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Walter Geller
Martin Schultze
Robert Kleinmann
Christian Wolkersdorfer *Editors*

Acidic Pit Lakes

The Legacy of Coal and Metal Surface Mines

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Venæ metallicæ lavantur, quæ lotura, quia venenis inficit rivos & fluvios, pisces aut necat, aut ex eis abigit.

Further, when the ores are washed, the water which has been used poisons the brooks and streams, and either destroys the fish or drives them away.

Georgius Agricola
De re metallica libris XII
1551
First book, page 5

English translation: Hoover & Hoover 1912

To my grandfather, who worked in the “Pütt”

W. Geller

Preface

Mine pit lakes and their unique features are largely neglected in the limnology literature. The standard textbooks on limnology (Margalef 1983; Schwoerbel and Bren-delberger 2010; Wetzel 2001) used in English, Spanish, and German speaking countries do not mention these types of lakes at all. Discussions on acidification of lakes and rivers were, and are, usually restricted to rain-acidified soft waters (O'Sullivan and Reynolds 2003, 2005; Stumm and Morgan 1996). Given the political and economic changes that have occurred in eastern and central Europe since 1990, limnologists have to recognize that a large number of new pit lakes now exist, constituting about 30 % of the total number of lakes in Germany

During a symposium in Magdeburg in 1995, the current state of knowledge on mine water and post-mining lakes was discussed by 60 participants from the UK, Canada, USA, and Germany. The results were published in a book on Acidic Mining Lakes (Geller et al. 1998). After a decade of continuing scientific research and increasing practical experience, some of the authors of the first book met again in 2008 during the International Mine Water Association (IMWA) congress in Karlovy Vary, Czech Republic and agreed to prepare a second book on Acidic Pit Lakes. Altogether, 43 authors and co-authors contributed. The first part of this book presents the state of knowledge on the origin, geochemistry, and limnology of acidic pit lakes and various remediation approaches. The second part contains nine regional surveys and case studies on single lakes. The book is complementary to two other books which appeared recently, Castendyk and Eary (2009), and McCullough (2011).

We initially planned to publish this book in 2010, but learned that the rigorous peer-review and graphic editing process we imposed on ourselves required more time than we expected. Then, given the passage of time, several chapters, and sections had to be amended or rewritten.

We acknowledge the work of all of the authors and anonymous reviewers. We also gratefully acknowledge the financial support of IMWA that made this book possible, in particular the color printing of figures and photographs.

Freiburg, Magdeburg, Germany, December 2011

Walter Geller
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Chapter 1
Introduction

1.1 Occurrence and Distribution of Pit Lakes

Walter Geller and Martin Schultze

Pit lakes develop in surface excavations at former mining sites. They can result from mining of sand, gravel, clay, lignite, hard coal, and metal ores, and in quarries. Synonymous terms used in the literature are "mining lake", "mine lake," and "mine pit lake". The emphasis of this book is on pit lakes in former lignite, hard coal, and ore mines that are affected by acid mine drainage (AMD), and on respective management options to ensure acceptable water quality. Other pit waters without AMD inputs, such as fluvial gravel pit lakes, quarry ponds, and neutral or alkaline pit lakes, are not addressed, though the case studies in Chap. 5 of this volume include pit lakes in former sulfur mines and remediating the harmful effects of mining on nearby natural lakes.

Pit lakes only occur in regions where mineral deposits are located relatively close to the earth surface. However, history shows that the suitability of deposits for surface mining changes, depending on technological progress and economic conditions. Open cast mines are much deeper today than in the past. One reason for this is the increased sophistication, size, and power of mining equipment, which now includes some of the world's largest machines (Fig. 1.1 and 1.2).

In hard rock mining for base and precious metals, the number and area of surface mines now greatly exceed the equivalent values for underground ore mines, since it is now economically possible to excavate increasing volumes of ore with decreasing grades of metal (Fig. 3.18; Sect. 3.2.2). Surface mining of hard coal and lignite is also increasing in some areas of the world, but is decreasing in other countries due to political and economical changes (e.g. Poland, Czech Republic, and East Germany since 1990). Laws and regulations (e.g. U.S. Surface Mining Control and Reclamation Act, 1977) now restrict and control surface mining in many countries to ensure that mining operations are conducted in an environmentally responsible manner and that the land is adequately reclaimed during and after mining.

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Fig. 1.1 Technology of industrial scale strip mining. **a** *Upper photo* overburden conveyor bridge (type: F60), 500 m long and 100 m high, is surpassing the size of Eifel's tower. It was used till 1992 for lignite strip mining and is shown in Lichterfeld mining museum (Lusatia, Germany; *Source* Lutz Bruno); **b** *lower photo* Bucket wheel (type: 288), 220 m long and 96 m high, moving 240,000 t/d of coal/overburden in Garzweiler mine/Rhenish lignite district (*Source* Wikimedia commons, panorama-photo by Martinroell)

Fig. 1.2 Technology of industrial hard-rock opencast-mining. Large size excavators loading ore on giant trucks in Aitik mine/Sweden. The trucks that haul the ore can carry from 255 to 360 tons of rock. Visitors for size comparison (By courtesy of Boliden/Photograper: Daniel Olausson)

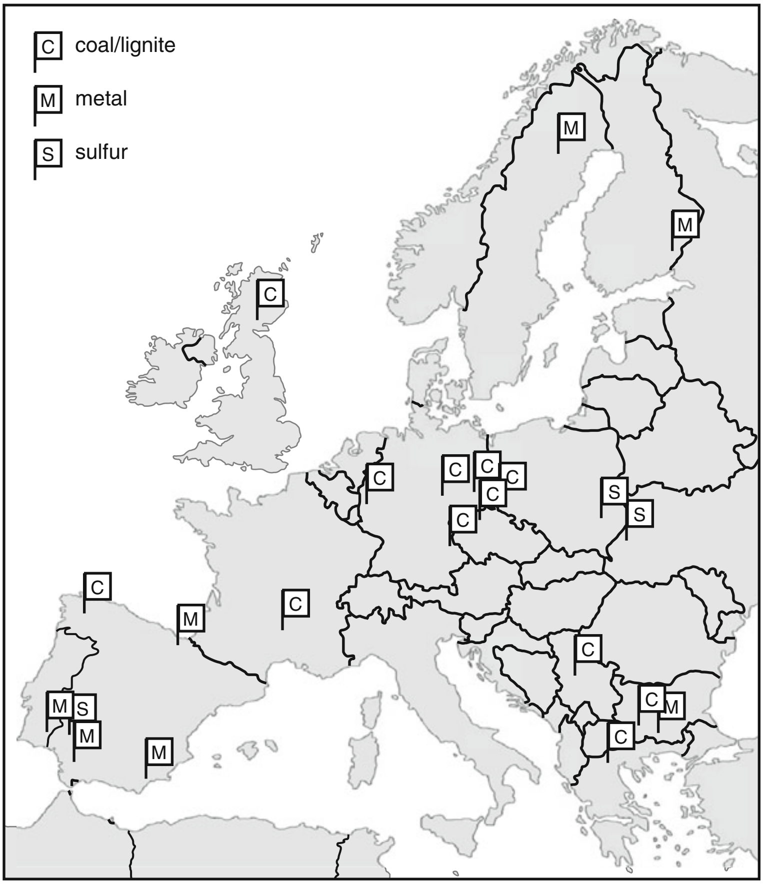

Fig. 1.3 Occurrence of pit lakes in Europe. Flags show the kind of mining causing the formation of the pit lakes. The feet of the flags roughly indicate the respective mining regions

Pit lakes are known worldwide, although the scientific literature on pit lakes is dominated by reports from Australia, North America, and Europe. The probable reason for this is that industrial development with its high demands for metals and energy started about 150 years ago in Europe and North America, so that large-scale surface mining (and pit lakes) occurred earlier. Driven by concomitant adverse side effects of industrialization, environmental legislation started to develop in these regions and stimulated research on pit lakes. Figure 1.3 indicates European regions where post-mining pit lakes emerged. Some of these are subject of special chapters of this book (Poland, Iberian Pyrite Belt, Germany). Ongoing metal mining operations (Sect. 3.2.2) are forming new pit lakes around the globe, and will likely continue to do so in the future.

Where deposits have a large areal extent, groups of pit lakes or lake districts may form, such as the Collie Coal Basin in Western Australia (Lund and McCullough 2008), the coal mine pit lakes in the Cedar Creek region in Missouri (Campbell and

Lind 1969; Parsons 1964), the pit lakes of the Iberian Pyrite Belt in Spain, and the Lusatian lignite-mining districts in Germany and Poland (case studies 5.1, 5.2, 5.3).

The degree of backfilling, which is another important factor that influences the occurrence and nature of pit lakes, largely depends on the ratio of overburden to coal or ore and on technological and economical factors. Strip-mining for coal and lignite usually includes backfilling of excavated voids with overburden during active mining, whereas in many open cast metal mines, backfilling is technologically impossible before mine closure. Backfilling after cessation of mining is relatively expensive and so is often not done, except where laws (such as the U.S. Surface Mining Control and Reclamation Act of 1977) require the approximate reshaping of the pre-mining landscape, which usually prevents the formation of pit lakes.

1.2 Morphology of Pit Lakes

The morphology of pit voids and lakes is distinctly different at mines in hard rock and unconsolidated rock. Surface mines in solid rock are typically deep, with steep side-walls, which results in crater-like lakes with large ratios of depth to surface diameter. The limited stability of unconsolidated rock and thick covers of soil and heavily fractured and weathered rock does not typically allow such void morphology. Depending on the nature of mining and the amount of backfilling, the final lake volume can range from the volume of the extracted mineral to the volume of the entire excavation, including overburden, waste rock, and tailings materials. In some of the lignite mining districts, the lignite seams are only a few meters thick, and large areas have to be strip mined. Large strip mining equipment, e.g. Fig. 1.1, produces narrow, deep trenches; the resulting pit lakes often have the form of a long, deep graben, accompanied by large, shallow areas (Sect. 2.1). Summarized, pit lake morphology is very diverse, creating lakes that range from small to large and from shallow to deep (Figs. 1.4, 1.5).

1.3 Local Hydrology and Lake Use

Pit lakes form where excavations leave voids with a positive water balance, which means that the sum of all inflows (groundwater, interflow, local runoff, streams, and precipitation) is greater than the sum of all outflows (surface and subsurface), withdrawals, and evaporation. Therefore, climate, hydrological and hydrogeological conditions as well as position in the landscape have decisive influence on the sustainable formation of pit lakes. The likelihood of formation of pit lakes is low in (semi-)arid regions, but where they do occur, they can be especially important as the only standing surface waters and important water reserves, e.g. in Australia (case study 5.4). Debates about the use and remediation of man-made lakes as by-products of mining might go beyond classical aspects such as tourism,

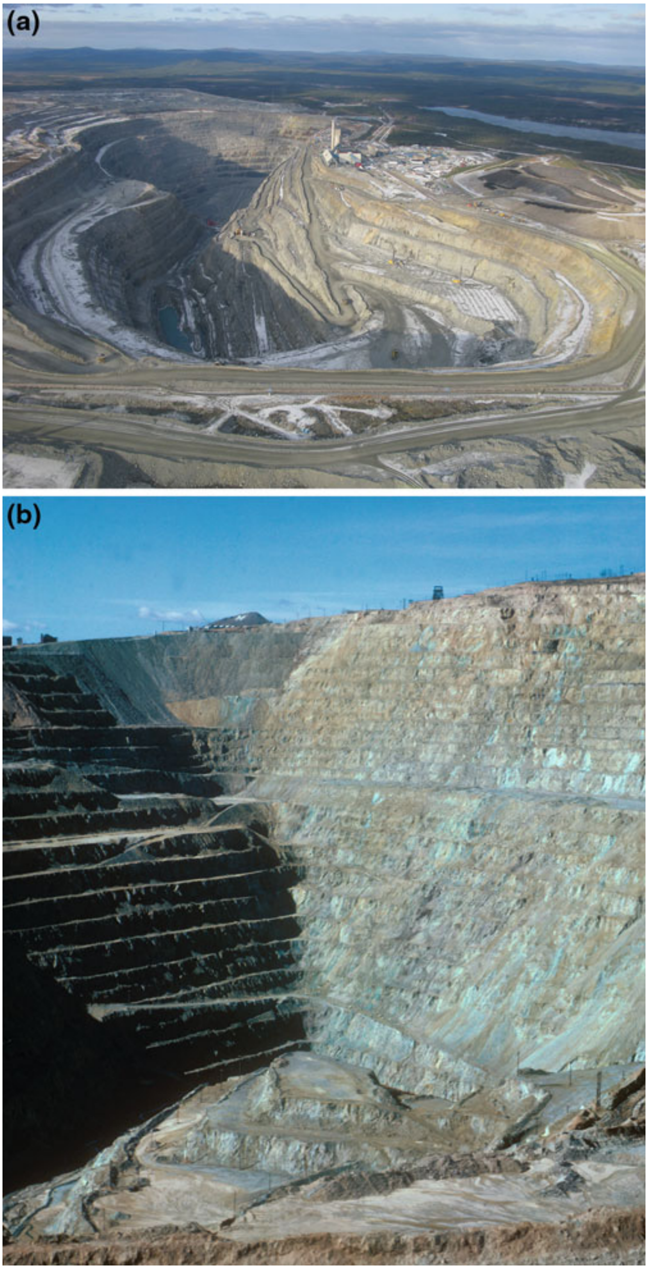

Fig. 1.4 Pit lakes from surface mining of ores: (**a**) *above* Aitik mine in Sweden (by courtesy of Boliden/Photographer: Lars Devall). The *below* (**b**) shows the Berkeley metal pit in Montana/USA left by industrial mining. The void was empty in 1983 (Photo: Ted Duaime, Montana Bureau of Mines and Geology)

Fig. 1.5 Pit lakes from surface mining of lignite *Above*: Pit lake district in Lusatia, Germany, in 2003. The lakes have surface areas of >10 km^2, and all lakes initially have acidic water, visible at brownish color near lake shores. The lakes in the center were only partially filled at the time when the photo was taken. The areas refilled with overburden appear as islands and developed to shallow-water areas with reaching the final water level. The *photo below* shows strips of old, small lignite pits created in Lusatia/Germany by hand-digging during the 19th century (Photos: Peter Radke/LMBV)

or fisheries, and include the status of water as a distinct human right (Kemp et al. 2010).

1.4 Acidification and Contamination of Lakes

Acidification is the central problem in many mining areas, affecting rainwater that seeps through dumps, contaminated groundwater, and surface water in pit lakes and rivers. The sources of acidity are generally sulfide minerals and sulfur components of coal and lignite. After contact of sulfide minerals (mainly pyrite) with atmospheric oxygen, roasting of sulfidic ore, or combustion of coal and lignite, the reduced sulfur components are oxidized and set free as sulfate or sulfur dioxide and acidity in the affected water. The acidity might be distributed over large areas by atmospheric transport (acid rain) and affect soils and waters, especially in regions with carbonate-poor geology. The direct transport path within the mine area is the flow of AMD into shallow ground- and surface-waters. Where the local geology is rich in minerals that produce acidity when oxidized, and poor in carbonates, severe acidification is generally an unavoidable side-effect of mining, as has been well known since medieval times (Agricola 1541–1561). A spectacular example of an acidic river is Rio Tinto in southern Spain (Fig. 1.6), the chemistry of which originates from natural sources as well as from mining activities that date back to pre-Roman times (de la Torre et al. 2011).

The range of lake acidification is shown in Fig. 1.7. Rain-acidified soft water lakes with low acidity and moderate pH form the lower end of this acidification scale, while volcanic lakes usually have the lowest pH and very high levels of acidity. Acidic pit lakes typically are in an intermediate range with lakes in former metal mines generally having lower pH and higher acidity than pit lakes in former lignite mines. High acidity is usually accompanied by elevated concentrations of total dissolved substances (TDS), sometimes reaching in brackish level salinities. Eary (1999) defined three main categories of pit lake chemistry: (1) acidic-high TDS, (2) alkaline-high TDS, and (3) circumneutral-low TDS. There are further examples beyond the scope of these findings, such as the German pit lakes with highly saline groundwater inflows. Their monimolimnia reach marine salinities (case study 5.1). Alkaline conditions in pit lakes may not only result from geologic conditions (e.g. Savage et al. 2009). Some pit lakes were used as deposits for industrial waste waters, such as red mud in the Gorka pit lake, in Poland, with water reaching a pH > 13 (Czop et al. 2011). However, this book is focused on acidic pit lakes.

The extremely acidic pit lakes show elevated concentrations of sulfate and iron, aluminum in coal and lignite pits, and additional contaminants (including potentially toxic metals and metalloids) in ore mines. Acidification and contamination degrade lake water quality with respect to both ecological value and human use. These quality problems demand remediation measures to avoid further contamination to rivers that receive the outflows from the contaminated

Fig. 1.6 Acidified river Rio Tinto dewatering parts of the Iberian Pyrite Belt in Southern Spain. The name describes the typical iron-red color of heavily AMD-affected mine waters. One of the biggest mining companies adopted the name. (Photographer: M. Koschorreck)

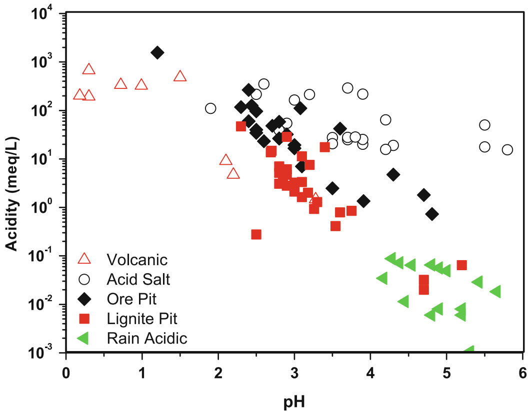

Fig. 1.7 Acidity and pH in lakes, that were acidified by acid rain (*green triangles*), in volcanic crater lakes and brines (*red triangles*), in acidic salt lakes (*black circles*), in ore pit lakes (*black diamonds*) and in German lignite pit lakes (*red squares*). The acidities in all waters are essentially based on oxidized sulfur. Values from different sources

lakes. In semi-arid areas, the pit lakes usually are the only existing lakes. They are especially important for nature and public use, and remediation appears as an urgent task.

1.5 Limnology of Pit Lakes

The limnology of pit lakes comprises the same basic processes as known from natural lakes. Pit lakes, however, show some peculiarities arising from special morphological, chemical, physical, and biological features, which are addressed in the Chaps. 2 and 3 of the first part of this book. Further comprehensive introduction to important processes and basics of pit lake limnology may be found in a report on northern pit lakes prepared for the government of Canada (Gammons et al. 2009) and in Castendyk and Eary (2009).

1.6 Modeling and Predictions

The pit lakes that exist after closure of ore and coal mines show a broad range of size, depth, water balance, and chemistry. Predicting the development of future pit lakes and the long-term management of water quality strongly depends on suitable modeling of the lakes and their catchment area, both surface and underground. In addition to the modeling code, a sufficient set of important features and basic data must be available, including morphology of the lake basin, data on temperatures, salinity, and pH, concentrations of all chemicals of interest, data on volumes and geochemistry of all in- and outflows, surface and groundwaters, and meteorological data (Sect. 3.4).

A crucial point for limnological modeling is the calculation of density stratification. Usually, densities are estimated from temperature and electrical conductivity (e.g. Sect. 3.4). However, a broad variability of water chemistry is found in different types of pit lakes, depending on their specific geological and hydrological environment. The weakness of current density estimates might be largely eliminated with actual progress in methods to achieve chemistry-specific density calculations (Sect. 3.1).

1.7 Remediation

Predictions and modeling of future pit lakes and their environments can help avoid acidification and contamination by inducing precautions and countermeasures during active mining (Sect. 4.6). Once acidification has occurred, however, remediation of whole lakes is a large-scale problem. Countermeasures might be composites of remediating AMD, ground- and lake-water on various levels, at inflowing water and with in-lake treatments. Finally, outflows might be treated to protect receiving surface waters. There is a broad set of active and passive options and approaches to treat acidified and metal-contaminated water, based on chemical or microbiological processes. Experience with experimental and field-scale applications are compiled in a general chapter of this book (Chap. 4).

1.8 Case Studies

Nine case studies are presented in the second part of this volume. The pit lakes of Germany (case study 5.1), Poland (case study 5.2), the Iberian Pyrite Belt in southern Spain (case study 5.3), and Australia (case study 5.4) are described in regional surveys. Two of the world's best investigated pit lakes are presented in detail, the copper-mine *Berkeley Pit Lake* in Montana (case study 5.5) and the lignite *Mining Lake 111* in Lusatia, Germany (case study 5.6). The role of different biological approaches to eliminate toxic metals (biological polishing, ecological engineering) from lake water (case study 5.7), and an innovative method to make economic assessments of pit lakes (case study 5.9) are presented in two additional case studies.

1.9 Aims of this Book

This book comprises a survey on the state of knowledge of pit lakes and the geochemical acidification processes that degrade the value of pit lakes. The book is not simply a second edition of Geller et al. (1998), despite comparable aims. Progress in research and practical experiences of the last decade have generated a new conceptual understanding of pit lakes. For example, the limnophysical character of pit lakes has emerged as an important field in recent years (case study 5.1). New facts have been compiled on the ecophysiology of acidophilic and acid-resistant organisms (Sect. 3.3). Findings about the interactions between organisms and water/sediment have helped us understand the simple but unique ecosystem structure and the food web of extremely acidic waters, which is characterized by a high degree of mixotrophy of various types. The approaches for remediation (Chap. 4) are understood in principle, but some approaches have worked well, while others did not meet initial expectations. Case studies and comprehensive regional surveys provide instructive examples of how acidic pit lakes can be remediated. Open questions, lessons learned that researchers can apply, technical developments, and important recent results are presented as conclusions in the final Chap. 6 of this book.

Chapter 2
Terrestrial Environment of Pit Lakes

2.1 Morphology, Age, and Development of Pit Lakes

Martin Schultze, Bertram Boehrer and Walter Geller

Several factors determine the shape of a mine pit at the time of decommissioning. The most important of these are the amount and distribution of coal, lignite, or ore in the ground and the stability of the surrounding material, which forms the side walls of the pit after closure. Other factors that play a role are backfilling (if it occurred), material movement and erosion, and the age of the pit lake.

In the case of steeply dipping ore veins, the open cast mine follows the veins from surface to depth. This is typical for many open cast metal mines. Coal and lignite deposits usually have a different shape since they originated from a horizontal deposit. The seams are confined by surrounding strata and extend horizontally (unless the strata have been folded or faulted) over wide areas. These deposits are often exploited by strip mining. Both types are illustrated in Fig. 2.1. Some mines may show features of both types.

The steepness of the side slopes of a decommissioned mine depends on the stability of host rock and overburden. Sidewalls of a mine in a hard rock environment can be designed at a steep angle, but slopes of much smaller inclination are mandatory in unconsolidated rock. Figure 2.1 illustrates this. Hard rock allows for steeper slopes not only during mining but also when a pit has been filled with water to form a lake, since hard rock walls are less susceptible to erosive wave action. Unconsolidated rock, however, are eroded rapidly by wave action. If the slopes of a mine void are not well prepared for wave action, this may result in permanent shore erosion and even in landslides.

Consideration of long term stability extends beyond the period of mining, to when a different hydrological setting has changed the boundary conditions. Cohesion of unconsolidated rock decreases when the underground fills with water. Landslides of enormous horizontal and vertical dimensions (Fig. 2.2) can result (Nestler and Stoll 2001). Where the rising groundwater meets the surface, springs

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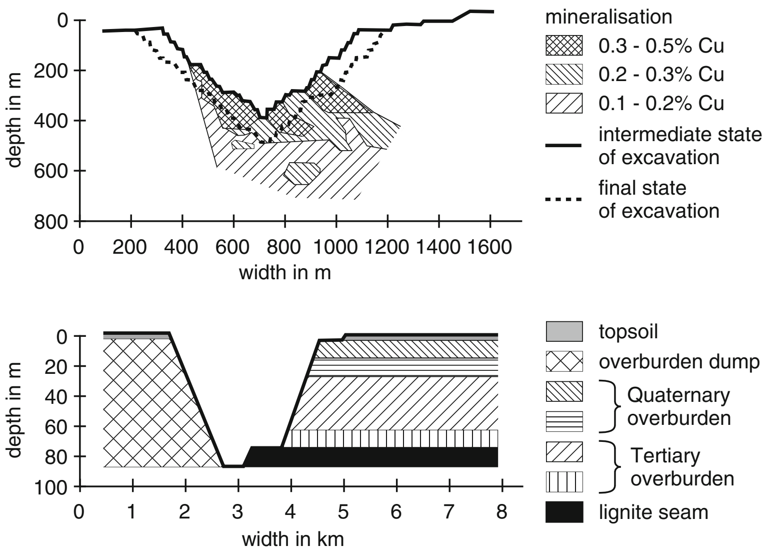

Fig. 2.1 Typical examples of open cast mines: *upper panel* from metal mining in solid rock, based on conditions at the Aitik mine in northern Sweden, with simplifications; *lower panel* from lignite mining in Germany, where seams are usually embedded in unconsolidated rock like gravel, sand, loam, and clay (based on conditions at the former mine Espenhain, with simplifications); note the different scales of the panels

can form, and the flowing waters can destroy the side walls. In addition, groundwater flow exerts pressure against the slope from the underground into the mine void and causes suffusion (transport and removal of smaller particles). Clay layers and fractures dipping into the mine void or earthquakes can also promote landslides. Some of these issues can be handled more easily when the water table inside the mine pit is raised rapidly by introducing water, e.g. by river diversion. Consequently, the filling procedure also influences the final shape of a pit, at least in cases of unconsolidated rock.

The steepness of a lake basin, i.e. the initial mine void, can be expressed by the relative depth, z_{rel}, which is defined as the ratio of the maximal depth of a lake z_{max} to the mean diameter of the lake surface A, often expressed in percent (Wetzel 2001):

$$z_{\mathrm{rel}} = \frac{z_{\max} \times \sqrt{\pi} \times 100\%}{2 \times \sqrt{A}} \tag{2.1}$$

Figure 2.3 illustrates differences between pit lakes in former lignite mines in Germany, former coal mines in Western Australia, and former metal mines. While the German lignite pit lakes are embedded in unconsolidated rock (gravel, sand, loam, and clay), requiring small slope inclinations, most pit lakes in former metal mines are embedded in solid, often crystalline rock (e.g. Dallmeyer and Martinez

Fig. 2.2 Landslide of dumped overburden in the former Spreetal Mine (Lusatian lignite mining district, Germany) at October 12, 2010. The ground broke over an area of ca. 1800 m × 600 m (ca. 110 ha), damaging the neighbouring pit lake (*upper margin of the photo*). It was caused by an initially local liquidation of deeper parts of the overburden dump and supported by extremely high water saturation of the entire dump as a result of a very rainy period of about 10 weeks. (Photo: Radke, LMBV)

Garcia 1990), allowing steep slopes. The pit lakes of the Collie Basin (Western Australia) are embedded in sandstone, mudstone, and shale (Le Blanc Smith 1993), resulting in an intermediate position regarding the relative depth (Fig. 2.3).

Backfilling of the mine void with overburden and waste rock will change the morphometry of a pit. Backfilling is common in strip mining, where overburden is deposited in areas where the coal has been previously excavated (Fig. 2.1, lower panel). Large strip mining technology, e.g. the conveyor bridge shown in Fig. 1.1 (see Chap. 1), can leave a narrow, deep trench as a final void. Many pit lakes of this type resemble a long, deep graben, often accompanied by large, shallow areas where extended stands of macrophytes may develop (Fig. 2.4).

In contrast, a mine that proceeds more vertically may not have space for dumping as long as mining is proceeding (Fig. 2.1, upper panel), but backfilling after decommissioning is typically too expensive. As a consequence, backfilling in open cast metal mines is unusual. The Aznalcollar pit lake (Spain) is an example for partial backfilling with waste rock from a neighbouring open cast mine (Schultze et al. 2008).

The available material for backfilling is limited by the removal of the exploited material. Coal and lignite are used for combustion. The residual ash has a much smaller volume, and depending on the contaminants it contains, it is often too toxic for placement in permeable mine spoil. Therefore, complete backfilling to the initial contour of the landscape would appear to be impossible. However, overburden material that has been fragmented takes up more space than it did before it was disturbed. This is often referred to as ‘swelling’; at many coal mines where the

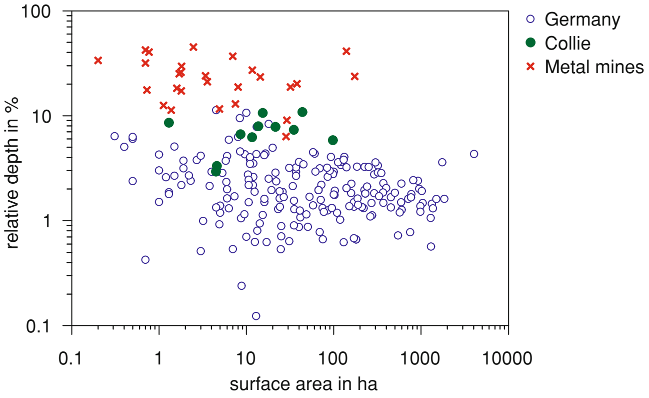

Fig. 2.3 Plot of the relative depth of German pit lakes in former lignite mines (database identical to the one used in case study 5.1), pit lakes in the Collie coal basin in Western Australia (database: McCullough et al. 2010), and pit lakes in former metal mines (database: Crusius et al. 2003; Doyle and Runnels 1997; Fisher and Lawrence 2006; Levy et al. 1995; Lu 2004; Lyons et al. 1994; Park et al. 2006; Sánchez-España et al. 2008; Steven and Lawrence 1997; Wyatt et al. 2006)

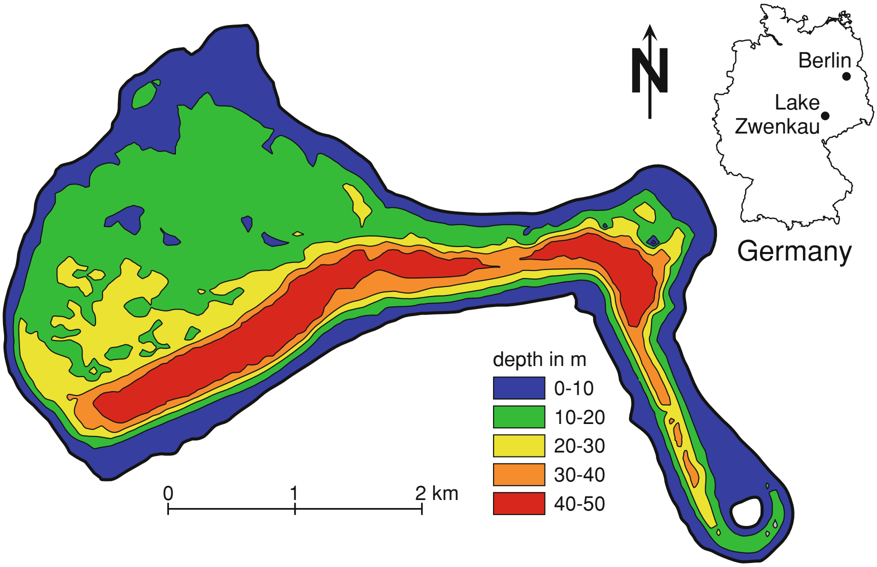

Fig. 2.4 Bathymetric map of Lake Zwenkau (Central German lignite mining district)

volume of overburden greatly exceeds the amount of coal extracted, this swelling more than makes up for the amount of material removed, and no pit lake forms. This commonly occurs in the eastern U.S.

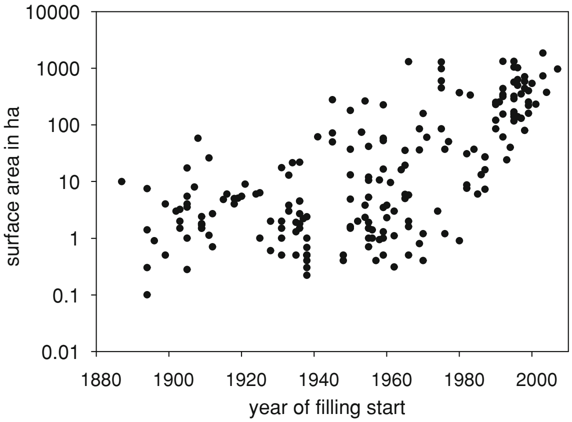

Fig. 2.5 Surface areas of German pit lakes in former lignite mines relative to the age of the pit lakes, reflecting the increased performance of mining equipment (database identical to that used in case study 5.1)

Pit lakes have formed since the end of the nineteenth century, e.g. in Germany. At that time, open cast mines were limited by the performance of the available mining equipment. Consequently, the resulting pit lakes were small, i.e. less than 1 ha surface area with a maximal depth less than 10 m. As mining equipment became more powerful, extraction depths and areas grew. Today, opencast mines and resulting pit lakes have surface areas of several square kilometres and depths of several hundreds of meters. Therefore, there is a correlation between age of pit lakes and their size (Fig. 2.5).

After a lake has formed, its morphometry is subject to changes due to sedimentation: the older the pit lake, the thicker the accumulated sediment at the lake bottom resulting from chemical precipitation, dead plankton, erosion of the shore, and allochthonous sediment input by streams or rivers feeding the pit lake. In unconsolidated rock, the sedimentation rate may be very high during filling and in the first years after filling, until the formation of the lake shore has reached equilibrium with the mean local wave action. Without landslides, however, sedimentation only changes the morphometry at a slow pace. Wagner (2010), for example, found that ca. 500 m^3/a of sand and finer material was transported along the shore of Lake Cospuden (4.3 km^2 surface area) by wind-driven surface waves and the resultant erosion of the shoreline.

To close this section, we introduce Lake Goitsche (Germany; Fig. 2.6) to illustrate different factors that influence the shape of the lake basin, including changes in morphometry caused by landslides and flooding. Lake Goitsche consists of three subbasins, named Mühlbeck, Niemegk, and Döbern, respectively (Fig. 2.6). The lake was formed by deviating water from the nearby Mulde River into the Mühlbeck subbasin. Subbasins Niemegk and Döbern were subsequently filled when the water overflowed into them (see Fig. 2.6, right panel).

The geology of the deposit created two islands in the central southern part of the lake and a sill north of them. They are the result of a paleo-dune, which resulted in the local absence of lignite. Consequently, the area of the current islands was not mined. The deepest locations of the lake basin result from local depressions in the

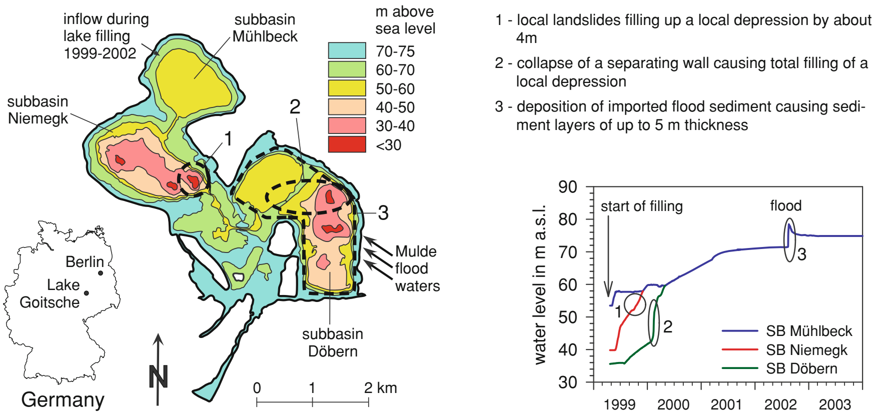

Fig. 2.6 Changes of morphoplogy in Lake Goitsche (Germany). *Left panel* Bathymetric map of Lake Goitsche showing the initial morphology of the lake basin at the start of filling in May 1999. The *dotted lines* indicate the regions within the lake basin where the morphologic changes occurred. *Right panel*, *upper part* Details of the morphologic changes. The numbers 1, 2, and 3 correspond to the spatial indication of morphologic changes in the *left panel* and to the temporal occurrence of the changes in the diagram in the *lower right panel*

lignite seam caused by the dissolution of salt deposits deeper underground (see Fig. 5.2 in case study 5.1).

The excavation technology and the spatial progress of the exploitation are the reasons for the shallow water depth in the western part of the Döbern subbasin and for the peninsula separating the Mühlbeck and Döbern subbasins. Both areas were used as dump sites for overburden in the final phase of mining. The mining started west of subbasin Niemegk, and initially proceeded southward. River Mulde initially crossed the eastern part of the current Lake Goitsche (mainly in the northern part of subbasin Döbern and the area between subbasins Mühlbeck and Niemegk). After diversion of the river, mining proceeded eastward in a northern and southern arc, in parallel, like a pincer. The subbasins Mühlbeck and Niemegk were not used as dump sites for overburden to allow later exploitation of amber deposits, which lie beneath the lignite seam in the area of these two subbasins (Wimmer et al. 2006).

During remediation, landslides and a flood produced further changes in the basin morphology. First, small-scale sediment transport and landslides near the former deepest point of the pit (the southwestern part of subbasin Niemegk; number 1 in Fig. 2.6), reduced the maximum depth in this area by about 4 m as this subbasin was filled (Boehrer et al. 2003). Then, when water started to spill from subbasin Niemegk into Döbern, the separating wall broke and much of it was flushed into Döbern and filled some deep areas in the northern part of the subbasin (number 2 in Fig. 2.6). Finally, an extreme event happened when the catchment of the nearby Mulde River received extremely high precipitation in summer 2002, causing record river water levels (Klemm et al. 2005). The flood water found a way into Lake Goitsche and created a river bed (about 1 km long, 100 m wide, and up to 5 m deep). About 100×10^6 m^3 of flood water entered the lake in less than 48 h, carrying a load of about 1×10^6 m^3 of suspended material into the lake. Most of this suspended material settled in the quieter waters of the lake. This changed the morphometry of the lake by up to 5 m over a considerable area (number 3 in Fig. 2.6; Boehrer et al. 2005).

Although the amount of such displaced material is small compared to lake volume (e.g. 109×10^6 m^3 in Lake Cospuden, 213×10^6 m^3 in Lake Goitsche), local depressions of a lake bottom can be filled and bathymetric maps of the anticipated morphology of the lake bottom, based on the final measurements of the mine surveyors before lake filling, will become inaccurate. In addition, erosion and landslides are accompanied by an intense washout of substances into the lake water, which can have considerable influences on the progress of neutralization processes (e.g. Schultze et al. 2002).

2.2 Influence of Groundwater on Pit Lakes

Martin Schultze

Surface mining for coal, lignite, and metals requires the total dewatering of the mined portion of the ground down to the deepest level of the mine. The hydraulic head of the groundwater below the surface mines has to be lowered, at least enough to prevent a dangerous uncontrolled inflow of groundwater through the bottom of the mine. Therefore, groundwater cones of depression form around the surface mines, as schematically shown in Fig. 2.7. The depression cone results in a groundwater flow to the mine from all directions.

The formation of the cone of depression exposes strata that were saturated with water to atmospheric oxygen. If the strata contain pyrite, it will begin to oxidize, producing acidity, sulfate, and dissolved iron, according to the Eqs. 2.2–2.5:

Oxidation of pyritic sulfur by oxygen

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \tag{2.2}$$

Oxidation of ferrous iron by oxygen

$$14Fe^{2+} + 3.5O_2 + 14H^+ \rightarrow 14Fe^{3+} + 7H_2O \tag{2.3}$$

Oxidation of pyritic sulfur by ferric iron

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{2.4}$$

Ferric iron that was not consumed by further oxidation of pyritic sulfur, hydrolyses and precipitates if the pH is above 3.5, according to the following reaction:

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+ \tag{2.5}$$

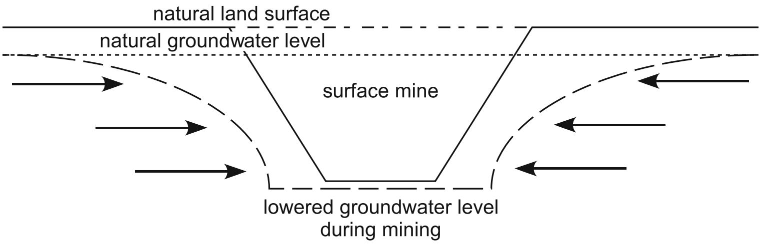

Fig. 2.7 Schematic cross section of a surface mine showing the groundwater levels before mining and during mining. The *arrows* indicate the flow direction of the groundwater under the conditions of mining

Often, other sulfide minerals are present, in addition to pyrite. At many metal mines, these other sulfide minerals are the target of the mining operations. They are also subject to oxidation and can contribute to acidification and water contamination.

The acidity reacts with other minerals that are present. This consumes a portion of the acidity and buffers the pH. The most important reactions are the consumption of dissolved bicarbonate, the dissolution of carbonates, silicates, metal hydroxides, and oxides, and ion exchange. Diverse ions, including aluminum, are mobilized, which causes many mine waters to be highly mineralized.

As long as the pyrite oxidation occurs underground, the availability of oxygen is limited. Therefore, not all of the dissolved iron is oxidized. The remaining ferrous iron represents hidden (mineral) acidity, which becomes relevant when the groundwater enters a pit lake or reaches the surface at springs and is exposed to higher oxygen concentrations.

This has to be considered when analyzing groundwater from mining-influenced sites and when interpreting the results. An initial oxidation step is recommended for the titrimetric determination of acidity and in order to prevent any misunderstanding, the procedure used to determine acidity should be clearly described (Kirby and Cravotta 2005a, b). A clear description of the analytical procedure used is even more important if the acid neutralization potential of the solid material along the flow paths of the water is to be considered (e.g. Morin and Hutt 2009). An accurate determination of acidity is an essential and powerful input for assessment and for planning remedial measures (e.g. Castendyk and Webster-Brown 2007; Kringel et al. 2000; Schöpke 2008).

Everything described so far applies to mines in both solid and unconsolidated rock. However, there are important differences between solid and unconsolidated rock regarding the flow of water and the interaction between air, water, and rock. In solid rock, water flow is restricted to faults, fractures, and fissures. In unconsolidated rock, the water also flows through the pore space. The interface between the fluid and the solid phase is usually much larger in unconsolidated rock than in solid rock.

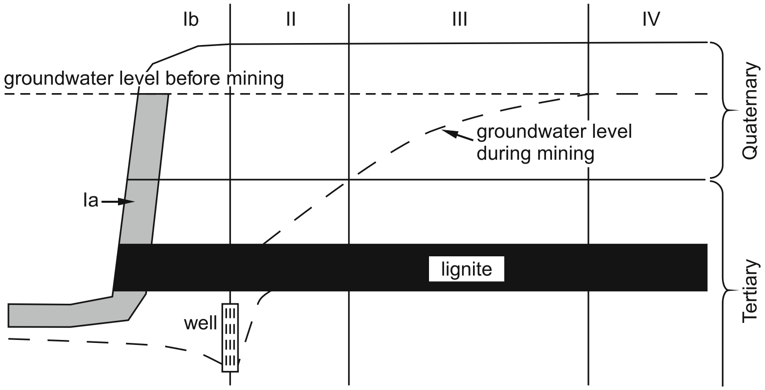

Fig. 2.8 Scheme of the concept of zones of different duration of mining related aeration of the underground in the vicinity of surface mines (modified from Grützmacher et al. 2001; for details on the characteristics of the zones see text)

A larger interface allows for more intense and faster interaction, including pyrite oxidation and dissolution of carbonates and feldspars.

Many publications on the influence of mining on groundwater exist. The following literature can be recommended for information on the relevant processes, including the long-lasting effects after mine closure: Grützmacher et al. 2001; McLemore 2008; Niccoli 2009a, b; Wisotzky and Obermann 2001; Wolkersdorfer 2008; Younger et al. 2002.

The spatial and temporal extent of aeration of pyritic material is one of the main factors influencing the amount of acidity formed during mining. Pyrite oxidation proceeds as long as pyrite, oxygen and humidity are available. After the dewatering of a surface mine ceases, the groundwater rebound usually reaches the underground areas closest to the remaining mine void later than areas that are further away. This led to classifying the underground in the vicinity of surface mines into zones based on the extent of groundwater lowering (Grützmacher et al. 2001). The concept was developed at German lignite mines where the Tertiary lignite seams are embedded in Tertiary and overlain by Quaternary unconsolidated rock. Figure 2.8 shows a schematic depiction of this concept.

The zones of groundwater lowering are characterized as follows for the typical hydrogeological conditions in German lignite strip mines (Grützmacher et al. 2001):

Ia the side walls and the bottom of the mine void below the pre-mining groundwater level with intensive contact with oxygen for a long period
Ib fully drained underground areas between zone Ia and the dewatering wells
II area where the Tertiary material below the lignite remained saturated except for a small cone of depression close to the wells and the Tertiary materials above the lignite was only drained partially, while the Quaternary material was fully drained

III area where the Tertiary material remained saturated with water and the Quaternary material was partially drained
IV area without groundwater lowering.

The separation of Tertiary and Quaternary strata in German lignite mines is important since the Quaternary material usually does not contain pyrite whereas it is common for the Tertiary strata. In other regions where such a separation is not necessary, the concept can easily be adapted by reducing the number of zones. Extension of the zones generally depends on the local hydrogeological conditions of a particular mine site. For the conditions of the Central German lignite mining district, Grützmacher et al. (2001) reported 1–6 m thickness for zone Ia, up to 500 m extension for zone II, and 500–2000 m extension for zone III.

As long as the water level in a pit lake is considerably lower than the groundwater level, a significant amount of the underground strata will remain aerated and may form a long term source of acidity until all of the pyrite is oxidized and the acidic products are washed out by interflow and groundwater recharge. The thickness of this aerated layer may vary over time if the groundwater level varies seasonally or inter-annually, and these variations can introduce periodic pulses of acidic inflow into the pit lake. Water level changes in the pit lake, which are typical in pit lakes that are used as reservoirs or for flood protection, will also cause groundwater level variations.

Groundwater observation wells are usually located a safe distance from the shores of pit lakes. The samples represent the quality of the groundwater, i.e. the water in the saturated part of the underground at a certain, site-specific distance from a pit lake, often located in zone III or even zone IV (Fig. 2.8). This is not necessarily the quality of the groundwater that eventually enters the pit lake because special sampling devices for the interflow and shallow groundwater observation wells very close to the shore of the pit lakes are not common. Therefore, the rate that acid is imported into pit lakes is often underestimated when it is only based on typical groundwater sampling.

An exception to this situation was reported by Heinrich et al. (2011). An investigation considering all components of potential acidity imported into Lake Bockwitz (Germany) included groundwater monitoring close to the lake shore and at the typical distance, seepage water from interflow and groundwater recharge, inflow from pit lakes located up-gradient, local precipitation, local surface runoff, erosion from the sidewalls above the water level of the lake, water quality inside the lake, interaction with the sediment of the lake and outflow from the lake. Column tests were operated to determine the rate of pyrite oxidation in the vadose zone and the elution rates in the permanently saturated zone. These results, combined with a groundwater flow model that was calibrated with actual observations, allowed for the development of a detailed balance of acidity in Lake Bockwitz. The result is depicted in Fig. 2.9. For more details, see Heinrich et al. (2011).

Interflow was a major influx of acidity into Lake Bockwitz in 2010, i.e. 5 years after reaching the final lake level (Fig. 2.9). The water level of Lake Bockwitz was about 15–20 m below the surrounding landscape, which may have caused the

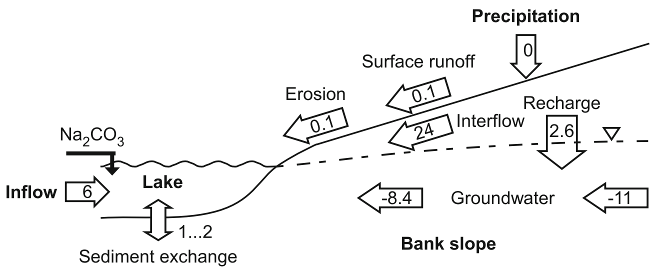

Fig. 2.9 Detailed balance of acidity for Lake Bockwitz (Germany; modified from Heinrich et al. 2011). The data give the average fluxes of acidity for 2010 in kmol d^{-1}. Negative values indicate alkalinity fluxes

interflow contribution to be exceptionally high. Nevertheless, Lake Bockwitz demonstrates the importance of interflow and the processes that take place above the water table in the vicinity of a pit lake on pit lake acidification. Therefore, this component should be considered and, as far as possible, quantified when establishing acidity-alkalinity-balances of pit lakes or designing neutralization measures.

Like the above-mentioned concept of zones of lowered groundwater, the example of Lake Bockwitz originates from Germany where mining takes place in unconsolidated rock. The basic ideas described above also apply to pit lakes in hard rock environments and intermediate conditions, such as porous rock, e.g. sandstone. Often, soil cover and the weathered zone provide conditions similar to that present in unconsolidated rock. Waste rock dumps are also similar to unconsolidated rock with respect to water flow and the interaction between the air in the underground pores and the minerals.

Of course, the relationship between groundwater and pit lakes is a two-way street; pit lakes are influenced by groundwater, but also influence groundwater. For example, evaporation from a lake surface and surficial outflows of pit lakes can cause a long term depression of the groundwater surface in the vicinity of the lakes. If there is a subsurface outflow from a pit lake, the lake is a source of water and contaminants to the down-gradient groundwater. Also, pit lakes often interconnect different aquifers, which may otherwise be separated; these pit lakes act like a mixing, aeration, and reaction chamber. The outflowing water has a different water quality than the influent groundwater. Even if groundwater of a deep aquifer only passes through the anoxic monimolimnion of a meromictic pit lake, the water quality will be changed in the lake, since the permanent input of substances into the monimolimnion by sedimentation changes the geochemistry of the water. Such aspects all have to be considered when assessing interactions between groundwater and pit lakes.

To summarize, there are often intense and important interactions between groundwater and pit lakes. Which kind of influence dominates at a particular pit lake depends on local conditions. However, this book is focused on the lakes, and so, such groundwater aspects are only addressed in Sects. 3.2.2, 4.6, 5.3, 5.5, 5.8, and Chap. 6.

The interactions of groundwater and a pit lake were extensively investigated at the Berkeley pit lake. They are briefly described in case study 5.5 in this book. More details can be found in Gammons et al. (2009), Pellicori et al. (2005), and in a special issue on the topic in *Mine Water and the Environment* (Kleinmann 2006). Further case studies on the interaction of groundwater and pit lakes in Germany exist, such as: Bozau and Strauch (2002), Trettin et al. (2007), and Werner et al. (2001, 2008).

Chapter 3
Limnology of Pit Lakes

3.1 Physical Properties of Acidic Pit Lakes

Bertram Boehrer

Mine water in pit lakes can have a pH of 3 or even less. In some cases, we find gradients of pH within the same lake extending from acidic to neutral. In addition, pH-neutral water can possess the potential to turn acidic when brought into contact with oxygen. In acidic waters, the concentrations of heavy metals can be high, which differentiates such lakes from 'natural' lakes, except for a few volcanic ones. Given these high concentrations, common approximations for electrical conductivity or density that may be reasonable in less contaminated water will not necessarily be accurate. In conclusion, alternative approaches need to be developed. In the following subsection, the most common approaches to deal with these properties are presented.

3.1.1 Electrical Conductivity

Acidity represents a reactive constituent. When iron rich, monimolimnetic waters of Waldsee are brought into contact with dissolved oxygen, iron is precipitated. The resulting hydrolysis of ferric iron, releases H^+ ions, which directly affect the carbonate buffering system and hence lower the conductivity. As a consequence, the implementation of electrical conductivity as a tracer underlies some severe restrictions.

Natural freshwater lakes usually have an electrical conductivity in the range of 0.1–0.5 mS/cm at 25°C. Mine drainage can have considerably higher conductivities (see Fig. 3.1). As a consequence, the precipitation versus evaporation deficit in the eastern German summer shows up in high values of conductivity during summer stratification (Karakas et al. 2003), while during deep circulation and in

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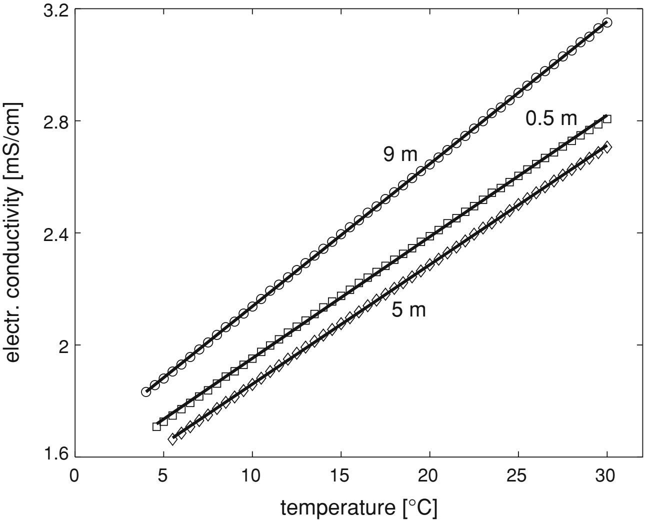


Fig. 3.1 Temperature dependence of electrical conductivity in water samples from several depths in Mining Lake 111 versus temperature (0.5 m—epilimnion, 5 m—hypolimnion, 9 m—monimolimnion; modified after Karakas et al. 2003)

the hypolimnion conductivity remains roughly constant. High concentrations of dissolved substances can contribute to epilimnetic water density. Especially in areas of dry summers, this effect can contribute to deep mixing when the higher epilimnetic concentrations of dissolved substances help overcome temperature stratification when falling autumn temperatures allow deep mixing. Ocean waters have an electrical conductivity of around 42 mS/cm at 25°C, while some (natural) salt lakes show an electrical conductivity even higher than 200 mS/cm (Dead Sea, Akawwi 2006; case study 5.3).

Acidic waters contain a considerable concentration of dissolved substances, i.e. the H^+ ions and corresponding ions to balance the electric charge. The specific electrical conductivity of H^+ is particularly high, i.e. a factor of 5–10 higher than most other ions (see Millero 2001). The conductivity contribution of H^+ ions (and OH^-) can be evaluated for infinite dilution, which of course is not realistic for pH values below 1 or above 13. The conductivity contribution of H^+ and OH^- give a lower limit of the electrical conductivity at 25°C of lake water (for the pH range 0–14, see Fig. 3.2). If the conductivity of a water sample is at least an order of magnitude above the curve in Fig. 3.2, H^+ (and OH^-) ions contribute a much lower portion to electrical conductivity, compared to other ions.

If lakes are neutralized by the addition of buffers, conductivity may remain high, as seen in the example of Lake Bockwitz, where soda was added to reduce acidity. The situation is less drastic if, during the filling period, water had been introduced from natural systems to dilute the highly mineralized (acidic) drainage from the mined area (e.g. Lake Goitsche, Boehrer et al. 2003).

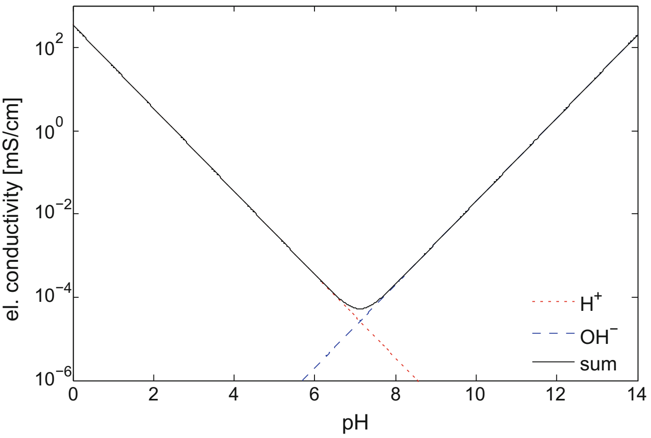


Fig. 3.2 Electrical conductivity at 25°C of the water ions, H^+ and OH^- and the sum against pH, calculated for infinite dilution

Electrical conductivity is a function of dissolved substances and temperature. To use it to assess the concentration of dissolved substances, the temperature effect is commonly removed by referring to the conductivity, as it were at a certain reference temperature, usually 25°C. Experience shows that the effect of temperature can be approximated quite well using linear regression, $C(T) = aT + b$ (see Fig. 3.1). This yields an equation for calculating κ_{25} from a field measurement of pairs of temperature T and in situ conductivity $C(T)$, using Eq. 3.1,

$$\kappa_{25} = \frac{C(T)}{\alpha_{25}(T - 25^{\circ}\mathrm{C}) + 1} \tag{3.1}$$

where α_{25} is commonly set to 0.02/K, or rarely to slightly lower values for natural neutral lakes.

All ions show specific temperature dependences, though, except for H^+, they lie within a relatively narrow band (see Sorensen and Glass 1987). As a consequence, the electrical conductivity of neutral waters calculated in this manner aligns well with Eq. 3.1. In acidic waters, however, the temperature dependence must be quantitatively analysed. In lakes with a low pH, a value for α_{25} considerably smaller than 0.02/K must be used (see Table 3.1).

For temperature compensation, the most common reference temperature is 25°C, though tables have also been developed for 20°C. Choosing a reference temperature closer to the temperatures found in the lake can improve the accuracy of the results (e.g. Boehrer et al. 2009b).

Oceanographers define salinity S as a function of temperature T and electrical conductivity C. Values are given in practical salinity units [psu], which give a good indication of dissolved salts in g/kg of ocean water and brackish water.

Table 3.1 List of empirically determined α_{25} values for various lakes

Lake	Sampling date	pH	α_{25}, 1/K	κ_{25}, mS/cm	Reference
Waldsee monimolimnion	2006-12-12	6.6	0.0194	0.974	Boehrer et al. (2009a)
Waldsee mixolimnion	2006-11-16	7.2	0.0194	0.481	Boehrer et al. (2009a)
RL 111 epilimnion	2001-08-21	2.67	0.0163	2.603	Karakas et al. (2003)
RL 111 hypolimnion	2001-08-21	2.67	0.0165	2.601	Karakas et al. (2003)
RL 111 monimolimnion	2001-08-21	2.8	0.0173	2.899	Karakas et al. (2003)
Moritzteich mixolimnion	2006-11-15	3.2	0.0178	0.970	Here
Moritzteich monimolimnion	2006-12-12	6.7	0.0194	1.497	Here

$$S = S(C, T) \tag{3.2}$$

Salinity is calculated over several steps, involving a number of empirical constants. The exact numerical approach can be read in the original literature or—in a more comprehensible way—in the review by Boehrer and Schultze (2008). At the time of writing this manuscript, UNESCO is providing a calculator on the internet for assessing properties of ocean water using coefficients by Fofonoff (1985). For low salinity limnetic water (<0.6 psu), Chen and Millero (1986) introduced a correction factor.

$$S = 1.00488_{\text{ocean}} \tag{3.2a}$$

In limnic waters, salinity has no clear definition. It would be better to refer to total dissolved substances, which is more clearly defined. However, as the most commonly accepted density formulae refer to this definition of salinity as an intermediate step, it is still in common use. Oceanographic equipment, e.g. multiparameter probes, often supply the salinity value in psu from measurements of temperature and electrical conductivity conveniently in the data output. It must be kept in mind that this value has been evaluated under ocean condition assumptions.

3.1.2 Density

Density gradients, i.e. potential density gradients contrary to in situ density (see e.g. Boehrer and Schultze 2008), in lakes control whether stratification is stable or whether density differences drive vertical exchange flows. An accurate approach for density is mandatory for any quantitative work on the stability of stratification. Density differences in lakes usually lie in the range of a few per mill, i.e. some kg/m^3, which are responsible for stable stratification during summer, and stable stratification in meromictic lakes.

There are four approaches to calculating density in lakes:

1. Using temperature and electrical conductivity data, while implementing ocean assumptions,

2. Making freshwater assumptions (of natural lakes) at low salinity,
3. Evaluating lake-specific regressions between temperature, conductivity, and density, and
4. By adding partial molal volumes and masses, when concentrations of all relevant dissolved substances are known.

1. Oceanographers use the so-called UNESCO formula by Fofonoff and Millard (1983) to evaluate density. This approach is valid only between 2 and 42 psu of salinity, and hence should only be used for a small number of lakes. In addition, the salt composition must be similar to brackish water (e.g. Rassnitzer See, Wallendorfer See in mining area Merseburg-Ost; Böhrer et al. 1998). This is the most commonly used approach for calculating density in numerical stratification models of lakes, and so this formula has become very important in limnology.
2. For natural lakes with salinities below 0.6 psu, Chen and Millero (1986) proposed using a different approach to calculate density. They suggested using a term that is based on the above definition of salinity for limnic waters to incorporate the density contribution of solutes. However, for acidic lakes, and also for most natural lakes, the composition of dissolved substances does not concur with the waters used for the regressions by Chen and Millero.

   An alternative was offered by Bührer and Ambühl (1975) for alpine lakes (in Europe): They used a third order polynomial for density against temperature and added the density of dissolved substances with a linear term for conductivity. This formula at least seems to satisfy the density requirements in several natural lakes, possibly with a small adjustment for the coefficients (e.g. Heinz 1990). The numerical approaches, including the required coefficients, were listed by Boehrer and Schultze (2008).
3. In many cases, these approaches are not accurate enough to calculate density in pit lakes, as the differences due to chemical composition of solutes lead to considerable errors. In these cases, an empirical approach should be used.

   If concentration changes of solutes are found, but the composition of the solutes does not change much, the best approach is probably the following: a lake water sample is investigated for its electrical conductance ($\kappa_{25\text{sample}}$ see Eq. 3.1) and its density over the required temperature range is measured in a densitometer. Usually a forth order polynomial is required to fit the density curve within the accuracy that is delivered from high accuracy densitometers (relative accuracy, e.g. PAAR Graz). A "pure water" sample is also measured in the same densitometer. The density difference between the samples is attributed to the conductivity of the lake water sample, as a measure of the solute concentration. The density formula hence has the general form (e.g. Karakas et al. 2003)

$$\rho = \rho_W + \frac{\kappa_{25}}{\kappa_{25\text{sample}}} \Delta\rho \tag{3.3}$$

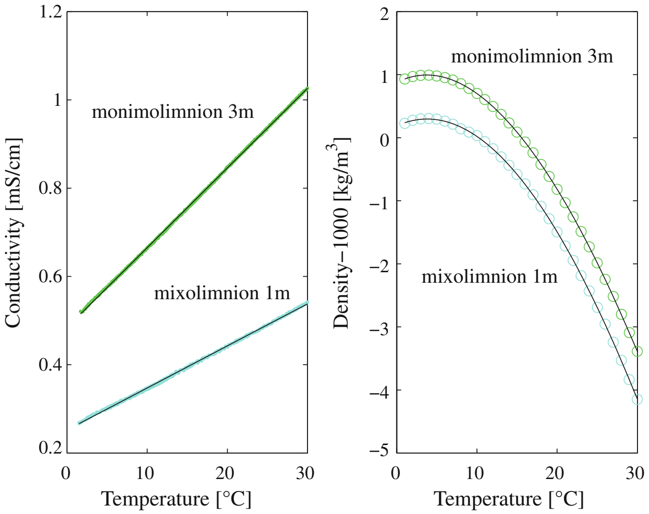


Fig. 3.3 Conductivity (*left panel*) and density (*right panel*) of a mixolimnion sample and a monimolimnion sample from Waldsee, Germany versus temperature (from Boehrer et al. 2009a, with permission of American Geophysical Union)

Nowadays, the pure water reference ρ_W can be taken from Kell (1975) or Tanaka et al. (2001). The density difference $\Delta\rho$ can be a constant or a polynomial in temperature $\Delta\rho(T)$. Conducting a dilution series can improve the accuracy, especially in highly saline systems (e.g. Jellison et al. 1999).

If a lake consists of two layers that differ in their chemical composition, as in meromictic lakes (see below), the gradient can be reflected in the following approach: starting from Eq. 3.3, the lake sample is replaced by the monimolimnion sample (higher conductance from deep waters) and the pure water sample by a mixolimnion sample (lower conductance from shallow waters), e.g. Boehrer et al. (2009a). A density regression $\rho_{\mathrm{mixo}} = \sum_{i=0}^{4} p_i T^i$ (see Fig. 3.3) is produced, and a corresponding ρ_{monimo} for the monimolimnion sample. The density difference between both samples $\rho_{\mathrm{monimo}} - \rho_{\mathrm{mixo}} = \sum_{i=0}^{4} q_i T^i$ is attributed to the higher conductance of the monimolimnion sample.

Now, any sample of conductance κ_{25} can be linearly interpolated for density calculation, under the assumption that any water parcel behaves similar to a linear combination of the samples measured in the laboratory. Thus, a lake-specific density function can be attained for calculating density profiles from field measurements of temperature, T, and in situ conductivity, C (yielding κ_{25} following Eq. 3.1):

$$\rho = \sum_{i=0}^{4} q_i T^i \rho_W + \frac{\kappa_{25} - \kappa_{25-\mathrm{mixo}}}{\kappa_{25-\mathrm{monimo}} - \kappa_{25-\mathrm{mixo}}} \cdot \sum_{i=0}^{4} q_i T^i \tag{3.4}$$

The evaluated coefficients for Waldsee (Boehrer et al. 2009a) are lake-specific and hence have not been listed here.

4. Finally, density of lake waters can be calculated from partial molal volumes of solutes. This approach requires that all substances contributing significantly to density are known. The approach is straightforward, but has not been widely used in limnological practice: adding the masses of water plus the concentrations in molal units b_n of substances of molar mass M_n yield the mass m of the solution, while the volume of water at the respective temperature plus the molal volumes $V_n = \frac{\partial V}{\partial b_n}$ yield the volume V of the solution (Millero 2001, Table 3.19).

$$\rho_{mv} = \frac{m}{V} = \frac{m_W + m_W \sum_n b_n M_n}{m_W/\rho_W + m_W \sum_n b_n V_n} = \frac{1 + \sum_n b_n M_n}{1/\rho_W + \sum_n b_n M_n} \tag{3.5}$$

Molar masses of solutes are easily available, but molal volumes depend on temperature and ionic strength. A numerical approach can be found in the work of Boehrer et al. (2010), where the required coefficients of limnologically important substances are also given. The numerical approach RHOMV can be accessed via the internet (www.ufz.de/webax).

3.1.3 Optical Properties of Lake Water

Due to high concentrations of dissolved substances, mine lakes can have very distinct coloring. Below pH of about 3, ferric iron is soluble in water; a pronounced red color is often encountered. In the aluminum buffered pH range of about 5, mine water can show a turbid blue to turquoise color. Light attenuation in these colored lakes can be very high.

Measurements in Moritzteich show the spectrum of irradiated light against depth (Fig. 3.4), which shows pH values of about 3.2 in the mixolimnion (above 10 m depth). While directly below the surface there is considerable input of near infrared light and near UV, wave lengths below 300 nm and above 750 nm have been (nearly) completely attenuated before reaching a depth of 1 m. Hence light attenuation is a function of wave length. This is also reflected in the perception of water color.

While light intensities of wave lengths between 400 and 700 nm can decrease by 50% from a depth of 0.01–1 m, attenuation is much less below 1 m. At a depth of 2 m, about 80% of the light intensity at 1 m depth can be recorded. Here, light attenuation is also a function of water depth. In conclusion, the common assumption of exponential light intensity decrease with depth is a rough approximation, at least in some cases.

Vertical gradients of dissolved substances result in variable water properties. In the case of meromictic lakes, such a transition can be very sharp, as seen in Moritzteich where water properties go from oxic mixolimnion to anoxic monimolimnion conditions within several decimeters (see Fig. 3.5). While mixolimnetic

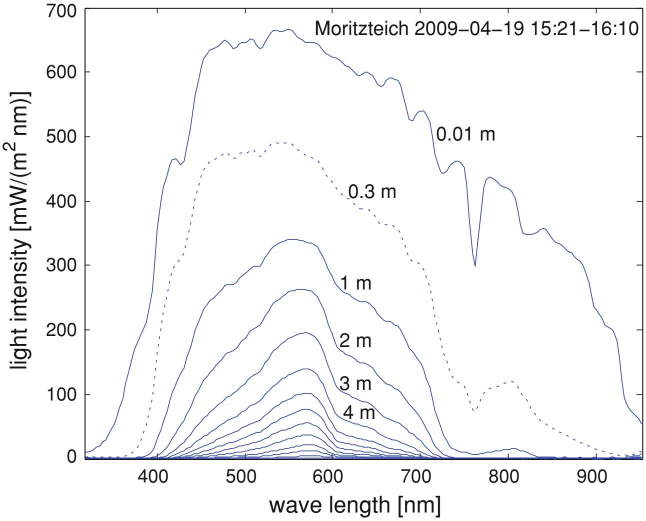


Fig. 3.4 Spectrum of irradiated light in Moritzteich against depth. Interval of solid lines is 1 m, broken line at 0.3 m depth. Measurements were taken under a clear sky in the afternoon between 15:21 and 16:10 Central European Time

waters are clear, monimolimnetic waters have a distinct reddish color, which is attributed to the very high concentrations of iron and dissolved organic matter. A narrow turbid band about 15 cm thick separates the two layers (Figs. 3.5 and 3.6).

Optical properties in these transitions can be investigated more closely with multiparameter probes. Profiles of turbidity (i.e. backscattered white light) and light transmissivity can be acquired. Data from Moritzteich (Fig. 3.5) quantify the optical impression of Fig. 3.6. The turbidity maximum and transmissivity minimum can be seen in acquired data sets at a depth of about 10 m, where oxygen drops from mixolimnetic values to monimolimnetic values and electrical conductivity rises sharply.

In addition to particularly high light attenuation, we can find extremely clear water in acidic pit lakes. Mine Lake 117 represents this type of lake, where visibility is very high, and the lake bed at a depth of about 7 m can be visible from the lake surface. The variability of optical properties in acidic lakes is demonstrated in Fig. 3.7. Light absorption data can be compared for clear Mine Lake 117, a residual turbid, acidic, iron-rich lake (residual lake Niemegk, now part of neutral Lake Goitsche), and a highly acidic, non-turbid, red mine lake (107). In general, the lakes form two groups, where the red color seems to dominate spectral absorption, while the effects of turbidity are reflected in the shallower depths, where similar light intensities are found (see depiction of the spectra in Fig. 3.7).

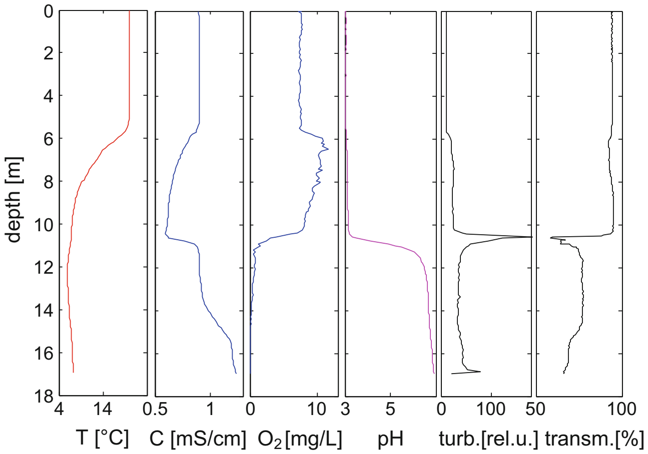
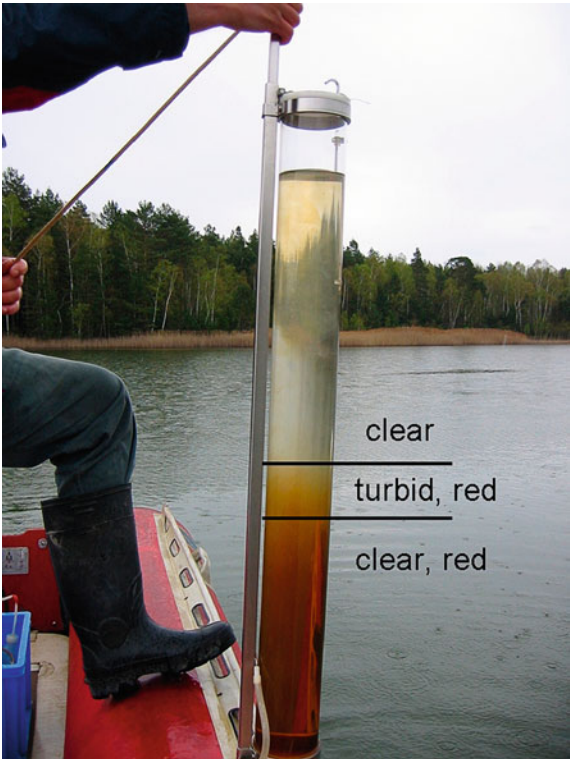


Fig. 3.5 Profiles of temperature, electrical in situ conductivity, dissolved oxygen (numerically corrected for response time of 5.5 s), pH, turbidity, and light transmissivity against depth in Moritzteich on 5th July 2007

Fig. 3.6 Water sample from a depth of about 10 m from Moritzteich, showing the transition from mixolimnion to monimolimnion



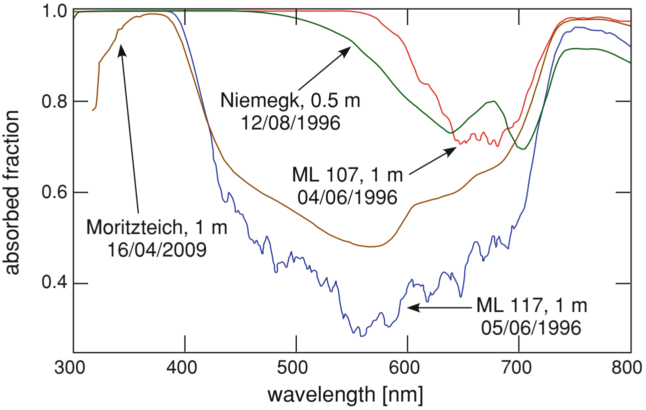


Fig. 3.7 Light attenuation in acidic pit lakes: ML 117: Mining Lake 117 (pH = 3, very clear), ML 107: Mining Lake 107 (pH = 2.4, clear and red) and residual lake Niemegk (acidic, pH = 2.7, turbid red; all data from Schimmele and Herzsprung 2000) in comparison to Moritzteich (mixolimnion pH = 3.2)

3.1.4 Stratification and Circulation

At the surface, lakes are exposed to seasonal changes in weather conditions. Exposed to sensible heat exchange with the atmosphere and irradiation from the sun, surface waters show a pronounced annual temperature cycle (see Fig. 3.8). As diffusive transport through water is slow, deeper layers are shielded from heat input from the atmosphere. Consequently temperature excursions at greater depths are generally much smaller over an annual cycle (Fig. 3.8). For general features of lake stratification, we refer to Boehrer and Schultze 2008.

During stratification, the density at the lake surface is less than in deeper water. As a consequence, vertical exchange of water parcels requires energy. If not enough energy is available to overcome the density difference, the lake remains stratified. Usually a strong temperature gradient (thermocline) is formed. Lower autumn temperatures allow deeper mixing due to falling surface temperatures and higher water density at the surface. As a consequence, the annual cycle of a lake is divided into stratification and circulation periods (see Fig. 3.9).

During stratification periods, vertical exchange of dissolved substances is very much restricted to vertical circulation of the epilimnion in cold and windy periods. Below the thermocline, vertical transport is generally small. In areas of high density gradients, transport coefficients can be close to the molecular level (von Rohden et al. 2009) while at depths that are weakly stratified, transport coefficients can be larger by several orders of magnitude (e.g. von Rohden and Ilmberger 2001).

In small- to medium-size lakes, this turbulent transport mainly happens at the side boundaries where waves and currents interact with the slope of the side walls (Gouldsmit et al. 1997). Turbulence created in the open water only contributes a

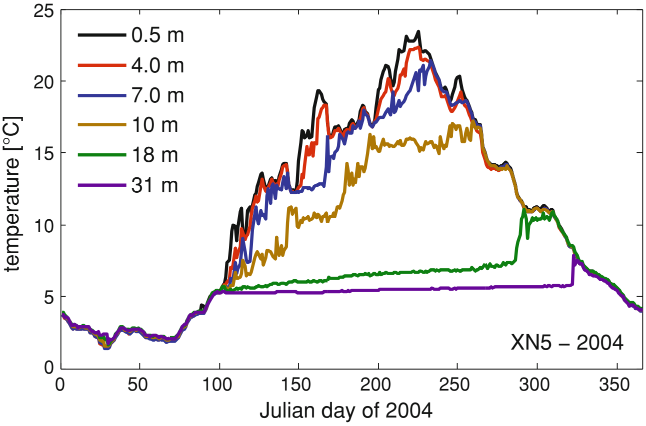


Fig. 3.8 Temperature time series acquired at several depths in Lake Goitsche at sampling site XN5

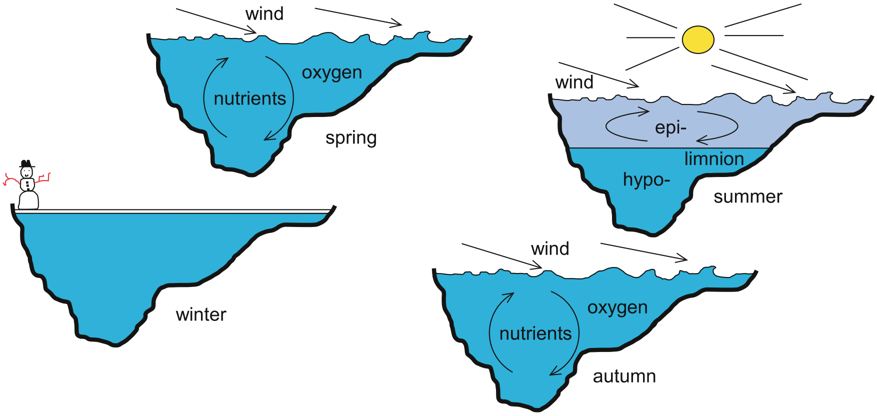


Fig. 3.9 Circulation pattern of a dimictic lake, with a circulation period in spring and autumn, separated by stagnation periods during summer, and periods of ice cover in winter

large portion of the vertical transport in larger lakes (e.g. Lake Constance, Boehrer et al. 2000; Kocsis et al. 1991). As the density gradient is the crucial quantity to overcome, transport coefficients have been correlated with the potential density gradient in the form of a stability frequency

$$N^2 = -\frac{g}{\rho}\frac{\partial \rho}{\partial z} \tag{3.6}$$

for an empirical correlation of transport coefficients under given stratification conditions (Heinz et al. 1990; von Rohden and Ilmberger 2001).

In contrast, during circulation periods, vertical transport happens at a fast rate. Oxygen is supplied to deeper layers of the lake and dissolved substances, which have accumulated in the deep waters during the stratification period, are redistributed through the lake.

If a lake is temperature stratified during summer and covered by ice during winter, it usually experiences two separate stratification periods (stagnation), separated by two deep circulation periods. Such lakes are called dimictic. Usually lakes without an ice cover circulate sporadically during winter under appropriate weather conditions. These lakes are called monomictic, as they show one extended period of stratification and one period of (intermittent) full vertical circulation over an annual cycle.

Only very deep lakes without gradients of dissolved substances can have continuous stratification throughout winter without an ice cover. These lakes may exhibit other specialties of permanent stratification due to pressure effects on the temperature of maximum density (see Crawford and Collier 1997; Petterson 1902; Yoshimura 1936). This kind of stratification has been observed in very deep crater lakes in Japan (Fig. 3.10, Boehrer et al. 2009b), which have a similar shape and size as large mine pits (several kilometres in diameter and depths that can exceed 200 m). Due to the small horizontal dimension, the deep water stratification in these lakes corresponds to model results derived under consideration of horizontal homogeneity and stability criteria (Boehrer et al. 2008).

Deep water renewal by thermobaric instabilities, as postulated for the deep water renewal in Lake Baikal (Weiss et al. 1991), do not play an important role at this size of lake basins. In very deep lakes, the difference between potential temperature and in situ temperature can become important, especially if deep water temperatures differ much from the temperature of maximum density (see e.g. Boehrer and Schultze 2008).

If surface temperatures of a lake never fall below the temperature of maximum density around 4°C, the deep water will have a temperature above 4°C. Hence, these lakes can only circulate vertically when surface waters have cooled sufficiently to overcome the density of the deep water. Due to the variability of winter temperatures, this is not necessarily the case every winter, especially if the lakes are deep. Such lakes are termed oligomictic.

In cases where gradients of dissolved substances contribute significantly to the density stratification, concentrations in the deep water may suffice to prevent a lake from a full overturn (e.g. Findenegg 1933; Hutchinson 1957). Isolated from exchange with the atmosphere, the deepest layers in the lake develop a chemical milieu different from the waters above. Such a bottom layer is called a monimolimnion, contrary to the mixolimnion, i.e. the ensemble of epilimnion and hypolimnion above (see Fig. 3.11). A zone of high chemical gradients, a 'chemocline' separates the two layers. Such lakes are called meromictic, as opposed to holomictic, when a full overturn of the water masses takes place at regular or irregular intervals.

Many lakes in deep mine pits will develop meromictic conditions (e.g. Boehrer and Schultze 2006; Stevens and Lawrence 1997, 1998). Analogies have been reported between volcanic lakes and lakes forming in abandoned opencasts

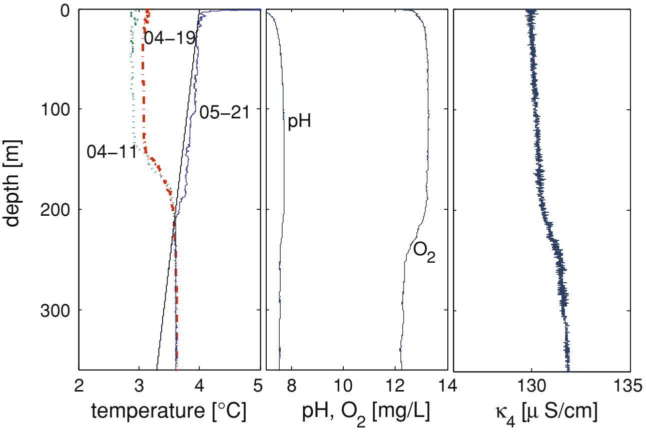


Fig. 3.10 Profiles of temperature, electrical conductivity, pH, and dissolved oxygen in Lake Shikotsu in Japan from 21st May 2005 (and other dates where annotated, modified after Boehrer et al. 2009b)

concerning shape and size (Boehrer et al. 2009b), geochemistry and microbial activity (e.g. Wendt-Potthoff and Koschorreck 2002), and meromixis (e.g. Boehrer and Schultze 2006; Murphy 1997; Sánchez-España et al. 2008; Stevens and Lawrence 2006).

A number of geochemical processes can be involved in sustaining the density stratification (see Table 3.2), including the iron cycle as the most prominent for lakes originating from mining (see Boehrer and Schultze 2006, 2008). In addition, the groundwater connection plays an important role in many meromicitic pit lakes (von Rohden and Ilmberger 2001; Seebach et al. 2008; von Rohden et al. 2009). Quantification and numerical simulation of processes controlling meromixis remain a challenge (Böhrer et al. 1998; Jellison et al. 1998; Heidenreich et al. 1999; Fig. 3.12).

Besides iron, the anoxic decomposition of organic material, manganese, and calcite precipitation must be included in stability considerations. Many other elements experience co-precipitation, when the above-mentioned chemicals form solids in the water column. For a proper meromixis prognostication, a full geochemical model is required. Geochemical models have been developed (Müller et al. 2008; Salmon et al. 2008), but they still require the proper coupling of geochemical processes to density effects to properly reflect the evolution of stratification (Moreira et al. 2011).

In many cases, mining has disrupted an equilibrium that had existed for many centuries or even millennia before. Removal of an overburden and lowering the water table has provided oxygen to layers where input had previously been very low. As a consequence, some mineral deposits have gained mobility, such as metal ions after oxidation of their sulfide deposits. Depending on the paths they have taken before entering a pit lake, groundwaters from various aquifers can greatly vary in their concentrations of dissolved substances. As a consequence, pit lakes in general are exposed to high mineral gradients.

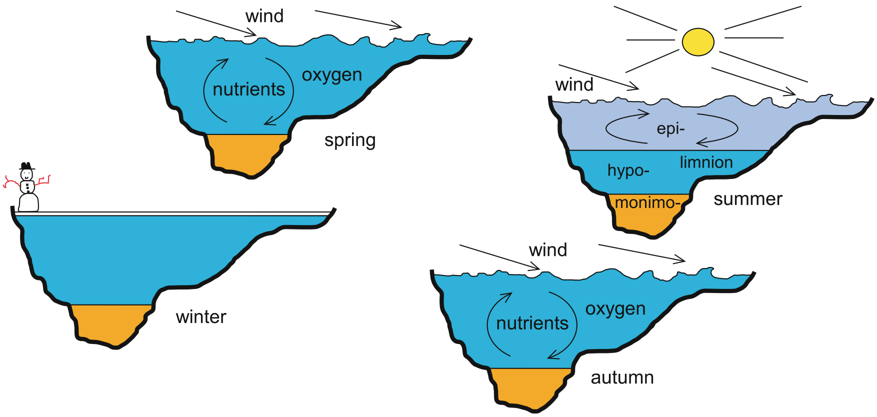


Fig. 3.11 Circulation pattern of a meromictic lake; the chemically different monimolimnion remains in the deepest depression of the lake bed throughout the year

Table 3.2 Documented precipitation processes responsible for sustaining meromixis

Substance	Lake, country	Reference
Sodium sulphate	Shield lakes, Canada	Rawson and Moore (1944)
Organic material	Längssee, Austria	Frey (1955)
Calcite	Lake La Cruz, Spain	Rodrigo et al. (1998)
Iron	Swinsjöen, Norway	Kjensmo (1967)
Manganese	Lake Nordbytjernet, Norway	Hongve (1997)

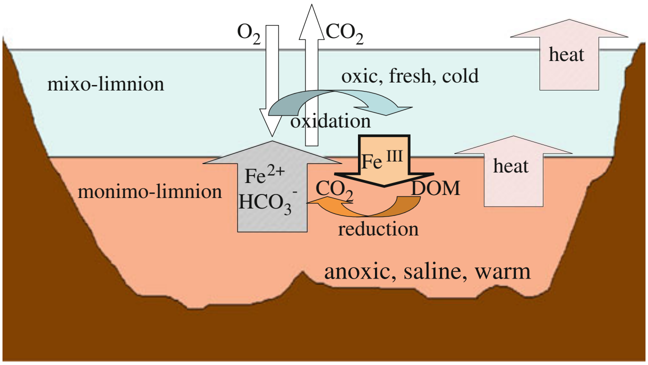


Fig. 3.12 Geochemical cycle sustaining the iron meromixis in Waldsee (from Boehrer et al. 2009a, with permission of the American Geophysical Union)

Monimolimnia, however, do not represent entirely isolated water bodies. There is a certain minimum diffusive exchange with the overlying mixolimnion. In addition, small-scale turbulence may transport dissolved substances across the chemocline.

In many cases, monimolimnia receive inflows from the groundwater domain, and discharge into it (Heidenreich et al. 1999). Pit lakes are young aquatic systems, where time has been short to form a sediment layer that could isolate the lake water from the groundwater domain. As a result, highly dynamic systems are formed that can be closely linked to groundwater flows that may have unusually high gradients.

To confine hazardous substances to deeper waters, it may be desirable to reduce vertical exchange (Schultze and Boehrer 2009). At least in two cases, resulting meromictic conditions have been induced or retained intentionally (Island Copper Mine Lake in Canada: Fisher 2002, Fisher and Lawrence 2006; Lake Vollert-Süd: Stottmeister et al. 1998). In both cases, dissolved substances were considered a hazard to the surface waters. Confined to deeper layers of the water column, they do not pose a danger to the fauna around the lake. In the case of Island Copper Mine Lake, anoxic conditions in the deep water are anticipated after oxygen is depleted, which should induce precipitation of metal sulfides.

Decomposition of organic material and co-precipitation leads to accumulation of dissolved substances in the deep water. These substances contribute to density and thus sustain the presence of meromixis. Accumulation continues until formation is balanced by exports out of the monimolimnion into the mixolimnion or groundwater space. Some of these dissolved substances are gases. In addition to passive transport by the water, gases can escape by forming bubbles, which move due to their own buoyancy. Bubbles form when the sum of partial pressures overcomes the local pressure (e.g. Halbwachs et al. 2004), which essentially is the sum of hydrostatic pressure and air pressure. Concentrations in the water and partial pressures are linked by the so-called Bunsen coefficient.

Amongst gases, carbon dioxide plays a particular role. As its Bunsen coefficient is much larger (≈ 1) than most other gases (≈ 0.01), a much higher volume of CO_2 can be dissolved in water. Above $pH = 5$, part of the carbonate is dissolved as bicarbonate ions or carbonate ions. In addition, the density contribution of CO_2 is positive, while other common gases such as O_2 and N_2 contribute negatively to density, i.e. dissolving oxygen in water decreases the density due to an expanding volume. As a consequence, a water column can be stably stratified due to its increasing CO_2 concentration towards greater depths.

The sudden release of large volumes of dissolved gases has been documented from tropical volcanic lakes. Such limnic eruptions have cost the lives of 1,700 human beings in the neighborhood of Lakes Monoun and Nyos, both located in Cameroon, in 1984 and 1986, respectively. Despite much research, the release mechanisms of these events are not agreed upon.

3.1.5 Waves and Currents in Mining Lakes

Like natural and neutral lakes, acidic lakes are exposed to meteorological forcing. Winds and differential cooling, for example, drive currents and create surface and internal waves. There are differences in the flow behavior of mine pit lakes and

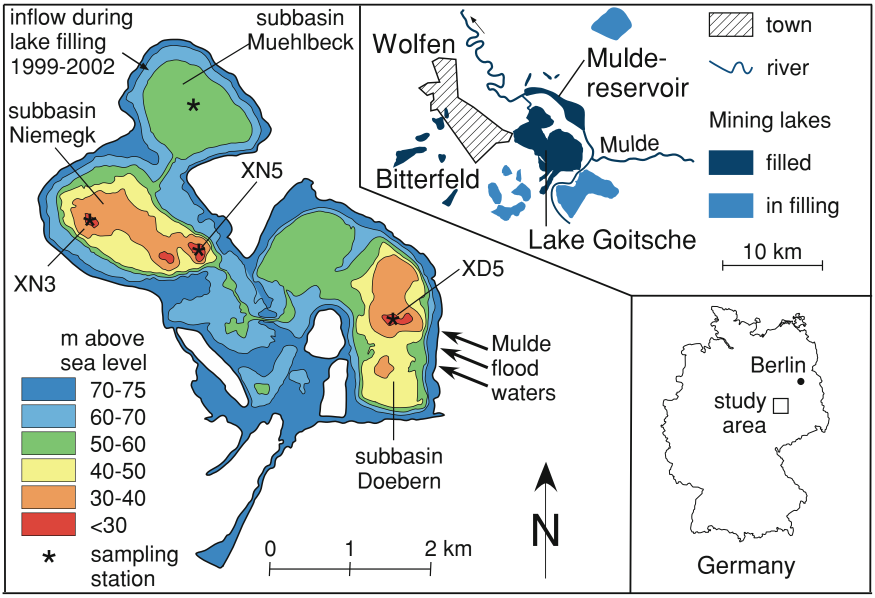


Fig. 3.13 Lake Goitsche and major measuring sites in the lake (map dated 2003; modified after Boehrer et al. 2003)

natural (and neutral) lakes, beyond what was discussed about deep recirculation, which are due in most cases to the morphometric peculiarities of the pits rather than the water properties. In this subsection, we refer to a number of special stratification and flow features that may be encountered in mine pit lakes and which are not commonly discussed when referring to currents in lakes in general. For the general context of currents in lakes, we refer to the literature of physical limnology (e.g. Fischer et al. 1974; Hutter 1987; Imberger and Patterson 1990; Imboden and Wüest 1995).

As mining followed the deposits, many mining lakes are subdivided at depth into basins, connected across sills that extend close to the surface (e.g. Mining Lake 111). This basin structure can result in different water conditions in the deep depressions as exchange between basins is very restricted below the sill depth (e.g. Boehrer et al. 2003, 2005). Between 1999 and 2006, Lake Goitsche contained meromictic patches in some places (e.g. XN3 see map in Fig. 3.13), while even deeper depressions of the lake basin (XN5, XD5) were filled with mixolimnetic waters (Boehrer et al. 2003).

Internal waves may be able to lift water from a greater depth across a sill (“internal wave pumping”, Van Senden and Imboden 1989). The excursion height and the amount of water that will cross a sill from a lower location are limited by the amplitude of internal waves and the number of events in a certain time period.

When lakes are stratified, internal seiches can form. Usually, the first internal vertical mode dominates the water movements in a lake during stratification periods. If the equilibrium position is disturbed by the surface stress of wind, the

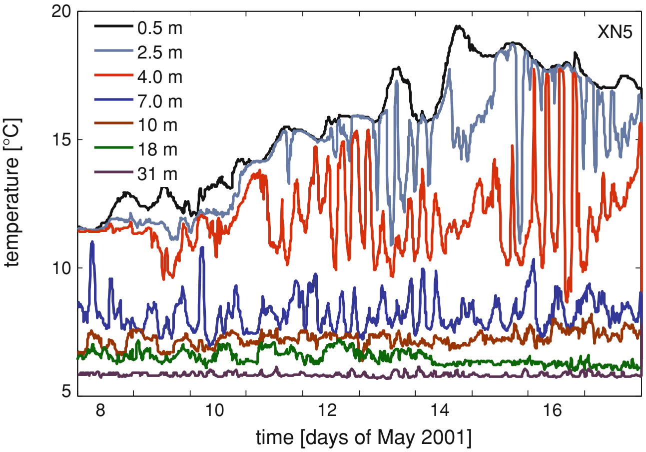


Fig. 3.14 Temperature time series at several depths in Lake Goitsche, subbasin Niemegk (position XN5), showing oscillations

cessation of the wind will result in internal waves, where the epilimnion and hypolimnion usually move in opposite directions in a frequency determined by the lake morphometry and the density stratification of the water column. At a fixed position, temperature oscillations of a distinct frequency can be recorded (Fig. 3.14). Higher modes have also been reported, and in a few cases, they are dominant (Vidal et al. 2005), but usually, their influence on currents is small, and can be quantified numerically (Boehrer 2000).

Lake Goitsche consists of several subbasins, which were interconnected by channels for the flooding procedure. By the year 2001, the subbasins had reached a common water surface, slightly greater than 70 m above sea level (see Fig. 3.13). The thermocline of the subbasin Niemegk (between 7 and 10 m water depth, Fig. 3.14) lay below the sill depth of the neighboring Mühlbeck and Döbern subbasins. Interfacial waves on the thermocline (i.e. first mode internal waves), were not able to leave the basin. The internal wave recorded at location XN5 had a period of 4 h. This oscillation period was clearly related to the size of the Niemegk subbasin. The oscillation of the thermocline induced currents in the epilimnion (and hypolimnion). However, as the thermocline oscillation was confined to the subbasin, surface currents must have felt the sill although they flowed clearly above the sill depth.

Boehrer and Stevens (2005) pointed out that the distribution of kinetic energy may be affected by the fact that reflection conditions for internal (ray) waves in many mine lakes are different than in natural lakes. Natural lakes typically have a shallow near-shore zone that acts as a ray wave trap (e.g. Turner 1973). In addition, benches left from mining produce even steeper walls. Furthermore, such benches act as discrete locations that can create internal wave rays of defined wave length and imposed frequency, such as the internal seiche in Island Copper Mine Lake. The observed turbulence pattern below the chemocline (Stevens et al. 2005) may be connected to the uniform wavelength (Boehrer and Stevens 2005).

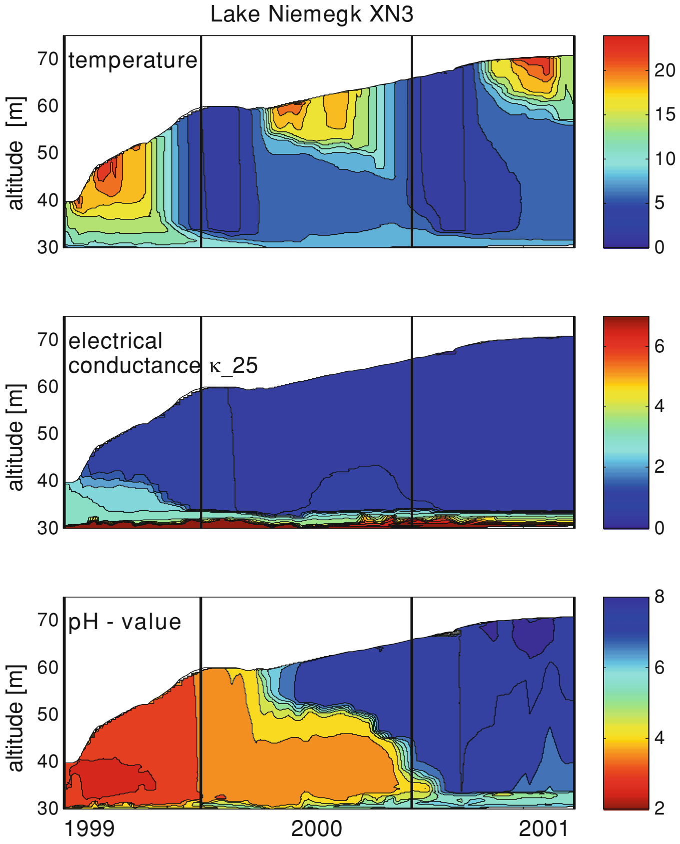


Fig. 3.15 Contour plots of temperature (in °C), electrical conductivity at 25°C (in mS/cm), and pH at measuring site XN3 over the period of regular flooding of the Goitsche pit (modified after Boehrer et al. 2003)

3.1.6 Mixing and Vertical Transport

Gradients of dissolved substances can be sustained for longer time periods, if density stratification restricts vertical transport. This was verified when the previously acidic residual lake Niemegk was filled with river water to reduce acidity. While the introduced flooding water had neutralized the epilimnetic waters within a short time period during 2000, the deep waters retained their low pH until deep recirculation later during the year allowed for vertical exchange of dissolved substances, such as buffering chemicals, into the deeper water (Fig. 3.15, Boehrer et al. 2003). Gradients of pH are stable over longer time periods only where density gradients reduce vertical mixing.

Meromictic lakes can show especially high vertical density gradients. Von Rohden and Ilmberger (2001) measured the spreading of an introduced tracer

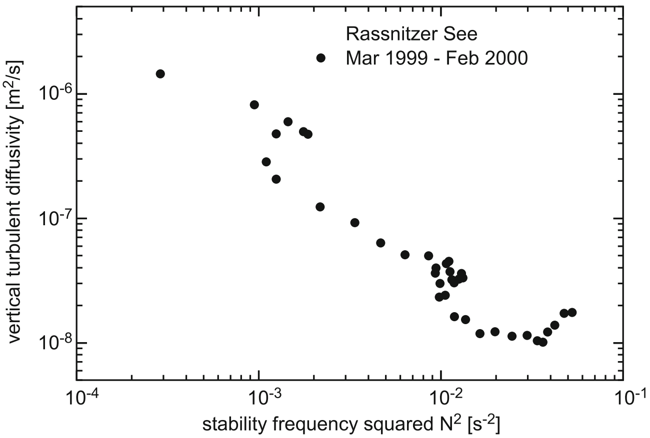


Fig. 3.16 Vertical diffusivity versus stability (modified after von Rohden and Ilmberger 2001)

cloud over periods of two years and calculated vertical transport coefficients from their measurements. A strong correlation of vertical diffusivity and density gradient could be verified. High gradients in the deep waters limited vertical transport to values little above molecular diffusion (Fig. 3.16; von Rohden and Ilmberger 2001; von Rohden et al. 2009).

Goudsmit et al. (1997) showed that in a lake that is several kilometers long (Alpnacher See), nearly all mixing happened along the side boundaries. Even in lakes as large as Lake Constance, mixing due to friction and shoaling at the side walls can still overcome pelagic mixing (Boehrer et al. 2000; Kocsis et al. 1998). Hence, the generally steep side walls in mine pits can affect vertical mixing. And, as mentioned above, the steepness of sidewalls and benches can produce different wave patterns and can alter distribution of internal wave energy at depth.

Transport can be established by double diffusion. This occurs when two species of different diffusivities contribute to density, one in a stabilizing and one in a destabilizing configuration. In meromictic lakes especially, we find examples where the temperature and concentration of dissolved substances both increase with depth. This usually results in staircases of temperature and conductivity profiles (Newman 1978; Schmid et al. 2005). This process is well established in tropical lakes, but has also been discovered in meromictic lakes of the temperate climate zone (von Rohden et al. 2010; case study 5.3).

Despite the overall stable density stratification in meromictic lakes, double diffusion can greatly enhance vertical transport (Brandt and Fernando 1995; Schmid et al. 2005). If temperature increases with depth, and hence opposes the density gradient implied by dissolved matter, the previously continuously density stratified water column is broken up into convection layers alternating with layers of high gradients.

Double diffusion also happens at chemoclines, where waters of different properties meet. In the case of Waldsee near Döbern, the density difference can be largely due to dissolved ferrous iron in the monimolimnion, which cannot enter the oxic mixolimnion, as biochemical oxidation will cause it to precipitate back into the monimolimnion (Boehrer et al. 2009a). The configuration approaches the case of two immiscible layers in thermal contact (Fig. 3.12). As a consequence, double diffusive convection cells are not restricted to the step size derived for conservative salts (e.g. Federov 1988), and a full monimolimnetic overturn has been observed, resulting in the redistribution of dissolved substances within the monimolimnion (Boehrer et al. 2009a).

3.1.7 Concluding Remarks

Pit lakes have quite a few peculiarities. This section has discussed special features of pit lakes that are not usually covered sufficiently in books about limnology. Some of these aspects have developed from site-specific solutions to more general considerations, e.g. temperature compensation of electrical conductivity, and the implementation of density functions based on partial molal volumes in numerical models. The effect of (biogeo-)chemical transformations on stratification still needs to be quantitatively investigated. Numerical models must be developed and used to improve prognostication of the evolution of water quality in pit lakes and to demonstrate remediation strategies for pit lakes. Such prognosticative tools may also prove useful for predicting changes in "natural" lakes that may result under change of use and climate variability.

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3.2 Limnochemistry of Water and Sediments of Acidic Pit Lakes

3.2.1 Pit Lakes from Coal and Lignite Mining

3.2.1.1 Water, Sediment, and Pore Water

Kurt Friese, Peter Herzsprung and Martin Schultze

Introduction

Hard coal and lignite are important raw materials for energy and steel production. Coal provides 26.5% of global primary energy needs and generates 41.5% of the world's electricity. Over 5,560 million tons (Mt) of hard coal and ca. 890 Mt of brown coal/lignite are currently produced worldwide. There are over 847 billion tons of proven coal reserves worldwide and recoverable reserves in about

Table 3.3 Top ten coal and lignite producers and worldwide production in 2008 (Mt—million tonnes; from Statistik der Kohlewirtschaft 2010)

Hard coal	(Mt)	Lignite	(Mt)
China[a]	2,586	Germany	175
USA	1,000	Russia	76
India	436	Turkey	71
Australia	334	USA	68
Russia	247	Australia	67
Indonesia	150	Greece	63
South Africa	250	Poland	59
Kazakhstan	104	Czech Republic	47
Poland	84	Serbia	36
Colombia	70	Romania	35
World	5,562	World	892

[a] including lignite

70 countries (World Coal Institute 2009). About 47% of power generated in Germany (the world's largest lignite producer), is provided by coal and lignite whereas, for example, in Poland, it exceeds 90% (Euracoal 2009). Hard coal and lignite is the principal source of energy production for several countries in Europe and elsewhere (e.g. Australia, China, India, Indonesia, Republic of South Africa, Russia (and the former states of the USSR), USA, and to a lesser extent, other countries in Africa, Asia, and Latin America). Table 3.3 shows the 10 major coal and lignite producing countries.

This chapter provides an overview of the chemistry of water and sediment in pit lakes from former coal and lignite open cast mines, mainly by comparing results from Australia, Germany, Poland, and the United States. Results of studies on pit lake water chemistry from India are considered as well. Generalized results of the chemistry of sediments and their pore waters were mainly deduced from studies on Australian and German pit lakes because comparable results were not found elsewhere. A review paper covering water chemistry and sedimentary processes of acidic coal mine pit lakes in Germany was published recently by Blodau (2006).

The geological conditions that lead to the formation of lignite and hard coal, mainly the anoxic conditions in the presence of sulfur and iron in a brackish environment, also favor the formation of pyrite or marcasite (FeS_s), and to lesser extent, mackinawite (FeS). Hence, lignite and hard coal deposits are often accompanied by pyrite/marcasite in the strata. The content and distribution of pyrite can vary over a broad range from 0.1 to 5% by weight (e.g. Knöller et al. 2004; Ludwig and Balkenhol 2001; Ludwig et al. 1999; Rolland et al. 2001; Seoane and Leiros 1997; Tiwary 2001) in disseminated occurrence, concentrated in clusters or in scattered pockets (Evangelou and Zhang 1995) depending on the mechanism of pyrite formation (e.g. syngenetic or epigenetic). Therefore, it is not surprising that mining opens the pathways for the oxidation of this pyrite. Surface mining needs dry conditions; consequently, before a mine pit can be opened, the groundwater table has to be lowered to an appropriate depth below the coal seams.

This is the first step in exposing the pyrite to oxygen, which afterwards is accelerated when the strata and coal are excavated.

When the mine is closed and operations cease, groundwater pumping, which normally is contemporaneous with increasing depth of the mine pit, stops. Consequently, the groundwater table rebounds until hydrological equilibration is reached. The ascending groundwater enters the pit by passing through the dewatered strata. On its way, the groundwater transports the products of pyrite oxidation, mainly sulfate, iron, and acidity (see Sect. 2.2) or dissolves secondary minerals that might have formed, in particular in overburden dumps.

The hydrochemistry of coal mine pit lakes is the result of the geological background, the hydrologic situation, the amount of sulfur within the strata, the extent of pyrite oxidation, and the mining technology used (e.g. Blodau 2006; Rolland et al. 2001; Wisotzky and Obermann 2001). Consequently, lake water chemistry has to be generalized with care and several exceptions might exist.

Pit Lake Water Chemistry

The first examples of strip mine pit lake water chemistry were from hard coal mining in the USA and were published by Campbell and Lind (1969), Campbell et al. (1964), and Parsons (1964), based on initial studies of Crawford (1942; cited in Campbell et al. 1964) and Heaton (1951, cited in Campbell et al. 1964) from coalfields in the Cedar Creek region of Missouri. Parsons (1964) described six acid strip mine pit lakes with a pH between 2.5 and 3.0 and ferric iron concentrations from 1 to 300 mg L^{-1} and sulfate concentrations from 2000 to 8,400 mg L^{-1}. Typically, all these lakes could be classified as acidic, hard water lakes of the Ca–SO_4-type. The Al concentrations in these lakes were quite high, ranging from 96 to 183 mg L^{-1}. In the same region (about 20 km north of the lakes investigated by Parsons (1964), Campbell et al. (1964) and Campbell and Lind (1969) investigated five acid strip mine pit lakes over a period of five to six years. The pH of these lakes ranged from 2.3 to 8.2. The concentrations of dissolved substances depended on the pH and on the depth of water sampling, showing increased concentrations with lower pH and greater depth. The maximum concentrations reported by Campbell et al. (1964) were 4,350 mg L^{-1} of ferric iron, 7,600 mg L^{-1} of sulfate, and 83 mg L^{-1} of manganese, whereas Campbell and Lind (1969) reported 426 mg L^{-1} of aluminum and 217 mg L^{-1} for zinc as maximum values from the bottom of the most acidic pit lake from this series. According to Campbell et al. (1964), similar conditions of strip mine pit lake water chemistry could be expected for coalfields in Arkansas, Oklahoma, Kansas, and Iowa from the same geological formation.

The first summary of existing and expected pit lake water chemistry of hard coal mines in the western USA was given by Miller et al. (1996). The main ion composition of these lake types defines them as Ca–SO_4 waters with high iron contents in the range of 200 mg L^{-1}. Due to the low sulfur content of the hard coal deposits in Montana, Wyoming, and Dakota (an average of about 0.6% S, Turbak et al. 1979) and alkaline groundwaters, most of these hard coal mine pit lakes have a neutral pH (Anderson and Hawkes 1985). Similar observations were reported from a set of coal mine pit lakes from Illinois (Gibb and Evans 1978, cited in Castro and Moore 2000).

Further sets of geochemical data were available from 14 pit lakes in former hard coal mines in the Collie region in Western Australia (Lund and McCullogh 2008; Salmon et al. 2008; McCullough et al. 2010; see also case study 5.4), from 71 pit lakes in former lignite mines in Western Poland (Samecka-Cymerman and Kempers 2001; Solski and Jedrczak 1990, 1991a, b; see also case study 5.2) and from even more pit lakes in former lignite mines in Germany (for data sources and further details, see case study 5.1). These data are used to illustrate how the concentrations of dissolved substances are related to pH (Fig. 3.17 a–c). The ranges within the datasets are compared and discussed (Figs. 3.18 and 3.19).

The solubility of many constituents increase with decreasing pH, in particular carbonates, metal (hydr)oxides, and silicates. Magnesium (Fig. 3.17a), aluminum, the heavy metals including iron (Fig. 3.17b), and silicon (Fig. 3.17c) follow this pattern. Whereas ferric iron and oxidized manganese species increasingly precipitate with increasing pH, concentrations of iron and manganese can still be elevated under neutral conditions due to the high solubility of iron(II) and manganese (II) at anoxic conditions. Figure 3.17 a–c shall be used for a brief discussion of some fundamental biogeochemical rules in pit lake water; these rules are well established in geochemistry and have been discussed in more detail by Eary (1999).

The relevance of iron and aluminum buffering in pit lakes has often been demonstrated (e.g. Totsche et al. 2004; Uhlmann et al. 2004). Totsche et al. (2006) demonstrated that zinc also may buffer pH. However, those investigations were done in water originating from a waste rock dump of a Canadian base metal mine. In pit lakes resulting from coal and lignite mining, only iron and aluminum reach concentrations high enough to form relevant buffering systems.

Calcium, sodium, and potassium (Fig. 3.17a) do not show a clear concentration dependence on pH. This may be due to the formation of secondary minerals, such as gypsum and jarosite. In the case of German pit lakes, another reason is the intrusion of saline groundwater from Permian salt deposits into some of the pit lakes (see case study 5.1). For at least some of the Australian pit lakes, the diversion of highly saline water into lakes from the local rivers during the first flush at the beginning of the wet season would have likely disrupted any relationship between these cations and pH. The source of the salt in the river water was agricultural land use (McCullough et al. 2010), which is causing salinization of soil, groundwater, and river water in many regions of Australia. For more details on the mechanisms behind this phenomenon see e.g. Jolly et al. (2001). The absence of any relationship of chloride concentrations to pH supports this conclusion (Fig. 3.17a).

The decrease of sulfate concentrations with increasing pH (Fig. 3.17a) probably reflects that less pyrite oxidation occurs in certain lake catchments, which therefore have higher pH-values and lower acidities. To some degree, this might also

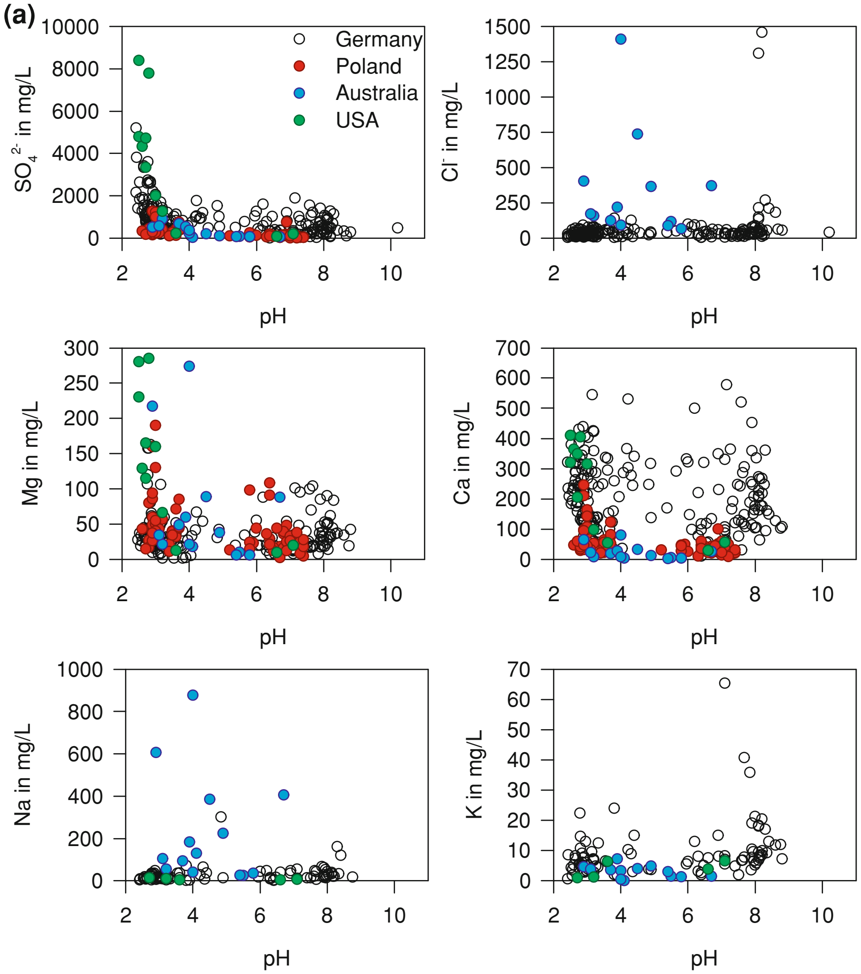


Fig. 3.17 Compilation of water chemistry data versus pH for pit lakes from Germany, West Poland, the Collie region (Australia), and the Cedar Creek region (USA). **a** Sulphate, chloride, magnesium, calcium, sodium, and potassium. **b** Acidity, Fe, Al, Mn, Zn, and Cu. **c** Ammonia, nitrate, SRP, TP, DOC, and Si

explain similar behavior of other constituents. In addition, pit lakes that became neutral over time due to natural flushing by neutral superficial and subsurface inflows are usually diluted with respect to all water constituents.

The decrease of ammonia concentrations with increasing pH (Fig. 3.17c) can likely be attributed to the inhibition of nitrification under acid conditions. Lignite is believed to be the source of ammonia in acidic pit lakes resulting from lignite mining. In former hard coal mines, where blasting is a common step in mining, explosives are probably the main source for ammonia. However, the missing inhibition of nitrification at neutral pH obviously did not result in a strong increase

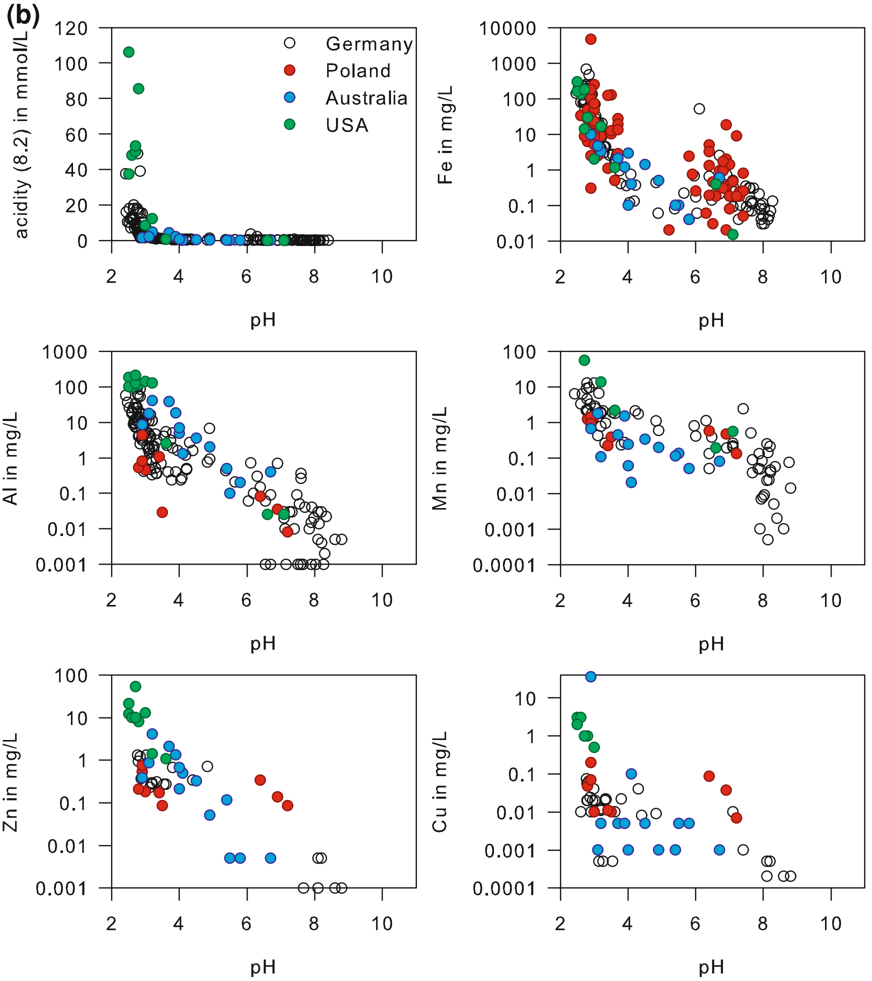
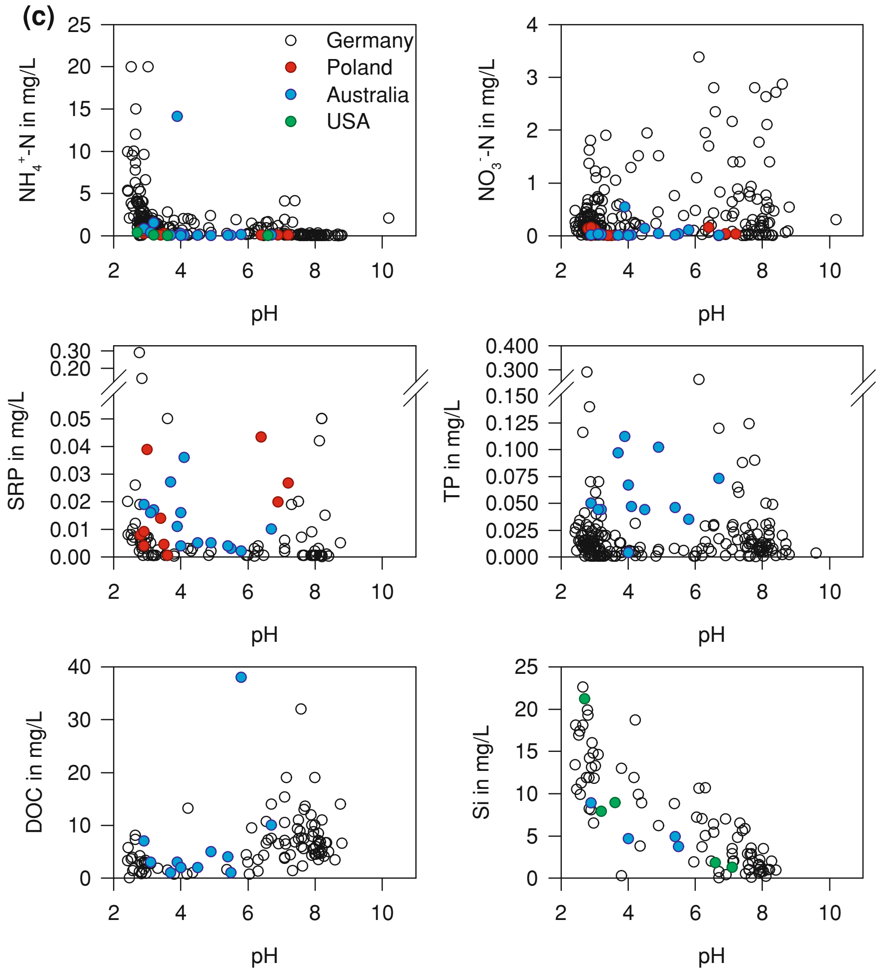


Fig. 3.17 (continued)

of nitrate with increasing pH (Fig. 3.17c). Other microbial processes, like uptake of nutrients and denitrification, may have also influenced the concentrations of nitrate.

The relation of pH to the concentration of dissolved organic carbon (DOC) is also not well understood (Fig. 3.17c). The increase of DOC at pH above 5 may result from better solubility of humic acids at higher pH and from less intense co-precipitation of organic compounds with precipitating iron and aluminum due to the much lower availability of the metals at neutral pH. Furthermore, the oxidation of organic carbon, i.e. its consumption during photo-reduction of ferric iron, is occurring only under acid conditions. The concentrations of SRP and total phosphorus (TP; Fig. 3.17c) are generally low. This is due to their strong binding



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to surfaces of precipitates of iron and aluminum (see Sect. 3.2.1.3). In the few cases where high concentrations occur, source contributions (i.e. high loads from the catchment areas, inflow of waste water, inadequate fishery) rather than pH was apparently responsible.

In summary, there are no clear differences obvious between the relationships of ion concentrations to pH for the compared mining regions.

Figures 3.18 and 3.19 compare the ranges of the data from the pit lakes in Australia, USA, Poland and Germany. There are several close similarities between the German pit lakes and the pit lakes in western Poland. In addition to the fact that both groups of lakes originate from lignite mining, the Polish lakes belong to a geological structure, a moraine arc formed by Quaternary glaciation (Kupetz

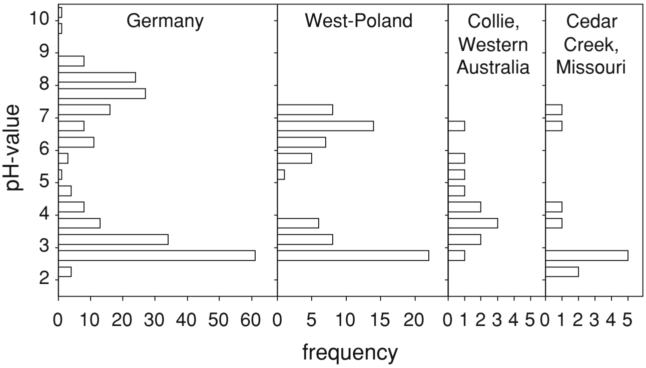


Fig. 3.18 Comparison of the frequency distributions of pH in pit lakes from Germany (data sources described in case study 5.1), from West Poland (data from Solski and Jedrczak 1990; Samecka-Cymerman and Kempers 2001), from the Collie region of Western Australia (data from McCullough et al. 2010) and from the Cedar Creek region in Missouri (data from Parsons 1964; Campbell and Lind 1969). Note the different scales for the frequency

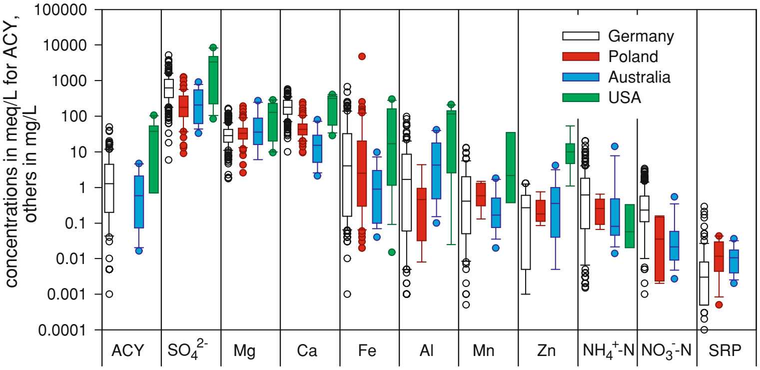


Fig. 3.19 Comparison of concentrations of major constituents characterizing the water chemistry in pit lakes from Germany (data sources described in case study 5.1), from West Poland (data from Solski and Jedrczak 1990; Samecka-Cymerman and Kempers 2001), from the Collie region of Western Australia (data from McCullough et al. 2010) and from the Cedar Creek region in Missouri (data from Parsons 1964; Campbell and Lind 1969). Lines within the boxes are median values, box limits 25 and 75%, and whiskers show the 10 and 90% values, respectively. ACY—acidity. Please note the different number of values behind the plots: 121–221 for the German pit lakes, 9–71 for West Poland, 12 for the Collie region and 4–11 for the Cedar Creek region

1996), that crosses the border into Germany. Lignite was mined there very early, mainly during the first half of the 20th century, since the seams reached the surface as a result of deformation by the pressure of the glaciation.

The frequency distribution of pH in the pit lakes in all of these regions had a statistical mode in the acidic range (Fig. 3.18). In Germany and in Missouri, the pH range indicated buffering by iron. The maximum frequency distribution of pH in the pit lakes of the Collie region lay at higher pH, which is closer to the pH range typical for buffering by aluminum. Only the Polish and the German pit lakes showed a second maximum in their pH frequency distribution in the neutral range. It could be that the datasets from the Collie region and from the Cedar Creek region were not large enough to show a second maximum. Alternatively, the relative absence of neutral pit lakes in the Collie and Cedar Creek regions may be due to the limited age of the pit lakes at the time of the investigation and the lack of broad remediation programs, comparable to those conducted in Germany during the last 20 years (see case study 5.1). The findings of Campbell et al. (1964) and Campbell and Lind (1969) support this assumption. They found that pH increased in three of the investigated lakes from 1940 to the 1960s due to natural processes like long term wash out, natural buffering by slow weathering processes (e.g. dissolution of silicates), and microbial alkalinity production by sulfate reduction.

On average, i.e. according to the median, the pit lakes in Missouri showed the highest concentrations of the solutes in Fig. 3.19, except for ammonia. The concentrations of acidity, sulfate, calcium, iron, and manganese all followed the same pattern: the highest concentrations were found in the pit lakes in Missouri, with intermediate concentrations in Polish and German pit lakes, and the lowest concentrations in the pit lakes in Western Australia. The concentrations of magnesium, aluminum, and zinc followed different patterns. Data on the concentrations of dissolved organic carbon (DOC) and the nutrients nitrogen and phosphorus were only available for the pit lakes of Germany and the Collie region in Western Australia (Figs. 3.17, 3.19). The occurrence of many neutral pit lakes in Germany is assumed to be one reason for the higher concentrations of DOC and nitrate in the German pit lakes. The embedding of the German pit lakes in sand and gravel additionally allows more intense interaction between remnant lignite in the overburden and the groundwater than is possible under the hydrogeological conditions of the Collie region (hard coal, sandstone, mudstone, shale). This probably also contributed to the lower concentrations of ammonia in the pit lakes of the Collie regions. The reasons for the differences in soluble reactive phosphorus (SRP) are not known. The different geological conditions of the various mining regions (hard coal in Missouri and Western Australia versus lignite in West Poland and Germany, and the different ages of the coal and lignite (Carboniferous in Missouri, Permian in the Collie region, and Tertiary in Poland and Germany)) probably contribute to the other notable differences in water quality, as do the different ages of the pit lakes at the time of their investigation and differences in how they were filled (natural rebound of groundwater or flooding with river water).

Published hydrochemical data from coal mine pit lakes outside of the United States of America, Australia, Poland, and Germany are rare. Denimal et al. (2005) reported on three pit lakes in former coal mines at the north-eastern edge of Massif Central (France). The lakes had a circumneutral pH and two of them were meromictic. Sulfate concentrations ranged from 500 mg L^{-1} to 1,500 mg L^{-1}. Iron concentrations were low at the surface (0.01–0.11 mg L^{-1}) and at depth (0.06–0.3 mg L^{-1}), whereas manganese concentrations were at rather typical levels (0.02–0.2 mg L^{-1} at surface, 1.4–4.5 mg L^{-1} at depth). Water chemistry comparable to the German lignite pit lakes was reported from acid mine waters (not pit lakes) from coalfields in India (Singh 1988; Tiwary 2001). Furthermore, there are also several coalfields in India producing neutral and less contaminated mine waters (e.g. Choubey 1991; Gupta 1999; Khan et al. 2005; Tiwary 2001). Similarly, few data (only sulfate and zinc) were given by Geldenhuis and Bell (1997) for acid overspill water (pH range 2.0–3.4) collected in control reservoirs of the Loubert Mine in South Africa (Witbank coalfield, eastern Transvaal). Although, electric conductivity (EC) in these overspill water was in the same range as EC values measured in lignite mine pit lakes of Germany (e.g. 2–6 mS/cm), sulfate and zinc concentration were much higher in the overspill water (up to 5 g/L and up to 4.7 mg/L, respectively).

Sediment Chemistry

The authigenic sediments from coal mine pit lakes are generally very fine grained with a near-surface (upper 5–10 cm) high water content (>40%; Friese 2004; Friese et al. 1998b). In several cases, water contents of 60–80% were detected in the top 5 cm (e.g. Fritz and Carlson 1982; Langner 2002). The amount of in-lake sedimentation depends strongly on local conditions (e.g. amount and rate of groundwater inflow or precipitation). As much groundwater and seepage or drainage water enters the lake, precipitation of solid phases from the oxidation of pyrite and—if they exist—secondary minerals will occur. Typical sedimentation rates are on the order of 5–10 mm/y (deduced from 10 to 20 cm sediment layers in 10–40 years old pit lakes; e.g. Bachmann et al. 2001; Friese 2004; Friese et al. 1998b; Peine 1998; Peine and Peiffer 1996, 1998; Peine et al. 2000).

The main component of the sediment is often iron (iron oxides, hydroxides, and hydroxosulfates), ranging from only 5% to 45% of the dry weight (Bachmann et al. 2001; Blodau et al. 1998; Brugam et al. 1988; Lessmann et al. 1999; Meier et al. 2004; Peine et al. 2000). Other major components are generally Si, Ca, Mg, Na, K, and Al (Friese 2004; Friese et al. 1998a, b; Read et al. 2009). All of these can be attributed to the dissolution of silicates, like quartz, feldspar, or clay minerals. Mineralogical analyses of sediments from coal mine pit lakes are scarce in the literature. Göttlicher and Gasharova (2000) described the precipitation of goethite and jarosite as the main iron precipitates in the lignite mine pit lake ML-111 (see also case study 5.6), whereas Peine et al. (2000) found mainly schwertmannite in mine pit lake 77 from the same German mining district. Our own mineralogical analyses (not yet published) of sediment cores from the Lusatian mine pit lakes ML-111 and ML-107 confirm the precipitation of iron hydroxosulfates, like K-jarosite, and of iron-oxides like goethite (Table 3.2) in the upper 15–20 cm of the lake sediments. Quartz and clay minerals are also common throughout the lake sediments. Geochemical analyses by XRF (X-ray fluorescence) show that iron predominates in these sediments.

A generalized sequence of typical sediment from the acid lignite mine pit lakes of Lusatia (Germany) is given in Table 3.4. Often, the top 1–2 cm layer of the

Table 3.4 Typical sequence of the sediment structure and composition in acid pit lakes of the Lusatian lignite mining district, Germany

	Unit	Depth (cm)	Color	Structure	Grain size	Main mineralogy	Main geochemistry
	1	0–2	Red–brown	Without any texture	Fine clay	Amorphous or less crystalline; Fe-hydroxosulfates (jarosite, schwertmannite)	Water content: 70–80%; LOI: 20–40 wt%; Fe_2O_3: 30–45 wt%; SiO_2: ≈ 10 wt%
	2	2–3	Black	Without any texture	Fine clay	Amorphous or less crystalline FeS, FeS_2, Me(Zn, Ni)S	Water content: 70–80%; LOI: 20–40 wt%; Fe_2O_3: 10–20 wt%; S: 2–3 wt%
	3	3–20	Reddish yellow to brown	Laminated	Clayey	Fe-oxides, Fe-hydroxides, Fe-hydroxosulfates, clay minerals, quartz, feldspar	Water content: 60–70%; LOI: 20 wt%; Fe_2O_3: 10–30 wt%; S: 1–2 wt%; Al_2O_3: 5–10 wt%
	4	>20	Grey	Grained	Silty to sandy	Quartz, feldspar	SiO_2: >80 wt%; Al_2O_3: 10–15 wt%

Please note that differences in the thickness of units occur from lake to lake as well as within a particular lake depending on the bottom morphology and the individual sedimentation. Additionally, unit 1 is not observed in every lake sediment is a very fluffy and water-rich layer of freshly precipitated iron hydroxosulfates. The form of the iron precipitated from the water column strongly depends on the pH-Eh conditions (e.g. Stumm and Morgan 1996). Since iron is a key factor in the water–sediment system for this type of lake, the iron cycle is described in detail separately (Sect. 3.2.1.2). In several cases, this layer is not apparent and the top unit consists of a very dark black, water- and organic-rich, strongly reduced layer (named unit 2 in Table 3.4) that is enriched with reduced sulfur compounds like FeS, FeS_2, and probably other metal sulfides (ZnS, NiS). The occurrence of reduced sulfur compounds and the precipitation of secondary iron sulfides within this layer were proven by sulfur isotope measurements (Fauville et al. 2004; Knöller et al. 2004). However, most of the sediment is a unit of laminated precipitates of iron-hydroxosulfates, -oxides and -hydroxides, quartz, and clay minerals (unit 3 in Table 3.4). Since this laminations is very fine (within the mm to sub-mm range), it is not yet clear what causes the lamination (Table 3.4).

In general, trace elements are of minor importance in German lignite mine pit lake sediments. As, Cd, Co, Cu, Cr, Pb, and Zn all display mass concentrations below 50–70 mg/kg (dry weight). In some cases, there is a close positive correlation found between iron and arsenic, iron and copper, and iron and cobalt within the depth profiles of the sediments, which is probably the result of co-precipitation onto iron-hydroxides/hydroxosulfates. On the other hand, in sediment cores with strong anoxic conditions and a pronounced unit 2 (Table 3.4), positive correlations can be found between S and Ni and S and Zn within the top 5 cm due to precipitation of metal sulfides, as mentioned above. Similar high correlations between S and Cu and Ni were reported by Brugam et al. (1988) from near-surface sediments of coal mine lakes from the mid-western U.S. (about 30 lakes). The amount and distribution of trace metals co-precipitated onto iron hydroxides/hydroxosulfates and the precipitation of metal sulfides varies from year to year and also within a year, depending on the stability of oxic and anoxic conditions at the sediment surface or within the top 5 cm, respectively.

Sediment Pore Water Chemistry

Pore water is an interface and transfer component between the solid (sediment) and liquid (lake water) phases, and between the groundwater and lake water, so its composition can play a major role in pit lake water chemistry. Thus, analysis of pore waters gives information about transport and transformation processes within the sediment (e.g. Blodau et al. 1998; Koschorreck et al. 2007 a, b; Regenspurg et al. 2004). Chemical (Knorr and Blodau 2006) and microbiological (Meier et al. 2004) transformative processes are both responsible for cycling elements between the pore water and sediment. Researchers have focussed on chemical processes that can be derived from pore water profiles in acid lignite and coal mine pit lake sediments (Herzsprung et al. 2002; Knorr and Blodau 2006; Peine et al. 2000);

the most important of these involve transformations of ferric and ferrous minerals (see also Sect. 3.2.1.2). Generally, the researchers analyzed pH, dissolved oxygen (or redox potential; Koschorreck et al. 2007a), ferrous iron, total dissolved iron, sulfate, and DOC (Laskov et al. 2002) in the pore water. To complete process understanding and enable geochemical modeling (PHREEQC or similar programs), additional analysis of remaining major ions (calcium, magnesium, sodium, potassium, and chloride), other metal ions like aluminum, manganese, and zinc, and nutrients like ammonia and soluble reactive phosphate may be required (Herzsprung et al. 2002).

Diagenesis of minerals like schwertmannite, jarosite, and goethite occurs in acidic pit lake sediments (Bozau et al. 2007; Knorr and Blodau 2006; Peine et al. 2000; Regenspurg et al. 2004). The pore water composition reflects the steady state resulting from all transformation and transport processes in the sediment (Knorr and Blodau 2006). The influence of biogeochemical transformations on pore water chemistry will be discussed using examples from the literature (Herzsprung et al. 2002; Knorr and Blodau 2006; Laskov et al. 2002; Peine et al. 2000).

Investigating the electron flow in the iron-rich Mining Lake 77, Peine et al. (2000) found a predominant pH gradient in the sediment pore water (Fig. 3.20). Protons are transferred by diffusion from acidic pelagic water to the sediment and are produced by transformation of schwertmannite to goethite and by precipitation of solid ferric iron minerals at the oxic/anoxic boundary. In deeper sediment layers, protons are consumed by reductive dissolution of ferric minerals and by sulfate reduction. The precipitation or dissolution of manganese oxides (MnOx) produces similar effects (Tan et al. 2010).

Figure 3.20 demonstrates the dependence of pore water chemistry on the geochemical conditions of acid pit lake sediments. ML 111 is extremely acidic; pore water pH values < 3.5 were found at sediment depths up to more than 20 cm (Herzsprung et al. 2002; Koschorreck et al. 2007a). ML 77 contains less acidity than ML 111. The pore water pH of ML 77 rises to higher values (up to 6) with increasing sediment depth (Peine et al. 2000). Ferrous iron and sulfate pore water concentrations are influenced by transport, dissolution, and precipitation processes. Knorr and Blodau (2006) demonstrated that pore water gradients change dramatically with groundwater percolation (upward). AMD-polluted groundwater (from dump sites with high ferrous iron and sulfate concentration) percolates the sediment of ML 77, so the concentration gradients are considerably less distinct than would be the case without percolation (Fig. 3.20). A local maximum of ferrous iron and sulfate pore water concentration (as shown in Fig. 3.20) qualitatively indicates transformation of schwertmannite to goethite (Knorr and Blodau 2006).

The DOC content in acid pit lake sediment pore water typically exceeds pelagial water DOC by at least an order of magnitude (Friese et al. 1998a, b; Laskov et al. 2002). As assumed by Laskov et al. (2002), the release of DOC into pore water is linked to the transformation of schwertmannite to goethite by desorptive processes. All parameters involved in redox cycling (ferric and ferrous iron, sulfate, pH, ORP, and DOC) were intensively investigated in pit lake pore waters, with minor consideration given to the other inorganic parameters mentioned above

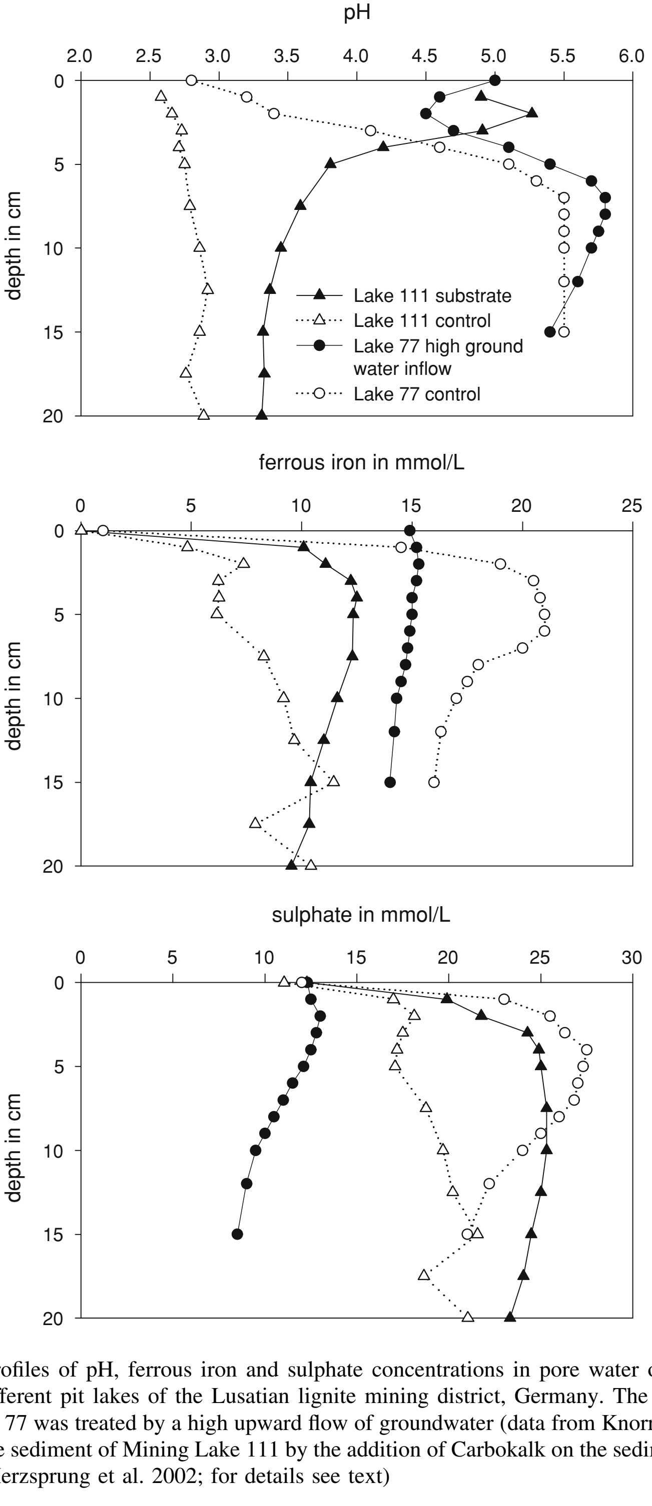


Fig. 3.20 Profiles of pH, ferrous iron and sulphate concentrations in pore water of sediments from two different pit lakes of the Lusatian lignite mining district, Germany. The sediment of Mining Lake 77 was treated by a high upward flow of groundwater (data from Knorr and Blodau 2006) and the sediment of Mining Lake 111 by the addition of Carbokalk on the sediment surface (data from Herzsprung et al. 2002; for details see text)

(other major ions, metal ions). Blodau et al. (1998) stated that concentration gradients of calcium, magnesium, potassium, sodium, and chloride were less pronounced. Herzsprung et al. (2002) investigated pore water chemistry after organic substrate (carbokalk, a by-product of the sugar industry, cf. Frömmichen et al. 2003, 2004) and lime were added to stimulate alkalinity production. As shown in Fig. 3.20, pH values were elevated in the uppermost sediment layers after addition of substrate to lake water in an enclosure of mine pit lake ML-111 (Lusatia, Germany; cf. Geller et al. 2009). The concentrations of sulfate and ferrous iron increased due to reductive dissolution of ferric minerals. The pore water composition changed considerably. Ferrous iron, sulfate, potassium, and ammonia were released into the pore water while aluminum and silica concentrations were depleted by precipitation. The release of potassium indicated the dissolution of K-jarosite, which is probably also the source of enriched ammonia concentrations within the pore water; both ions have a similar ionic radius and so NH_4^+ might replace K^+ in K-jarosite.

In a similar study conducted by Read et al. (2009), the change of pore water pH, iron, and sulfide after addition of DOC was investigated in a laboratory experiment on sediments from two Australian pit lakes and compared to the ML-111 results. Reductive processes were induced in all experiments, leading to increased concentrations of iron and ammonia in the overlying water, but sulfide was only measurable in the pore water in the Australian pit lake sediments. The high concentrations of ferric iron in the ML-111 sediment inhibited the formation of sulfide (see also Sect. 3.2.1.2). Consequently, a shift to increased pH within the top layer of the sediment was only observed in the Australian pit lake sediments.

Observations (Blodau et al. 1998; Herzsprung et al. 2002; Peine et al. 2000) indicate that the concentrations of calcium, magnesium, sodium, and chloride in pore water are not very different from pelagial water concentrations (exception: calcium in pore water after treatment with lime). These parameters seem to be neither involved in biogeochemical transformations nor in groundwater/lake water interactions. The concentration of manganese is elevated in acidic lake water and nearly equal in pore water and pelagial water (Herzsprung et al. 2002). In neutral coal mining affected lakes, manganese concentrations are low under oxic conditions (Wu et al. 2001). However, in the corresponding pore water, peak manganese concentrations can be found near the sediment water boundary. Manganese cycling in pit lake sediments after remediation and neutralization by flooding with river water is discussed by Herzsprung et al. (2010) and Wu et al. (2001). The behavior of phosphorus in acidic pit lake sediment pore water was explored by Kleeberg et al. (2005, see also Sect. 3.2.1.3).

Concluding Remarks

In the past 15 years, remarkable progress has been made in understanding pit lake chemistry and pit lake processes, mainly through research at pit lakes in Germany and Australia. Lakes in former hard coal mines have been much less intensively investigated than at lignite mines. Although many results from the German and Australian pit lakes can be generalized, a more international database is needed to better understand the relationships between the geological conditions of the deposits and the final chemical conditions in the lakes. This includes differences resulting from being in unconsolidated or in solid rock, which affects the interaction between the pit lakes and groundwater, and the contribution of residues of coal and lignite to the organic matter in the pit lakes. Furthermore, a detailed structural characterisation of this organic matter and quantification of its degradability and its contribution to reductive alkalinity production is needed.

3.2.1.2 The Role of Iron Minerals in the Biogeochemistry of Acidic Pit Lakes

Stefan Peiffer, Klaus-Holger Knorr and Christian Blodau

Predominant Iron Minerals in Acidic Mine Pit Lakes

Environments affected by acidic mine drainage (AMD) are characterized by the occurrence of a large variety of iron oxy (hydroxy) sulfates. Depending on the redox state of Fe and the degree of dilution, a broad range of sulfate and hydroxide minerals can form, ranging from pure melanterite ($FeSO_4$) in highly concentrated very acidic waters to goethite (FeOOH) in dilute waters (for a review cf. e. g. Nordstrom and Alpers 2000). A mineral characteristic to rivers affected by AMD is schwertmannite. It has the general formula, $Fe_8O_8(OH)_x(SO_4)_y \times n\ H_2O$, where $(8–x)/2 = y$ and $1.0 < y < 1.75$ and a mineral structure probably akin to akaganéite (γ-FeOOH; Bigham et al. 1994). The exact structure is, however, still a matter of discussion (Majzlan and Myneni 2005; Waychunas et al. 2001). The occurrence of schwertmannite was demonstrated also in the sediment of an acidic pit lake (APL) in layers up to 5 cm thick (Peine et al. 2000). In a survey performed in APLs from 17 pit lakes of three different lignite mining districts (Regenspurg et al. 2004), schwertmannite was the predominant iron mineral in fresh sediments. In addition to environments affected by AMD, it has been found in acidic sulfate soils, where it is subject to a dynamic iron turnover (Burton et al. 2006)

Schwertmannite is restricted to a geochemical window characterized by pH values between 2.5 and 4.5 and sulfate concentrations between 10 and 30 mmol L^{-1} (Bigham et al. 1994; Yu et al. 1999). At pH < 2.5, jarosite predominates (Cravotta et al. 1999). Geochemical modelling revealed that there is a chemical equilibrium between Fe^{3+} dissolved in lake water sampled from these lakes and schwertmannite (Regenspurg et al. 2004, Fig. 3.21). It can therefore be postulated that the geochemical window reflects a pH buffering system established by schwertmannite precipitation. This seems to be characteristic for many APLs, buffering the pH to values between 2.6 and 3.3 (Peine et al. 2000). An extensive review on acidity generation and consumption in APLs has been provided by Blodau (2006).

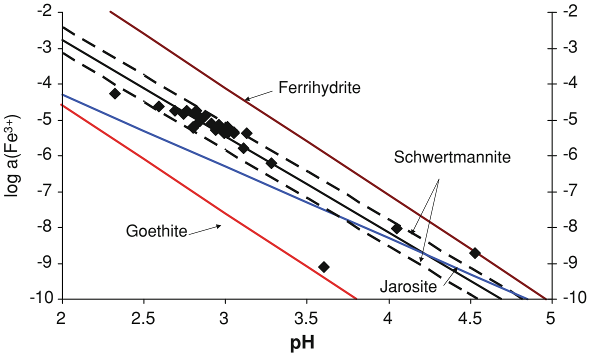


Fig. 3.21 Plot of the logarithm of the Fe^{3+} activity (mean values of measured data) versus pH for surface waters of 17 APLs. Solubility lines were calculated for goethite (log $a(Fe^{3+}) = 1.4–3$ pH), ferrihydrite (log $a(Fe^{3+}) = 4.83–3$ pH), K-jarosite (*mid-line* log $a(Fe^{3+}) = -0.19 - 2$ pH), and schwertmannite (*mid-line* log $a(Fe^{3+}) = 2.7–2.63$ pH). Maxima and minima (*dashed lines*) for the solubility window of schwertmannite are for the range of log $a(SO_4^{2-}) = -1$ to -1.5, that of jarosite -1.85 to -2.5, and for log $a(K^+) = -3.5$ to -4.07 (after Regenspurg et al. 2004)

Formation and Stability of Schwertmannite

In the APLs studied by Regenspurg et al. (2004), a redox equilibrium between Fe^{2+} and schwertmannite was detected, which implies that schwertmannite is the first mineral formed after Fe(II) oxidation in these environments. Given the slow oxidation kinetics of Fe(II) at low pH, this observation implies that schwertmannite formation is controlled by the oxidation kinetics of Fe^{2+}. This assumption was confirmed by a mass balance of dissolved Fe(II) and suspended Fe(III) established for a specific, yet typical APL studied by Peine et al. (2000). In this lake, solid Fe(III) was identified to be exclusively bound to schwertmannite, of which the sedimentation rate was measured to be 2.6×10^{-3} mol Fe(III) m^{-2} $year^{-1}$ on average, which agreed well with the Fe(II) oxidation rate of 3.0×10^{-3} mol Fe(II) m^{-2} $year^{-1}$.

Schwertmannite formation seems to be directly linked to bacterial oxidation of Fe^{2+} (Kawano and Tomita 2001). The bacterial cell appears not to be involved in the precipitation of either jarosite or schwertmannite (Eneroth and Bender Koch 2004), although direct contact between the bacterial cells and the crystal surface was demonstrated (Ferris et al. 2004). In a study of the bacterial community at a plant that generates pure schwertmannite while treating acidic waters from an active lignite surface mine (Glombitza et al. 2007), strains of Fe(II) oxidizing bacteria belonging to the class of beta-proteobacteria, closely related to the neutrophilic iron-oxidizing *Gallionella ferruginea*, were the dominant group (Hedrich et al. 2007; Heinzel et al. 2008).

Schwertmannite has been demonstrated to be metastable with respect to goethite (Bigham et al. 1996). Once suspended in water, it ultimately transforms into goethite, thereby lowering the pH (Jönsson et al. 2005; Knorr and Blodau 2007;

Regenspurg et al. 2004; Schwertmann and Carlson 2005). The transformation rate is slow under acidic conditions (pH $\approx$ 3) and increases significantly at higher pH (Regenspurg et al. 2004; Schwertmann and Carlson 2005), being driven by a supply of alkalinity (Peine et al. 2000). This transformation also seems to be dependant on temperature and concentrations of sulfate and dissolved organic carbon (DOC; Jönsson et al. 2005; Knorr and Blodau 2007), factors that can be highly variable under field conditions. High concentrations of sulfate and DOC probably also impede or at least retard the formation of well-crystalized goethite; instead; low-sulfate but poorly crystalline, x-ray amorphous iron oxyhydroxides form (Knorr and Blodau 2007).

Transformation to goethite has been demonstrated to occur in the sediment of an APL (Peine et al. 2000) at a rate of 3.5 mol m^{-2} year^{-1}. This reaction generates additional acidity in the sediment:

$$2y\ H_2O + Fe_8O_8(OH)_x(SO_4)_y \rightarrow 8FeOOH + y\ SO_4^{2-} + 2y\ H^+ \qquad (3.7)$$

The Role of Schwertmannite for the Element Cycles in APLs

As discussed above, schwertmannite plays a prominent role in the acid–base budget of APLs and is abundant in their sediments (e.g. Sánchez-Espana et al. 2008). This has consequences for the nature and rates of elemental cycling in APLs. The stability of acidic conditions in APLs is enhanced by the acidity-driven iron cycle at the sediment–water interface, where acidity generated by oxidation of Fe^{2+} to schwertmannite (1.0–4.7 mol m^{-2} year^{-1} in the sediment of Mining Lake (ML) 77, Lower Lusatia, Eastern Germany; Eq. 3.2) is balanced by alkalinity gained by microbial reduction of schwertmannite in this zone (0.65–4.0 mol m^{-2} year^{-1} in ML 77; Peine et al. 2000).

$$\begin{aligned} &8Fe^{2+} + y\ SO_4^{2-}(24 - 2y + x)/\ 2\ H_2O \\ &\quad \rightarrow Fe_8O_8(OH)_x(SO_4)_y + (24 - 2y)\ H^+ + 8\ e^- \end{aligned} \qquad (3.8)$$

Contrary to other minerals, schwertmannite is easily microbially reduced under acidic conditions by acidophilic bacteria, such as *Acidophilium cryptum JF*-5 (Küsel et al. 1999). This is reasonable, minding the strong dependence of microbial reducibility of iron minerals on factors such as crystallinity and surface area (Lovley and Phillips 1988; Roden 2003). Goethite is reduced at significantly lower rates by acidophilic bacteria than dissolved Fe(III) or amorphous ferric hydroxide by *Acidiphilium SJH* (Bridge and Johnson 2000). The reducibility of jarosite by *Acidiphilium SJH* is even lower than that of goethite (Bridge and Johnson 2000). In the acidic, schwertmannite-enriched zone of APL sediment, a rate of 6–25 nmol g^{-1} h^{-1} (Peine et al. 2000) was measured. Addition of schwertmannite to APL sediment-peat slurries also stimulated the Fe(II) release rate compared to both unamended controls and goethite addition in incubation experiments (Blodau and Gatzek 2006), which clearly indicated Fe(III) reduction.

Table 3.5 Quality of organic carbon in different density fractions as indicated by C/N-ratio, lignine content, and the amount of aromatic polycarbonic acids, a marker for coal carbon

Density (g cm^{-3})	C/N ratio (g/g)	Σ Lignine (μg/mg C)	aPCA (μg/mg C)
<2.0	56	9.0	95
2.0–2.4	23	4.0	68
>2.4	19	3.3	48

The lowering of pH and potentially the increase in dissolved ferric iron appeared to be critical to the increase in bacterial iron reduction in these schwertmannite-amended incubation experiments.

The alkalinity derived from reductive dissolution was, however, completely consumed by the transformation of schwertmannite into goethite and the reoxidation of Fe(II) (Peine et al. 2000). Sulfate reduction only took place at a depth where the transformation was complete and the pH increased. The rate of alkalinity formation from sulfate reduction (2.0 eq m^{-2} year^{-1}) in deeper zones ($\approx$10 cm) of the sediment from ML 77 was in the range of the acidity generated by schwertmannite transformation (3.5 eq m^{-2} year^{-1}) at $\approx$5 cm depth. It appeared that these two processes balanced each other. Thus, the pH did not increase in the lake water or in the top 5 cm of the sediment (this picture can, however, be changed by advective groundwater flow conditions, cf. below). Under these low pH conditions and without a supplemented carbon source, sulfate reduction is inhibited (Küsel and Dorsch 2000; Meier et al. 2004), so that Fe(II) cannot be fixed as iron sulfide in the top layers of the sediment. Reprecipitation of iron sulfides, however, would be a prerequisite for long-term neutralization of APLs (Blodau 2006).

Moreover, schwertmannite also appears to control metabolic activity in the sediment by selectively retaining microbially labile organic carbon (Laskov et al. 2002). Less than 10% of the organic carbon in the top sediment of a lignite APL were identified as autochthonous; the other fractions were either terrestrial (30–40%) or coal carbon. A density fractionation revealed that in the upper 4 cm of the sediment, 70% of the total carbon were associated with the heaviest, hence, iron-containing fraction, which itself made up 95% of the total mass. The iron fraction consisted of pure schwertmannite (Peine et al. 2000). A detailed analyis of the quality of the carbon pools in the three density fractions revealed that the carbon associated with the iron fraction was of the "best" quality with respect to its microbial availability (Table 3.5). It had the lowest C/N ratio, and the lowest content of lignite and aromatic polycarbonic acids, a marker for coal carbon (Glaser et al. 1998).

These observations may imply restrictions with regard to the primary production in APLs. Primary production in APLs seems to depend on the benthic supply of dissolved inorganic carbon (DIC), due to the low concentrations of DIC in acidic waters (Nixdorf and Kapfer 1998; see also Sects. 3.3.1.1 and 3.3.1.4). This supply may be severly affected by the availability of labile organic carbon being used for respiration by dissimilatoric bacteria associated with the large iron (schwertmannite) pool.

In addition to the impact of schwertmannite on pit lake geochemistry and metabolism, the mineral may also strongly influence the mobility and sequestration of trace elements. The mineral has a high affinity to anions and is, due to its large surface area, an efficient sink for As(V) (e.g. Acero et al. 2006; Schroth and Parnell 2005) and As(III) (Paikaray et al. 2011) in mine waters (see also case study 5.5). The adsorption of arsenate has been demonstrated to be an exchange reaction with non-structural sulfate (Fukushi et al. 2003). Similarly, phosphate can be retained, although at high concentrations, phosphate and arsenate may lead to destruction of the schwertmannite structure (Regenspurg and Peiffer 2005). Schwertmannite may therefore be regarded as an effective sink for both toxic anions and essential nutrients that control primary production, and can also enhance carbon sequestration in these waters.

Hydrogeochemical Effects on Schwertmannite Stability Under Transient Hydrological Conditions

APLs are hydrologically characterized by a strong interaction with groundwater (Werner et al. 2005; Fleckenstein et al. 2009). Influent groundwater tends to be only weakly acidic, due to intensive buffering activites in the adjacent dump materials, but rich in Fe(II) and sulfate (Bozau and Strauch 2002; Rolland et al. 2001; Werner et al. 2001). The extent of exchange with groundwater has a significant effect on biogeochemical processes in the sediments. Pore-water pH values, concentrations of Fe(II), sulfate reduction rates, and iron sulphide content were higher in areas of groundwater inflow (Blodau 2004, see also Sect. 3.2.1.1). The proton balance within the sediments was negative in areas with groundwater inflow and positive in those without groundwater inflow (Blodau 2005).

It appears that these observations are strongly linked to the reactivity of schwertmannite exposed to different flow rates in combination with different loads of $FeSO_4$ and DOC (Blodau und Knorr 2006; Knorr und Blodau 2006). Percolation in columns filled with schwertmannite-containing sediment material stimulated transformation of schwertmannite and thus acidity export. Mobilization increased with flow rates and decreased $FeSO_4$ concentration.

In order to quantify these relationships, we reanalyzed the data from Knorr and Blodau (2006) under conditions of pseudo steady-state. Acidity formation rates were calculated as the difference between acidity concentration at the inflow and the outflow of the columns times the flow rate. Acidity was calculated from the concentration of the following species and components

$$\begin{aligned}\text{Acidity} = {} & 2\,c(\mathrm{Fe}^{2+}) + 3\,c(\mathrm{Fe}^{3+}) + 2\,c(\mathrm{FeOH}^{2+}) + 3\,c(\mathrm{Al}^{3+}) \\ & + c(\mathrm{HSO}_4^-) + c(\mathrm{H}^+)\end{aligned} \tag{3.9}$$

The acidity formation rate decreased non-linearly with the load of sulfate (Fig. 3.22). This variable shows the same dependence on sulfate load as the ratio between inflow and outflow sulfate concentration, which suggest a relationship between the dissolution rate of schwertmannite and sulfate load. The acididity

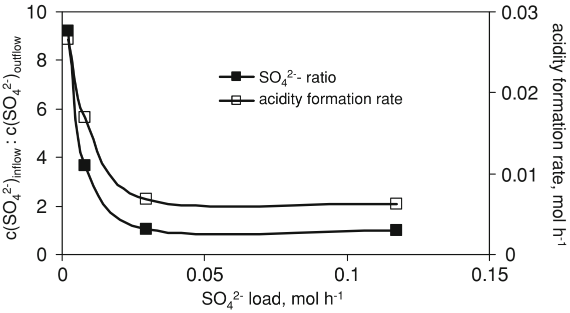


Fig. 3.22 Acidity formation rate and ratio between inflow and outflow sulfate concentration as a function of sulfate load measured in column experiments by Knorr and Blodau (2006) under pseudo steady-state conditions

formation rate therefore seems to be proportional to the degree of undersaturation $(K_{sp} - IAP)/K_{sp}$, with IAP being the ion activity product of schwertmannite and K_{sp} its solubility product.

The implication of these considerations for APL water quality could be severe when groundwater inflow changes compared to conditions under which schwertmannite deposits formed. Such a scenario can be expected when the regional groundwater flow field is altered by the cessation of water drainage in pit mines. Influent groundwater will tend to dissolve sedimentary schwertmannite, thereby amplifying acidity flow into a lake. This effect becomes even more relevant if sulfate load is low. On the other hand, exfiltrating lake water will export acidity into the groundwater. The sediment layers underlying the schwertmannite-containing layer in such areas will thus receive acidity, inhibiting sulfate reduction and long-term neutralization of the acidity.

3.2.1.3 Phosphorus in Acidic Mining Lakes: Importance and Biogeochemical Cycling

Björn Grüneberg and Andreas Kleeberg

Because phosphorus (P) availability often limits phytoplankton growth, elevated concentrations of P usually accelerates freshwater eutrophication. A large body of knowledge exists on P in neutral freshwater lakes and lakes acidified by airborne pollutants, but the role of P as a key nutrient in geogenically acidified mining lakes (MLs) is not adequately considered. This is important because many MLs are subject to rapid P import by ecotechnological measures or flooding with river water. Changes in pelagic and benthic conditions (e.g. pH, redox potential, C, and Fe supply), either through natural development or due to anthropogenic manipulations, affect P mobility (Kleeberg and Grüneberg 2005). Independent of velocity and grade of manipulation during ML development, a low trophic state (oligo- to mesotrophic) has to be maintained, either to satisfy utilization concepts (e.g. recreation) or to meet regulatory standards (e.g. the EU water framework directive).

Acid MLs are usually characterized by low pelagic concentrations of total P (TP, < 5–38 μg L^{-1}, $n = 23$ MLs; Nixdorf et al. 1998; Fig. 3.23) and soluble reactive P (SRP, 6–26 μg L^{-1}, $n = 4$ MLs; Spijkermann 2008). These lakes are usually oligotrophic (Nixdorf et al. 2003). High TP concentrations (42–230 μg L^{-1}) occur in meromictic or sewage-impaired MLs (Fig. 3.23). Exceptionally high SRP concentrations (3.5–14.8 mg L^{-1}), derived from the dissolution of phosphorite-nodules by highly aggressive acid mine drainage (AMD), were reported for an acid (pH 2.5) pond (Woelfl et al. 2000).

The vulnerability of MLs to critical P loads from river flooding (Schultze and Klapper 2004), P loading due to in-lake measures (e.g. Lessmann et al. 2003), and fish farm emissions for neutral MLs (Axler et al. 1996, 1998; Rümmler et al. 2003; Yokom et al. 1997) is of present and future concern. Hence, the prediction of future trophic state requires knowledge of mechanisms of import and accumulation of P in relation to that of other substances during ML succession, particularly on P pelagic settling and scavenging, benthic P diagenesis, and mobility aspects known to influence P retention and pelagic P availability.

The objectives of this section are to: (1) review the state of knowledge concerning P in acidic MLs in order to evaluate its actual import paths, accumulation, and retention mechanisms, (2) assess recent and future sedimentary P mobility in young MLs, and (3) address open and critical research and management questions. Due to the dynamic development of the young (only a few decades old) MLs, the discussion refers in some cases (e.g. sedimentation, P forms) only to conditions of the current (acid) phase of succession. Furthermore, the number of studies on P in MLs is limited and little long-term data exists, so some conclusions are preliminary.

Import of Phosphorus

Soil erosion, in the form of transported suspended sediment in overland flow, is often associated with high rates of particulate P transfer from land to water bodies. A review of P loss from land to water by Sharpley et al. (2001) revealed that the loss of P originates mostly from small areas within watersheds, and typically during a few periods of high rainfall intensity. However, the results of common soil erosion processes are not transferable to the dumps of the post-mining landscape (e.g. Abel et al. 2000; Biemelt et al. 2005).

A year of monitoring and ten short rainfall simulations have revealed high erosion rates and loss rates for P and Fe from bare lignite mining dumps at Schlabendorf, Lusatia, Germany (Kleeberg et al. 2008). The hydrophobicity led to very low infiltration, thus generating surface runoff even at low rainfall intensities. The mean annual soil erosion rate from the monitoring site was 18×10^6 kg km^{-2} $year^{-1}$. Loss rates for P and Fe were 470–650 kg km^{-2} $year^{-1}$ and 37.9×10^3–71×10^3 kg km^{-2} $year^{-1}$, respectively. These rates are equivalent to those of intensively used agricultural catchments. However, P import from these P-poor (17–90 μg g^{-1}) tertiary spoil materials into MLs will hardly affect their trophic state due to the accompanying high Fe import (Fe:P $\approx$ 60).

The diversion of river water into mining pits, both to quickly fill the pit and, at some sites, as flow-through to maintain sustainability, is one of the major management strategies to prevent (hydraulic gradient towards the dumps) or to combat acidification by dilution and import of alkalinity (see Sects. 4, 5.1).

Primary filling can cause extremely high short-term P loading for the new pit lakes. For example, various MLs in Saxony-Anhalt, Germany, have been flooded with river water (TP 110–160 μg L^{-1}), resulting in short-term P loading between 0.07 and 3.15 g m^{-2} $year^{-1}$ for ML Merseburg Ost to 3.6 g m^{-2} $year^{-1}$ for ML Runstädt (Schultze and Klapper 2004; see also case study 5.1). In-lake TP concentration during flooding ranged between <3 and 160 μg L^{-1} and usually decreased rapidly for MLs with significant 'mining impact' (metal import). As documented for ML Goitsche, Germany, which was flooded by River Mulde water (TP $\approx$ 110 μg L^{-1}), P was efficiently removed from the water column by Fe- and Al-compounds adsorbing riverine P, leading to low TP concentrations of 6–11 μg L^{-1} a few months after flooding (Duffek and Langner 2002; Herzsprung et al. 2010). However, elevated TP concentrations (12–70 μg L^{-1}) after flooding of other MLs, such as ML Runstädt, depict the limits of this technique and the risk of eutrophication.

Through flow of alkaline river water is required for many MLs as a continuous management measure to buffer acidity (Senftenberger See, ML Dreiweibern) or to use MLs as reservoirs to buffer variable discharge. Most examples show that MLs can compensate for this extra nutrient load (e.g. 20% for ML Dreiweibern) by high P retention, depending on the degree of mining impact, thus retaining a meso- or oligotrophic state.

Groundwater (GW) often dominates the water budgets of acid and neutral MLs after cessation of flooding (Hofmann et al. 2008; Werner et al. 2001). Despite the availability of high quality water mass balances from three-dimensional GW modeling (Heidenreich et al. 1999; Knoll et al. 1999), it is difficult to quantify P import because: a) TP concentrations in GW vary over a wide range (e.g. 101–254 μg L^{-1} for ML 117; 50–1,700 μg L^{-1} for ML Dreiweibern, Germany), and b) the P concentration is altered substantially during sediment passage.

The composition of GW after sediment passage as measured by seepage meters differs considerably from that in the vicinity of a lake (e.g. Driescher et al. 1988; John and Lock 1978). During passage through mining-influenced sediment, which typically has an elevated Fe content in both acid and neutral MLs compared to sediment of near naturally neutral lakes (Fig. 3.23), it is very unlikely that substantial amounts of P initially reach the ML water. Due to the high P sorption capacity of Fe-rich sediments (e.g. 5.6–9.1 mg g^{-1} in ML 117), predominantly adsorption of P onto Fe oxyhydroxides, P levels rarely exceed the sorption equilibrium concentration of about 3 μg L^{-1}. With typical Fe contents >70 mg g^{-1} and Fe:P ratios >60 for acid ML sediments (Fig. 3.23) there is no case where P is close to saturation, i.e. Fe:P $<$ 10 (Lijklema 1977).

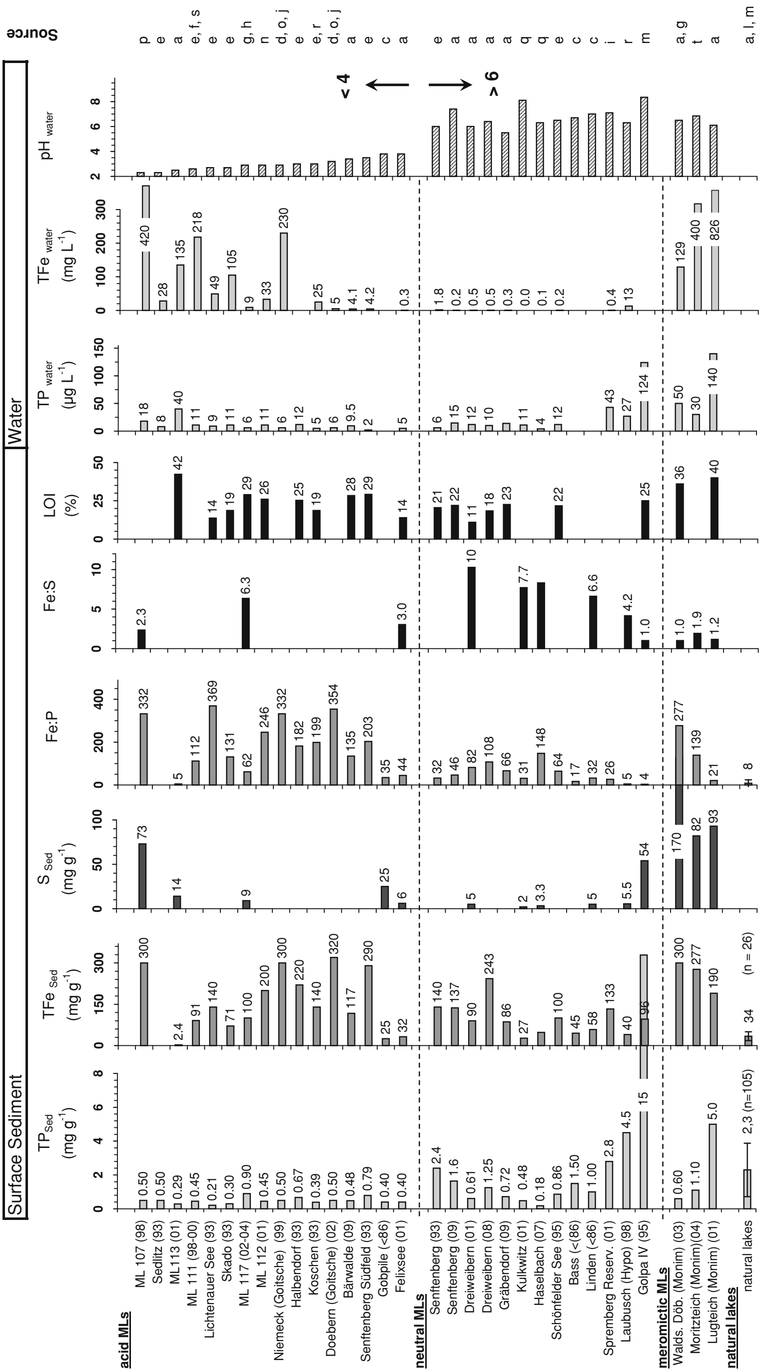
Complete P mass balances allow the estimation of the TP concentration in GW after sediment passage if whole lake retention (R) is assumed. For ML Dreiweibern, a GW TP concentration of 0–75 $\mu g\ L^{-1}$ was calculated (for $R = 0.85$–0.88), which is considerably less than measured in GW wells. However, preferential flow is probably important due to small-scale bottom inhomogeneities that are influenced by the regional surface excavation technique. Preferential flow into deeper parts of e.g. ML 117 by means of electrical conductivity and seepage meter measurements revealed a 82–93% reduction of TP concentration to 17–71 $\mu g\ L^{-1}$, compared to GW, despite high discharge at these locations and a short, i.e. <10 cm sediment passage (Hofmann 2003; Hofmann and Lessmann 2006). From a whole-lake sediment P budget, we estimated that the GW infiltrating the sediment had a TP concentration of 200–300 $\mu g\ L^{-1}$, which was almost completely adsorbed during sediment passage, generating a mean in-lake SRP concentration of <4 $\mu g\ L^{-1}$.

Role of Phosphorus in Mine Lake Remediation

In the dumps, phosphate (PO_4^{3-}) additions can reduce the potential of Fe^{3+} to act as a pyrite oxidant if PO_4^{3-} precipitates with Fe^{3+}, forming relatively insoluble iron phosphate minerals, such as amorphous $FePO_4$ and $FePO_4 \cdot 2H_2O$ (strengite; e.g. Baker 1983; Hood 1991). However, experiments to verify the P control on pyrite oxidation indicated that the inhibition is only temporary because of iron armoring (Huang and Evangelou 1992; Fytas and Evangelou 1998). An example of natural phosphate rock application to precipitate iron is also described in case study 5.7. To our knowledge, practical application of this technique is limited because of the high costs, and the potential adverse environmental effects of P fertilization.

The approach of neutralizing poorly buffered airborne acidified lakes by treatment with P fertilizer has been known for a long time (Davison et al. 1995). In recent years, some have attempted to use single P amendments to reduce AMD from mine dumps, or to stimulate a ML's primary production to enhance the C supply for benthic alkalinity generation. Additions of P should be most effective in removing acidity via iron sulfide sequestration. Theoretically, to remove 1 mol acid, it is necessary to form 1 mol of FeS_2. This can be achieved by applying either 0.05 mol PO_4^{3-} ('controlled eutrophication', Fyson et al. 1998a), or 0.5 mol $CaCO_3$ ('lake liming', e.g. Lindmark 1982), or alternatively 3.75 mol of organic matter $<CH_2O>$ ('saprobization', Fyson et al. 1998b). However, the following few examples show that single P additions have had limited effects.

Fyson et al. (1998a, b) tested amendments of organic C and hydroxyapatite in lab mesocosm experiments with sediment of an acid (pH 3.1) ML. Additions of potatoes at rates of 51–348 g dry weight (dw) m^{-2}, equivalent to a P load of 0.13–0.88 g m^{-2} (P content 1.8 mg g^{-1}) resulted in anoxic conditions above the sediment, and an increase in dissolved Fe, SRP, NH_4^+, and organic and inorganic C as the potatoes decomposed. In contrast, a single hydroxyapatite addition (692.9 g P m^{-2}) was not effective in supplying organic C via planktonic


Surface Sediment
Water
Source
TP Sed (mg g-1)
0 2 4 6 8
TFe Sed (mg g-1)
0 150 300
S Sed (mg g-1)
0 50 100
Fe:P
0 200 400
Fe:S
0 5 10
LOI (%)
0 25 50
TP water (µg L-1)
0 50 100 150
TFe water (mg L-1)
0 100 200 300
pH water
2 4 6 8
< 4
> 6
acid MLs
ML 107 (98)
Sedlitz (93)
ML113 (01)
ML 111 (98-00)
Lichtenauer See (93)
Skado (93)
ML 117 (02-04)
ML 112 (01)
Niemeck (Goitsche) (99)
Halbendorf (93)
Koschen (93)
Doebern (Goitsche) (02)
Bärwalde (09)
Senftenberg Südfeld (93)
Gobpile (<86)
Felixsee (01)
neutral MLs
Senftenberg (93)
Senftenberg (09)
Dreiweibern (01)
Dreiweibern (08)
Gräbendorf (09)
Kulkwitz (01)
Haselbach (07)
Schönfelder See (95)
Bass (<86)
Linden (<86)
Spremberg Reserv. (01)
Laubusch (Hypo) (98)
Golpa IV (95)
meromictic MLs
Walds. Döb. (Monim) (03)
Moritzteich (Monim)(04)
Lugteich (Monim) (01)
natural lakes
natural lakes
p e a e, f, s e e g, h n d, o, j e e, r d, o, j a e c a
e a a a a q q e c c i r m
a, g t a
a, l, m
0.50 0.50 0.29 0.45 0.21 0.30 0.90 0.45 0.50 0.67 0.39 0.50 0.48 0.79 0.40 0.40
2.4 1.6 0.61 1.25 0.72 0.48 0.18 0.86 1.50 1.00 2.8 4.5 15
0.60 1.10 5.0
2,3 (n=105)
300 2.4 91 140 71 100 200 300 220 140 320 117 290 25 32
140 137 90 243 86 27 100 45 58 133 40 96
300 277 190
34 (n = 26)
73 14 9 25 6
5 2 3.3 5 5.5 54
170 82 93
332 5 112 369 131 62 246 332 182 199 354 135 203 35 44
32 46 82 108 66 31 148 64 17 32 26 5 4
277 139 21
8
2.3 6.3 3.0
10 7.7 6.6 4.2 1.0
1.0 1.9 1.2
42 14 19 29 26 25 19 28 29 14
21 22 11 18 23 22 25
36 40
18 8 40 11 9 11 6 11 6 12 5 6 9.5 2 5
6 15 12 10 11 4 12 43 27 124
50 30 140
420 28 135 218 49 105 9 33 230 25 5 4.1 4.2 0.3
1.8 0.2 0.5 0.5 0.3 0.0 0.1 0.2 0.4 13
129 400 826

◀**Fig. 3.23** Sediment and water data for MLs with emphasis on sediment P and mining indicators (Fe, S) for acid, neutral, and meromictic MLs; (Hypo: hypolimnion; Monim: monimolimnion). Sources: a) own unpublished data; b) Borovec and Hejzlar (2001); c) Brugam et al. (1988); d) Duffek and Langner (2002); e) Friese et al. (1998); f) Frömmichen et al. (2004); g) Grüneberg and Kleeberg (2005); h) Grüneberg (2006); i) Heidenreich and Kleeberg (2003); j) Herzsprung et al. (2004); k) Herzssprung et al. (2010); l) Hupfer (1998); m) Hupfer et al. (1998); n) Kleeberg and Grüneberg (2005); o) Langner (2004); p) Lessmann et al. (1999); q) LMBV (various unpublished reports and monitoring data from state company responsible for the remediation of former lignite mines in eastern Germany; www.lmbv.de); r) Nixdorf et al. (2000); s) Saballus (2000); Stellmacher (2004)

production. The studies demonstrated that organic wastes remove acidity in the short-term by generating reducing conditions around the sediment surface and stimulating P release to the overlying water.

To study whether self-sustaining acidity removal is possible by 'controlled eutrophication', enclosure experiments were run in dimictic, acidic (pH $\approx$ 3) ML 117-Grünewalder Lauch ($A = 0.94$ km^2, $z_{max} = 14.4$ m) from August to October 2002. 12 enclosures ($\varnothing = 1$ m) were installed at a water depth of 6 m. Two were neutralized by adding Na_2CO_3, two were neutralized and fertilized ($Na_2CO_3 + P$ with 3 g m^{-2}), two were only fertilized with P (3 g m^{-2}), two were neutralized and fertilized with 3 kg fresh potatoes (309 g C m^{-2} incl. 1.44 g P m^{-2} on a dw basis), two were only fertilized with 3 kg potatoes, and two were left untreated as controls.

Neutralization and C addition in combination was most efficient in terms of sustainability of increased pH and decreased Eh at the sediment water interface and secondary supply of particulate organic C (POC) from primary production towards the sediment. There was no permanent effect after single neutralization, C addition, or P fertilization. In the neutralized and P-fertilized enclosures, the Na_2CO_3 additions led to a rapid decrease of TP concentration from 500 to 15 µg L^{-1} by co-precipitation with Fe carbonate and Fe hydroxide, and so significantly decreased the pelagic P availability for primary producers. Consequently, there was (at least for the amounts added) no long-term effect as a consequence of the diminished phytoplankton production and the corresponding POC flux. In summary, there was a gradual component-specific effect on pH in the sequence: 'potatoes' > '$Na_2CO_3 + P$' > 'P' > 'control' indicating that biogenic alkalinity generation due to organic C supply is more efficient than liming or P amendments.

Lessmann et al. (2003) reported on in-lake treatment by the addition of organic waste material to increase primary production and to form anoxic microbial reaction compartments and thereby stimulate biogenic alkalinization via sulfate reduction. The small ($A = 10$ ha, $V = 10^5$ m^3), shallow ($z_{max} = 2.5$ m) acidic mining lake Koyne 113, Germany, was treated four times in three consecutive years with a total of 243 t of a mixture (C: 486 g kg^{-1}, N: 6.36 g kg^{-1}, P: 94 mg kg^{-1}) of cut-up beer and water bottle labels in jute bags. These additions resulted, from before the treatment to the third year, in increased lake water concentrations of organic C from 2.9 to 8.0 mg L^{-1}, of TP from 10 to 43 µg L^{-1}, and of chlorophyll a from 28 to 85 µg L^{-1}. However, acidity ($K_{B4.3} = 10.4 \pm 0.4$ mmol l^{-1}; $K_{B8.2} = 13.9 \pm 0.6$ mmol l^{-1}) and pH (2.5 ± 0.05) did not change.

This approach obviously failed because the import of acidity-forming constituents was not stopped. For example, within the observation period, sulfate concentrations increased from 1.59 to 2.86 g L^{-1}, i.e. by 79.9%. This increase showed that either no sulfate reduction occurred in the shallow lake, or sulfides were re-oxidized due to constant high oxygen saturation >90% in the water column. Even if part of the sulfate was stored in the sediment, such an oxygen supply favors a re-oxidation of sulfides as shown by Koschorreck et al. (2002).

Furthermore, the addition of C (mostly C_{org}) with 1,181 g m^{-2}, of N with 15.5 g m^{-2}, and of P with 0.23 g m^{-2} corresponds to a ratio of $C_{13,356}$:N_{150}:P_1. This ratio differs quite a lot from the mean composition of phytoplankton with C_{106}:N_{16}:P_1 (Redfield 1934), which indicates that the nutrient mixture was not appropriate. The total P amount of waste material addition should theoretically lead to a pelagic TP concentration of 228 μg L^{-1}, representing an already highly eutrophic lake. However, the TP concentration monitored after the measure (43 μg L^{-1}) revealed that most of the P (77.6%) was precipitated due to surplus of P-binding partners, such as Fe, Al, and Mn (Fe:P 6366, Al:P 4248, and Mn:P 180) in the water. Metal concentrations even increased during the experiment.

Phosphate and nitrate have also been directly applied to surface waters of pit lakes to reduce metal concentrations and toxicity. Island Copper pit lake (Fisher and Lawrence 2006; Pelletier et al. 2009), and enclosures in Main Zone and Waterline pit lake, Canada (Martin et al. 2003) received P additions between 0.1 and 2.0 mmol m^{-2} d^{-1}. Due to increased primary production, a pronounced removal of dissolved and total Zn, Cu, and Cd was attained by active uptake or sorption to algal surfaces and subsequent particle settling, and by metal-sulfide precipitation under anoxic conditions. Combined limestone neutralization and P amendment reduced Al and Zn metal toxicity by shifting metal species to predominantly non-bioavailable forms in mesocosms with Lake Kepwari water, West Australia (Neil et al. 2009; case study 5.4).

To summarize, it is best to lower the import of AMD to a minimum prior any in-lake manipulations. In the case of P fertilization, the concomitant import or pelagic and benthic surplus of P-binding partners, such as Fe, Al, and Mn, has to be adequately considered in terms of a mass balance and respective sediment. Even a surplus of P and organic C by waste materials does not guarantee effective acidity sequestration, even though it bears the risk of eutrophication.

Sedimentation and Accumulation of Particulate Matter and Phosphorus

Composition and sedimentation of particulate matter in MLs has rarely been studied. High deposition rates for dry weight (dw; 3.8 g m^{-2} d^{-1}) and Fe (1.45 g m^{-2} d^{-1}) were reported for acidic (pH 2.9) ML 77, Germany (Peine et al. 2000). Similar dw deposition rates (2.1 g m^{-2} d^{-1}) were reported for meromictic ML Waldsee, Germany (Dietz, unpubl.), and considerably lower rates (dw: 0.94 g m^{-2} d^{-1}, Fe: 0.2 g m^{-2} d^{-1}) for ML 117 (Grüneberg 2006). Due to the high Fe content of settling matter (210–363 mg g^{-1}), Fe fluxes are an order of

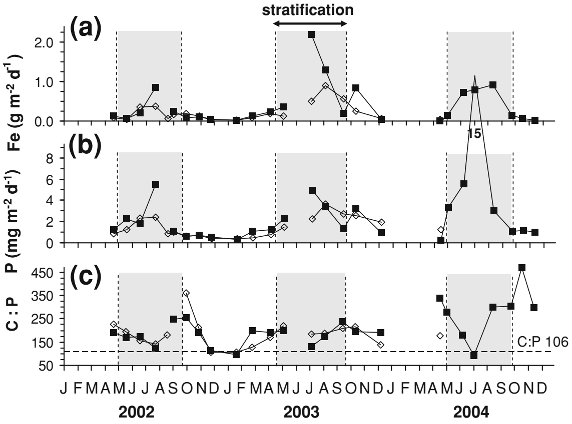


Fig. 3.24 Monthly mean of sedimentation rate at the deepest site of acid (pH ≈ 3) ML 117, Germany, for the epilimnetic 7 m trap (open symbol) and hypolimnetic 12 m trap (closed symbol) for: **a** total Fe, **b** total P, and **c** the atomic C:P ratio of material entrapped

magnitude higher than in natural lakes. A three-year sediment trap study in acidic (pH 3.0) dimictic ML 117, representing moderate Fe concentrations (9.3 mg L^{-1}) revealed, first, annual mean epilimnetic sedimentation rates of organic C (101 mg m^{-2} d^{-1}) and TP (1.4 mg m^{-2} d^{-1}) were similar to those of natural oligotrophic lakes. Second, Fe oxyhydroxide precipitation dominated sedimentation only for a short time, between mid June and August (max. 2.2 g Fe m^{-2} d^{-1}; Fig. 3.24a), inducing low C:P ratios during summer (Fig. 3.24c) by scavenging of organic C, a seasonal trend opposite to that of natural neutral lakes. Third, even during periods of intensive Fe oxyhydroxide floc formation, low concentrations of SRP ≈ 3 µg L^{-1} limited P adsorption, so downward P transport was mainly organic (algae; 39–71% TP).

Sediment composition and accumulation rates differ for shallow and deep parts of ML 117 due to different rates of lateral Fe oxyhydroxide and organic particle transport and mobilization. The sediment formed at a shallow water depth (2.5–8 m) has a high P sorption potential due to a high Fe (400 mg g^{-1}) and low P content (0.4 mg g^{-1}). In contrast, an Fe-poor (24–250 mg g^{-1}) but C- and P-rich (loss on ignition: 32–70%; TP: 0.9–3.4 mg g^{-1}) sediment formed at deeper (8–14 m) water depths. Although these results are from a single case study, differentiation in small deep and extended shallow areas is characteristic for a number of MLs (Nixdorf et al. 2001). Thus, the effects of morphometry-triggered sediment accumulation and composition patterns for P retention or for processes depending on POC supply have to be considered as likely to occur in other MLs as well.

Phosphorus Adsorption Properties of Mining Lake Sediments

The low trophic state of acid MLs is, to a great extent, a consequence of the high P adsorption capacity of metal oxyhydroxides (e.g. 37.3 mg P g^{-1} Fe for fresh Fe hydroxide at pH 7; Parfitt et al. 1975). Phosphorus adsorption capacities (batch experiments, Langmuir isotherm) varied between 0.3 and 3.3 mg g^{-1} dw for sediment of neutral Spremberg reservoir, Germany, receiving river water discharged by AMD (Heidenreich and Kleeberg 2003), and 3.8–9.1 mg g^{-1} dw for three ML sediments (Grüneberg 2006) with P adsorption clearly depending on sedimentary Fe content ($R^2 = 0.90$; $n = 8$). These numbers are significantly higher than those known from natural lakes ranging from 0.03 to 3.0 mg g^{-1} dw (e.g. Detenbeck and Brezonik 1991; Pant and Reddy 2001), and are similar to other Fe hydroxide media (Adler and Sibrell 2004; Zeng et al. 2004).

Working with these numbers, it should be considered that P adsorption a) is lower (e.g. 5.6–8.5 mg g^{-1} for ML 117) if determined in continuous flow experiments as to mimic GW sediment passage with more realistic (0.4 and 2.0 mg L^{-1}) adsorbate concentrations (Grüneberg 2006), and b) may significantly decline under anoxic conditions (e.g. Pant and Reddy 2001).

The significance of the very efficient non-redox sensitive Al–P sorption (Lijklema 1980; Parfitt 1989) has been documented for rain-acidified lakes (e.g. Kopáček et al. 2004), but not for MLs. There are contradictory views on the influence of humic substances on metal-P adsorption, which compete with P for adsorption sites at metal surfaces (Antelo et al. 2007; de Vincente et al. 2008), but may also increase P sorption (Bloom 1981; Gerke and Herman 1992). This might be especially significant for MLs, giving the substantial amounts of partly lignite-derived C associated with metal oxyhydroxides (Laskov et al. 2002).

Phosphorus Forms in Mining Lake Sediments

The stability of P binding in acid ML sediments was highlighted by Brugam et al. (1988). They found that only a small fraction of P dissolves in 0.1 N HCl (representing inorganic metal-bound P) and that most P (and other elements) is released only in ashed sediment by hot HCl. Thus, most P is strongly adsorbed or in organic form.

Many authors apply a sequential extraction (e.g. Hupfer 1998; Psenner et al. 1984) to identify operational phases and to interpret pools and mobility of benthic P forms. Because of the high Fe contents of ML sediments, the procedure was modified (Grüneberg 2006; Saballus 2000), and a simple method for TP and TFe determination was tested for sediments with Fe contents up to 450 mg g^{-1} (Grüneberg and Kleeberg 2005).

Iron is regarded the predominant sorption partner for P in MLs due to the abundance of Fe oxyhydroxides. However, BD-P (Fe-bound P) comprised only 17–30% of TP in oxic sediments of acid ML 112 (Kleeberg and Grüneberg 2005) and ML 117 (Grüneberg and Kleeberg 2005). The potential for P adsorption to Fe oxyhydroxides (BD-P) is not completely fulfilled in these acid MLs due to an excess of Fe compared to P.

Aluminum contributes differently to P sorption in MLs depending on the geochemical setting. Despite high atomic Al:P ratios ($13 - 440$; $n = 8$) in acid ML surface sediments, Al is of minor importance for P binding if mainly present as constituent of clay particles, as found for ML Golpa IV (Hupfer et al. 1998), and by means of energy-dispersive X-ray analysis and sequential extraction for ML 117 (Grüneberg and Kleeberg 2005). The increase of NaOH-P (metal-bound P, mainly Al, and organic P) at the expense of BD-P between pH 4 and 7 was interpreted as a shift of relevance from Fe— to Al—oxydroxides for P sorption in ML Goitsche (Duffek and Langner 2002; Duffek and Schultze 2002). Dominance of Al–P binding was also demonstrated for rain-acidified (pH 4.9) Lake Plešne due to high Al import (Kopáček et al. 2004) and for Mud Pond Lake (pH 4.8), as evidenced by 80% solubility of Al and >95% solubility of P in the NaOH-fraction (Wilson et al. 2008).

Vivianite [$Fe_3(PO_4)_2$] is known to be a long-term P sink in anoxic lake sediments (e.g. Holdren and Armstrong 1980; Nriagu and Dell 1974). Positive vivianite saturation indices were determined by chemical equilibrium calculations for the highly anoxic deeper sediment of ML Golpa IV (Hupfer et al. 1998) and in mesocosm experiments with organic C and P additions to ML sediments (Grüneberg 2006; Langner 2004). These authors concluded that the high Fe content of ML sediments and the dominance of Fe reduction over SO_4^{2-} reduction result in excess Fe^{2+} in pore water, which allows concurrent sulfide and vivianite formation not possible under most conditions (Nriagu 1972).

Metal–organic complexation was assumed to be an important P binding mechanism as it offers an explanation for the high BD- and NaOH-NRP (non-reactive P) content of ML sediments (Grüneberg and Kleeberg 2005) that is consistent with the finding that organic matter is preserved after degradation due to adsorption to Fe oxyhydroxide surfaces (Antelo et al. 2007; Laskov et al. 2002; Tipping 1981).

To summarize, there are indications of Al control of P binding for MLs at pH 4–6.5, based on one case study and analogous rain-acidified lakes. For acid ($pH < 4$) MLs, high organic P contents were found in two cases (up to 36–42% NaOH-NRP in ML 112 and 117 surface sediment), while most Fe-based P adsorption capacity remains unfulfilled due to the high Fe contents. Evidence for vivianite as well as metal–organic complexation is vague despite their potentially high relevance as long-term sinks for P in MLs.

Phosphorus Mobility and Availability: Implications for Mine Lake Succession

There are mechanisms and indications for both very efficient P binding in ML sediments and also for increased mobility of P with ML succession. Four mechanisms that could lead to increased P mobility and potentially higher trophic state have been identified. First, the import of Fe and Al into MLs will decrease with maturation and reclamation of their catchments; thus, the supply of P binding partners will decline (Kleeberg and Grüneberg 2005). Second, the P adsorption capacity of Fe oxyhydroxides will decline with increasing pH due to transformations to more crystalline forms. Third, the burial of metal-rich sediments by particles from river flooding or increased primary production may render the Fe oxyhydroxides from the acid phase inactive for P adsorption (Schultze and Klapper 2004). And finally, natural maturation or artificial neutralization will lead to P and C accumulation in MLs, which may cause anoxic conditions at the sediment, reductive dissolution of Fe oxyhydroxides, immobilization of Fe as FeS_x, and consequent mobilization of Fe-bound P analogous to natural lakes (Caraco et al. 1993; Kleeberg 1998).

However, anoxic conditions do not inevitably cause P release. SRP concentration remained close to the detection limit of $\approx 3\ \mu g\ L^{-1}$, despite anoxic conditions (Eh < 150 mV) and periodic neutralization of hypolimnetic water to pH 5–6.4 in ML 117 (Grüneberg 2006). The meromictic and anoxic ML Goitsche showed no sign of eutrophication (TP 8 $\mu g\ L^{-1}$), despite a short-term high P import by a river flood (Herzsprung et al. 2010). In both cases, the re-oxidation of Fe^{2+} from reductive dissolution in anoxic sediment layers at the sediment water interface ('ferrous wheel'; Campbell and Torgersen 1980; Davison 1993) allowed continuous P precipitation by newly-formed Fe oxyhydroxides. Thus, a high Fe:P ratio in pore water ($\approx$10,000 for ML Goitsche, basin Niemegk) was suggested as an indictor for a low trophic state (Herzsprung et al. 2010; Sect. 3.2.1.1).

The longevity of an effective Fe–P co-precipitation is elucidated by the case of natural lake Groß-Glienicker See, Germany ($A = 0.67\ km^2$, $z_{max} = 10.8$ m). P sorption capacity has remained high for 16 years (13 cm of new sediment) after iron hydroxide and iron chloride treatment (Hupfer 2004), as evidenced by an elevated Fe content, low pore water SRP, and a high Fe:P ratio in sediment (7.5) and pore water (15.0; Fig. 3.25).

Conversely, batch and column experiments involving the addition of organic C have shown that P release from Fe-rich ML sediments is possible under permanent anoxic conditions. However, P release rates between 0.15 and 0.46 mg $m^{-2}\ d^{-1}$ (Grüneberg 2006) and 6.2 mg $m^{-2}\ d^{-1}$ (Langner 2004) are low compared to those of oligotrophic (0–1 mg $m^{-2}\ d^{-1}$) and mesotrophic (2.1–6.7 mg $m^{-2}\ d^{-1}$) lakes (Nürnberg and Lazerte 2004). Grüneberg (2006) found that P release occurred only from ML sediments where Fe was largely immobilized as FeS_x, as evidenced by a low atomic Fe:S ratio (1.4–2.0). The measured SRP pore water concentrations were in adsorption equilibrium with the fraction of Fe not immobilized as FeS_x.

Explanations for high P retention, the limits of P binding, and conditions that cause high pelagic P concentrations can also be derived by analyzing the geochemisty of ML water and sediment (Figs. 3.23 and 3.26): MLs without additional nutrient inputs are characterized by low TP concentrations in water column (<12 $\mu g\ L^{-1}$) and sediment (<0.5 mg g^{-1}). Additional nutrients provided by river flooding or wastewater discharge results in high sediment TP, but pelagic TP concentration increases only if the P loading exceeds sedimentary P sorption capacity (e.g. ML Golpa IV). Elevated P concentrations (30–50 $\mu g\ L^{-1}$) in the monimolimnion of meromictic MLs Moritzteich and Waldsee Döbern, which receive only natural low P imports, highlight that high Fe contents ($\approx$300 mg g^{-1}) and Fe:P ratios (140–280) in the sediment are insufficient indicators for P mobility (Fig. 3.26c). For most cases, prerequisites for high P concentrations are anoxic conditions in the hypolimnion and sediment as well as immobilization of Fe as FeS_x as indicated by low atomic Fe:S ratio <2 (Fig. 3.26e). Kleeberg (1998) already identified the 'degree of pyritization' (DOP),

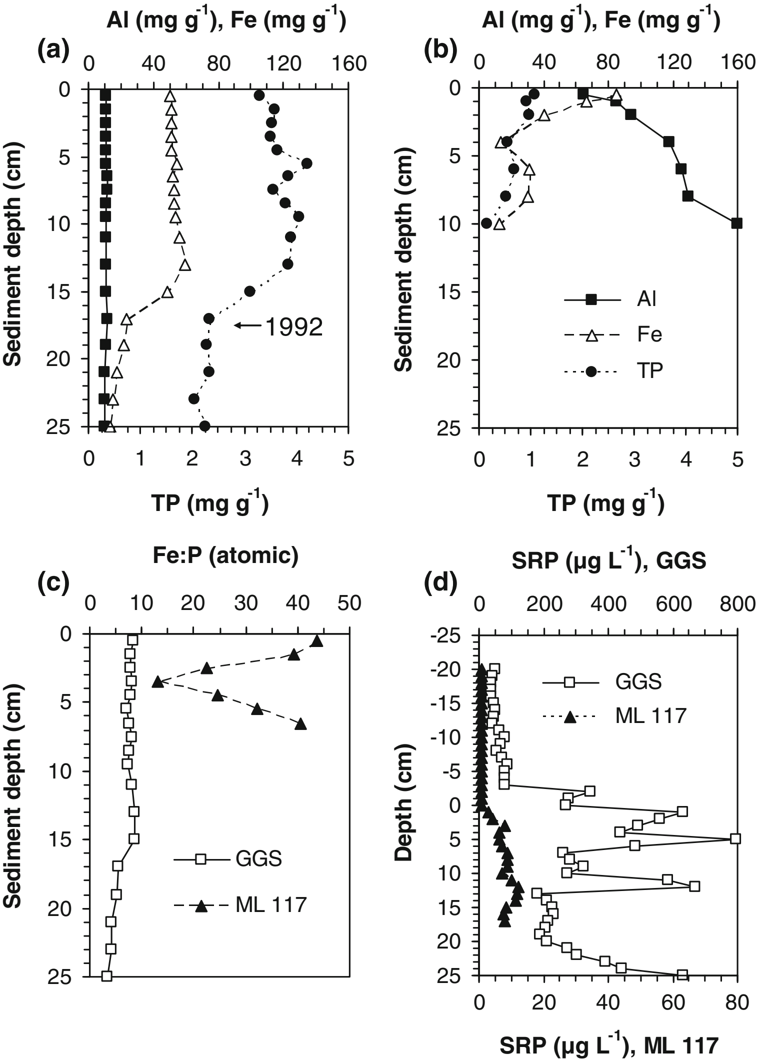


Fig. 3.25 Vertical profile of sedimentary Al, Fe, and total P (TP) for **a** neutral lake Groß Glienicker See, Potsdam, Germany, which has been treated by ferric Fe in 1992 (see *arrow*), and **b** for acid ML Grünewalder Lauch (ML 117), Lauchhammer, Germany; **c** respective atomic Fe:P ratio for both lakes; **d** vertical profile of soluble reactive P (SRP) in pore water at the deepest site of lake Groß-Glienicker See (GGS) in September 2008, and for ML 117 in June 2003

an expression of the percentage of Fe sequestered in FeS_x form, as an essential indicator for P mobility.

Groundwater seepage into MLs largely determines water geochemistry due to the import of elevated quantities of dissolved metals and sulfur associated with mining activities (Blodau et al. 2006; Graupner et al. 2005; Wisotzky and Obermann 2001). As the cycling of P relates to the quantity of this mining impact, various indicators for P mobility have been used, reflecting the interconnections between P, Fe, Al, and S (Fig. 3.27). A high mining impact (metal import and their pelagic precipitation as oxyhydroxides) leads to very low benthic P mobility in acid MLs. Under anoxic conditions, P mobility remains low due to: a) upward propagation of the aforementioned 'ferrous wheel,' which leads to a high P binding capacity of Fe-rich ML sediments beyond the period of a massive AMD, despite decreasing Fe- and Al-import and ongoing deposition of organic and P-rich sediment; b) the possibility of vivianite formation as a permanent P sink concurrent with sulfide formation, given a Fe^{2+} surplus; and c) the higher thermodynamic stability of the $Fe(OH)_3$–P complex, compared to $Fe(OH)_3$, so that an almost complete transformation of ferric Fe to FeS_x (>75%) is required before P release becomes significant (Golterman 1995).

A high pore-water Fe:P ratio and low SRP concentrations was found to assure efficient adsorption onto re-precipitated Fe oxyhydroxides, an indicator concept also suggested for natural lakes (e.g. Baccini 1985). The surface sediment Fe:P ratio, suggested as an indicator for shallow oxic lakes (Jensen et al. 1992; Sondergaard et al. 1993), can be used for MLs only when the DOP is low. Analogously, the Al:P ratio (Rydin et al. 2000; Welch and Cooke 1999) may be used with Al hydroxide as the binding partner. Kopáček et al. (2005) proposed the ratio $\text{NaOH-Al: BD} + H_2O\text{–P} > 25$ as an indicator for efficient Al-based P sorption. Maaßen (2003) and Jin et al. (2006) suggested combined Al and Fe indicators, a concept not tested for MLs yet. We recommend the application of the Fe:S ratio or $\log(\text{Fe:S}) \times \log(\text{Fe:P})$ ratio to account for the fact that DOP determines the availability of Fe as binding partner.

Phosphorus Retention in Mining Lakes and Prognosis of Trophic State

Acid MLs exhibit a high availability of P binding partners as a result of mining activities, as indicated by sediment Fe:P ratios up to 370 (Fig. 3.23). Even neutral MLs (without unusually high P loading) have significantly higher sediment Fe:P ratios (17–148) than natural lakes (≈ 8; Fig. 3.23). As a consequence of this elevated sediment-based P binding capacity, whole lake P retention for a set of eight Lusatian MLs was $14.7 \pm 5.5\%$ higher than predicted from the empirical OECD (1982) model (Grüneberg, unpublished). Data indicate that even a slight mining impact (e.g. Fe surplus) leads to significantly increased P retention. We suggest that empirical P retention models be adapted for MLs since this underestimation of permissible loading may, for instance, lead to usage restrictions.

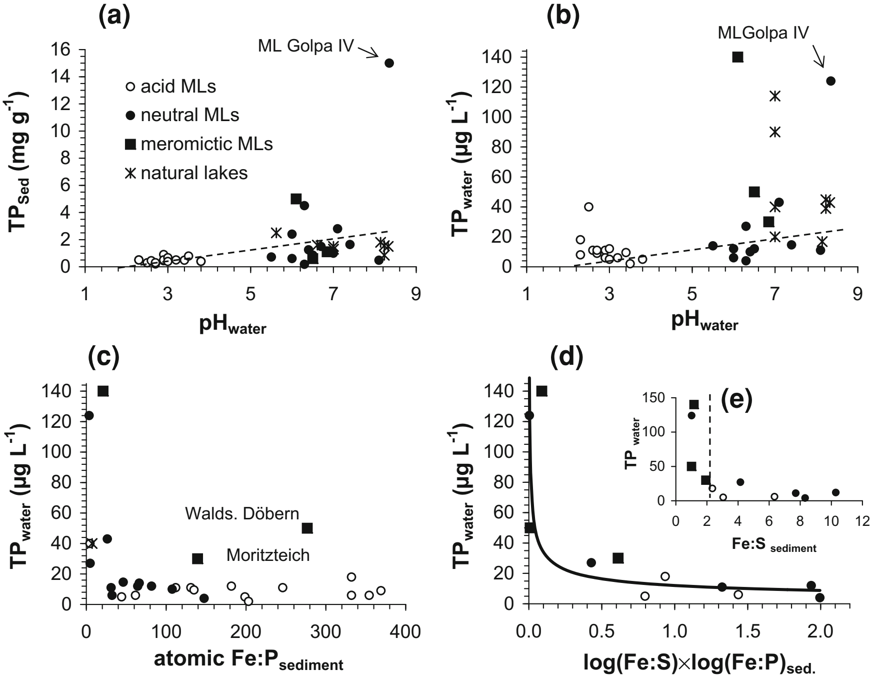


Fig. 3.26 Concentration of total P of water (TP_{water}) and sediment ($TP_{sediment}$) versus indicators (ratios in water and sediment) supposed to indicate conditions of low and high P concentrations in MLs ($n = 27$, see Fig. 3.23) compared to natural lakes ($n = 5$)

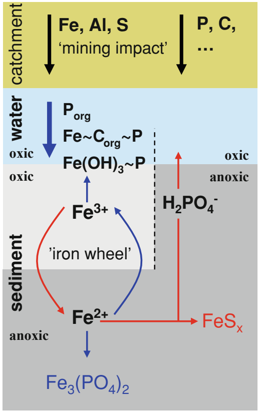
3.2.2 Hardrock Metal Mine Pit Lakes: Occurrence and Geochemical Characteristics

L. Edmond Eary and Devin N. Castendyk

3.2.2.1 Introduction

Pit lakes are an increasingly common legacy of modern, large-scale surface mining operations. Pit lakes formed in open pit metal mines, where base and precious metals are extracted from ore deposits hosted in predominantly igneous and metamorphic silicate rocks, comprise one category of pit lakes. This category is referred to as hardrock metal-mine pit lakes, to distinguish them from pit lakes formed in above-ground hydrocarbon, industrial minerals, and aggregate mining operations.

Ore deposits exploited by mining consist of rock assemblages with naturally elevated concentrations of metals. These include the base metals (e.g. Co, Cu, Pb, Mo, Ni, and Zn) and precious metals (e.g. Ag and Au). Base metals are typically



process / mechanism		P mobility Low	P mobility High
Import	at present: Fe, Al >> P	x	
	future: Fe, Al decrease; P, C increase		x
	river flooding → burial of Fe/Al-layer		x
Sedimentation and sediment P binding	Fe/Al-oxides high sorption capacity	x	
	C_{org} scavenging, metal-organic complexation	x	
Diagenesis and release	$Fe(OH_3)$ reductive dissolution, FeS_x formation		x
	Fe^{2+} upward diffusion and re-oxidation	x	
	vivianite formation due to Fe^{2+} surplus	x	
Indication for P mobility	pore water: Fe:P *	~10.000	0.04 - 4
	sediment: Fe:P **	< 5.5-8.3	
	Al:P ***	4.6-27.5	
	Fe:S	2 - 12	< 2
	log(Fe:P)×log(Fe:S)	0.7 - 2	< 0.7

Fig. 3.27 Processes in MLs with implications for low or high P mobility and indicators for P mobility; (*) no quantitative relation for P mobility versus pore water Fe:P or threshold value for MLs established yet; (**) only if Fe is not immobilized as FeS_x; (***) only as Al hydroxide, not as clay constituent

found as metal sulfides and sulfosalt minerals, and precious metals as sulfide minerals (e.g. acanthite—Ag_2S) or as native metals (gold, silver, electrum), in association with iron sulfides. Accessory minerals containing As and Se are common. Due to the ubiquitous presence of iron sulfides, acid rock drainage is a major water quality problem in metal-mine pit lakes. Thus, the environmental problems with metal-mine pit lakes are similar to those at coal and lignite pit lakes, where acid rock drainage from iron sulfide oxidation occurs, but hardrock metal-mines often have a more diverse set of metals at high concentrations available for dissolution and release to surface and groundwater systems, compared to coal and lignite pit lakes.

Water quality in pit lakes is often an important issue that affects permitting of new mines, expansion of existing mines, and planning for closure. There are numerous approaches for using numerical models to predict future water quality in pit lakes (e.g. Balistrieri et al. 2006; Castendyk and Webster-Brown 2007a, b; Eary et al. 2008; Kempton et al. 1997; Schafer et al. 2006). However, one of the best ways to assess whether predictions are credible is to compare them to water quality patterns that occur in existing pit lakes located in ore deposits with similar geo-environmental characteristics. This chapter provides an overview of the geoenvironmental characteristics and associated water quality patterns for metal-mine pit lakes that provides a starting point for comparative purposes. The frequency of occurrence of metal-mine pit lakes is also discussed. These topics are fundamental to understanding the importance of geoenvironmental models for guiding the setup of numerical models of future pit lake water quality and assessing the credibility of the resulting numerical predictions.

3.2.2.2 Occurrence of Hardrock Metal-Mine Pit Lakes

The metal mining industry has faced an increasing challenge of meeting society's demand for metals to maintain economic growth while ore grades in metallic ore deposits have steadily declined. For example, worldwide production of copper has steadily increased at an annual rate of about 4% since 1910 while average ore grades have declined by about 50% (Fig. 3.28). The long term trends in worldwide gold production and ore grade are similar to copper (Fig. 3.29), although the trend data for gold show more ups and downs due to various factors, such as economic disruptions, opening of new mining districts, and improvements in extraction technologies. Since 1910, worldwide gold production has increased from about 700–2,500 t/year in 2006. This increase in production has taken place even though ore grades have decreased by 50–75% since the early 1900s (Fig. 3.29). Obviously, gold recovery from lower and lower grade ores has become increasingly important for maintaining production rates.

An important technology for efficiently extracting gold from low grade oxide ores is heap leaching with cyanide. In this process, crushed ore is saturated with a cyanide solution which dissolves microscopic grains of gold. The solution is recovered and processed to extract the gold. First trialed in New Zealand at the turn of the 20th century, gold heap leaching became a primary extraction method for oxide ores starting in the 1970s. By 1986, about 30% of the world's production of gold was through heap leaching with cyanide (Dorey et al. 1988).

Increasing metal production from decreasing ore grades requires processing more material. Thus, open pit mining has become the dominant method for metal recovery over time because it is a more efficient method of excavating huge amounts of ore. The dominance of open pit mining can be seen in a compilation of data on yearly worldwide investments in mining projects from 2001 to 2007, which was a period of rapid increase in mine production. Figure 3.30 shows these data for all base metals, precious metals, iron, and diamonds. Figure 3.31 shows data specifically for gold and copper. Each of these charts shows that the proportion of mines planned to be operated as open pits has increased coincident with the recent increase in mining activity. This trend is especially evident for gold and copper mines (Fig. 3.31). For all metal mines, the proportion planned to be operated as open pits increased from 61% in 2001 to 79% in 2007 (Fig. 3.31). For copper and gold mines, the proportion planned as open pits increased from 63% in 2001 to 87% in 2007 (Fig. 3.31). While these data represent only a short time span, they show how open pits have become the dominant mining method for metals due to the need to increase production while ore grades have decreased.

The data on mining project investments also provides a good depiction of where metal mines are located and where they will be located in the future. Figure 3.32 shows the trends in investment by region. Australia (included as part of Oceania) has consistently been the leading country for investments in metal mining projects since 2001. Overall, investments are distributed across all geographic regions, and the proportions of investments by region have remained roughly constant, except for small increases for Latin America at the expense of other regions.

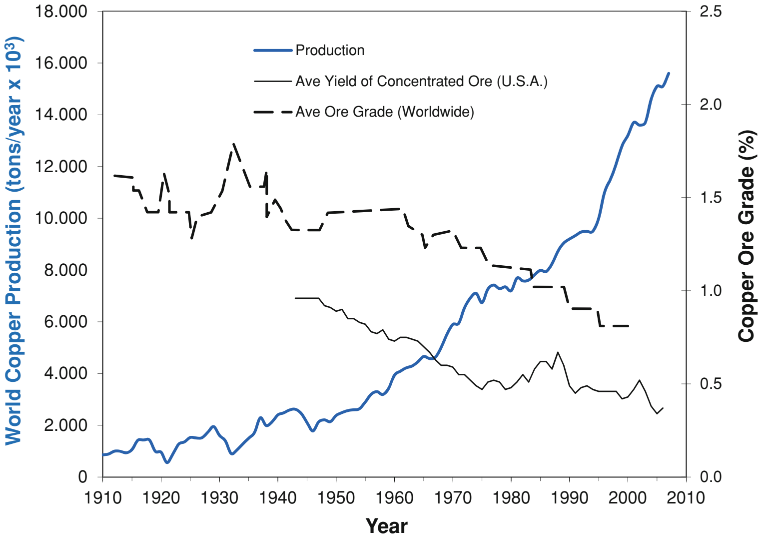


Fig. 3.28 Trends in worldwide copper production (Kelly and Matos 2008a) and ore grades (Kelly and Matos 2008a; Gerst 2008) since 1910

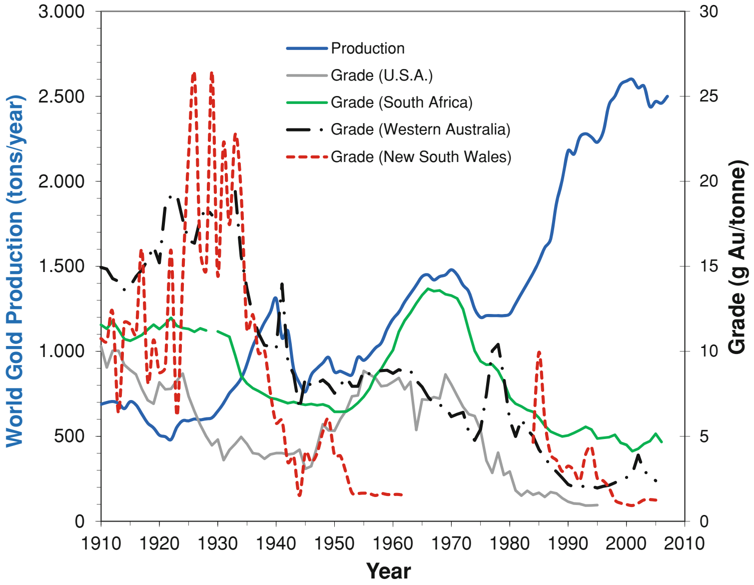


Fig. 3.29 Trends in worldwide gold production (Kelly and Matos 2008b) and gold ore grades (Craig and Rimstidt 1998—U.S.A.; Mudd 2007—South Africa and Australia) since 1910

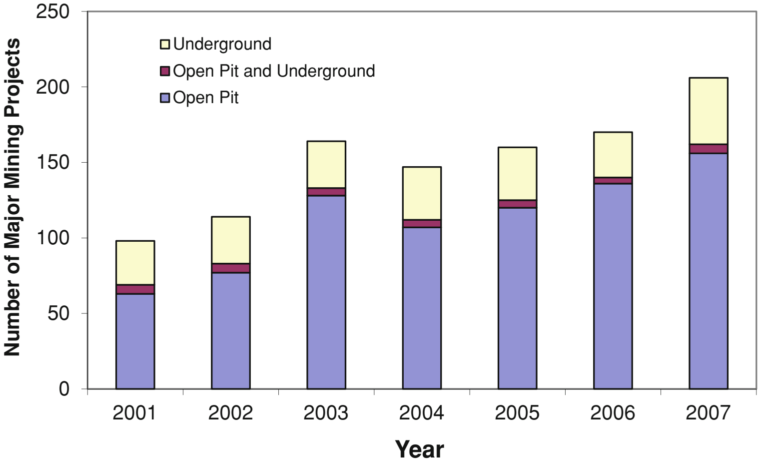


Fig. 3.30 Trends in major mining projects (copper, gold, iron, lead, nickel, platinum group metals, silver, diamonds, zinc; E&MJ 2002–2008)

The global distribution of pit lakes can be expected to resemble the distribution of investments in mining (Fig. 3.32) because the trends shown in Figs. 3.30 and 3.31 indicate that a high percentage of metal mines will be open pit operations. Given the past exploitation of many prospects in the established mining districts of Canada, the United States, and South Africa, it is anticipated that the number of open pit mines (and therefore pit lakes) in East and Central Africa, Central Asia, and Latin America will increase in the future (Castro and Moore 2000).

Metal-mine pit lakes have the potential to cause long-term changes to hydrologic systems and water quality (National Research Council 1999). The creation of lakes in areas where no lake existed prior to mining can potentially affect the viability of nearby water resources. Given their potential volumes, mine pit lakes comprise a potentially large water resource in arid to semi-arid regions and mountainous areas, where potable water is a valuable commodity. For example, Miller (2002) estimated that 35 pit lakes in Nevada have the potential to store 1.85×10^9 m^3 of water, compared to 0.74×10^9 m^3 of water in all the reservoirs in Nevada constructed for water storage. However, the resource value of water in pit lakes is greatly diminished if the water is of poor quality or lost to evaporation. Evaporative loss from large-surface-area pit lakes in arid regions effectively "pumps" stored groundwater from aquifers to the atmosphere while simultaneously increasing the concentration of dissolved metals in residual lake water. Conversely, pit lakes in humid climates may undergo more extensive sulfide oxidation and generate larger volumes of acidic discharge owing to higher inputs of direct precipitation, runoff, and groundwater.

The sections below describe the typical causes of poor water quality at metal-mine pit lakes based on known geochemical processes and observed trends in chemical compositions of existing pit lakes. While these descriptions are useful for making generalizations about the characteristics of metal-mine pit lakes, there are

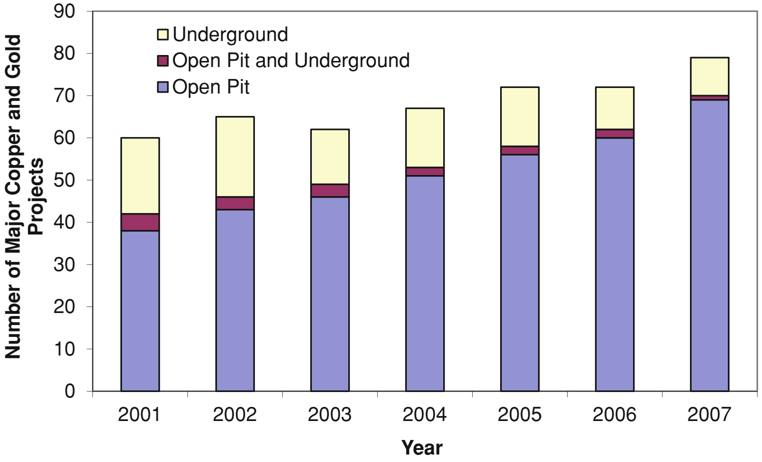


Fig. 3.31 Trends in major mining projects for copper and gold (E&MJ 2002–2008)

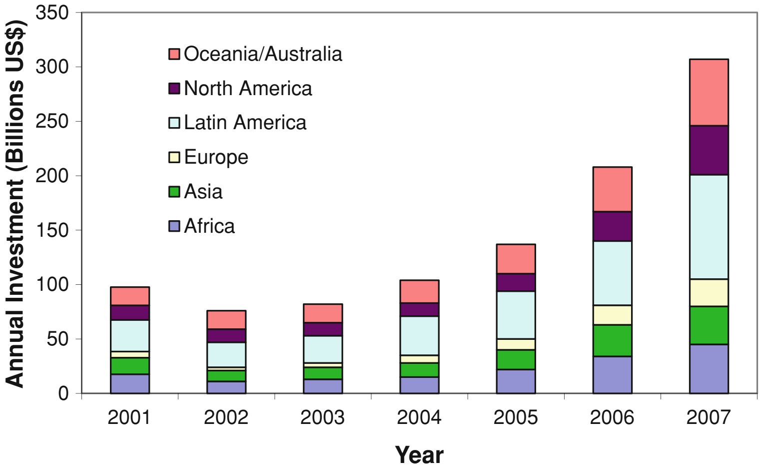


Fig. 3.32 Annual investments in metal mining projects by region (E&MJ 2002–2008)

many deviations from such generalizations due to differences in the geoenvironmental characteristics of specific mine sites.

3.2.2.3 Hydrogeochemical Processes in Metal-Mine Pit Lakes

There are a number of hydrochemical processes that can affect water quality in metal-mine pit lakes over the long term, including:

- Geoenvironmental characteristics
- Sulfide mineral oxidation
- Water balance
- Mineral solubility
- Surface adsorption
- Water column dynamics
- Sediment biogeochemical processes
- Mitigation and remediation efforts

This list of processes is not meant to imply rank in importance but is merely a generalized compilation of the numerous factors that influence water quality in pit lakes. The following sections discuss the importance of these processes in more detail.

3.2.2.4 Geoenvironmental Characteristics

The geoenvironmental characteristics of an ore deposit generally exerts the primary influence on water quality in pit lakes in the absence of remedial measures. The characteristics of ore deposits are often discussed in terms of geoenvironmental models, which are a convenient way to categorize geologically similar mineral deposits and their wastes with respect to their geochemical, mineralogical, geological, geophysical, hydrological, and climatic properties. Summaries and examples of geoenvironmental models can be found in duBray (1995), Plumlee (1999), Plumlee and Nash (1995), Plumlee et al. (1999) and Seal et al. (2007).

Two of the more important aspects of geoenvironmental models are host rock reactivity and alteration mineralogy. Host rock reactivity is important because a portion of the wallrock that surrounds a pit lake is usually comprised of partially mineralized and/or sub-ore grade host rocks that typically contain metal sulfides. Alteration mineralogy is important because the secondary minerals left exposed in the pit walls (host rocks, remnant ore, and adjacent rocks) after mining is completed represent potential sources of leachable metals and acidity. Table 3.6 provides a list of ore deposit types arranged by major metal commodity and their typical assemblages of host rocks. The reactivities of the host rocks are also indicated for each deposit type in terms of typical acid neutralization potential and acid generation potential. The predominant theme that can be gained from the data in Table 3.6 is that most metal ore deposits are contained in silicate rock types that typically have more acid generation potential than acid neutralization potential. The few exceptions to this generalization, such as the lead–zinc Mississippi Valley deposits and Carlin-type gold deposits, are hosted in carbonate rocks, and hence tend to have moderate to high acid neutralization potential. However, the host rocks of most metal ore deposits have an excess of acid generation potential relative to acid neutralization potential.

Table 3.7 lists typical alteration types and secondary mineral assemblages that may be overprinted on host and ore rocks at metal ore deposits. The effects of the secondary minerals on acid neutralization and acid generation potential are also qualitatively estimated in Table 3.7. Most types of alteration result in a decreased potential for acid neutralization because the metasomatic processes involved in secondary mineral formation usually remove or replace reactive primary carbonate and silicates with less reactive silicates and, in some cases, iron sulfides and metal sulfates (e.g. alunite, jarosite), depending on redox conditions. The primary exception to this generalization is carbonitization, in which primary minerals are replaced by carbonate minerals.

The geoenvironmental characteristics of an ore deposit, such as those listed in Tables 3.6 and 3.7, cannot be used to predict absolute values of water quality parameters, such as pH or metal concentration, but they can provide a useful qualitative guide about what type of water quality should be expected in a pit lake. For example, a prediction of neutral pH and low metal concentrations for a future pit lake in a porphyry copper deposit with pervasive argillic alteration should be questioned to identify what mitigating characteristics make it an exception when its geoenvironmental characteristics would predict that acidic water quality should occur. For existing pit lakes, an examination of the geoenvironmental characteristics of the deposit can provide context for explaining observed water qualities. This information may be used to identify the range of conditions that may occur based on comparison to pit lakes in similar deposit and host rock types, which may be useful in the design of remedial strategies for final closure of the pit lake.

3.2.2.5 Sulfide Mineral Oxidation

The primary processes responsible for poor water quality in metal-mine pit lakes is acid mine drainage due to the oxidation of iron sulfide minerals, such as pyrite, marcasite, and pyrrhotite. Sulfides are present in the floors and wallrocks of most metal-mine pit lakes and in the groundwater flow paths leading to pit lakes. In the groundwater flow paths, oxidation may take place in dewatered aquifers, providing a potential source of solutes that could be rinsed and transported into a mine (above and below ground) after mining has ended and the groundwater level recovers to its natural elevation. Sulfides may also be present in waste rock and ore stockpiles sometimes left in the pits after closure.

Iron sulfide is oxidized by molecular oxygen and ferric iron through reactions such as:

$$\mathrm{FeS_2} + 7/2\ \mathrm{O_2} + \mathrm{H_2O} \rightarrow \mathrm{Fe^{2+}} + 2\mathrm{SO_4^{2-}} + 2\mathrm{H^+} \tag{3.10}$$

$$\mathrm{FeS_2} + 14\mathrm{Fe^{3+}} + 8\mathrm{H_2O} \rightarrow 15\mathrm{Fe^{2+}} + 2\mathrm{SO_4^{2-}} + 16\mathrm{H^+} \tag{3.11}$$

A similar type of reaction can be written for pyrrhotite oxidation. Depending on pH conditions, dissolved oxygen concentrations, and microbial activity, ferrous

Table 3.6 Summary of major ore types and acid–base characteristics for hardrock metal-mine pit lakes

Primary metal	Deposit type	Typical host rocks	Host rock acid–base character[a]	Expected lake water quality
Au	Adularia-sericite epithermal vein	Silicic—volcanics: rhyolite, dacite, latite, andesite	Low NP; moderate to high AGP	Acidic to circumneutral
	Epithermal quartz-alunite	Silicic—volcanics	Low NP; high AGP	Acidic
	Carlin type (silicic)	Silicic—siltstone, sandstone, shale, ± igneous intrusive	Low NP; low to moderate AGP	Mildly acidic to circumneutral
	Carlin type (calcareous)	Carbonates—calcareous siltstone, silty, cherty or dolomitic limestone, siltstone, limestone	Moderate to high NP; low to moderate AGP	Circumneutral to alkaline
	Low sulfide quartz-gold veins	Silicic—granitic intrusives, greenstone, gneiss	Low NP; moderate AGP	Acidic
	Au–Ag telluride veins	Silicic—alkalic porphyritic igneous (syenite, monzonite diorite, phonolite), volcanic breccia, diatremes, stockworks	Low NP; moderate AGP	Acidic
	Quartz-pebble conglomerate	Silicic—Clastic sediment, igneous (granite, greenstone, ± volcanics)	Low NP; moderate AGP	Acidic
	Skarn	Carbonates—limestone, dolomite, marble, metasediments	Moderate to high NP; moderate AGP	Acidic to alkaline
Ag	Sedimentary exhalative	Silicic—silicified metasediments, sandstone, siltstone, mudstone, shale	Low NP; moderate AGP	Acidic
	Adularia-sericite epithermal vein	Silicic—volcanics (rhyolite, dacite, latite, andesite)	Low NP; moderate to high AGP	Acidic
	Polymetallic veins	Silicic—igneous intrusives (diorite, granodiorite, monzonite), volcanics (andesite to rhyolite), metasediments	Low NP; moderate to high AGP	Acidic
	Au–Ag telluride veins	Silicic—alkalic porphyritic igneous (syenite, monzonite diorite, phonolite), volcanic breccias, diatremes, stockworks	Low to moderate NP; moderate to high AGP	Acidic

(continued)

Table 3.6 (continued)

Primary metal	Deposit type	Typical host rocks	Host rock acid–base character[a]	Expected lake water quality
Cu	Seafloor massive sulfide	Silicic—mafic to felsic volcanics, metasediments	Low to moderate NP depending on mineral assemblage; high AGP	Acidic
	Magmatic massive sulfide	Silicic—mafic volcanic: diabase, gabbro, pyroxenite	Low to moderate NP depending on mineral assemblage; high AGP	Acidic to neutral
	Sedimentary exhalative	Silicic—silicified metasediments, sandstone, siltstone, mudstone, shale	Low to moderate NP; moderate AGP	Acidic
	Porphyry	Silicic—igneous intrusives (tonalite to monzogranite, syenite porphyries)	Low NP; moderate to high AGP	Acidic
	Sediment hosted	Silicic—red-beds (green shale, gray shale, siltstone, sandstone, ± carbonates, evaporites)	Low to moderate NP; low to moderate AGP	Acidic to neutral
	Skarn	Carbonate—Limestone, dolomite, marble, calc-silicate metasomatic, igneous intrusives (tonalite to monzogranite, syenite porphyries)	Moderate to high NP; moderate AGP	Neutral
Mo	Porphyry	Silicic—igneous intrusive: granitic-rhyolitic porphyries	Low NP; moderate AGP	Acidic
Pb–Zn	Seafloor massive sulfide	Silicic—mafic to felsic volcanics, metasediments	Low to moderate NP depending on mineral assemblage, High AGP	Acidic
	Sedimentary exhalative	Silicic—silicified metasediments, sandstone, siltstone, mudstone, shale	Moderate NP; low to moderate AGP	Acidic
	Mississippi Valley type	Carbonate—dolostone, ± limestone, sandstone–siltstone, shale	Moderate to high NP; moderate AGP	Neutral to alkaline
	Manto/skarn	Carbonate—limestone, dolomite, sandstone–siltstone	Moderate to high NP; moderate AGP	Acidic to alkaline

[a] *NP* neutralization potential, *AGP* acid generation potential

Table 3.7 Summary of acid–base characteristics of major alteration types found in metallic ore deposits based on the summary in Plumlee (1999)

Alteration	Secondary minerals	Acid–base characteristics[a]
Acid sulfate (alunite)/ advanced argillic	Quartz/chalcedony, pyrite, alunite, jarosite, kaolinite, ± pyrophyllite, dickite	Greatly decreases NP, increases AGP; increases potential for rapid initial release of acid + sulfate
Argillic	Kaolinite, illite, montmorillonite, ±pyrite, ±chlorite	Decreased NP; possible increase in AGP
Phyllic	Quartz, sericite, pyrite	Decreased NP; increased AGP
Potassic	K-feldspar, biotite, ±anhydrite	Decreased NP; possible rapid release of sulfate
Propylitic	Epidote, chlorite, calcite, albite, ±pyrite	Increased NP depending on amount of calcite formed; Possible increase in AGP from pyrite
Silica	Silica (quartz, chalcedony)	Decreased NP; AGP not substantially changed
Jasperoid	Silica (quartz, chalcedony)	Greatly decreased NP due to replacement of sedimentary carbonates with silica; AGP not substantially changed
Greisen	Quartz, muscovite, fluorite, cassiterite, magnetite	Potential for decreased NP; AGP not substantially changed
Skarn	Ca silicates, silica, magnetite, ±pyrite	Decreased NP; increased AGP
Dolomitization	Dolomite	Decreased effective NP due to formation of potentially less reactive dolomite; AGP not substantially changed
Carbonitization	Calcite, dolomite, siderite, rhodochrosite	Potentially large increase in NP (but neutralization from siderite is countered by oxidation of Fe^{2+}; AGP not substantially changed)
Sulfidation	Pyrite	Decreased NP; increased AGP

[a] *NP* neutralization potential, *AGP* acid generation potential

iron is fairly rapidly oxidized to ferric and precipitated as ferric hydroxide and schwertmannite, producing more acid, as in:

$$Fe^{2+} + 1/4O_2 + 5/2H_2O \rightarrow Fe(OH)_3 + 2H^+ \tag{3.12}$$

$$8Fe^{2+} + SO_4^{2-} + 2O_2 + 10\ H_2O \rightarrow Fe_8O_8(SO_4)(OH)_6 + 14H^+ \tag{3.13}$$

It is generally recognized that dissolution reactions involving carbonates (calcite and dolomite) have a high potential to neutralize the acid generated by sulfide oxidation through reactions such as:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \tag{3.14}$$

Silicates also have the capacity to neutralize acidity through dissolution reactions, such as the following reaction for anorthite:

$$CaAl_2Si_2O_8 + 2H^+ + 6H_2O \rightarrow Ca^{2+} + 2Al(OH)_3 + 2H_4SiO_4 \tag{3.15}$$

There are numerous detailed descriptions of the above types of reactions involved in sulfide mineral oxidation in the literature (e.g. Nordstrom and Alpers 1999; White et al. 1999) and it is not the purpose of this paper to discuss them in detail. However, a comparison of the kinetics of acid generation reactions (Eqs. 3.10 and 3.11) to the rates of acid neutralization (Eqs. 3.14 and 3.15) is useful for illustrating why some metal-mine pit lakes become acidic and some do not.

Williamson and Rimstidt (1994) describe the abiotic rate of pyrite oxidation by oxygen for a reference system with a surface area to water ratio of 1 m^2 pyrite/1 kg of solution:

$$\mathrm{Rate(mol\,pyrite}\,m^{-2}s^{-1}) = 10^{-8.19}\left(\frac{\mathrm{m}_{\mathrm{O_2}}^{0.5}}{\mathrm{m}_{\mathrm{H^+}}^{0.11}}\right) \tag{3.16}$$

These authors also describe the abiotic rate of pyrite oxidation by ferric iron for conditions where both dissolved oxygen and ferric iron are present in solution for a reference system (Williamson and Rimstidt 1994):

$$\mathrm{Rate(mol\,pyrite}\,m^{-2}s^{-1}) = 10^{-6.07}\left(\frac{\mathrm{m}_{\mathrm{Fe^{3+}}}^{0.93}}{\mathrm{m}_{\mathrm{Fe^{2+}}}^{0.4}}\right) \tag{3.17}$$

For carbonate minerals, Palandri and Karaka (2004) describe the rates of calcite and dolomite dissolution:

$$\mathrm{Rate(mol\,calcite}\,m^{-2}s^{-1}) = 10^{-0.3}[H^+]^{1.0} + 10^{-5.81} + 10^{-3.48}P_{\mathrm{CO_2}} \tag{3.18}$$

Finally, the rates of dissolution of silicates can be described by the general form of the following rate expression (Casey and Ludwig 1995; Chou and Wollast 1985; Palandri and Karaka 2004):

$$\mathrm{Rate}(\mathrm{mol\,silicate}\,m^{-2}s^{-1}) = k_H[H^+]^a + k_w + k_{OH}[OH^-]^b \tag{3.19}$$

Palandri and Karaka (2004) provide a detailed summary of the values of rate constants and exponents for Eq. 3.19 for silicate minerals.

Figure 3.33 shows a comparison of the above reaction rates for a range of pH for equivalent quantities and surface areas. The rates of pyrite oxidation by both oxygen and ferric iron are more rapid than neutralization by the types of silicates most commonly found in silicic intrusive rocks hosting metal sulfide ores, such as quartz, feldspars, clays, and micas. The dissolution rates of some mafic silicates (e.g. olivine and anorthite) approximate the rate of pyrite oxidation by oxygen, suggesting that they may be good sources of neutralization. However, few economic grade metallic ore deposits mined in open pits are hosted in mafic silicates; hence, their importance for preventing acid generation for most pit lakes is minimal.

In comparison, the rates of carbonate mineral (calcite and dolomite) reactions are more rapid than pyrite oxidation (Fig. 3.33). That is why carbonate minerals, when present in sufficient quantities, can prevent acid generation in metal-mine pit lakes; they react rapidly enough to keep up with the rate of iron sulfide oxidation, assuming that they are not completely consumed before the sulfides.

The conclusion that can be drawn from Fig. 3.33 is that most silicate minerals generally do not dissolve fast enough to preclude acid generation under most circumstances, in contrast to carbonate minerals. This conclusion is not surprising; otherwise, acid rock drainage would not be the common phenomena that it is given the predominance of silicate rock types over carbonates in most mineralized districts. Similar observations have been made for natural, closed-basin lakes located in volcanic terrains with high sulfur contents where the buffering capacities of silicate minerals have been overwhelmed by pervasive acid alteration from sulfur and sulfide oxidation, resulting in naturally acidic, saline lakes (Risacher et al. 2002).

3.2.2.6 Water Balance

Water balance, which describes the inputs and outputs of water and their associated solute loads to a pit lake, has a fundamental control on water quality in metal-mine pit lakes, especially during the initial period of infilling. Solutes enter the lake primarily through groundwater inflow, leaching of wallrocks, leaching of backfill material (if present), and the dissolution of secondary minerals and metal-salts, some of which may exist as efflorescence on pit walls and in pore spaces prior to lake filling. Salts may also exist in the dewatered parts of aquifers surrounding a mine due to oxidation processes. Because solute influxes are functions of flow rates, they are directly dependent on the rates of water inflow from the different hydrologic sources that make up the water balance of the pit lake watershed. Sources may include groundwater, pit wall runoff, direct rainfall, and

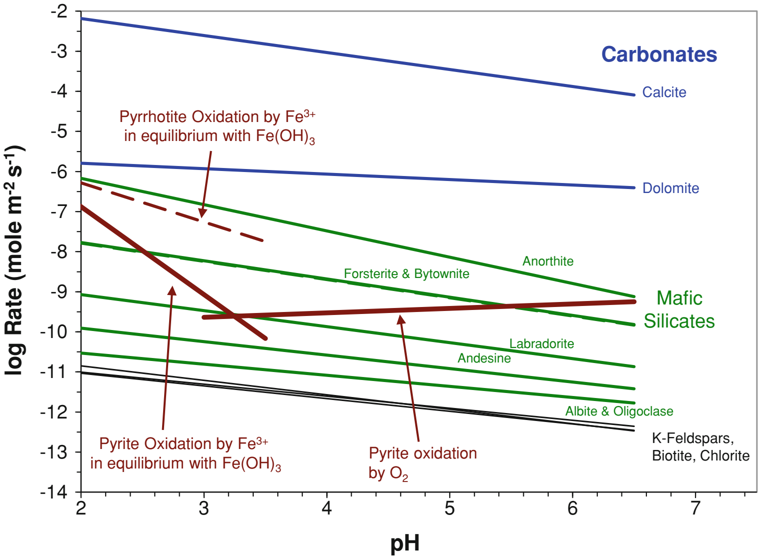


Fig. 3.33 Comparison of reaction rates for acid generation and acid neutralization reactions relevant to metal-mine pit lakes (reference surface area to solution ratio of 1 m^2/kg H_2O). Sources of rate data are Williamson and Rimstidt (1994) for pyrite and Palandri and Karaka (2004) for pyrrhotite, carbonates, and silicates

possibly surface water diverted into the open pit to accelerate lake filling. The rates of inflow of different hydrologic sources may change over time as the pit lake fills. For example, the proportion of the water balance from groundwater inflow may decrease over time as the local groundwater table recovers and hydrologic gradients diminish, whereas the relative proportions of water from runoff and direct precipitation may increase, depending on the pit morphology and catchment area. Sulfide mineral oxidation will slow as the wallrocks are increasingly inundated, thereby slowing the rates of acid and metals release. In some cases, the rinsing of sulfide oxidation products from wallrocks and backfill materials may provide a short-term high influx of solutes during the early stages of pit filling (see also case study 5.1). If evaporation is the only route for water loss from the pit lake, many solute concentrations not affected by solubility will increase slowly over time due to evapoconcentration. Biogeochemical processes and surface adsorption reactions taking place in the water column and sediments may moderate the concentrations of some solutes, but for the most part, the water and chemical balance will primarily control water quality.

The water balances for most hardrock mining pit lakes can be categorized in general terms as either: terminal pit lakes, in which outflow occurs only as evaporation or; flow-through pit lakes, in which surface and/or groundwater flow into and out of the pit lake (see also Sect. 4.1.2). The typical trends in water quality dynamics for each type are likely to be different for different water balance scenarios.

A common situation for many hardrock mining pit lakes is that the wallrock leachates are acidic due to sulfide mineral oxidation, whereas the inflowing groundwater has a circumneutral to alkaline pH and some amount of acid-buffering capacity. As a result, the dynamics in water quality are controlled by the relative influx proportions from these two sources. For example, most terminal pit lakes with low influxes of acid solutes from wallrock leaching and high influxes of alkalinity from groundwater will evolve to water qualities with one of the following sets of characteristics: (1) circumneutral pH values, gypsum saturation, and low cationic and anionic metal concentrations due to solubility and adsorption constraints, or (2) alkaline pH values, calcite saturation, and low cationic metal concentrations but potentially elevated concentrations of arsenic and selenium (Davis and Eary 1997; Eary 1998). In either case, the total dissolved solids concentrations will continue to increase over time in terminal pit lakes due to evapoconcentration (Fig. 3.34). Pit lakes formed in Carlin-type gold deposits are examples of circumneutral to alkaline pit lakes with occasional instances of elevated arsenic and selenium (Davis and Eary 1997; Eary 1998).

For pit lakes with high influxes of acid equivalents from wallrocks compared to groundwater inflow, the initial and long-term water quality can be expected to be acidic, with high total dissolved solids (TDS) due to elevated metal concentrations and sulfate (Fig. 3.34; Eary 1999). The pH will most commonly stabilize over time between 2.5 and 4, but the TDS will continue to increase due to evapoconcentration (Fig. 3.34). Over the long-term, some amount of microbial activity in the sediments of anoxic lower layers of meromictic lakes may produce small increases in pH and decreases in metal concentrations due to sulfate reduction, but the lakes are likely to remain acidic in the absence of remedial measures due to their large volume and the isolation of meromictic waters from shallower lake layers. The acidic pit lakes of the Iberian Pyrite Belt (Sánchez-España et al. 2008) associated with polymetallic massive sulfide deposits and the former Spenceville pit lake (Levy et al. 1997), which formed in a silicic polymetallic vein deposit, are examples of terminal pit lakes with high rates of acid influx and evapoconcentration.

Bowell and Parshley (2005) documented the existence of a variety of secondary iron sulfates and arsenic oxyhydroxides on pit wallrocks that may act as sources of easily leachable metals to pit lakes during the initial stages of pit infilling and potentially on a seasonal basis thereafter. Pit lakes receiving high initial loads of metals and sulfate from the wash off of oxidation products may initially have acidic pH values that eventually rise as the effects of the wash off of acidic solutes diminish and the pit walls become inundated, slowing further sulfide mineral oxidation (Fig. 3.34). The TDS trends for this situation may show an initial period of decrease due to dilution from inflowing groundwater with lower TDS concentrations, but over time, the trend for TDS will be upward (Fig. 3.34). This type of TDS trend may be most applicable to arid climate pit lakes.

Flow-through and terminal pit lakes with high influxes of acidity from wallrocks relative to groundwater inflow are likely to remain acidic in the absence of

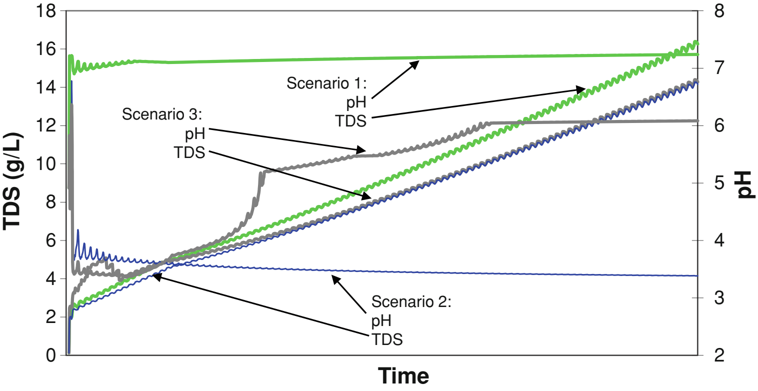


Fig. 3.34 Generalized time trends in pH and TDS for terminal pit lakes for Scenario 1—high groundwater alkalinity and low wallrock acidity; Scenario 2—high wallrock acidity and low groundwater alkalinity; and Scenario 3—moderate groundwater alkalinity with initial acid wash off

remedial measures (Fig. 3.35). Conversely, flow-through pit lakes with low acid loads from wallrocks and high influxes of alkalinity from groundwater are most likely to have circumneutral pH values. An important difference with terminal pit lakes is that TDS concentrations in flow-through pit lakes will only increase until the lake reaches hydrologic steady state with the groundwater system (Fig. 3.35). At that point in time, the TDS should stabilize as a balance is reached between chemical inputs and losses to and from the pit lake. The Berkeley pit lake is an example of an eventual flow-through system in which total solute concentrations have slowly increased over time as the lake approaches its hydrologic spill-over point (Gammons and Duaime 2006), although its water quality dynamics are also affected by water management systems associated with metal extraction and inflows from underground workings. An important consideration for both terminal and flow-through pit lakes is that the time scale for the dynamics in chemical processes may be different from hydrologic processes (Schafer and Eary 2009). A flow-through pit lake may reach hydrologic equilibrium in a relatively short period of time, but various chemical processes and water column dynamics in terminal pit lakes may continue to evolve and result in changes in water quality.

3.2.2.7 Water Column Dynamics

It is generally recognized that metal-mine pit lakes have substantially different shapes than natural lakes. Pit lakes tend to have lower ratios of surface area to depth and are steep-sided compared to natural lakes. This difference is evident in a comparison of relative depths for pit lakes. (Relative depth is defined by Wetzel (2001) as the ratio of the maximum depth to the average diameter, in percent.

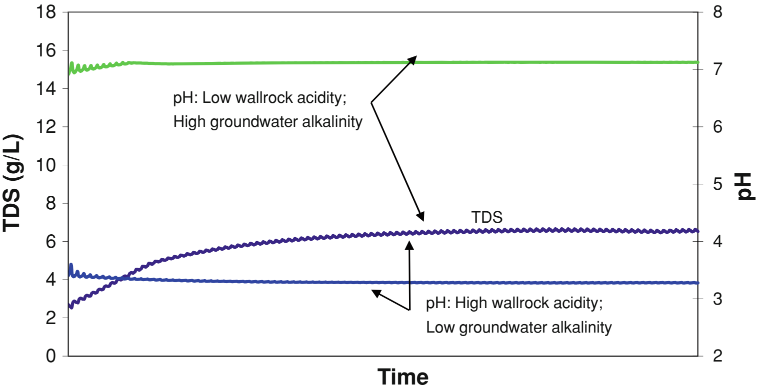


Fig. 3.35 Generalized time trends in pH and TDS for flow-through pit lakes

See also Sect. 2.1) Natural lakes usually have relative depths in the range of 2% or less, whereas metal-mine pit lakes have much higher values, from 15 to 45% (Castendyk 2009). Highwalls, which are common on one or more sides of pit lakes, may also decrease the transfer of wind energy to the lake surface, decreasing the potential for mixing of the water column.

Based on these general characteristics, it has been thought that pit lakes should be more likely to be permanently stratified (meromictic) than natural lakes, which commonly experience seasonal overturn (holomictic), and that a calculation of relative depth may be sufficient to predict water column dynamics (Castro and Moore 2000; Doyle and Runnells 1997; Lyons et al. 1994). However, Schultze and Boehrer (2009) and Castendyk (2009) independently showed that relative depth is a poor predictor at best of the tendency for stratification in pit lakes. For example, a plot of maximum depths against surface areas for metal-mine pit lakes shows that, as might be expected, meromictic lakes tend to have slightly higher depths than holomictic lakes, there is a great deal of overlap between the two sets of data (Fig. 3.36). Many steep-sided pit lakes have high depths and small surface areas yet show holomictic water column dynamics. These data indicate that while the shape of a pit lake undoubtedly has an important influence on the water column dynamics, numerous other factors, such as the chemistry and density of lake water inputs, climate, and hydrology, are also important (see also Sect. 3.1).

The data in Fig. 3.36 show that predicting whether a pit lake will become permanently stratified or experience seasonal or occasional overturn cannot be based solely on shape. Knowledge of water column dynamics is important for predicting long term water quality and designing mitigation strategies to improve water quality. For example, a lake that experiences seasonal overturn may be expected to remain oxygenated for most of the year. This factor that can be used to parameterize predictive models for future pit lakes or interpret water quality models of existing pit lakes where redox processes are important for controlling metal concentrations. In comparison, a pit lake that experiences permanent

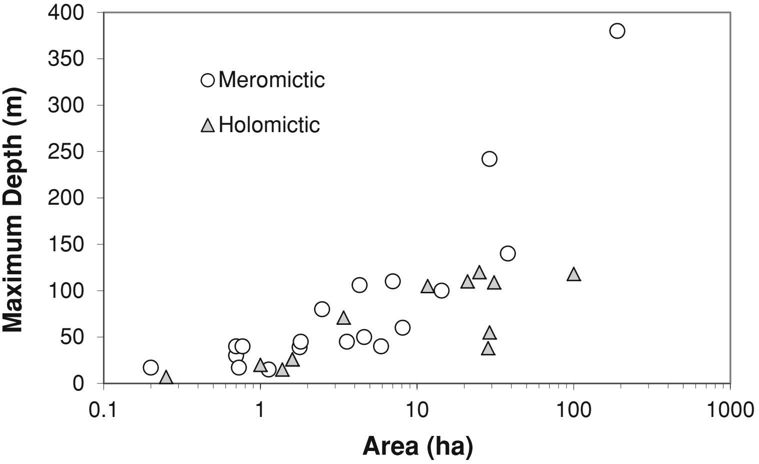


Fig. 3.36 Maximum lake depth versus area for meromictic and holomictic metal-mine pit lakes from the compilations of Castendyk (2009) and Sánchez-España et al. (2008)

stratification may have substantially different redox conditions and water qualities in different lake layers. Oxygenated conditions may exist near the surface whereas anoxic conditions may exist at depth, leading to sulfate reduction and alkalinity production in bottom sediments.

Permanent stratification and associated effects on biogeochemical processes may be incorporated into approaches for improving water quality. For example, the strategies employed at the Island Copper pit lake in British Columbia have resulted in greatly improved water quality in surface layers, even though the lake experienced inputs of acid mine drainage water (Pelletier et al. 2009). In a different study, Colarusso et al. (2003) determined that density stratification of the water column in the South Mine Pit lake at the Copper Basin Mine, Tennessee would be stable for a range of potential conditions. This result was used by Wyatt et al. (2006) to justify development of an in-pit lime treatment system to improve the water quality of discharges from the top, low-TDS water layers.

3.2.2.8 Mineral Solubilities

Mineral and gas solubilities play an important role in affecting rates of solute release in pit lakes similar to contaminant attenuation processes observed in some surface groundwater systems. Numerical models of pit lakes typically rely at least in part on thermodynamic-based geochemical models of aqueous speciation, solubility, and surface adsorption, as well as kinetic formulations for predicting water quality trends in future pit lakes and interpreting water quality conditions in existing pit lakes. Pit lakes, however, are dynamic systems in which both kinetically controlled abiotic and biotic chemical processes occur, producing conditions of disequilibrium that may metastably persist. Eary (1999) reviewed equilibrium trends in pit lakes to provide guidance to numerical modelers about which solubility reactions are reasonably well represented by chemical equilibrium and which are more likely to be affected by kinetic processes.

A summary of potential solubility controls for different solutes from Eary (1999) and supplemented by a few more recent studies is given in Table 3.8. The review by Eary (1999) showed that sulfate is the dominant solute in most metal-mine pit lakes, especially acidic pit lakes, and sulfate concentrations are typically limited by gypsum solubility. Gypsum is indicated to be a solubility control based on its trend in saturation indices calculated for a number of metal-mine pit lakes as a function of sulfate concentration (Fig. 3.37). Other important solubility controls for major ions indicated from saturation indices were calcite, fluorite, and barite. In addition, the data trends from numerous acidic pit lakes indicated that reasonably well defined solubility controls include alunite for aluminum, ferrihydrite for iron, and manganite and birnessite for manganese. Schwertmannite may also be an important solubility control for iron in acidic pit lakes, based on evaluations provided by Nordstrom and Alpers (1999) and Sánchez-España et al. (2009).

Solubility controls for divalent minor metals are much less well established, but data trends suggest otavite for cadmium, brochantite and malachite for copper, cerrusite and pyromorphite for lead, and hydrozincite and zinc silicate for zinc (Table 3.8). Concentrations of As and Se are not represented by any established mineral solubilities and may be primarily affected by adsorption to aluminum and iron oxyhydroxide minerals under acidic conditions. For example, Sánchez-España et al. (2008) report that arsenic concentrations are significantly lower in acidic pit lakes that have pH values within the pH stability field of schwertmannite (i.e. pH $< \approx 4$) compared to pit lakes in which schwertmannite is not stable. Arsenic may also be incorporated into uncommon mixed hydroxyl sulfate minerals, such as beudantite [$PbFe_3(AsO_4)(SO_4)(OH)_6$] (Romero et al. 2007). Adsorption processes are less effective for removing arsenic and selenium from solution in high sulfate concentrations or in higher pH (i.e. >pH 6) solutions and their concentrations can be expected to increase linearly with evapoconcentration.

In summary, mineral solubilities provide reasonable representations of maximum concentrations for many major solutes (e.g. Ca, Mg, HCO_3^-, SO_4^{2+}, F, Al, Fe^{3+}, and Mn) in metal-mine pit lakes (Eary 1999; Eary and Schafer 2009), but they are much less reliable for predicting the concentrations of divalent minor metals (e.g. Cd, Cu, Pb, and Zn) and metalloids (e.g. As and Se). In most cases, predictive models will need to rely on empirical formulations to represent metal and metalloid concentrations derived from either experimental, field data, and/or comparisons to existing pit lakes in similar geoenvironmental settings.

Trend data for $CO_{2(g)}$ partial pressures as a function of pH for metal-mine pit lakes are shown in Fig. 3.38. These $CO_{2(g)}$ levels are calculated from measurements of pH and bicarbonate alkalinity and carbonate equilibrium speciation. They show that most acidic metal-mine pit lakes can be expected to be oversaturated with $CO_{2(g)}$ compared to the atmospheric level of $10^{-3.5}$ atm (Fig. 3.38). The degree of oversaturation increases in acidic pH conditions and reaches about

Table 3.8 Summary of potential solubility controlling minerals for metal-mine pit lakes (Bowell and Parshley 2005; Eary 1999)

	Acidic (pH < ≈4.5)	Circumneutral (pH ≈ 4.5 to ≈ 7.5)	Alkaline (pH > ≈ 7.5)
Al	Alunite, basaluminite	Gibbsite, kaolinite, allophane, sericite	Gibbsite, kaolinite, allophone, sericite
Alkalinity	Not applicable	Calcite[b]	Calcite[b]
As	Adsorption to ferrihydrite and schwertmannite[h], scorodite[j], bukovskyite[k], scorodite-mansfieldite[k], weilite[k], pharmacolite[k]	Adsorption to ferrihydrite[h]	None identified
Ba	Barite	Barite, witherite	Barite, witherite
Cd	None identified	Adsorption to ferrihydrite	Otavite
Ca	Gypsum	Gypsum	Gypsum, calcite
Cu	Copper sulfates[j]	Brochantite[g]	Malachite, brochantite[g]
Fl	Fluorite	Fluorite	Fluorite
Fe[c]	Ferrihydrite, schwertmannite, melanterite[j]	Siderite (Fe^{2+})[j]	Siderite (Fe^{2+})[j]
Pb	Anglesite[f], chloropyromorphite[d], plumbojarosite[j],	Anglesite[f], chloropyromorphite[d], adsorption to ferrihydrite	Cerrusite, chloropyromorphite[d]
Mn	Manganite, birnessite	$MnHPO_4$[d]	Rhodochrosite
Se	Adsorption to ferrihydrite[i]	Adsorption to ferrihydrite	None identified
Strontium	Celestite	Celestite, strontianite	Celestite, strontianite
Sulfate	Gypsum, copiapite[k], melanterite[k], mirabolite[k], halotrichite-pickeringite[k]	Gypsum	Gypsum
Zinc	None identified	Hydrozincite[e], $ZnSiO_4$[g]	$ZnSiO_4$[g], zincite, smithsonite[j]

[a] Oversaturation with calcite is typical in most pit lakes; [b] Oversaturation with CO_2 at $10^{-3.5}$ atm typically occurs for pH < 8.5 and undersaturation for pH > 8.5; [c] Assumed to be ferric iron; [d] Dependent on the presence of phosphate; [e] Requires the presence of carbonate alkalinity; [f] Requires relatively high sulfate concentration such as those reached at gypsum saturation; [g] Requires the presence of dissolved silica near or approaching saturation with chalcedony; [h] Decreases in efficiency with increases in sulfate concentration; [i] Negligible for sulfate concentration >100 mg/L; [j] From compilation for acid mine waters in Nordstrom and Alpers (1999) [k] From compilation of Bowell and Parshley (2005)

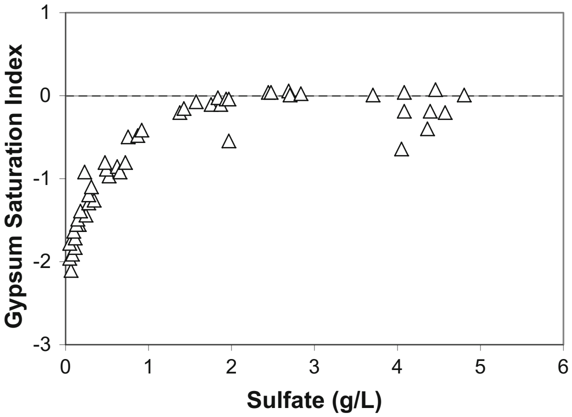


Fig. 3.37 Gypsum saturation indices for metal-mine pit lakes (Eary 1999)

10^{-2} atm or about 30 times atmospheric $CO_{2(g)}$ for pH less than 7. These data are important for providing information on the levels of oversaturation that should be expected to occur when parameterizing geochemical models of pit lakes. Models of metal-mine pit lakes should expect conditions of disequilibria with respect to $CO_{2(g)}$, particularly for lakes with pH less than the circumneutral range. This is an important point for modelers to remember when predicting pit lake geochemistry. By specifying $CO_{2(g)}$ in equilibrium with the atmosphere, the model will force $CO_{2(g)}$ out of solution, resulting in a higher pH than would otherwise be calculated. This can lead to predicted higher pH values than observed pH values.

3.2.2.9 Surface Adsorption

At a microscopic scale, charged ions and molecules are attracted to electrically-charged surfaces of suspended particulate matter (SPM) within pit lake water. Positively-charged cations (e.g. Cu^{2+}, Pb^{2+}, Zn^{2+}) are attracted to negatively-charged surfaces, whereas negatively-charged anionic metalloids (e.g. SeO_4^{2-}, SeO_3^{2-}, AsO_3^{3-}, AsO_4^{3-}) are attracted to positively-charged surfaces. Once the ion or molecule adsorbs onto a surface, it will remain there until the pH of the surrounding solution changes or the SPM decomposes. Under optimal conditions, the water quality of a pit lake may improve due to metal adsorption to SPM and the SPM settles to the bottom of the pit lake where it is buried. With this goal in mind, improving water quality via surface adsorption forms the basis of many contemporary remediation strategies for pit lakes (Kalin and Wheeler 2009; Pelletier et al. 2009).

Hydrous ferric oxides (HFO), such as ferrihydrite and schwertmanite, which are produced by the oxidation of iron sulfides in acidic pit lakes, typically provide abundant surface area for adsorption. Webster et al. (1998) discuss the effects of surface adsorption on the water quality of acid mine drainage. Castendyk and Webster-Brown (2007b) demonstrate the effects of surface adsorption on predicted pit lake water quality by comparing As, Cd, and Cu concentrations modeled

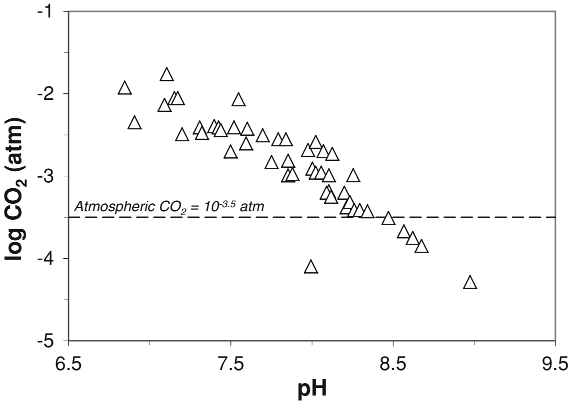


Fig. 3.38 Trends in equilibrium partial pressures of $CO_{2(g)}$ in metal-mine pit lakes (Eary 1999)

without surface adsorption to concentrations modeled with surface adsorption onto freshly precipitated ferrihydrite.

The surfaces of other particles, such as Al and Mn hydroxides and clays minerals (e.g. smectite, illite, kaolinite) that develop surface charges in response to cation substitutions may also be adsorption substrates. Furthermore, the surfaces of suspended organic matter, such as phytoplankton and diatoms spines, provide adsorption sites; hence, some remediation strategies endeavor to stimulate biological productivity of pit lakes by the addition of nutrients (Kalin and Wheeler 2009; Pelletier et al. 2009).

General depictions of percent adsorption of various dissolved cations and anionic metalloids onto a sample of HFO as a function of pH (Figs. 3.39 and 3.40 partially explain why low pH pit lakes tend to have elevated concentrations of cationic metals whereas high pH pit lakes may exhibit elevated concentrations of anionic metalloids (see below). However, these diagrams should only be used as general indicators of adsorption trends as each pit lake will contain different surface adsorption surfaces and different water chemistry.

3.2.2.10 Sediment Biogeochemical Processes

Geochemical processes occurring in bottom sediments have the potential to affect metal cycling in metal-mine pit lakes in ways similar to natural water bodies. These reactions are driven in large part by the oxidation of carbon catalyzed by microbial processes. In simple terms, the oxidation of organic carbon can be described by:

$$C_{organic} + 2H_2O = CO_2 + 4H^+ + 4e^- \tag{3.20}$$

In the anaerobic environment at the bottom of a pit lake, anaerobic microorganisms derive energy from the oxidation of organic carbon coupled with the following reduction reactions, which are listed in order of decreasing redox potential:

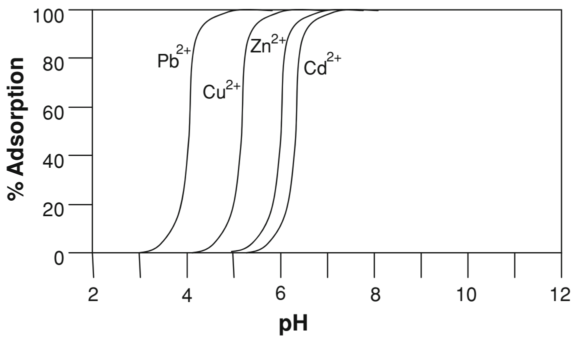


Fig. 3.39 Approximate adsorption of cations onto generic HFO as a function of lake pH (after Drever 2002, with data from Dzombak and Morel 1990)

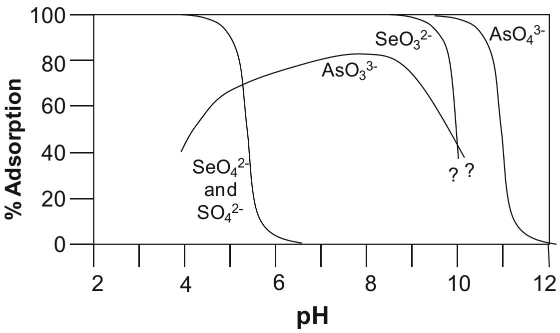


Fig. 3.40 Approximate adsorption of anionic metals onto generic HFO as a function of lake pH (after Drever 2002, with data from Dzombak and Morel 1990)

$$2NO_3^- + 10e^- + 12H^+ = N_2 + 6H_2O \text{ (denitrification)} \tag{3.21}$$

$$MnO_2 + 2e^- + 4H^+ = Mn^{2+} + 2H_2O \text{ (manganese reduction)} \tag{3.22}$$

$$Fe(OH)_3 + e^- + 3H^+ = Fe^{2+} + 3H_2O \text{ (iron reduction)} \tag{3.23}$$

$$SO_4^{2-} + 8e^- + 10H^+ = H_2S + 4H_2O \text{ (sulfate reduction)} \tag{3.24}$$

When combined with reaction 3.20, the net oxidation–reduction reactions for iron and sulfate by organic carbon may be written as follows:

$$C_{organic} + 4Fe(OH)_3 + 8H^+ = CO_2 + 4Fe^{2+} + 10H_2O \tag{3.25}$$

$$2C_{organic} + SO_4^{2-} + 2H_2O = H_2S + 2HCO_3^- \tag{3.26}$$

While these types of reactions are well established as important controls on sediment chemistry, there are few investigations specific to metal-mine pit lakes available in the literature that can be used to develop detailed understanding of sediment mineralogy, chemical composition, pore water chemistry, biogeochemistry, and their effects on water quality. Information gleaned from a few available studies is summarized in Table 3.9, although most of these studies were focused on acidic, stratified (i.e. meromictic) pit lakes. The common characteristics of the lakes summarized in Table 3.9 are acidic compositions, seasonal or permanent stratification, oxygenated upper portion of the water column, and anoxic conditions at depth and in sediments. Iron and aluminum oxyhydroxide and sulfate minerals are commonly found in sediments along with gypsum. These minerals are most likely to have formed as secondary phases in wallrocks and carried into the pit lakes by erosion or formed in the water column and subsequently settled to the bottom. Triantafyllidis and Skarpelis (2006) also report the presence of a number of metal sulfate minerals present as a thin layer of precipitants in the bottom of a shallow, highly acidic pit lake that is oxygenated throughout the water column.

Accompanying the anoxic conditions at depth are increases in pH in the sediment pore water relative to the overlying water column and occasional presence of hydrogen sulfide (Table 3.9). These characteristics are indicative of biologically-mediated reduction of sulfate and Fe^{3+}, potential for release of metals due to reductive dissolution of metal oxyhydroxides, and potential for re-precipitation of some metals as metal sulfides. Biological reduction of sulfate requires an energy source for microbial activity in the form of organic carbon. However, there are few data on organic carbon levels in metal-mine pit lakes. Levy et al. (1997) found low concentrations of dissolved organic carbon (DOC) in the water column of the acidic Spenceville pit lake, although concentrations were greater in the sediment pore water (Table 3.9). Levy et al. (1997) speculated that the low DOC levels in combination with high Fe^{3+} levels limited the extent to which microbial processes resulted in sulfate reduction in the sediments of the Spenceville pit lake. Cameron et al. (2006) reported low DOC concentrations in the water column but relatively high concentrations in the sediment pore water from the acidic Berkeley pit lake (Table 3.9). However, there is little evidence of sulfate reduction in the Berkeley pit lake sediments, which Cameron et al. (2006) interpreted as an indication that highly acidic, metal laden conditions are hostile to supporting high populations of sulfate-reduction bacteria. In contrast, the less acidic Udden pit lake shows low TOC and evidence of some amount of sulfate reduction. Some of the highly acidic pit lakes of the Iberian Pyrite Belt also show increased pH values in sediments compared to the overlying water column and hydrogen sulfide has been detected in some deep water samples, indicative of sulfate reduction (Sánchez-España et al. 2009).

It is important to note that biogeochemical reactions do not always improve pit lake water quality. Wendt-Pottoff et al. (2004) observed that stimulation of sediment biogeochemical processes in an acidic pit lake in Germany released Fe^{2+} to the overlying water column, which in turn oxidized and counteracted neutralization.

Also, the concepts and data discussed in this chapter are directed at natural factors that affect water quality in metal-mine pit lakes in the absence of mitigation and remediation efforts. Many different remedial approaches exist for improving water quality in pit lakes. The reader is referred to the appropriate chapters or sections in this volume and also discussions in Kalin and Wheeler (2009), Pelletier et al. (2009), and Wielinga (2009).

Table 3.9 Summary of sediment geochemistry characteristics for acidic, metal-mine pit lakes

Pit lake	Limnology	pH/Redox conditions	Organic carbon	Secondary minerals in sediments	Reference
Spenceville Pit, California[b]	Meromictic	pH 2.4–2.9 in water column; pH 3.42 in sediment pore water; DOC and H_2S in sediments	DOC: 7 mg/L water column; DOC: 110 mg/L in sediment pore water	Jarosite, gypsum[a], unidentified amorphous Al phase	Levy et al. (1997)
Kirki (Agios Filippos) Pit, Greece	Not reported	pH 2.9–3.1 in water column; oxidizing	Not reported	Jarosite, wroewolfeite, beaverite, gypsum, anglesite, scorodite, bukovskyite, goethite, melanterite, rozenite, butlerite	Triantafyllidis and Skarpelis (2006)
McLaughlin South Pit, California	Holomictic	pH 4 in water column; anoxic in lower lake layers	Not reported	Ferrihydrite floc in water column adsorbs As and Sb	Rytuba et al. (2000)
Udden Pit, Sweden	Dimictic	pH 4.8 in surface increasing to 6.4 at the bottom of water column; anoxic in lower lake layers; increased Fe, As, and Mn with depth	TOC: 0.4–0.6 mg/L in surface layers increasing to 2.7 mg/L at depth	Ferrihydrite[a], gibbsite[a]	Ramstedt et al. (2003)
Berkeley Pit, Montana	Meromictic (may have been holomictic in the past)	pH 3.1–3.4 in sediment pore water; anoxic at depth	TOC: 0.3–0.4% in sediments; DOC: 2.5–4.5 mg/L in water column and 50–380 mg/L in sediment pore water	Jarosite, gypsum, $AlOHSO_4^a$, schwertmannite (water column)[a]	Twidwell et al. (2006; Cameron et al. 2006)
Numerous pit lakes of the Iberian Pyrite Belt	Meromictic and holomictic	pH 1.2–4.7 in water column; typically oxidizing in surface water layers and anoxic at depth; evidence of Fe^{3+} and SO_4 reduction in sediments in the form of H_2S odor	Not reported	(Ferrihydrite, alunite, schwertmannite, jarosite, gibbsite, jurbanite)[c]; Efflorescent minerals on shorelines include gypsum, pickeringite, and hexahydrite	Sánchez-España et al. (2008; 2009)

[a] Inferred from solubility calculations

[b] Spenceville pit was backfilled in 2001

[c] Inferred from elemental analyses of colloids collected from the water column and solubility calculations

3.2.2.11 Water Quality Trends

Inspection and analysis of data trends from existing metal-mine pit lakes can provide useful knowledge about important factors affecting water quality, such as ore deposit type, geochemical processes, and hydrologic cycles. However, there are no publicly accessible, comprehensive international databases on pit lake water quality currently in existence that can be used for thorough assessment of chemical trends. Various amounts and detail on water quality data are available in open literature reports and scientific papers for individual and collections of pit lakes. The water quality data collected for this paper and discussed below are summarized in Table 3.10. Data from these sources were compiled for the purpose of summarizing trends in water quality and comprise 144 water quality analyses for 49 pit lakes. This dataset is predominantly reflective of pit lakes formed in gold mines in the western U.S. and is relatively old. Hence, it is recognized that these data represent, at best, only snapshots of water quality at the time of study and thus not a completely accurate representation of all types and variabilities of all types of metal-mine pit lakes. However, taken together, these water quality data do provide useful context for identifying trends generally common to metal-mine pit lakes.

TDS is an important parameter in the evaluation of water quality trends to provide context for more detailed inspection of other solutes, such as metals (discussed below). Figure 3.41 shows a plot of TDS as a function of pH for metal-mine pit lakes where the data are categorized according to the ore deposit type. The TDS concentration can be strongly affected by evapoconcentration; hence, the age of the pit lake may be an important factor. The data shown in Fig. 3.41 represent lakes at all ages of maturity. While the factor of age may obscure some details in TDS trends, the data in Fig. 3.41 indicate that elevated TDS concentrations occur most frequently under acidic conditions ($\mathrm{pH} < \approx 4.5$), although a few alkaline ($\mathrm{pH} > \approx 7.5$) pit lakes also show elevated TDS (Fig. 3.41). Lakes with a pH between pH 4.5 and 7.5 generally have low TDS concentrations. Overall, the highest TDS concentrations occur for acidic pit lakes formed at mines of massive sulfide, high sulfidation polymetallic vein, and porphyry types of deposits.

A closer inspection of the major components of TDS indicates that the percentage comprised of sulfate increases as TDS increases (Fig. 3.42). The percentage of TDS as alkalinity decreases as TDS is increased as it is increasingly supplanted by sulfate. Sulfate is, by far, the dominant solute in nearly all pit lakes with highly elevated TDS concentrations. The majority of the high TDS, high sulfate pit lakes included in the datasets shown in Figs. 3.41 and 3.42 are acidic. A direct reflection of high acidity can be seen by the increase in the percentage of TDS comprised of metals ($\mathrm{Al} + \mathrm{Fe} + \mathrm{Mn}$) with an increase in TDS. These metals comprise 5–20% of the TDS concentrations in most acidic pit lakes, such as those of the Iberian Pyrite Belt in Spain (Sánchez-España et al. 2008) and the Berkeley pit lake in Montana (Pellicori et al. 2005). These highly acidic pit lakes contain predominantly acidic sulfate solutions in which metals, sulfate, hydrogen ion, and to a lesser extent, base cations, make up most of the TDS concentrations.

Table 3.10 Summary of water quality data sources for metal-mine pit lakes

Deposit	Pit lakes	Location	Number of water quality values	Reference
Low sulfide gold-quartz deposit	Harvard	California	1	Ashley and Savage (2001)
Volcanogenic low sulfidation	Sleeper	Nevada	8	Dowling et al. (2004)
Quartz adularia	Boss, Aurora, Tuscora	Nevada	25	Price et al. (1995)
Carlin-type	Cortez, Big Springs, Adelaide, Getchell (south, center, north)	Nevada	16	Price et al. (1995)
Porphyry	Yerington, Liberty, Ruth, Kimbley, Cypress-Tonapah, Anaconda, Berkeley	Nevada Montana	35	Bird et al. (1994; Davis and Ashenburg 1989; MacDonald 1993; Price et al. 1995; Pellicori et al. 2005)
Quartz alunite	Ketchup Flat	Nevada	6	Price et al. (1995)
Skarn	Fortitude	Nevada	3	Price et al. (1995)
High sulfidation polymetallic vein	Spenceville McLaughlin (south, north), Kirki	California California Greece	16	Levy et al. (1997; Rytuba et al. 2000; Triantafyllidis and Skarpelis 2006)
Massive sulfide	22 Iberian District pit lakes, Udden, Elizabeth (south, north)	Spain Sweden Vermont, New Hampshire	34	Sánchez-España et al. (2008; Ramstedt et al. 2003; Seal et al. 2006)

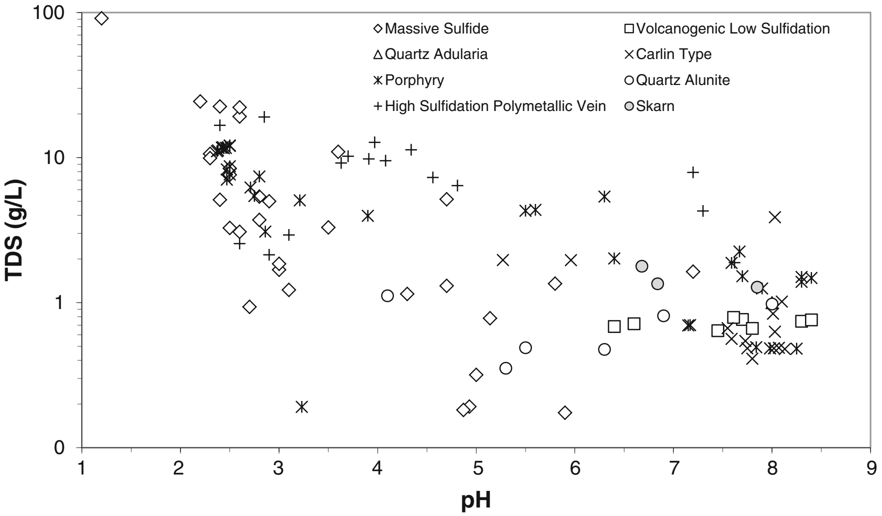


Fig. 3.41 Trends in total dissolved solids in metal-mine pit lakes

Iron, Al, and Mn are most commonly the dominant dissolved metals in acidic pit lakes due to the increased solubilities of the minerals that contain these elements. This effect can be seen in plots of Fe, Al, and Mn as functions of pH (Figs. 3.43, 3.44 and 3.45 respectively). Iron concentrations may exceed 1,000 mg/L in the most acidic pit lakes formed in massive sulfide, polymetallic high sulfidation, and porphyry deposits (Fig. 3.43). Only total Fe concentrations are shown in Fig. 3.43, but both ferrous and ferric iron are usually present when pH values are less than about 4.5 due to slow oxidation kinetics and absence of dissolved oxygen in the lower layers of acidic pit lakes. Iron concentrations tend to be low in pit lakes formed in Carlin type, quartz adularia, and low sulfidation deposits due to circumneutral to slightly alkaline pH conditions resulting from low sulfide content in the host rocks of many of the pit lakes included in this dataset. The secondary minerals reported to best explain iron concentrations in acidic pit lakes are schwertmannite and ferrihydrite, whereas siderite may be a reasonable solubility control for neutral to alkaline pit lakes (Table 3.8), depending on redox conditions. Trends in Al and Mn concentrations with pH (Figs. 3.44 and 3.45) are similar to Fe, although there are fewer data for Al, and Mn shows much more variability through the mid-pH range. Most secondary oxyhydroxide and sulfate minerals containing Fe, Al, and Mn have amphoteric solubilities, and hence show similar trends in concentrations with pH. Secondary solids such as gibbsite and various Al-sulfates, such as jurbanite, alunite, and basaluminite, are important solubility controls for dissolved Al in acidic pit lakes. For slightly acidic to alkaline pit lakes, poorly crystalline clay-type minerals, such as kaolinite and allophane, may be the most common secondary minerals incorporating dissolved Al.

Concentration data for divalent cationic metals are shown in a Ficklin-type plot in Fig. 3.46. These metals show the expected trend of greatly increased

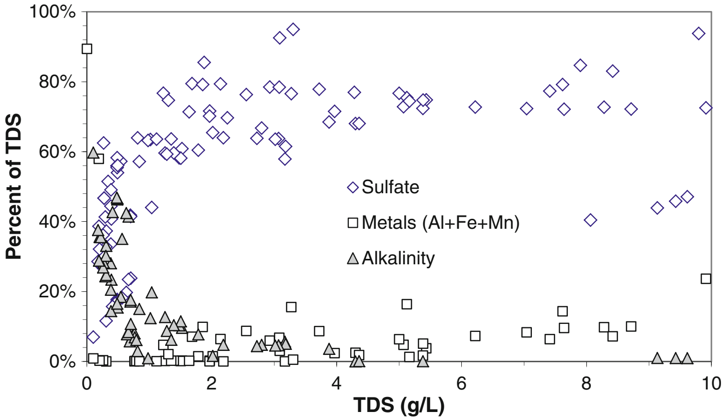


Fig. 3.42 Major components of TDS in metal-mine pit lakes expressed as percentages of TDS

concentrations in acidic pit lakes formed in massive sulfide, polymetallic high sulfidation, and porphyry deposits. A number of circumneutral lakes (pH $> \approx 4.5$ and $< \approx 8$) formed in massive sulfide and porphyry deposits also show relatively high metal concentrations due primarily to Cu and Zn (Fig. 3.46). Secondary minerals incorporating Cu and Zn are relatively soluble in the slightly acidic to neutral pH range. High solubilities allow high concentrations of these metals to occur in pit lakes due to the combined effects of sulfide oxidation and evapoconcentration, although adsorption to iron oxides may partially moderate cationic metal concentrations under these conditions (Fig. 3.39).

A final group of solutes is the anionic metalloids of As and Se. The trends for As concentrations in metal-mine pit lakes show a more complex relationship to pH than the cationic metals. Arsenic concentrations are highest at low pH, decrease to their lowest values in the pH range from about 4.5–7, and then tend to be higher at pH > 7 (Fig. 3.47). On the acidic end, pit lakes formed in massive sulfide deposits have the highest As concentrations due in part to the mineral arsenopyrite, whereas pit lakes formed in quartz adularia deposits tend to have the highest As concentrations for alkaline pH conditions. Selenium concentrations show a different pattern: the lowest concentrations (generally below detection limits) occur in acidic pit lakes and the highest concentrations occur in neutral to alkaline pit lakes (Fig. 3.48). Pit lakes formed in quartz adularia and porphyry deposits tend to have the highest Se concentrations (Fig. 3.48).

The tendency for elevated As and Se concentrations to occur in quartz adularia and porphyry pit lakes has been previously recognized by Shevenell et al. (1999), who examined water quality trends for 16 pit lakes in Nevada. Neither As or Se form low solubility secondary minerals under most pH conditions and the adsorption of As and Se anions is minimized under alkaline pH conditions. Because of these adsorption characteristics, the highest concentrations of As and Se tend to occur in alkaline pit lakes that have or are expected to evapoconcentrate (Eary 1998). A similar phenomenon is seen in natural evaporative lakes of the

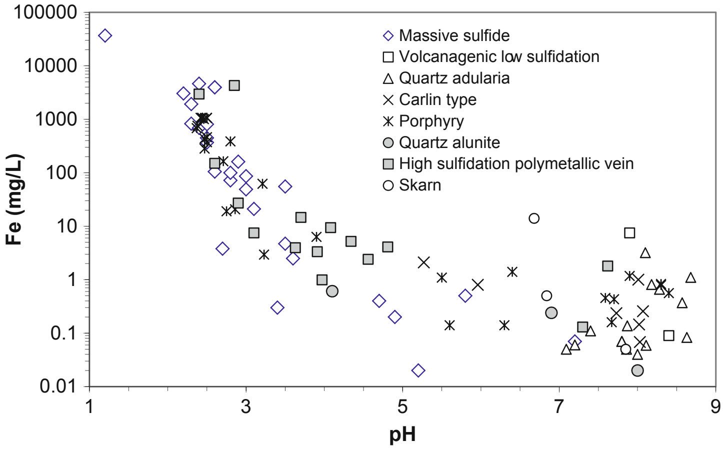


Fig. 3.43 Trends in total Fe concentrations with pH in metal-mine pit lakes

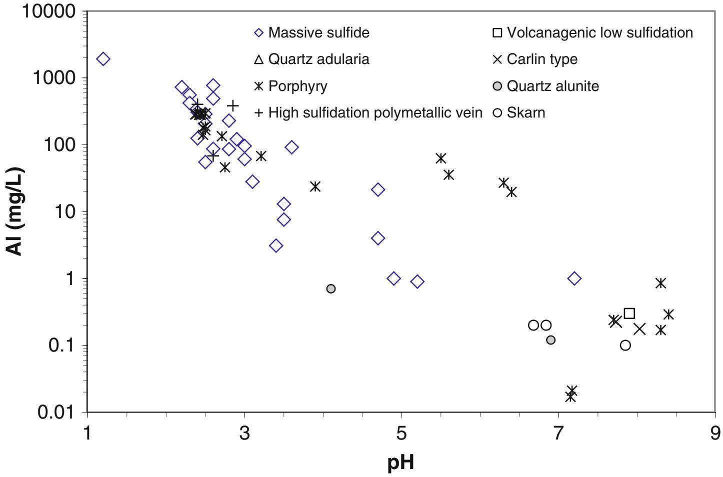


Fig. 3.44 Trends in Al concentrations with pH in metal-mine pit lakes

western USA that also contain elevated alkalinities and As concentrations, such as Mono Lake, California (Maest et al. 1992), Toulon and Upper Humboldt Lake, Nevada (Seiler et al. 1993), and Abert Lake, Oregon (Whitehead and Feth 1961).

3.2.2.12 Conclusions

The concentrations of solutes in metal-mine pit lakes show distinct trends that are primarily related to pH. The pH, in turn, is a complex function of the geoenvironmental characteristics, sulfide mineral content and oxidation rates, water

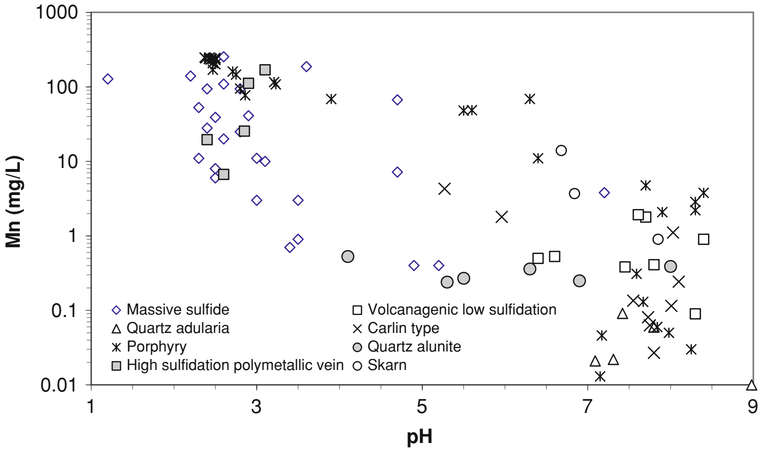


Fig. 3.45 Trends in Mn concentrations with pH in metal-mine pit lakes

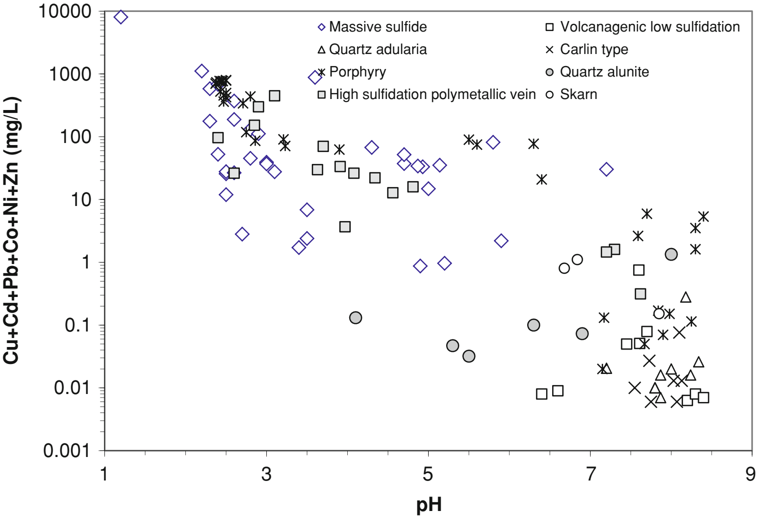


Fig. 3.46 Ficklin plot of divalent cationic metal concentrations with pH in metal-mine pit lakes

balance, solubilities of secondary mineral phases, water column dynamics, sediment biogeochemical processes, and remediation efforts. Thus, geoenvironmental characteristics can provide a useful framework for interpreting the hydrochemistry of existing pit lakes, making predictions of water quality for future pit lakes, and designing remedial strategies. However, there are still many areas where research could greatly improve our understanding of metal-mine pit lakes. A regularly

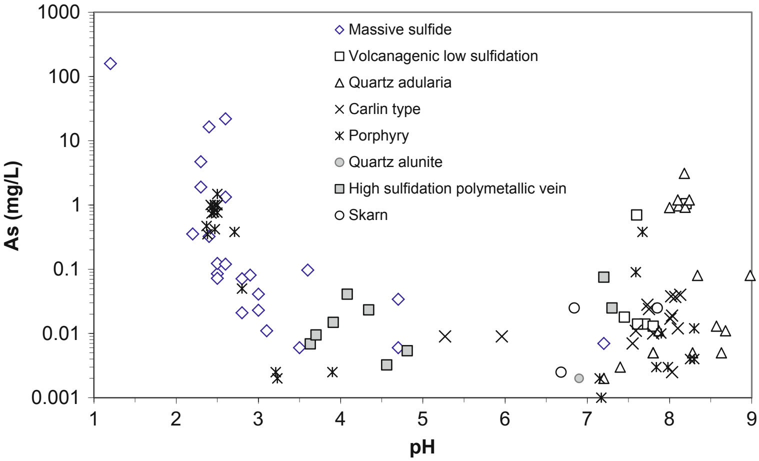


Fig. 3.47 Trends in As concentrations with pH in metal-mine pit lakes

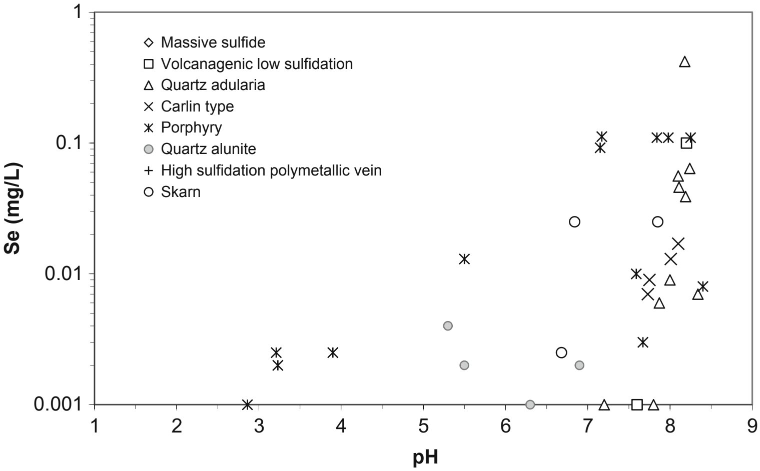


Fig. 3.48 Trends in Se concentrations with pH in metal-mine pit lakes

updated, international database on water quality from existing pit lakes in different types of mining regions, deposit types, metal resource, climate, and hydrologic environment could be valuable for identifying important factors affecting water quality, testing numerical models, and tracking remediation effectiveness. In addition, detailed studies on metal and nutrient cycling in the water column and sediments of pit lakes are needed to better understand the role of biogeochemical processes on water quality.

3.3 The Biology and Ecosystems of Acidic Pit Lakes

Katrin Wendt-Potthoff

Acid Pit Lakes as Special Habitats

Compared to typical acid mine drainage and chemically-similar hydrothermal solutions, the ionic composition of acid pit lakes is generally less concentrated, due to dilution of acid-generating oxidation products with groundwater or rainwater. The dissolved metal concentrations are typically elevated compared to natural lakes, but not necessarily at levels considered toxic for freshwater biota—this depends largely on the origin of the pit (lignite/coal versus metal ore mining, Sects. 2.2 and 3.2). As in natural lakes, stratification and mixis depend on the ambient climate, but also on the chemical influence of catchment and in-lake processes (Sects. 3.1 and 3.2.2). Iron and sulfur cycling determine the biogeochemistry, especially in the anoxic zones, in contrast to natural freshwater lakes, where the main anaerobic process is typically methanogenesis. The high iron concentrations of pit lakes also bring about significant photochemical reduction of Fe(III) near the lake surface, which is coupled with photochemical oxidation of dissolved organic carbon, a process that further diminishes the available organic carbon for organisms. The food webs of acidic pit lakes have much fewer levels and species than those of natural freshwater lakes. This makes them interesting locations for studying fundamental ecological processes. Therefore, the trophic interactions and flow of energy have been comprehensively investigated (Sect. 3.3.1.4). Much less is known about the taxonomy and physiology of bacterioplankton components and fungi in the water column, since microbiological studies have mainly focused on the sediments, where anaerobic, alkalinity-generating processes are common. Besides their extreme chemistry, many pit lakes are quite young (decades or years), which might also explain deficits in their colonization.

3.3.1 Plankton

3.3.1.1 Phytoplankton

Dieter Lessmann and Brigitte Nixdorf

Phytoplankton plays a key role in the biocoenotic structure of lakes—in acidic lakes just as in pH neutral lakes, although the importance of biotic factors decreases with increasing acidity, in contrast to abiotic conditions (Arnott and Vanni 1993). Phytoplankton species composition, in terms of species-related characteristics such as size, edibility, preferred nutrient sources, together with species abundance and biomass, profoundly influence other trophic levels (see also Sect. 3.3.1.4).

Phytoplankton coenoses of acidic pit lakes differ considerably from those of lakes in the circumneutral pH range due to their low species diversity, low biomass, different seasonal patterns, and utilization of resources. This is similar to findings for the phytobenthos of these lakes and of rivers and lakes that are acidified by acid mine drainage (AMD) or from volcanic sources.

During the past 15 years, scientists from different institutions have focussed their research on acidic pit lakes in the Lusatian and central German lignite mining district in the southeastern part of Germany, where this specific type of lake is relatively abundant. Other acidic water bodies that have been studied intensively by limnologists recently include streams in the Iberian Pyrite Belt (e.g. Sabater et al. 2003; Aguilera et al. 2007), streams affected by AMD in New Zealand (e.g. Niyogi et al. 1999, 2002; Bray 2007), and lakes and streams influenced by volcanism in the Argentinean Andes (e.g. Beamud et al. 2007; Pedrozo et al. 2010).

Species Diversity and pH

The biocoenotic structures of acidic lakes are determined by multiple abiotic stressors (Frost et al. 1999; Nixdorf et al. 2003b), which becomes especially evident in the correlation of species diversity with pH (Fig. 3.49). The plankton coenosis is less diverse as pH decreases, and the structure of the food web becomes simpler (see also Sects. 3.3.1.2 and 3.3.1.4). Only a small number of phytoplankton species tolerate the high proton and metal concentrations; the latter are site-specific and of different composition and importance. The loss of biodiversity and its effects are also well known from waters acidified by acidic deposition, whose lowest pH is around 3.5 (e.g. Baker and Christensen 1991; Matschullat et al. 1994; Steinberg and Wright 1994).

In Lusatian pit lakes, which have been regularly sampled for several years, the number of phytoplankton taxa in the pH range 2.5–3 is mostly between 7 and 9, whereas at pH values around 4, the taxa number increases to 17–25 (Fig. 3.49; Lessmann and Nixdorf, unpubl.; 2000). The majority of these algae belong to the nanoplankton or picoplankton (20–2 and 2–0.2 μm, respectively). These groups are usually underestimated in Lugol's samples (Sorokin 1999; Woelfl and Whitton 2000), and many algae have not yet been identified to the species level due to a lack of distinctive morphological characteristics. Comprehensive molecular biological studies are needed. The approach of Aguilera et al. (2007) for the investigation of the eukaryotic benthic community of Rio Tinto is an example how molecular approaches and traditional techniques can be combined to analyse the biocoenoses of acidic waters with greater accuracy.

Algal Communities at a pH of About 3

Most acidic pit lakes have a pH of about 3 due to iron buffering (Geller et al. 1998; Totsche et al. 2003). In Lusatian pit lakes with pH ≤ 3, the typical phytoplankton community is dominated by the genera *Ochromonas* and

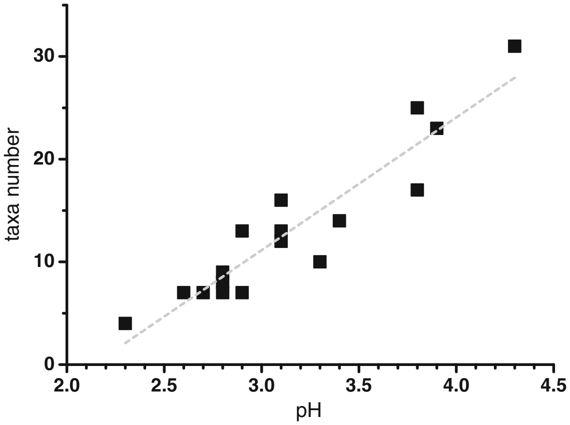


Fig. 3.49 Relationship between the number of phytoplankton taxa and the mean pH of 17 acidic pit lakes in Lusatia regularly sampled for several years, based on microscopic analyses

Chlamydomonas (Table 3.11; Lessmann et al. 2000; Nixdorf et al. 1998). Both are ubiquitous taxa in waters acidified by AMD (Lackey 1939; Sheath et al. 1982). *Chlamydomonas acidophila* is probably the only widespread species of its genus in these lakes and can be the most abundant phytoplankton taxon (Spijkerman 2008; Spijkerman et al. 2007). It is also a very common species in other extremely acidic waters, such as volcanic lakes, which can have even lower pH ranges than acidic pit lakes (Rhodes 1981; Satake and Saijo 1978; Sheath et al. 1982; Twiss 1990). The genus *Ochromonas*, with six morphologically distinct types, was eudominant in all lakes surveyed by Lessmann et al. (2000), who found that it constituted more than 50% of the annual total biovolume. *Lepocinclis teres*, *Euglena mutabilis* and *Chromulina* sp. can also be found frequently in several lakes. Two phytobenthic diatom species, *Eunotia exigua* and *Nitzschia* sp., occurred in most samples, but their contribution to total phytoplankton biomass is low in deep lakes (Lessmann et al. 2000). *E. mutabilis* is especially abundant in the littoral zone of the lakes, forming dense mats on the sediment surface (Kapfer 1998a, b).

Nevertheless, there is high variability in the phytoplankton community. Recent data show that *Peridinium umbonatum* and *Scourfieldia cordiformis* can be common in some of these lakes, in addition to *Chlamydomonas* and *Ochromonas*, and can represent a high portion of the annual total biovolume (Lessmann and Nixdorf, unpubl.).

In acidic pit lakes of the central German mining district around Leipzig, with a pH of 2.7–3.3, the dominant taxa, before remediation, were *Ochromonas* and *Chlamydomonas*, together with *Cryptomonas* and *Chrysococcus*, respectively (Rönicke et al. 2001, 2010). Another pit lake in that region that had a pH 3.4–3.6 was inhabited by five phytoplankton species, with *Chlamydomonas* being the most dominant, followed by *Chrysococcus* (Rönicke et al. 2002).

Many diatom species are unable to maintain a population at pH values below 4.5. DeNicola (2000) reviewed the occurrence of diatom species at pH $\leq$ 3.5. He identified less than nine species as real inhabitants in this pH range, most belonging to the phytobenthos.

Table 3.11 Presence and dominance of phytoplankton taxa that occur in pit lakes with pH ≤ 3. Data are based on 14 pit lakes of the Lusatian mining district

Class	Taxon	Presence (%)	Dominance
Chrysophyceae	*Chromulina* sp.	53	subd–eu
	Ochromonas spp. (6 types)	100	eu
Bacillariophyceae	*Eunotia exigua* Rabenhorst	73	subr–dom
	Nitzschia sp.	40	subr–dom
Cryptophyceae	*Cyathomonas* sp.	40	subr–eu
	Rhodomonas minuta Skuja	7	eu
Dinophyceae	*Gymnodinium* sp.	20	subr–eu
	Peridinium umbonatum Stein	13	subr–rec
Euglenophyceae	*Euglena mutabilis* Schmitz	60	subr–dom
	Lepocinclis teres f. *parvula* (Schmitz) Francé	67	subr–eu
Prasinophyceae	*Scourfieldia cordiformis* Takeda	27	subr–eu
Chlorophyceae	*Chlamydomonas* spp.	100	subd–eu
Trebouxiophyceae	*Nanochlorum* sp.	7	eu

Range of mean dominance: eu (dominant) with >10% of the total annual biovolume; dom(inant) with 5–10%; subd(ominant) with 2–5%; rec(edent) with 1–2%; subr(ecedent) with <1% (acc. to Schwerdtfeger 1975; after Lessmann et al. 2000)

Usually, Cyanobacteria are absent in such acidic water. Steinberg et al. (1998) detected the phycobilins phycocyanin and phycoerythrin (using fluorescence signals in flow-cytometry) in a pit lake with pH 3.0 and attributed them to filamentous Cyanobacteria. However, these fluorescence signals could not be assigned to specific cells by direct microscopic evidence (Whitton, Wendt-Potthoff, pers. comms.); so the detected pigment fluorescence might have come from eukaryotic algae with phycobilins (Rhodophyta, Cryptophyta, Glaucophyta). Unquestionable is that the green sulphur bacterium *Chlorobium limicola* can occur in extremely acidic waters (Overmann, pers. comm.).

The phytoplankton inhabitation of extremely acidic pit lakes can be compared with acidic volcanic water systems and streams receiving AMD. An unknown green alga occurs in high densities in the Indonesian crater lake Kawah Ijen with pH < 0.3 (Löhr et al. 2006). *Ch. acidophila* is known to be highly productive in the Japanese volcanic lake Katanuma at a pH of 1.9 (Satake and Saijo 1974).

The volcanic Río Agrio/Lago Caviahue acidic water system in the Argentinean Andes has been studied intensively for more than 10 years. The system comprises a crater lake from which the upper Río Agrio originates, which has a pH gradient of 0.4–1.5, Lago Caviahue, with a pH of about 2.3, and the lower Río Agrio (Pedrozo et al. 2010). In contrast to most pit lakes, the waters are rich in metals and phosphorus. The chemistry varies due to fluctuations in the activity of the volcano Copahue. While the crater lake lacks any phototrophic organisms, the upper Río Agrio is inhabited predominantly by the Chrysophycean genus *Gloeochrysis* (Table 3.12), which contributes 99% of the relatively low epilithon biomass, which totals <5 mg m^{-2} Chl-*a* (Baffico 2007; Baffico et al. 2004). The Chlorophycean species *Keratococcus rhaphidoides* represents more than 90% of the total annual abundance in Lago Caviahue, with eight other algal taxa also present (Table 3.12; Beamud et al. 2007; Pedrozo et al. 2001, 2010).

Table 3.12 Algal species, pH, and electrical conductivity (EC, mS cm^{-1}) in the upper Río Agrio/Lago Caviahue water system (after Pedrozo et al. 2010)

Site	pH	EC	Taxa
Crater Lake	1.2	500	(no phototrophs)
Upper Río Agrio	1.3–1.8	7.9–14.2	*Gloeochrysis* sp., *Euglena mutabilis*
Lago Caviahue	2.3	2.1	*Keratococcus raphidioides*, *E. mutabilis*, *Watanabea* sp., *Palmellopsis* sp., *Ulothrix* sp., *Nitzschia capitellata*, *Diatoma mesodon*, *Mougeotia* sp., Haptophyta

In addition to high acidity and high metal concentrations, autotrophs in streams that receive AMD are usually confronted with metal oxide deposition, which can cover all substrates where flow velocity is low (Bray 2007; Niyogi et al. 1999, 2002). Bray (2007) analysed the effects of AMD on algae in streams that show acidity gradients and identified pH as the most important controlling factor of the algae assemblage structure. With 15 taxa, algal diversity is low at pH < 3.6. This corresponds with the taxa number of the phytoplankton occurring in pit lakes with the same pH range. Certain species tend to dominate, especially filamentous *Klebsormidium acidophilum*. Other abundant species are *E. mutabilis*, *Navicula cincta*, *Microspora quadrata*, and *Microthamnion kuetzingianum*.

The benthic eukaryotic community of Rio Tinto, with a pH between 0.9 and 2.5 due to pyrite oxidation and AMD, comprises 10 algal taxa. The lowest taxa numbers are associated with the most acidic sites. Members of Chlorophyta, such as *Chlamydomonas*, *Dunaliella*, *Chlorella*, and *Euglena*, are the most frequent species, forming large green patches along the riverbed. *Dunaliella* and *Cyanidium* related species inhabit the most acidic site (Aguilera et al. 2007). Sabater et al. (2003) found low taxa and dominance structure fluctuations in Rio Tinto within the year and that the dominant taxa were *Klebsormidium flaccidum*, *Pinnularia acoricola*, and *Euglena mutabilis*. In acidic effluents from abandoned mines in Portugal, Valente et al. (2007) observed an algal flora that was dominated by *Euglena mutabilis* and *Klebsormidium* sp.

According to these findings, the dominant phytoplankton taxa in extremely acidic pit lakes are typically *Ch. acidophila* and species of the genus *Ochromonas*. The most common species in all kinds of extremely acidic waters is *E. mutabilis*. *Klebsormidium* appears to be a typical algal taxon in extremely acidified streams. However, large fluctuations in the biocoenotic structures can occur in these extremely acidic waters.

Phytoplankton Communities at pH 3.5 to 5

The phytoplankton community changes with increasing pH. Compared with lakes with a mean pH of 3 or lower, the taxa number increases and other species become dominant. At pH 4, the most common species in Lusatian pit lakes are *Peridinium umbonatum*, *Cryptomonas* spp., and in some lakes, *Amphidinium elenkinii*. Due to the lack of a stabilising buffering system, only a small number of these lakes show pH values between about 4.3 and 5.5. In this pH range, the phytoplankton community of Lusatian pit lakes is mostly formed by *Scourfieldia cordiformis*, *Cryptomonas* spp., *Peridinium umbonatum*, *Amphidinium elenkinii*, and *Gymnodinium* sp. (Lessmann and Nixdorf, unpubl.).

A few studies have monitored changes in the phyoplankton during an increase of pH due to remediation. Rönicke et al. (2010) found an increase in diversity slowly following the changes in pH during chemical neutralisation. The most common phytoflagellates (*Chlamydomonas*, *Ochromonas*, *Chrysococcus*) from the extremely acidic phase continued to dominate at the beginning of lake neutralisation. *Chromulina*, diatoms (*Synedra acus*, *Nitzschia acicularioides*, *Eunotia exigua*), Cryptomonads (*Cryptomonas ovata*, *Rhodomonas minuta*) as well as Dinoflagellates (*Peridinium umbonatum*) became increasingly important during the following years. Cyanobacteria did not occur until circumneutral conditions were achieved.

Kalin et al. (2006) describe the effects of pH changes in a pit lake in Canada where pH decreased from 5 to 3. Phytoplankton diversity dropped from 52 to 42 taxa, the number of taxa with a frequency >10% from 39 to 10. Only *Ochromonas* and *Chlamydomonas* were consistently present. *Peridinium*, *Pinnularia*, and *Euglena* were frequent during the pH 5 phase and declined at lower pH. *Lepocinclis* proliferated when pH decreased and metal concentrations increased.

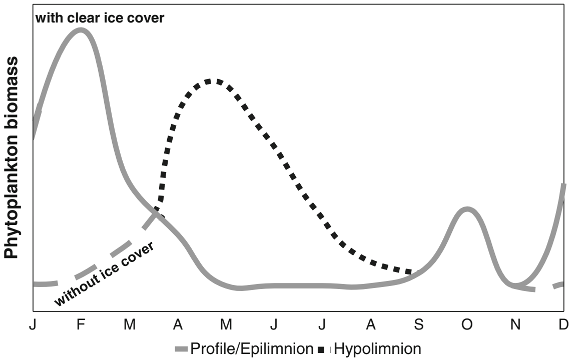
Control Mechanisms of Primary Production and Seasonal Succession of Phytoplankton

The biocoenotic structures are not the only difference between acidic pit lakes and circumneutral lakes; primary production control mechanisms also differ. Intense productivity studies and analyses of primary production and seasonal phytoplankton succession are available, especially from pit lakes of the Lusatian mining district.

Primary production is low in most lakes and does not exceed bacterial production, even during daylight. This leads to high differences on daily basis, with an average primary production rate of about 31 mg C m^{-3} d^{-1}, in contrast with a bacterial production rate of 186 mg C m^{-3} d^{-1}. The algal to bacterial production ratio identifies the lakes clearly as heterotrophic systems, which results in oxygen undersaturation of the water bodies (Nixdorf et al. 2003a). Beulker et al. (2002, 2004) measured autotrophic production of mining lake (ML) Plessa 117 (mean pH 2.9) regularly for more than a year. Primary production rates ranged from less than 1– 12.5 mg C m^{-3} h^{-1} in the upper water body. The wide range reflects the high seasonal fluctuation. With 278 mg C m^{-2} d^{-1}, the mean annual lake area related rate was low compared with natural lakes of the region (Beulker et al. 2004).

In general, mean annual phytoplankton biomass seems to be independent of the degree of acidification and to depend primarily on the availability of nutrients. In oligotrophic acidic pit lakes at pH values around 3 and 4, mean phytoplankton biovolume is within a similar range, between 0.3 and 0.7 mm^3 L^{-1}. At certain

Fig. 3.50 Scheme of the seasonal pattern of phytoplankton biomass succession in ML Plessa 117 (pH 2.9), usually formed by specific algae and indicating, in particular, the significance of the availability of increased inorganic carbon concentrations for phytoplankton growth in this lake



times of the year, maxima of 2–3 $mm^3 L^{-1}$ can occur (Lessmann and Nixdorf unpubl.; Nixdorf et al. 1998). As in natural pH-neutral lakes, the increase in phosphorus concentrations can significantly increase phytoplankton biomass and can lead to eutrophication despite the high phosphorus binding capacity of the iron-rich water and sediments (Lessmann et al. 2003; Tittel and Kamjunke 2004; Woelfl et al. 2000).

Nevertheless, large seasonal fluctuations of primary production and biomass are typical for oligotrophic acidic pit lakes and can generally be attributed to inorganic carbon limitation rather than to changes in phosphorus concentrations. Under acidic conditions below pH 4.3, CO_2 is the only available inorganic carbon source for photosynthesis. As long as the water body is in exchange with the atmosphere, the equilibrium between water and atmosphere and the uptake by autotrophs lead to dissolved inorganic carbon (DIC) concentrations that are far lower than in pH-neutral waters with bicarbonate buffering and their high availability of inorganic carbon.

However, CO_2 can accumulate in water layers isolated from the atmospheric exchange, i.e. in the hypolimnion or under ice. This can cause a fast increase in phytoplankton biomass. In contrast, during circulation periods and especially in the epilimnion of the summer stagnation phase, CO_2 concentrations are low. Increasing CO_2 concentrations are typical for the hypolimnia due to the inflow of CO_2-rich groundwater and respiration and decomposition of organic matter as major sources. During winter, ice cover can significantly reduce inorganic carbon loss to the atmosphere and lead to an increase in DIC concentrations and in phytoplankton biomass, if there is no shading by snow.

As an example, in ML Plessa 117 a typical pattern of seasonal phytoplankton succession was observed with the highest biomass in winter under an ice cover free of snow, followed by a second phytoplankton bloom in the upper hypolimnion at the beginning of the summer stratification and a small increase during the autumnal overturn (Fig. 3.50). In ML Plessa 117, these blooms are usually formed by a small number of species, with *Ochromonas* and *Chlamydomonas* being the most important ones. In consequence, mild winters without long-lasting ice cover show no algal bloom, and the maximum phytoplankton biomass occurs during the summer stratification as a deep chlorophyll maximum (DCM) in the metalimnion and upper hypolimnion (Lessmann and Nixdorf 2002; Beulker et al. 2003; Lessmann et al. 2006). DCMs are also characteristic of other oligotrophic acidic pit lakes (Tittel et al. 2003).

In addition to pelagic primary production, benthic algae can be important contributors to primary production of acidic lakes. A dense layer of the diatoms *Eunotia* spp. and *Pinnularia obscura* covers the sediment surface in a lake with pH 2.6 (Koschorreck and Tittel 2002, see also Sects. 3.3.2.2 and 3.3.2.3). The microphytobenthos in the littoral zones of the Lusatian pit lakes Plessa ML 111, ML 108, and ML 117 is dominated by *E. mutabilis*, *Eunotia* spp., and *Nitzschia paleaeformis*. Chlorophyll-*a* concentrations, primary production rates, and specific primary production were strikingly higher at *Euglena* dominated sites (12–176 mg Chl-*a* m^{-2}; 2.99–7.84 mg C m^{-2} h^{-1}; 0.30–0.47 mg C (mg Chl-$a)^{-1}h^{-1}$) than at sites dominated by *Eunotia* (1–89 mg Chl-*a* m^{-2}; 0.46–3.84 mg C $m^{-2}h^{-1}$; 0.03–0.35 mg C (mg Chl-$a)^{-1}h^{-1}$) (Kapfer 1998a, b). Elevated phytobenthos production may be attributed to higher concentrations of soluble reactive phosphorus (SRP), dissolved inorganic carbon (DIC), and dissolved organic carbon (DOC) in the sediment pore water than in the pelagic water, especially where groundwater inflow occurs (Hofmann and Lessmann 2006; Kapfer 1998a, b).

The presumed limitation of primary production by phosphorus and inorganic carbon in ML Plessa 117 is supported by laboratory experiments. To increase the volume-specific primary production rates, it was necessary to increase the inorganic carbon concentrations above 0.6 mg L^{-1} and the total phosphorus concentrations above 10 μg L^{-1} (Beulker et al. 2002, 2004).

Calculation of the carrying capacity for autotrophic phytoplankton shows changes in primary production limitations with water depth during the summer stratification of partly meromictic ML 111. While primary production is limited by inorganic carbon in the epilimnion, phosphorus becomes the limiting nutrient in the hypolimnion. Light limitation occurs only in the deepest parts of the lake (Fig. 3.51; Krumbeck et al. 1998).

In contrast to Lusatian mining lakes, in volcanic Lago Caviahue (pH about 2.5), primary production is primarily limited by nitrogen (dissolved inorganic nitrogen: 30–150 μg L^{-1}; compare also Berkeley Pit Lake, case study 5.5). The N:P ratio ranges from 0.03 to 0.11. A seasonal succession is missing and variations can mostly be attributed to volcanic activity. In addition to ammonium, phytoplankton biomass is also controlled by inorganic and, for mixotrophic species, by organic carbon (Pedrozo et al. 2008, 2010). Despite the lack of seasonal gradients of phytoplankton biomass in the water column, sometimes DCMs can be observed in the upper hypolimnion due to locally increased nutrient concentrations (Beamud et al. 2010).

Adaptation Strategies of Phytoplankton

Protists with fast asexual reproduction potential under favourable conditions form the most important group of the phytoplankton in the most acidic pit lakes. *Ch. acidophila* is able to survive at pH 1.0 for short time; its limit for sustained growth

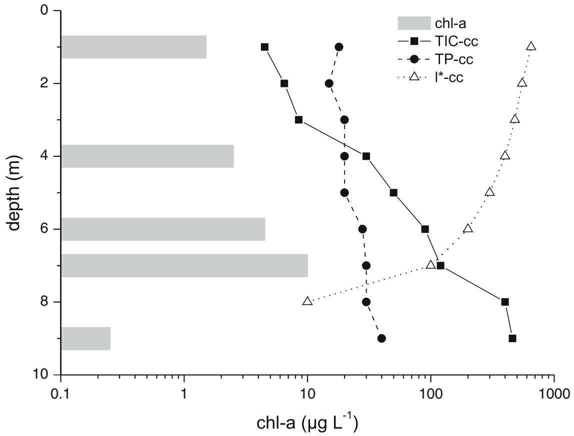


Fig. 3.51 Realized biomass and carrying capacity (cc) of phytoplankton expressed as Chl-*a* concentrations with regard to the available resources of inorganic carbon (TIC), phosphorus (TP), and light (I*) in the water column of ML 111 during summer stratification. The water column is divided into the epilimnion, down to a depth of about 3 m, the hypolimnion, from about 3 m to about 7 m, and the monimolimnion below (after Krumbeck et al. 1998)

is pH 1.5–2.0 (Pollio et al. 2005). Acidophilic algae developed different physiological adaptations to be able to maintain their cytoplasmatic pH in the circumneutral range or to increase pH in the water layer adjacent to their cell surface for the control of their osmoregulation (Pick 1999).

The two most common taxa *Ch. acidophila* and *Ochromonas* have a different pH niche width. While *Ch. acidophila* is an obligate acidophilic species, *Ochromonas* is acidotolerant, because *Ch. acidophila* has its fitness optimum under extremely acidic conditions, whereas *Ochromonas* grows best under moderately acidic conditions. That shows that in extremely acidic pit lakes, the phytoplankton coenosis is formed by a mixture of acidophilic specialists and acidotolerant generalists (Moser and Weisse 2011).

With regard to the occurrence of light and nutrient gradients, especially the lack of inorganic carbon in the epilimnion during summer, motility and the ability for fast reproduction under optimized conditions (C-strategists acc. to Reynolds 1997) are major advantages for phytoflagellates in acidic pit lakes (Fyson and Rücker 1998; Lessmann and Nixdorf 2000; Nixdorf et al. 1998).

Analysing the trophic spectrum that the dominant species are able to use, it is apparent that there is a high proportion of mixotrophs (Beulker et al. 2004; Nixdorf et al. 1998). These can either live as photoautotrophic organisms or (additionally) change to osmotrophy and feed on the organic carbon available in the water column or on bacteria, as phagotrophic organisms. *Chlamydomonas* and *Scourfieldia cordiformis* combine phototrophy with osmotrophy; *Ochromonas*, *Gymnodinium*, *Lepocinclis*, and *Cryptomonas* combine phototrophy with phagotrophy. In this group, *Ochromonas* can also feed on *Chlamydomonas* (Beulker et al. 2004; Tittel et al. 2003).

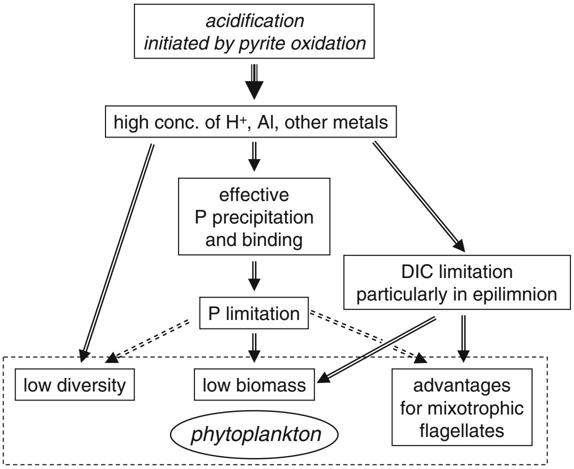


Fig. 3.52 Major control mechanisms of phytoplankton coenoses in acidic pit lakes (modified after Lessmann and Nixdorf 2000)

The ecosystem of ML 111 is very well investigated (see also Sects. 3.3.1.4 and 5.6). The plankton consists of single-celled and filamentous bacteria, mixotrophic flagellates with *Ch. acidophila* and *Ochromonas*, the Rotifera *Elosa worallii* and *Cephalodella hoodi*, and Heliozoa as the most important taxa of the food web. Heterotrophic flagellates, Crustacea, and fish are missing; Ciliata and Rhizopoda are rare. While bacterial filaments, *Ochromonas*, *Elosa*, and Heliozoa dominate in the epilimnion, the hypolimnion is dominated by single-celled bacteria, *Chlamydomonas* and *Cephalodella*. *Chlamydomonas* is primarily phototrophic and limited by light and inorganic carbon and is grazed by *Ochromonas* in the epilimnion. However, *Ochromonas* is primarily phagotrophic and controlled by prey availability (Kamjunke et al. 2004). Tittel and Kamjunke (2004) and Tittel et al. (2005) were able to show in experiments that the phototrophic growth of *Ch. acidophila* is limited at the water surface and that the addition of DIC leads to an increase in the growth rate. Despite significant photosynthetic activity, the alga also reduced the high DOC concentrations. Mixotrophic phytoflagellates are also important bacterial grazers. In ML 111, *Ochromonas* grazes 88% of the daily bacterial production of the epilimnion and 68% of that of the hypolimnion (Schmidtke et al. 2006).

Top-down control of the phytoplankton is only likely with the occurrence of larger zooplankton in high abundance, such as *Brachionus sericus* and *Chydorus sphaericus* (Wollmann and Deneke 2004; Wollmann et al. 2000); otherwise, the influence of higher trophic levels on phytoplankton is negligible (Lessmann et al. 1999; Weithoff 2004; see also Sects. 3.3.1.2 and 3.3.1.4).

To summarize, the extreme environmental conditions of acidic pit lakes, with high proton and metal, and low nutrient concentrations (limitation of primary production by P and C), control phytoplankton coenoses, resulting in low diversity and biomass (Fig. 3.52). On the other hand, several taxa show adaptations to the extreme habitat, especially physiological adaptations to the low pH, which allow them to thrive there. Mixotrophy, motility, and high reproduction potential are additional features for successful colonization of acidic pit lakes.

3.3.1.2 Zooplankton

Maria Belyaeva and Rainer Deneke

Relationship of Species Occurrence and Taxonomic Diversity to pH

Species richness of metazoan zooplankton is typically very low in acidic pit lakes, as few species can tolerate their harsh abiotic conditions (Nixdorf et al. 1998). As in other extreme environments, one or very few species dominate, resulting in low community evenness. Regarding the taxonomic composition of zooplankton in acidic pit lakes at pH 2.3–4.5, rotifers clearly outnumber crustaceans. Cladocera are represented by few species, but they can be important colonizers in lakes with pH $\geq$ 3, whereas Copepoda are rare (Deneke 2000).

Despite unfavorable abiotic conditions, even extremely acidic lakes are colonized by zooplankton: at pH 2.3, two rotifer species—*Cephalodella hoodi* and *Rotaria rotatoria*—were observed in the pelagic zone of Lake Plessa 107—a pit lake in northeast Germany (Lessmann et al. 1999). These two species, together with *Elosa worallii*, *Cephalodella gibba*, and *Brachionus sericus* constitute the core zooplankton community in highly acidic pit lakes with pH around 3 (Deneke 2000). A number of rotifer species from the genera *Lecane*, *Colurella*, *Trichocerca*, *Lepadella*, and *Philodina* are occasionally found in highly acidic pit lakes, but they are never very abundant (reviewed in Deneke 2000). All of the acid-tolerant rotifer species also occur in less acidic pit lakes (Wollmann et al. 2000), above their species-specific lower in situ pH thresholds (Table 3.13); however, they disappear from the pelagic zone of neutral and alkaline pit lakes, being replaced by a species assemblage typical of natural non-acidic lakes (Nixdorf et al. 1998). *Chydorus sphaericus* (Cladocera, Chydoridae) is the most acid-tolerant crustacean species that colonizes acidic pit lakes, with an in situ pH threshold of 3.0 (Wollmann et al. 2000). At pH $>$ 3.5, two more crustaceans occur in acidic pit lakes—another cladoceran, *Scapholeberis mucronata*, and the most tolerant cyclopoid copepod, *Diacyclops* sp. (Wollmann et al. 2000). Remarkably, calanoid copepods that often dominate zooplankton communities in soft-water acidic lakes (Brett 1989) are completely lacking in acidic pit lakes.

The majority of acidic pit lakes fall into the pH range of 2–4.5. At pH 4.5–6, chemical conditions become unstable due to the lack of a buffer system; thus, weakly acidic pit lakes are rare (Nixdorf et al. 2003). Hence, field studies on colonization patterns along the entire pH gradient from acidic to circumneutral conditions in pit lakes are methodologically hampered. The very few pit lakes with a pH range of 4.5–6 are recently or incompletely neutralized lakes, where water chemistry has not yet stabilized. These lakes are valuable sites to study colonization patterns and ecology of colonizing species under weakly acidic pit lakes conditions. For example, littoral Cladocera have been studied within a horizontal pH gradient in Lake Senftenberger See, formed within a channel connecting the acidic (pH 3) and the neutral (pH 7.5) basins of the lake (Belyaeva and Deneke

Table 3.13 Zooplankton species occurring in acidic pit lakes and the lowest in situ pH at which they were recorded

Taxonomic group	Species	pH	Sampling site	Reference
Extremely acidic pit lakes				
Rotifera, Monogononta	*Cephalodella hoodi* (Gosse 1896)	2.3	Lake Plessa 107	Lessmann et al. (1999)
Rotifera, Bdelloidea	*Rotaria rotatoria* (Pallas 1766)	2.3	Lake Plessa 107	
Rotifera, Monogononta	*Cephalodella gibba* (Ehrenberg 1838)	2.5	Pit lakes, Illinois, USA	McConathy and Stahl (1982)
Rotifera, Bdelloidea	*Philodina* sp.	2.5	Pit lakes, Illinois, USA	
Rotifera, Monogononta	*Elosa worallii* Lord 1891	2.6	Lake Plessa (ML 111)	Wollmann et al. (2000)
Rotifera, Monogononta	*Lecane* (*Monostyla*) *lunaris* Ehrenberg 1832	2.6	Pit lakes in Lusatia	Deneke, unpubl
Very acidic pit lakes				
Rotifera, Monogononta	*Brachionus urceolaris* O. F. Müller 1773[a]	2.6	Pit lakes, Illinois, USA	McConathy and Stahl (1982)
Rotifera, Monogononta	*Colurella* sp.	2.7	Pit lakes in Lusatia	Deneke, unpubl
Rotifera, Monogononta	*Trichocerca similis* Wierzejski 1893	2.7	Pit lakes in Lusatia	
Rotifera, Monogononta	*Lecane stichaea* Harring 1913	3.0	Pit lakes in Lusatia	
Rotifera, Monogononta	*Lepadella* sp.	3.0	Pit lakes in Lusatia	
Rotifera, Monogononta	*Lecane* (*Monostyla*) *bulla* (Gosse 1886)	3.0	Pit lakes, Illinois, USA	McConathy and Stahl (1982)
Cladocera, Chydoridae	*Chydorus sphaericus* (Müller 1776)	3.0	Grünewalder Lauch (ML 117)	Wollmann et al. (2000)
Moderately acidic pit lakes				
Cladocera, Daphniidae	*Scapholeberis mucronata* (Müller 1776)	3.5	Geierswalder See	Belyaeva and Deneke, unpubl
Copepoda, Cyclopidae	*Diacyclops* sp.	3.5	Felixsee	Wollmann et al. (2000)
Weakly acidic pit lakes				
Rotifera, Monogononta	*Polyarthra* sp.	4.7	Gräbendorfer See	Deneke, unpubl
Rotifera, Monogononta	*Keratella cochlearis* (Gosse 1851)	4.7	Gräbendorfer See	
Rotifera, Monogononta	*Keratella testudo* (Ehrenberg 1832)	4.7	Gräbendorfer See	
Rotifera, Monogononta	*Filinia longiseta* (Ehrenberg 1834)	4.7	Gräbendorfer See	
Cladocera, Daphniidae	*Ceriodaphnia* sp.	4.7	Gräbendorfer See	
Cladocera, Bosminidae	*Bosmina coregoni* Baird 1857	4.7	Gräbendorfer See	
Cladocera, Chydoridae	*Eurycercus lamellatus* (Müller 1776)	4.9	Senftenberger See	Belyaeva and Deneke (2007)

(continued)

Table 3.13 (continued)

Taxonomic group	Species	pH	Sampling site	Reference
Cladocera, Chydoridae	*Pleuroxus truncatus* (Müller 1785)	4.9	Senftenberger See	
Cladocera, Bosminidae	*Bosmina longirostris* (Müller 1785)	5.0	Senftenberger See	
Cladocera, Sididae	*Sida crystallina* (Müller 1776)	5.0	Senftenberger See	
Cladocera, Chydoridae	*Alona affinis* (Leydig 1860)	5.0	Senftenberger See	
Cladocera, Chydoridae	*Acroperus harpae* (Baird 1835)	5.7	Senftenberger See	
Cladocera, Chydoridae	*Alona costata* Sars 1862	5.7	Senftenberger See	
Cladocera, Daphniidae	*Ceriodaphnia pulchella* Sars 1862	5.7	Senftenberger See	
Cladocera, Polyphemidae	*Polyphemus pediculus* (Linne 1761)	5.7	Senftenberger See	
Cladocera, Chydoridae	*Alona guttata* Sars, 1862	5.7	Senftenberger See	
Cladocera, Sididae	*Diaphanosoma brachyurum* (Liévin 1848)	5.7	Senftenberger See	
Cladocera, Daphniidae	*Simocephalus vetulus* (Müller 1776)	6.1	Senftenberger See	

Classification of lakes is according to Nixdorf et al. (2005), slightly modified. Core species that dominate zooplankton communities in acidic pit lakes are underlined. Lakes are in Germany unless otherwise specified

[a] Although this species was recorded from North American pit lakes as *Brachionus urceolaris*, it is likely *B. sericus*, which appears to be much more acid-tolerant than the former species. The observed minimum in situ pH of 2.6 for the North American populations differs from that in German lakes, where this species has only been found at a pH of 2.7 and above (Deneke 2000)

2007). Only two cladoceran species, *C. sphaericus* and *S. mucronata*, were found at pH below 4.9, whereas rather diverse communities occurred at pH $\geq$ 4.9 (Table 3.13). Dramatic changes in cladoceran species composition were observed within a distance of several hundred meters along the pH gradient, despite the lack of any physical barriers that might have limited the dispersal of species. Thus, the loss of species towards the acidic part of the lake can be attributed to the adverse effects of the chemical conditions. To our knowledge, no published studies report on the species composition of Copepoda and Rotifera within the pH range of 4.5–6 in pit lakes, although both groups do occur at these conditions (Belyaeva and Deneke unpubl.; Woelfl et al. 1998).

Most zooplankton species that are found in acidic pit lakes have been recorded from different continents and appear to be cosmopolitan. However, it should be noted that most data on zooplankton communities come from studies on pit lakes in Germany, while less is known about the biota of these habitats outside Europe. *C. hoodi*, *C. gibba*, and *B. sericus* have been recorded in both European and North American acidic pit lakes (Deneke 2000). There is a lack of detailed taxonomic studies confirming the co-specificity of geographically distant populations. Particularly, uncertainties exist concerning the taxonomic status of *B. sericus*. Although Rousselet (1907) described *B. sericus* as a separate species, it was often later regarded as a variety of *B. urceolaris* (e.g. Koste 1978). Hence, some records of *B. sericus*, *B. urceolaris* var. *sericus*, and *B. urceolaris* by different authors may possibly refer to the same taxon. If so, it colonizes acidic hard-water lakes separated by large geographical distances, being also found in Australian billabong ponds affected by mine drainage (Tait et al. 1984), geogenically acidified lakes in Japan (Uéno 1958), and in the Canadian Arctic ponds acidified by burnt bituminous shales (Havas and Hutchinson 1983). On the other hand, *Elosa worallii* is very common in acidic hard waters, but only in Europe (Nixdorf et al. 1998; Vallin 1953), while a detailed study of North American pit lakes by McConathy and Stahl (1982) did not detect this species. *C. sphaericus* has been recorded in hard-water acidic lakes on different continents (Deneke 2000). Yet, these populations probably belong to distinct, though closely related species (Belyaeva and Taylor 2009).

Volcanic and coastal sulfur lakes are natural analogues of acidic pit lakes, with similar water chemistry (Geller et al. 1998); they are also inhabited by similar zooplankton communities (Deneke 2000). However, there are some differences in species occurrence patterns, e.g. occurrence of copepods at pH around 3 in volcanic lakes in Japan (Uéno 1958), but not in pit lakes. This may be related to adaptation of species in the regions, where hard-water acidic lakes have existed over evolutionary relevant time scales.

Factors Influencing Colonization of Acidic Pit Lakes by Zooplankton

Zooplankton species richness and community composition in acidic pit lakes are both highly predictable from the lake pH value (Deneke 2000). The strong correlation between zooplankton species richness and pH (Fig. 3.53) exists

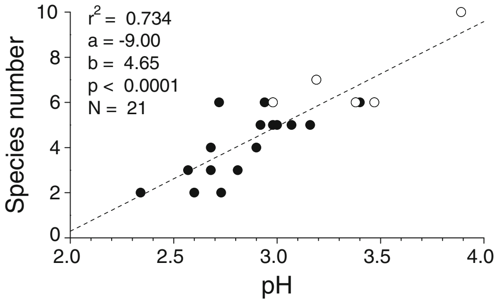


Fig. 3.53 Zooplankton species richness along a pH gradient in acidic pit lakes, based on monthly samples from 21 lakes in Lusatia, Germany, over a period of at least one year. Indicated are parameters of linear least square regression fitted to the data. Filled circles indicate that the communities lacked crustaceans; open circles indicate that crustaceans were observed

despite considerable variability in lake morphology, mixis regime, and trophic status of pit lakes. This, however, does not necessarily mean that high concentration of protons alone limits species occurrence. Generally, multiple abiotic stressors act in acidic lakes (Frost et al. 1999). Zooplankton species composition in acidic pit lakes differs greatly from that in soft-water acidic lakes, which indicates that other water chemistry parameters might be crucial for biological colonization. Laboratory tests with cladocerans have shown that aluminum, iron, and heavy metal ions (Lopes et al. 1999; Soucek et al. 2001) as well as high sulfate content (Kennedy et al. 2005) can contribute to the toxicity of waters affected by acid mine drainage. Metal ions may be elevated in soft-water acidic lakes as well, but their toxicity is mitigated by colored dissolved organic carbon (cDOC; Williamson et al. 1999). As cDOC content is usually very low in acidic pit lakes (Friese et al. 2002), its beneficial effects are diminished. Therefore, abiotic conditions in acidic pit lakes should be more toxic for organisms than those in naturally acidic lakes at the same pH values. Indeed, in our study on littoral Cladocera (Belyaeva and Deneke 2007), we reported higher species-specific in situ pH thresholds for most species in a pit lake vs. soft-water acidic lakes (Fig. 3.54). As a result, species diversity in acidic pit lakes is expectedly lower than in naturally acidic soft-water lakes.

Acidity reflects buffering capacity, i.e. the stability of pH conditions. Soft-water lakes are rather poorly buffered, and spatial as well as seasonal pH fluctuations occur, whereas acidic pit lakes at pH < 4.5 are well-buffered and display very little within-lake variation in pH, with the exception of meromictic pit lakes. At pH > 4.5, soft-water lakes are buffered by cDOC, but in pit lakes, this buffer system is lacking, and so the pH is very unstable (Nixdorf et al. 2003). Precipitation of metal compounds occurs during pH changes, which can adversely affect organisms (Belyaeva and Deneke 2007; Weatherley et al. 1991). This may occur, for example, during whole-lake neutralization or within mixing zones, where neutral river water enters a highly acidic pit lake. Thus, the detrimental effect of metal precipitation should be taken into account while planning neutralization measures.

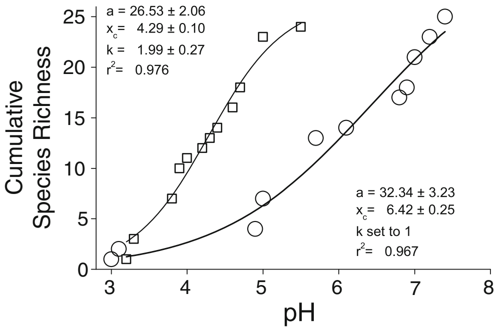


Fig. 3.54 Logistic regression curves for the potential cumulative species richness of littoral Cladocera within a horizontal pH gradient from 3 to 7 in a pit lake Senftenberger See (*circles*) and natural soft-water lakes (*squares*) based on in situ pH thresholds for individual species. Lower potential species richness predicted for acidic pit lakes, as compared to soft-water lakes, results from higher species-specific pH thresholds (modified from Belyaeva and Deneke (2007), with kind permission from Springer Science + Business Media)

Evidently, specific water chemistry in acidic pit lakes exerts profound effects on the zooplankton species diversity and composition. Secondary production and biomass in acidic lakes seem to be less affected, due to compensating shifts in biomass of tolerant species (Frost et al. 1995). On the other hand, food availability is believed to control zooplankton biomass in acidic lakes (Havens and Carlson 1998; Nixdorf et al. 1998) as well as within-lake distribution (Weithoff 2004) and seasonal dynamics of populations, but it is unlikely to limit species occurrence. Another limiting factor is, possibly, availability of micro-habitats in the littoral zone. Many acidic pit lakes are characterized by low macrophyte growth (Pietsch 1998); hence, plant-associated zooplankton species may be rare or completely excluded due to a lack of suitable micro-habitats. Biotic factors, such as predation and competition, play an important role in natural lakes. Yet, in acidic lakes, the importance of biotic factors decreases at low pH, where abiotic conditions become increasingly more stressful (Arnott and Vanni 1993). In the most extremely acidic pit lakes ($pH < 2.8$), neither predation nor competition seem to be important (Weithoff 2004), whereas at $pH > 2.8$, some effects of biotic interactions may be present, although water chemistry is still the major determinant of zooplankton community structure (Wollmann and Deneke 2004).

Dispersal of zooplankton may be hindered by the young age and/or isolated character of many acidic pit lakes. However, no published data is available on the primary colonization of newly created pit lakes, and it is unknown how long it takes the core zooplankton community to get established. Another interesting question for future studies would be the genetic structure and exchange among populations colonizing acidic pit lakes, i.e. metapopulation dynamics. It is possible that it would be reduced due to isolation of pit lakes, yet, many zooplankton species colonizing these habitats are pioneer species with high dispersal capabilities (see below), which can enhance metapopulation dynamics.

Ecology of Species Colonizing Acidic Pit Lakes

Anthropogenically stressed environments, such as acidic pit lakes, are commonly colonized by extremophilic specialists as well as generalist species with broad tolerance ranges to a number of environmental factors. In contrast to bacteria, algae, and protists, which are often represented by acidophiles in acidic pit lakes, the evidence for acidophily among zooplankton is rather weak (but see Sect. 3.3.1.4). Most of the zooplankton species occurring in acidic pit lakes have been also found in natural lakes at acidic and neutral conditions (Deneke 2000), although they exhibit somewhat different abundance patterns and habitat preferences there (see below). Furthermore, core species from acidic pit lakes—*C. sphaericus*, *B. sericus*, *E. worallii*, and *C. hoodi*—cultured at ambient pH, could be successfully transferred to neutral pH under laboratory conditions (Belyaeva and Deneke 2007; Deneke unpubl.). Hence, zooplankton community in acidic pit lakes largely, if not exclusively, comprises generalist species. In contrast, there are possibly some specialists among zooplankton species colonizing acidic soft-water lakes that have not been recorded in acidic pit lakes or in neutral hard-water lakes, e.g. the rotifers *Lecane acus*, *Habrotrocha lata*, *Keratella serrulata* (Bērziņš and Pejler 1987), and the cladocerans *Acantholeberis curvirostris* and *Streblocerus serricaudatus* (Flößner 2000). However, the designation of these species as specialists is derived from field occurrence data alone. It remains unclear whether their physiological optima lie under soft-water acidic conditions, or if they are simply weak competitors that are outcompeted in species-rich neutral lakes. Still, many soft-water acidic 'specialists' have not been found in species-poor acidic pit lakes, which suggests that they are not capable of tolerating the abiotic stresses there. The complete absence of specialists in acidic pit lakes is probably explained by insufficient time for adaptive evolution, since those are young habitats with peculiar abiotic conditions, and their natural counterparts, such as volcanic lakes, are rare.

Zooplankton species found in acidic pit lakes can be characterized as pioneers that also colonize newly created and perturbed water bodies. Pioneer species are r-strategists (meaning they have high growth rates) with efficient dispersal mechanisms, and they are able to use a wide range of food sources. For example, *C. sphaericus* is often the first crustacean species colonizing new sites (Louette et al. 2008); it is capable of using different food sources (De Eyto and Irvine 2001), tolerates a wide range of abiotic conditions (Belyaeva and Deneke 2007), and is often abundant in anthropogenically disturbed environments, e.g. highly eutrophic lakes (De Eyto 2001). Despite their large potential for colonization, pioneer species are presumably weak competitors. Their mass development is only observed in species-poor communities, such as acidic pit lakes, or in natural lakes, when superior competitors are (temporarily) absent, e.g. *C. sphaericus* developing in the absence of *Daphnia* and copepod nauplii (Matveev 1986).

Absence of pelagic forms and a simultaneous habitat shift of littoral species to the pelagic zone is a common observation in all kinds of acidic lakes, including soft waters (Nilssen 1980; Nilssen and Wærvågen 2003). This is probably due to the lack of competition and predation pressure under acidic conditions (Locke and

Sprules 2000). In European acidic pit lakes, no zooplankton species were found exclusively in benthic or littoral habitats (Deneke 2000), although rotifers and crustaceans exhibited heterogeneous distributions within the water column (Weithoff 2004; Wollmann and Deneke 2004). In North American acidic pit lakes, two species, *Lecane bulla* and *Philodina* sp., were found only in benthic algal clumps, but not in plankton (McConathy and Stahl 1982). The absence of large pelagic species in acidic pit lakes results in a shift towards species with body size <500 μm. A similar shift in size structure has been documented for naturally acidic and atmospherically acidified lakes (Schindler et al. 1985).

It is not quite clear what physiological adaptations of tolerant zooplankton species have led to successful colonization of acidic pit lakes. In general, organisms living at low pH are capable of maintaining a circum-neutral internal pH via passive or active mechanisms (Rothschild and Mancinelli 2001). Additional challenge for colonization of pit lakes is seemingly provided by the high total ionic content and high metal concentrations typical of these waters. Hence, it is possible that survival of zooplankton in acidic pit lakes is ensured due to different physiological mechanisms than those that are employed in soft-water acidic lakes. There is still a lack of knowledge concerning particular mechanisms of ion regulation in metazoan zooplankton species under acidic hard-water conditions. A study on a rotifer, *C. hoodi*, from extremely acidic pit lakes failed to detect any additional physiological costs or specific ecological adaptations (Weithoff 2005).

Ecological Characteristics of Zooplankton Communities in Acidic Pit Lakes

The major features of biological communities in acidic pit lakes are greatly reduced species diversity and extirpation of fish, so that the role of top predators is taken over by invertebrates (Wollmann et al. 2000). This leads to truncated and very simple food webs (Sect. 3.3.1.4). In acidic pit lakes, zooplankton community composition is controlled by pH and related water chemistry parameters, whereas zooplankton biomass is possibly controlled by food availability (Wollmann and Deneke 2004; Sect. 3.3.1.4), as in soft-water acidic lakes (Havens and Carlson 1998). Biotic interactions seem to be rather weak, at least in the most acidic pit lakes (Weithoff 2004). However, some ecological patterns occurring in natural lake ecosystems, such as niche separation among different species (Weithoff 2004), seasonal succession, and top-down and bottom-up effects on zooplankton (Wollmann and Deneke 2004; Wollmann et al. 2000), have been observed in acidic pit lakes as well. On the other hand, zooplankton community composition is rather peculiar and unique in acidic pit lakes, what may result in rather specific biotic interactions.

Nixdorf et al. (2005) proposed a classification scheme for acidic pit lakes based on pH, chemical buffer system, and colonization patterns by phyto- and zooplankton (Table 3.14). The defined lake groups can also be viewed as successive stages of habitat maturation, as acidic lakes should become neutral with time due to natural alkalinity generation by chemical and biological processes. Characteristic core species occur in each group of lakes (Table 3.14), whose presence often has a pronounced

Table 3.14 Classification of acidic pit lakes based on water chemistry and zooplankton colonization (modified from Nixdorf et al. 2005)

Lake group	pH	Conductivity ($mS\ cm^{-1}$)	Acidity ($mmol\ L^{-1}$)	Buffer system	Characteristic zooplankton species
Extremely acidic	<2.8	>3	>15	Iron	*Cephalodella hoodi*, *Elosa worallii*
Very acidic	2.8–3.5	1.5–3.0	>1.6–15	Iron	*Brachionus sericus*, *Chydorus sphaericus*
Moderately acidic	3.5–4.5	< 1.5	0–1.6	Aluminum	*Diacyclops* sp., *Scapholeberis mucronata*
Weakly acidic	4.5–6.5	< 1.5	ca. –0.5	Lacking buffer system	Diverse littoral Cladocera

effect on the food web structure and seasonal population dynamics (Wollmann and Deneke 2004). In ‘extremely acidic’ pit lakes ($pH < 2.8$), the zooplankton community is dominated by two small rotifer species, *C. hoodi* and *E. worallii*, and potential community grazing rates are very low (less than 1% per day). Hence, the impact on primary producers is negligible; indeed, no top-down effects on phytoplankton have been observed in extremely acidic pit lakes even during metazooplankton abundance peaks (Lessmann et al. 1999; Weithoff 2004). Heliozoa play the role of top predators in the pelagic food web; however, it appears that they are not capable of exerting any noticeable effect on zooplankton (Weithoff 2004).

In ‘very acidic’ pit lakes ($2.8 \leq pH < 3.5$), the appearance of larger zooplankton species with higher clearance rates—*B. sericus* and *C. sphaericus*—leads to top-down effects on phytoplankton (Wollmann and Deneke 2004). As a result, a seasonal pattern is observed with a break-down of phytoplankton biomass following mass development of both zooplankton species in summer (Wollmann et al. 2000). Corixidae prey on both dominant zooplankton species here, while heliozoans disappear from pit lakes at $pH > 2.8$. As corixids can feed both on benthos and zooplankton, they enable benthic-pelagic coupling in the food webs (Wollmann et al. 2000).

In ‘moderately acidic’ pit lakes (pH 3.5–4.5), zooplankton communities are more diverse, including several additional rotifer species, a cladoceran *S. mucronata*, and copepods (Wollmann et al. 2000). The community composition is intermediate between the acidic and neutral pit lake communities (Wollmann and Deneke 2004). Still, acid-tolerant species that are characteristic of very acidic pit lakes also dominate here. Weakly acidic pit lakes with $pH > 4.5$ are very rare due to the lacking buffer system.

The metazooplankton community can serve as a reliable and simple biological indicator of water quality in acidic pit lakes (Nixdorf et al., 2005). Colonization patterns mostly reflect physiological thresholds of individual species. Hence, species composition and community structure is intimately related to chemical conditions, whereas variation due to biotic interactions and within-lake habitat heterogeneity is almost absent. Pit lakes with similar water chemistry conditions, though they might be different in their morphology, mixis regime and trophic status, are still remarkably similar with respect to their zooplankton communities. All this makes zooplankton well-suited for bio-indication of ecological quality in acidic pit lakes.

3.3.1.3 Prokaryotic Microorganisms, Protists, and Fungi

Katrin Wendt-Potthoff

Bacterial Numbers and Biomass in Acidic Pit Lakes

Total bacterial numbers determined by epifluorescence microscopy in acidic pit lakes are similar to those of natural lakes and in many cases correspond to the trophic state of the lake inferred from primary production. Most acidic pit lakes in Germany are oligotrophic, and their bacterial counts normally do not show distinct vertical or seasonal patterns. Generally, the bacterial counts are roughly 10% of those from natural hard-water lakes (Nixdorf et al. 2003). Spanish pit lakes, which result from ore mining and include many meromictic lakes, often show pronounced vertical differences in bacterial numbers. For the numerous Australian pit lakes, no data on bacterioplankton, fungi, or heterotrophic protists are available.

Bacterial cell counts in acidic pit lakes are positively correlated to DOC concentrations (Kampe et al. 2010). In a comparative study of four pit lakes in Lusatia, average values lay between 1.6 and 3.4×10^5 cells mL^{-1}, with the highest values found in the most acidic (and oldest) lake. However, a neutral pit lake in the same region, which was studied as a reference, had bacterial counts of 4.9 (±4.4) $\times 10^5$ cells mL^{-1} (Table 3.15). For Lake 111, bacterial cell numbers were confirmed by subsequent studies (Müller 2004; Pöhler et al. 2002), so they appear to be stable with time. The bacterial counts of acidic lakes correspond to bacterial biomass and production, which are negatively correlated with pH and in the same range as those of natural lakes (Kamjunke et al. 2005). In contrast to the Lusatian lakes, pronounced vertical gradients of bacterial counts were found in Spanish pit lakes, with maxima at the surface in a dam (Malki et al. 2006) and in the rather young and meromictic San Telmo lake (Sánchez-España et al. 2007). In the latter, bacterial counts reached 10^8 cells mL^{-1} in the upper 5 m, showed a minimum of $\approx 10^6$ cells mL^{-1} in the deeper mixolimnion, and increased again to 3.6×10^6 cells mL^{-1} in the anoxic monimolimnion. The Berkeley Pit in Montana, USA, had bacterial counts around 10^5 mL^{-1} in the upper part and lower counts at depths >55 m (Mitman 1999).

The percentage of filamentous organisms in bacterioplankton is often high in pit lakes and seems to be negatively correlated with pH. When filaments longer than 10 μm were considered, their proportion was below 1% in 11 of 12 samples in the neutral pit lake, Lake B. Bacterioplankton of the acidic pit lakes, Lake 111 (pH 2.6) and Lake 107 (pH 2.3), comprised 13 ± 9 and 17 ± 7% filaments (median ± standard deviation, $n = 12$ and 10, respectively; Babenzien and Meier

Table 3.15 Bacterial counts and percentage of cells forming microcolonies on polycarbonate filters (mean ± standard deviation), determined by epifluorescence microscopy after staining with acridine orange

Lake	117 (pH 3.0)	107 (pH 2.3)	111 (pH 2.6)	B (pH 8.0)	F (pH 2.8)
Total bacterial counts (mL^{-1})	$1.8 \pm 0.5 \cdot 10^5$ ($n = 12$)	$3.4 \pm 2.0 \cdot 10^5$ ($n = 8$)	$2.8 \pm 2.0 \cdot 10^5$ ($n = 24$)	$4.9 \pm 4.4 \cdot 10^5$ ($n = 23$)	$1.6 \pm 1.0 \cdot 10^5$ ($n = 23$)
% of cells forming microcolonies	23 ± 12 ($n = 12$)	n.d.	26 ± 9 ($n = 20$)	23 ± 10 ($n = 22$)	25 ± 19 ($n = 21$)
% of microcolonies with 2–3 cells	82 ± 8 ($n = 11$)	n.d.	60 ± 25 ($n = 20$)	70 ± 21 ($n = 22$)	71 ± 12 ($n = 20$)
% of microcolonies with 4–11 cells	11 ± 6 ($n = 11$)	n.d.	15 ± 11 ($n = 20$)	21 ± 17 ($n = 22$)	21 ± 19 ($n = 20$)
% of microcolonies with >12 cells	7 ± 3 ($n = 11$)	n.d.	9 ± 8 ($n = 20$)	9 ± 8 ($n = 22$)	9 ± 5 ($n = 20$)

Sampling took place between 1995 and 1997. Microcolony formation was not determined (n.d.) for Lake 107 because of the large fraction of filamentous cells. Applying one way ANOVA and subsequent pairwise comparison by the Holm-Sidak method, total bacterial counts in the neutral Lake B were significantly different from Lake 117, 111 and F, but not from the most acidic Lake 107

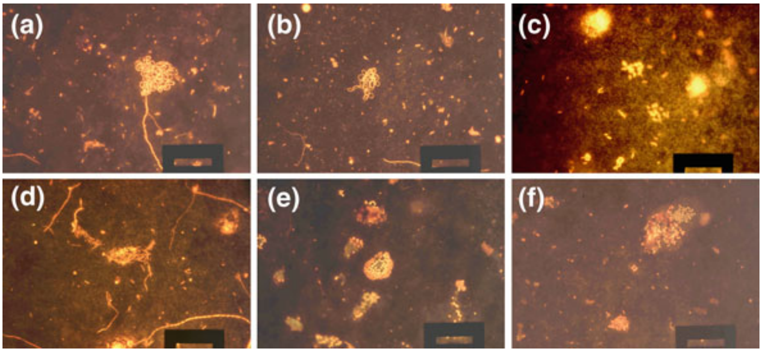


Fig. 3.55 Micro-organisms with "curled" morphology from **a** Lake 111 and **b** Lake 107. Microcolonies grown on polycarbonate filters from **c** Lake 117, **d** Lake 107, **e** Lake F, **f** the neutral pit lake, Lake B. Bars indicate 10 μm

1998, unpublished report); a later study (Müller 2004) reported around 11% filamentous cells in Lake 111 with a total cell count around 10^6 mL^{-1}. In addition to straight filaments of various sizes, conspicuously curled morphologies also occurred (Fig. 3.55a, b). A high proportion of filamentous forms can be a consequence of grazing pressure. In acidic pit lakes, bacteria are mainly grazed by phago-mixotrophic flagellates of the genus *Ochromonas* (Sect. 3.3.1.4).

Since microscopic counts of fixed cells not necessarily represent viable organisms, and microorganisms from the environment mostly fail to grow on solid culture media, dilution cultures in liquid media or microcolony assays using membrane filters (Straskrabova 1972) are used to enrich organisms or to test the viability of microscopically visible cells. Microcolony assays using white polycarbonate membranes have been successfully applied for acidophiles (de Bryun et al. 1990); this method has been modified to assess the ability of acidic pit lake microorganisms to divide with only their original 0.2 μm filtered lake water as a substrate (Wendt-Potthoff, unpublished). After 48 h, cells were fixed and stained with acridine orange following the protocol of Binnerup et al. (1993), and cell and microcolony numbers were counted using a filter immediately fixed after sampling as a reference. Some typical microcolonies are shown in Fig. 3.55 (c–f). Roughly 25% of total cells were able to divide on the polycarbonate membranes in both the neutral and acidic pit lakes. Most of the colonies (around 70%) were small, indicating that time and resources were only sufficient for one to two divisions (Table 3.15). However, larger colonies also formed with all of the studied lake waters, and their percentages were similar (Table 3.15). There is little published information to rank these results. They are within the range found for marine bacteria in membrane cultures with seawater and mud extract (0.8–66.1%, Bianchi and Giuliano 1996) and similar to those obtained with a slide culture approach without additional nutrients on freshwater and sewage samples (Fry and Zia 1982). Bartscht et al. (1999) found a higher percentage of 58.3 ± 23.1% dividing cells with a synthetic freshwater medium, but in this case, 15 mg L^{-1} of natural DOC was added, and the incubation time was 10 days.

In addition to the high percentage of cells able to divide with only lake water as a substrate, pit lake microbiota also showed a high potential to utilize ^{14}C-glucose during incubation at in situ temperature (Babenzien and Meier 1998, unpublished report). The process was temperature-dependent; in summer, uptake rates of 0.13–0.67 μg C L^{-1} h^{-1} were measured in Lusatian acidic pit lakes. These are in the range of activities measured in natural mesotrophic lakes and above that of the neutral reference pit lake, Lake B (0.12 μg C L^{-1} h^{-1}). The fraction of ^{14}C-glucose converted to CO_2 was not considered in these experiments. Metabolism of ^{14}C-glucose was also studied in summer samples from Reservoir 29, a lake that receives acidic drainage from coal refuse piles (Gyure et al. 1987). In this study, both uptake and respiration were considered, and there was a clear trend of increasing glucose utilization with depth. When converting these data, their range was either 0.04–8.6 or 0.2–43 μg C L^{-1} h^{-1} because of inconsistent information about label addition. Assuming that respiration accounts for approximately 30% of the measured activity (Hobbie and Crawford 1969), rates are comparable except for the deep-water measurements from Lake 29, which are roughly tenfold higher. Together with the fact that bacterial growth in acidic pit lakes was greatly limited by DOC availability (Kamjunke et al. 2006), this confirms the importance of heterotrophic metabolism in acidic pit lakes. The role of substrates and energy flow within the pit lake food web is discussed in detail in Sect. 3.3.1.4.

In conclusion, the numbers, biomass, viability, and thus the acclimatization of acidic pit lake bacterioplankton to the prevailing conditions appears to be comparable to that of other aquatic habitats.

Taxonomic Composition of Bacterioplankton in Acidic Pit Lakes

Information regarding the taxonomic composition of bacterioplankton in acidic pit lakes is scattered and inconsistent. The diversity of bacteria does not generally decline with sinking pH values, and the bacterial community composition in geographically close pit lakes of different pH appears to be similar (Kampe et al. 2010). The communities consisted mainly of alpha-, beta-, and gamma-Proteobacteria (>90% in most samples); Actino- and Acidobacteria were only minor components. Despite similar bacterial counts throughout the year, strong seasonal changes of community composition became evident by sequencing PCR products obtained with universal bacterial primers after denaturing gradient gel electrophoresis (DGGE; Kampe et al. 2010).

In a separate study, a clone library was prepared from Lake 111 water by 16S rDNA amplification with bacterial primers. Sequences of obligately anaerobic microorganisms were not detected in the clone library, corresponding to the oxic status of the water column. Here, the most prominent groups among the bacteria were *Acidobacteria*, *Acidiphilium* and, surprisingly, organisms affiliated with *Nitrosomonas* and *Legionella* (Müller 2004, Fig. 3.56). Ammonia oxidizers have also been found to be important in mine waters in North Wales (Hallberg et al. 2006). The presence of *Legionellae* was confirmed by Kampe et al. (2010). Members of the genus *Legionella*

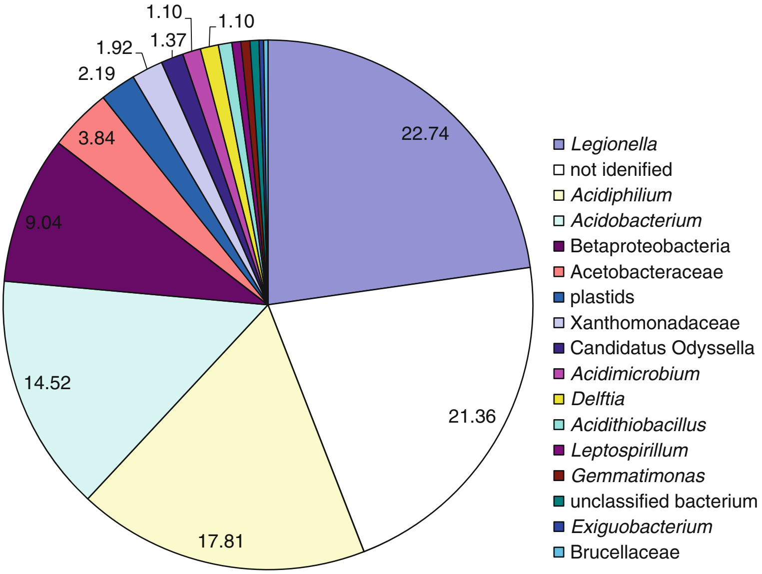


Fig. 3.56 Phylotypes detected in a clone library from a mixed water sample of Lake 111. The legend denotes taxa in decreasing order of percentage from *top* to *bottom*. The high fraction of clones that were not identified includes very rare phylotypes that were not further characterized. Percentages are given for taxa comprising more than 1% of the clones (data from Müller 2004)

(and of candidatus *Odyssella* as well) occur as endosymbionts in free-living amoebae (see review by Horn and Wagner 2004), and appreciable numbers of amoebae were also detected in Lake 111 (Müller 2004, see below). Although this association of microorganisms has not been reported from any other acidic pit lake, Legionellae and their potential host amoebae have been detected in a pH 2.7 geothermal stream in Yellowstone National Park (Sheehan et al. 2005). The fraction of unidentified clones in the Lake 111 clone library includes many rare phylotypes that were not further characterized. This indicates that the true diversity of Lake 111 bacterioplankton was not fully resolved by this clone library, though the phylotypes most frequent at the time of sampling could be classified. Müller (2004) also investigated Lake 111 bacterioplankton by whole cell hybridization. With eubacteria-directed probes, approximately 57% of all cells were marked. Among these, alpha-proteobacteria (27.6% of total cells) were most prominent, followed by gamma- and beta-proteobacteria and acidobacteria (7.2, 4.3, and 6.4% of total cells, respectively). The probe for alpha-proteobacteria stained many of the filamentous cells. For *Acidobacteria* subdivision 1, an improved oligonucleotide probe for whole cell hybridization was designed, and seasonally varying counts of $0.4–3.7 \times 10^4$ cells mL^{-1} were detected with this probe in Lake 111 bacterioplankton. This is equivalent to 37–70% of cells detected by the probe EUB338, and to 1.4–7.9% of all DAPI-stained cells (Kleinsteuber et al. 2008).

The Spanish pit lake San Telmo also showed a high percentage (47–78%) of alpha-proteobacteria (which include *Acidiphilium*) in the upper mixolimnion; in the lower part of the mixolimnion, *Leptospirillum*-like organisms (17–22%) were also important (Sánchez-España et al. 2007). *Acidithiobacillus*-related bacteria were generally rare in pit lake waters (Kamjunke et al. 2005; Sánchez-España et al. 2007). This is remarkably different from the prokaryotic diversity in the water column of the Río Tinto, about 80% of which was attributed to *Acidithiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*, and *Acidiphilium* spp., all of which are involved in iron cycling (González-Toril et al. 2003).

Two reservoirs associated with the largest open pit copper mine in China (termed YTW and ZJ, both pH 3), which contained a mixture of acid mine drainage, infiltration water, and rain, were obviously dominated by gammaproteobacteria (61 and 90.1% of clones, Yin et al. 2008). This group includes *Acidithiobacillus ferrooxidans*, and 28.2 and 27.5% of clones from YTW and ZJ were related to this species. Despite their equal pH, the chemistry of the reservoirs exhibited pronounced differences, with YTW having similar concentrations of iron and aluminum (both between 900 and 100 mg L^{-1}) and ZJ being rich in aluminum and copper (1,588 ± 206 and 213 ± 26 mg L^{-1}) associated with moderate (198.61 ± 17.9 mg L^{-1}) iron concentrations. This may explain the much lower total bacterial diversity (a Shannon–Weaver diversity index of $H = 2.23$ compared to 4.16 in YTW) in that reservoir (Yin et al. 2008). Although much effort has been made to cultivate bacteria from tailings and acid mine drainage streams in recent years (e.g. Diaby et al. 2007; Johnson et al. 2001), there seems to be no such study on acidic pit lake water. However, an isolate from Lusatia was identified as *Acidiphilium organovorum* by fatty acid analysis (Wendt-Potthoff et al., unpublished).

In contrast to findings from extreme acid mine drainage, where archaea can account for up to 50% of prokaryotic cells in summer samples (Edwards et al. 1999), archaea seem to be less important in the cooler and more dilute waters of acidic pit lakes. Few archaea (3%) were detected in the water of the Spanish pit lake San Telmo (Sánchez-España et al. 2007). In Lake 111, abundance and diversity of archaea was also low. Except for some non-thermophilic Crenarchaeota, they were affiliated to Thermoplasmatales (Müller 2004). No archaea were found in clone libraries from three samples of the acidic river Rio Tinto in Spain, and few archaeal cells were detected by whole cell hybridization (Garrido et al. 2008).

The occurrence of live cyanobacteria has not been reported from acidic pit lakes so far, but related sequences have been detected in PCR products obtained with universal bacterial primers following DGGE and sequencing (Kampe et al. 2010). Sequences of other phototrophic prokaryotes were not found, and bacterial pigments indicative of such organisms are also generally absent (Kamjunke et al. 2005). A special situation may arise in meromictic pit lakes. If the monimolimnion is close to neutral and sulfidic, anoxygenic phototrophic bacteria may establish a presence at the chemocline. So far, only two such cases have been reported, in the small lakes Waldsee and Lugteich in Lusatia (Rücker et al. 1998). Waldsee has a naturally high input of organic matter in the form of leaf litter, and Lugteich had received municipal sewage that had only been mechanically treated from approximately 1970–1990.

Pigment analyses revealed the presence of green sulfur bacteria, Chlorobiaceae, with bacteriochlorophyll –d concentrations of up to 500 μg L^{-1}.

Generally, the taxonomic composition of bacterioplankton from pit lakes exhibits marked similarities with those of concentrated acid mine drainage and geothermally influenced waters. As a rule of thumb, acidic pit lakes tend to have a higher prokaryotic diversity as well as a higher proportion of heterotrophs and a lower proportion of archaea.

Fungi and Yeasts

Fungi and yeast are known to occur over a wide pH range, and a considerable diversity of isolates has been obtained from acidic habitats (e.g. Das et al. 2009; Joseph 1953). A high percentage (43% of 274 strains) of hyphomycete isolates from Rio Tinto was demonstrated to grow in Rio Tinto conditions (Lopez-Archilla et al. 2001). Fungal communities in pit lakes have not been as systematically studied as streams influenced by acid mine drainage or volcanic activity. Fungi in general have been termed "tolerant" to "common" in a collection of more than 200 mine water samples, which included pit lakes, as they were found in 8.05% of spring and 18.05% of summer samples (Lackey 1939). Yeast and fungal colonies regularly appeared on solid culture media inoculated with water samples from Lusatian lakes and were sometimes hard to separate from bacterial isolates, because fungicides were either not fully effective at pH 3, or the organisms were resistant to them. When carbon substrates were added to acidic pit lake water, fungal proliferation was observed within 24 h (Babenzien and Meier 1998, unpublished report). A yeast bloom has also been observed in situ after the addition of whey to an enclosure experiment in Lake 111 that was intended to consume the oxygen in the water column. However, none of these findings are quantitative. Colony counts of 6×10^4–6×10^5 mL^{-1} have been reported from acid streams in northern West Virginia and Pennsylvania (Joseph 1953), and Gadanho et al. (2006) counted between 2 and >15,000 L^{-1} yeast colony forming units (cfu) in water samples from ponds and creeks in the Sao Domingos and Rio Tinto mines of the Iberian Pyrite Belt (pH 1.8–2.9). They used an acidified (pH 3) medium, which yielded higher counts than the conventional medium with pH 5.7. Tests with some samples revealed even higher counts when an acidic medium with water from the original sites was prepared. This shows that the yeast present in the acidic waters were well adapted to their habitat.

Using the same cultivation approach on a naturally volcanic-acidic water system in Argentina, Russo et al. (2008) counted lower yeast numbers (30–1,200 cfu L^{-1} for Rio Agrio and only 30–60 cfu L^{-1} for Lake Caviahue). Yeast diversity in a pit lake and a pond increased from spring to autumn, an as-yet unexplained observation that deserves further study (Gadanho et al. 2006). In total, 27 yeast species (both ascomycetous and basidiomycetous) were isolated, of which 48% might represent undescribed taxa. Among these, a *Cryptococcus* sp. required low pH for growth, a property that had not been observed before in yeasts (Gadanho et al. 2006). The acid-tolerant yeasts belonged to other *Cryptococcus sp.*, *Lecytophora sp.*, *Candida fluviatilis*, *Rhodosporidium toruloides*, *Williopsis californica*, and *Rhodotorula* sp. A truly acidophilic *Cryptococcus* sp. was also isolated by Russo et al. (2008) from the volcanic-acidic Rio Agrio-Lake Caviahue environment. Moreover, a *Cryptococcus* sp. with a growth optimum at pH 3 and almost no growth at pH 8 was isolated from an acidic pond at Smoking Hills in Canada, and was shown to live in a mutualistic relationship with the acidophilic alga *Euglena mutabilis* (Nakatsu and Hutchinson 1988). This possibly indicates a widespread occurrence and environmental significance of such *Cryptococcus* species.

Regarding the in situ activity of fungi, Satake and Saijo (1974) postulated that the heterotrophic activity in waters below pH 3 were mainly attributed to molds, but at that time, there was no substantiating in situ data. Schlief and Mutz (2005), investigating fungal biomass and respiratory activity in a Lusatian pit lake, found maximum fungal biomass in autumn and winter, probably caused by leaf fall. At the time of maximum leaf-associated respiration, fungi were responsible for 47 (±7.7) % of total respiration.

After decades of acidic pit lake research, the taxonomic structure and in situ activity of their fungal communities is still not well known. However, refinement of culture media and isolation and molecular identification of both highly acid- and metal-tolerant as well as truly acidophilic species from various acid waters will hopefully help to close this gap in the near future.

Heterotrophic Protists in Acidic Pit Lakes

Heterotrophic protists found in acidic pit lake plankton comprise mainly heliozoa, ciliates, and amoebae; sometimes, heterotrophic nanoflagellates are also present. Due to the delicate structure of protists and the extreme chemical matrix of the lake water, sampling and preservation of protists requires special care (Woelfl and Whitton 2000). Among the ciliates, members of the orders Prostomatida, Hypotrichida, and Peritrichida were detected. They typically reached maximum cell densities of 5,000–30,000 cells L^{-1} or even 335,000 cells L^{-1} in an extreme case, which are comparable to densities known from natural lakes (Packroff 2000). Hypotrichida, mostly represented by large, slow-swimming forms, was also the dominant ciliate taxon in the Río Tinto system (Aguilera et al. 2007). The regular finding of hypotrich ciliates in plankton, which are typically benthic organisms, is an unusual feature of acidic pit lakes and acid rivers and may be attributed to a lack of predatory pressure (Aguilera et al. 2007; McConathy and Stahl 1982; Packroff 2000).

In some acidic pit lakes, heliozoa appear to be the main protistan component of the plankton. They can reach cell densities of 26,000 cells L^{-1} (Packroff 2000), and be the top predators in some acidic pit lakes (Bell et al. 2006; Woelfl et al. 1998). The heliozoa present in Lake 111 were putatively identified as *Actinophrys sol*, but their cells were smaller than those of the same species found in other aquatic habitats. They exhibited pronounced temporal and vertical patterns in abundance, biomass, and cell volume, with abundance and biomass maxima in late

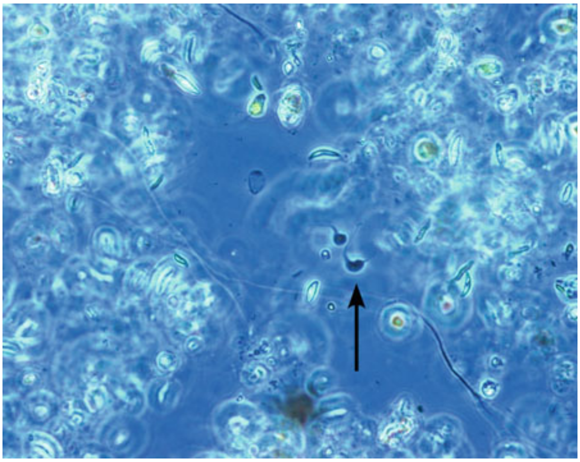


Fig. 3.57 Phase contrast image of sediment trap material from Lake 111 with cercomonad flagellates (*arrow*)

June/early July and September (Bell et al. 2006; for growth characteristics and food web relations, see Sect. 3.3.1.4).

Müller (2004) reported 2.5×10^4 amoebae per mL in Lake 111. A high diversity of amoebae has also been isolated from the extremely metal-rich Berkeley Pit Lake in Montana, USA (Mitman 1999), and *Arcella vulgaris* has been found to thrive in a highly acidic (pH 2.0) AMD-polluted lake in Ontario (Kumar and Patterson 2000). Considerable benthic recruitment of heliozoa and rhizopods takes place in Lake 111 (Bell and Weithoff 2003); this aspect deserves further investigation in other acidic pit lakes.

Data on heterotrophic nanoflagellates in acidic pit lakes are scarce. As the phytoplankton in these lakes is dominated by mixotrophic flagellates, their heterotrophic counterparts are generally outcompeted in the illuminated part of the water body (Rothaupt et al. 1996; Tittel et al. 2003). Packroff (2000) reported an average heterotrophic flagellate density of 2.3×10^6 cells L^{-1} for Lake Cospuden (East Germany), and Müller (2004) counted an almost identical value of 2.4×10^6 cells L^{-1} for Lake 111. Sediment traps deployed in Lake 111 regularly contained some heterotrophic flagellates with a peculiar morphology, possessing flexible cells with two flagella on opposite sides (Fig. 3.57). They were identified as cercomonads. In addition, the widespread flagellates *Bodo saltans*, *Neobodo designis*, *Neobodo covifilus*, and a taumathotomatid type were also found in these samples (Markus Weitere, personal communication). A *Cercomonas* species was also detected in a rRNA gene diversity study of the acidic river Rio Tinto (Amaral Zettler et al. 2003), indicating that there might be cercomonads specifically adapted to acid waters. Aguilera et al. (2007) observed a higher abundance of cercomonads in winter months. This confirms the above-mentioned importance of light for their distribution and biomass.

From the accessible data, it is hard to definitely judge microbial diversity in acidic pit lakes. Often, species identification has not been possible, or clone libraries are small and the information on seasonal patterns is missing. It appears that microbial diversity in acidic pit lakes is higher than at extremely acidic mine sites, but lower than in natural lakes. Prokaryotic diversity is, however, higher in sediments than in the water column of acidic pit lakes (Sect. 3.3.2). Additional research is needed to understand the relationship between microbial community composition and environmental factors other than pH in acidic pit lakes.

3.3.1.4 Trophic Interactions and Energy Flow

Guntram Weithoff, Elly Spijkerman, Norbert Kamjunke and Jörg Tittel

Survival in acidic mine pits is possible for only a limited number of planktonic species (e.g. Lessmann et al. 2000; Wollmann et al. 2000; Sect. 3.3.1.1). Growth of the plankton and especially phytoplankton species has been suggested to be limited by pH, light quality and quantity, concentrations of ferric iron, zinc, aluminum, and manganese, CO_2, and inorganic phosphorus (P_i). The effects of these parameters will be evaluated separately, followed by field measurements of primary production, bacteria production, and their relation to each other. An analysis of the food web in extremely acidic lakes is provided, and the potential of “controlled eutrophication” for the abatement of acidification is discussed.

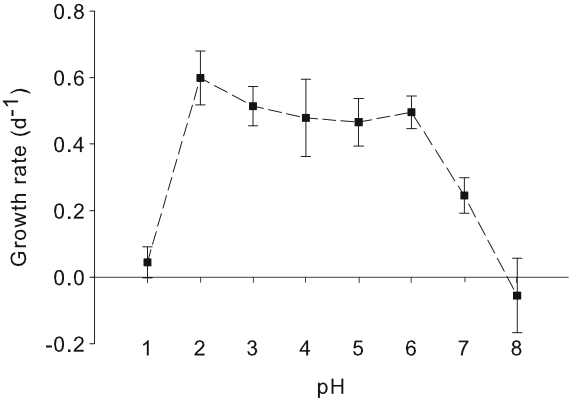
Adaptations to the Chemical Environment and to the Unusual Light Climate

pH

In many acidic mine pits, pH values are relatively stable over long time periods because the systems are buffered by high iron concentrations, which only fluctuate to a minor extent. Generally, pH values range between 2.0 and 3.5. Therefore, the lakes must be inhabited by species that are either acid tolerant or true acidophiles. In many such mine pits, a *Chlamydomonas* species can be found, often identified as *Chlamydomonas acidophila* (e.g. Gerloff-Elias et al. 2005a). *C. acidophila* can grow over a wide range of pH values, the lower pH limit lying at pH 1.5 and the upper limit at pH 7 (Fig. 3.58, Gerloff-Elias et al. 2005a; Nishikawa and Tominaga 2001; Spijkerman 2005). Its growth is optimal between a pH of 2.5 and 3.5, coinciding with the pH range of most acidic mine pits, and declines strongly at pH > 6. Maximum growth rates of *C. acidophila* at low pH are comparable to those of *Chlamydomonas reinhardtii* at pH 7 (Förster et al. 2001), indicating that low pH *per se* does not necessarily result in reduced growth.

Also, the maximum net photosynthetic rates of *C. acidophila* at pH 2.6 (308 mmol O_2 (g Chl a h)$^{-1}$) is comparable to that of *C. reinhardtii* at pH 7.0 (265 mmol O_2 (g Chl a h)$^{-1}$, Gerloff-Elias et al. 2005a; 300 mmol O_2 (g Chl a h)$^{-1}$, Förster et al. 1999), indicating that low pH also does not hamper maximum photosynthetic capacity. These results indicate that *C. acidophila* is well adapted to low pH and as this species is a main contributor to primary productivity

Fig. 3.58 Exponential growth rates of *Chlamydomonas acidophila* under non-aerated conditions over a range of external pH. Mean and SE of 3 independent replicates (modified after Spijkerman 2005)



(Kamjunke et al. 2004), the relatively low primary production rates in acidic mine lakes (Kamjunke et al. 2005; Nixdorf et al. 2003) do not result from the low pH (Gerloff-Elias et al. 2005a).

Ochromonas spp. often dominates the plankton in the acidic mine pits in Germany, constituting 45–80% of plankton biomass (Kamjunke et al. 2004; Wollmann et al. 2000). An isolate of *Ochromonas* from one of these lakes, Lake 111, grew at pH 2.6 phototrophically with a rate of 0.07 d^{-1}, but could reach growth rates of 0.27 and 0.32 d^{-1} mixo- or phagotrophically, respectively (Tittel et al. 2003). These rates are much lower than those obtained with neutral relatives who on average have growth rates of 0.46 d^{-1} (max. 1.3 d^{-1}) under autotrophic, and 2.0 d^{-1} (max. 3.14 d^{-1}) under mixotrophic conditions (Andersson et al. 1989; Maranger et al. 1998; Rothhaupt 1996; Sanders et al. 2001).

A dominant littoral microorganism in acid mine drainage is *Euglena mutabilis*. This algal species tolerates acid conditions down to pH 1.7, and its distribution is restricted to habitats with pH < 4.6, with prolific growth between pH 3.0 and 3.5 (Brake et al. 2001), possibly not much slower than mesophilic *Euglena* species.

Experiments with rotifer species from the genera *Cephalodella* and *Elosa* isolated from Lake 111, neighbouring lakes, and an acidic lake in Austria revealed a pH tolerance of 2.7–5 and 6, respectively (Weithoff, unpublished data). These results suggest that these rotifers are acidophiles. The calculated gross growth efficiency of *Cephalodella* sp. was in the range of isolates from neutral lakes (Weithoff 2005). In addition, the ciliate *Oxytricha* sp., also isolated from Lake 111, realised growth rates at pH 2.6 similar to that of mesophiles. It therefore appears that most species inhabiting acidic mine pits are acidophilic rather than acidotolerant, and most perform just as well at pH 2.6 as do their neutral relatives at pH 7.

Light

The underwater light spectrum in acidic mine pits is distorted and red-shifted. Contrasting to neutral lakes, only red light with a wavelength over 550 nm penetrates into the deeper water strata, whereas the blue light ($\lambda < 450$ nm) is already absorbed in the surface strata (Koschorreck and Tittel 2002;

Gerloff-Elias et al. 2005b). The light absorption in acidic mine pits results mainly from the high concentrations of dissolved ferric iron (for more detailed information, see paragraph 3.1). Consequently, the iron-rich Lake 111 (122 mg Fe L^{-1}) had an attenuation coefficient K_d(PAR) of -0.7 m^{-1}, whereas it was only -0.2 m^{-1} in Lake 117 (5.5 mg Fe L^{-1}). In situ experiments revealed that *C. acidophila* exhibited a significantly higher absorption efficiency and a higher cellular chlorophyll b content when incubated in the red-shifted underwater light of Lake 111 than in the more typical, blue-green dominated light spectrum of Lake 117 (Gerloff-Elias et al. 2005b). At a depth of 7 m, where only 0.1–0.3% of surface irradiation arrives as a result of the high absorption coefficient of iron-rich lake water, benthic algal mats can still photosynthesize, using the red light very efficiently (Koschorreck and Tittel 2002).

Metals

In acidic mine lakes, concentrations of many metals are enhanced (Friese et al. 1998; Nixdorf et al. 1998; Packroff 2000), with high iron concentrations being the most striking feature. Compared with neutral lakes, Fe concentrations in acidic mine pits are about a thousand-fold higher, and they are a million-fold higher than in the Pacific Ocean, where Fe may limit phytoplankton growth (Timmermans et al. 2004). High concentrations of many metals can be toxic (Gross 2000), although acidophilic organisms are generally rather tolerant (Gimmler et al. 1991). A principal component analysis on data from the Rio Tinto (Spain) showed a cluster consisting of concentrations of most of the analyzed metals with *Dunaliella* sp., and an inverse relationship between this cluster and *Chlamydomonas* sp. (Aguilera et al. 2006). Possibly, *Chlamydomonas* sp. inhabits this site despite the high metal contamination, but its lesser pH tolerance than *Dunaliella* sp. should also be considered when looking at component analyses, as low pH and metal solubility negatively correlate (and *Dunaliella* sp. grows well at $pH < 2.0$).

There are several suggested compensatory mechanisms in extremophiles, such as increased accumulations of heat shock proteins (Hsps; Laksanalamai and Robb 2004). In comparison to the mesophilic *C. reinhardtii*, *C. acidophila* exhibited significantly higher accumulations of Hsps under non-contaminated culturing conditions, and an increased accumulation of small Hsps when incubated in metal-rich lake-water (Spijkerman et al. 2007a). Increased levels of small Hsps can protect photosynthesis from metal stress, as it supposedly does in higher plants (Heckathorn et al. 2004).

Gross (2000) evaluated a possible defence mechanism for acidophiles to withstand high metal concentrations via a highly positive surface charge of the outer cell membrane. The positively charged membrane and positive zeta potential allow *Dunaliella acidophila* to maintain a neutral intracellular pH, and results in both a high acid resistance and a high resistance against toxic di- and trivalent cations (Gimmler and Weiss 1999). The observed metal resistance in acidophiles can therefore be due to a general cation resistance rather than to a specific H^+ or metal resistance.

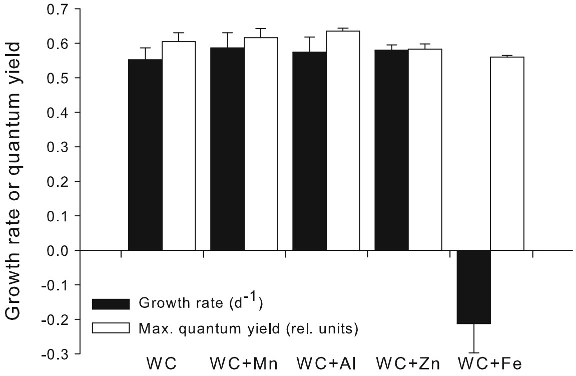


Fig. 3.59 Exponential growth rates over 5 days and maximum quantum yield after 3 days of *Chlamydomonas acidophila* cultivated in a minimal (WC) medium enriched with 11 mg Mn L^{-1}, 60 mg Al l^{-1}, 3.3 mg Zn L^{-1} or 800 mg Fe L^{-1}, reflecting metal concentrations in Lake 107 (modified after Spijkerman et al. 2007a). Results are mean and SE of 3 cultures

In *C. acidophila*, a large tolerance for Zn, Cd, Cu, and Co was described (Nishikawa and Tomanaga 2001). In contrast, after culturing the species in an Fe-rich medium, the maximum quantum yield was reduced, whereas high concentrations of Zn, Mn, or Al had no effect (Fig. 3.59, Spijkerman et al. 2007a). Repeating these experiments with $Fe_2(SO_4)_3$ instead of $FeCl_3$ revealed that it was the Fe speciation that caused the effect, and only very high concentrations of $Fe_2(SO_4)_3$ could inhibit the photosynthesis of *C. acidophila* (Spijkerman, unpublished data).

The periphytic green alga *Stigeoclonium tenue*, isolated from ditches containing mine water, was Zn-tolerant. It was able to grow and reproduce at external Zn concentrations $-\geq 1$ mg Zn L^{-1} (Pawlik-Skowronska 2003). In contrast to what would be expected, the Zn-tolerant ecotype of *S. tenue* significantly accumulated more Zn and Pb than a Zn-sensitive ecotype. Zn-toxicity experiments on neutrophiles often cover rather low concentrations; for example, the maximum concentration tested was 2.6 μg Zn L^{-1} in a marine *Chlamydomonas* sp., but resulted in a 10% decrease in growth rate (Sunda and Huntsman 1998), and similarly 5 μg Zn L^{-1} inhibited growth in *Selenastrum capricornutum* (Kuwabara 1985).

Similarly, the acidophilic protozoan *Euglena mutabilis* can grow at extremely high Fe concentrations (0.7–1.7 g Fe L^{-1}, Casiot et al. 2004) and has the ability to bio-accumulate Fe (Mann et al. 1987, 1989). *E. mutabilis* also contributes to formation of Fe-rich stromatolites by releasing intracellularly stored Fe compounds after death, which contribute to the solid material of stromatolites and act as nucleation sites for precipitation of authigenic Fe minerals (Brake et al. 2002). In addition, the acidophilic red alga *Cyanidium caldarium* also accumulated iron in acidic mine pits (Nagasaka et al. 2003). For neutrophilic algae, no Fe-toxicity values were found in the literature.

Little is known about the combined effect of metal ions and low pH on zooplankton. However, a study on several littoral crustaceans revealed that the harmful effect of low pH can be enhanced by high concentrations of aluminum (Havens 1991a). Total cation concentrations in these experiments were much lower than concentrations typically found in acidic mine lakes. High concentrations of less toxic cations may counteract the harmful effect of low pH and high heavy metal concentrations.

In summary, multiple adaptations of acidophiles (high Hsp levels, decreased metal uptake as a result of a positive cell membrane, or storage and de-toxification of metals) increase their tolerance to high metal concentrations.

Phosphorus

One possible factor limiting primary production and biomass yield in acidic mine lakes is inorganic phosphorus (P_i; Nixdorf et al. 1996; Beulker et al. 2003, see also Sect. 3.2.1.3). Experiments performed using pulsed amplitude modulation (PAM) techniques suggested a P_i-limitation in the phytoplankton of some mine lakes in Lusatia, Germany (Lake 117 and 111, but not in Lake 107; Beulker et al. 2002). This result was explained by the higher P_i concentrations in Lake 107 (25 μg P L^{-1}) compared with those in Lake 117 (6 μg P L^{-1}) and 111 (12 μg P L^{-1}). Comparing the phytoplankton from 4 lakes containing different P_i concentrations showed a large biomass increase after P_i- enrichment experiments, suggesting that P_i is the main nutrient limiting algal growth (Fig. 3.60; Spijkerman 2008a). Also, in other acidic mine pits, P_i was acknowledged as the most important limiting factor for phytoplankton productivity (Simmons et al. 2004).

In an enrichment study performed on 4 acidic Lusatian lakes, *C. acidophila* appeared to be the most severely P_i-limited phytoplankton species (Spijkerman 2008a). In these lakes *Ochromonas* sp. dominates the biomass, but it is phagotrophic in nature and may avoid a P_i-limitation by engulfing P-rich particles such as bacteria (Schmidtke et al. 2006). *C. acidophila* is the dominant photo-autotrophic species and therefore primary productivity in the acidic mine lakes is most likely decreased by a P_i-limitation.

The minimum cell quota for phosphorus (Q_0) of *C. acidophila* (2.0–2.1 mg P g C^{-1}) was similar to that of *C. reinhardtii* (2 mg P g C^{-1}; Lürling and van Donk 1997), indicating no enhanced metabolic costs by the extreme environment (Spijkerman 2007; Spijkerman et al. 2007b). Enhanced metabolic costs should result in a higher cellular ATP content under all growth conditions, but it is best to compare species using a well-defined parameter, such as Q_0. Metabolic costs have been suggested in an isolate of *C. acidophila* from the Rio Tinto, but might consist of only a slightly increased ATP consumption rates (Messerli et al. 2005). Interestingly, the Q_0 of *C. acidophila* was higher at low than at high CO_2 conditions (Spijkerman 2007; Spijkerman et al. 2007b), demonstrating a relationship between CO_2 and P_i acquisition. Possibly, growth of *C. acidophila* in the acidic mine lakes is co-limited by CO_2 and P_i.

For bacterial production in Lake 117, indications were found for a P_i-limitation (Spijkerman 2008a), but it is acknowledged that bacterial production is generally limited by the low concentrations of organic carbon.

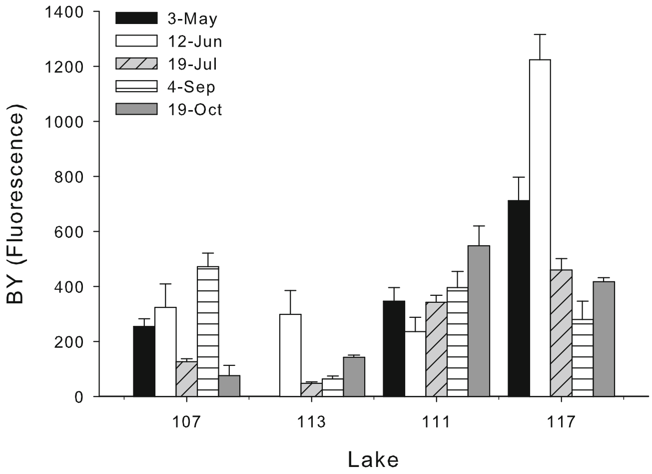


Fig. 3.60 Biomass yield (*BY*) of P-enrichment experiments after a one week incubation as measured by fluorescence of chlorophyll *a*. Lake P_i concentrations increase from *left* to *right*. Mean ± SD of 4 replicate measurements (from Spijkerman 2008a)

Carbon

In acidic waters below pH 4.0, inorganic carbon (C_i) is present only as CO_2, and HCO_3^- is virtually absent. Algae growing in acidic lakes are therefore often assumed to be C_i-limited in their natural environment (e.g. Nixdorf et al. 2003). However, adding CO_2 did not clearly enhance electron transport rates in phytoplankton samples from Lake 107, Lake 111, or Lake 117 (Beulker et al. 2002), although the phytoplankton succession revealed a clear dependence from the C_i concentration (Beulker et al. 2003). More precisely, rapidly increasing phytoplankton densities that were observed under ice and in the hypolimnion, correlated with enhanced C_i concentrations (Sect. 3.3.1.1). In addition, laboratory experiments with *C. acidophila* showed an increased maximum growth rate under high CO_2 conditions (Tittel et al. 2005). Concentrations of C_i in the upper water strata of acidic lakes are typically not much higher than equilibrium concentrations of CO_2 with the air (about 0.2 mg C l^{-1}, Tittel et al. 2003). This concentration of total C_i would limit photosynthesis and growth of algae in a neutral environment (e.g. Bozzo and Colman 2000). However, *C. acidophila* has a high affinity uptake system for CO_2 by photosynthesis, with an affinity constant of 0.025 mg C l^{-1} (Cuaresma et al. 2006; Spijkerman 2005, 2008b), similar to that in *C. noctigama* at pH 6.3 (van Hunnik et al. 2000) and *C. reinhardtii* (Bozzo and Colman 2000). Consequently, maximum photosynthetic rates can be realised in situ. Recent experiments suggest that high population densities, a P_i limitation and/or high concentrations of Fe might result in a CO_2 limitation, but much work still needs to be done. Only CO_2 enrichment experiments can reveal if C_i is indeed a growth limiting factor for the phytoplankton in acidic mine pits. These experiments will be difficult as the increased maximum growth rate at high CO_2 will likely not be realised in the field due to other population regulating factors.

Mixotrophy and Resource Limitation of Consumers

Mixotrophy as a Strategy to Overcome Resource Limitation

Mixotrophic organisms combine photosynthesis and the uptake of organic resources as modes of nutrition (Jones 1994, 2000). This phenomenon is especially common in flagellates. The relative contribution of mixotrophs to total phytoplankton biomass increases with increasing "extremeness" of the habitat. Two ways of mixotrophy can be distinguished: osmo-mixotrophy and phago-mixotrophy. Osmo-mixotrophic organisms can take up dissolved organic carbon compounds of both autochthonous and allochthonous origin. Phago-mixotrophic flagellates are able to ingest particles, e.g. bacteria or small algae. Both types supplement their photosynthetic carbon fixation by uptake of organic carbon when photosynthesis is limited. The degree of mixotrophy varies among species, that is, some use both carbon sources simultaneously most of their life, and some are mainly restricted to one carbon source and use the other only when the favourable carbon source is limited (Jones 1994). The uptake of dissolved organic carbon (DOC) in osmo-mixotrophic flagellates leads to potential competition with bacteria. In laboratory experiments, *C. acidophila* isolated from Lake 111 was capable of using the natural lake DOC for growth in the light, in the dark, and also in the presence of bacteria competitors. In addition, the alga readily assimilated aromatic compounds, typically occurring as light-degradation products of humic carbon of terrestrial origin (Tittel et al. 2009). In contrast, phago-mixotrophic flagellates act as predators on bacteria and algae. Since bacteria typically have a lower C: P ratio (i.e. they are relatively rich in phosphorus) than algae, phago-mixotrophs benefit from bacteria ingestion due to both the uptake of phosphorus and of carbon (Gaedke et al. 2002). This might be one driving factor for the high abundance of the phago-mixotrophic *Ochromonas* sp. in acidic mine pits.

Resource Limitation of Consumers

In principal, consumers can be limited either by resource quantity or by resource quality. When the first trophic level (i.e. the primary producers, such as phytoplankton) are limited by nutrient availability or other factors, then this translates directly to the first consumer level. Food supplement studies with rotifers from Lake 111 exhibited a quantitative resource limitation in the epilimnion over the whole vegetation period under ambient food conditions (Weithoff 2004). Indeed, artificially enriched enclosures in this lake exhibited both a higher biomass of phototrophs and an increased abundance of rotifers (unpublished data). Food quality also affects consumer growth in acidic lakes; besides potential mineral limitation due to low phosphorus availability, biochemical limitation might be important. Mixotrophic protists are abundant in extreme habitats and can adapt their mode of nutrition according to environmental conditions. These may change seasonally or vertically in the water column. Since the physiological pathways differ between autotrophic and heterotrophic nutrition, the biochemical

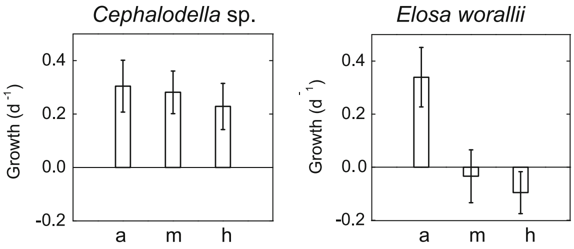


Fig. 3.61 Exponential growth rates of the rotifers *Cephalodella* sp. and *Elosa worallii* feeding on autotrophic (*a*), mixotrophic (*m*) and heterotrophic (*h*) *Chlamydomonas acidophila*. Data from life table experiments, error bars denote the 95% confidence interval (modified from Weithoff and Wacker 2007)

composition of protists strongly depends on their resource supply (Boechat et al. 2007; Poerschmann et al. 2004). Significant differences in the biochemical composition were found (e.g. in the composition and total amount of fatty acids). In particular, concentrations of polyunsaturated fatty acids are reduced when the heterotrophic pathway is employed (Boechat et al. 2007; Poerschmann et al. 2004). These fatty acids are often essential in zooplankton consumers and the lack of them may significantly reduce their growth. A case study with the osmo-mixotrophic *C. acidophila* grown heterotrophically (in the dark with glucose), mixotrophically (in the light with glucose), and autotrophically (in the light without any organic carbon source) demonstrated species-specific effects on the life history of rotiferan consumers. *Cephalodella* sp. achieved similar growth rates with all three types of *Chlamydomonas*, whereas *Elosa worallii* exhibited positive population growth only with autotrophic *Chlamydomonas* (Weithoff and Wacker 2007; Fig. 3.61). Thus, the competitive abilities of the consumers change according to the mode of nutrition of the mixotrophic flagellates (Hartwich et al. 2010). These results reveal that the performance of consumers is not only determined by the physical and chemical characteristics of mine lakes, but also by the biochemical composition of their resource.

Pelagic Primary Production and Bacterial Production in Lusatian Mine Lakes

In Lusatian mine lakes (Germany) of different pH, there was no relationship between pelagic primary production (PP) and pH. The highest PP was measured in the least acidic lake (Lake 117, pH 3.0), moderate values in the most acidic lake (Lake 107, pH 2.3), and the lowest PP in the lake with a pH of 2.6 (Lake 111). Overall, mean PP in all three mine lakes (14 μg C L^{-1} d^{-1}) was far below the means observed in many other lake systems (184 μg C L^{-1} d^{-1}, median 72 μg C L^{-1} d^{-1}; Cole et al. 1988). PP was in the range of values observed in polyhumic lakes, where PP was mainly limited by light (Ahtiainen et al. 1985;

Arvola 1984). PP in the acidic mine lakes could therefore be light limited, due to the high concentrations of dissolved ferric iron. Alternatively, the high seston C: P (mol:mol) ratio, ranging between 500 and 650 (Spijkerman 2008a), suggests that a P_i-limitation lowers PP. Overall, PP might be limited by a complex interaction of factors and vary with water depth (light availability), season, and among different lakes.

Bacteria

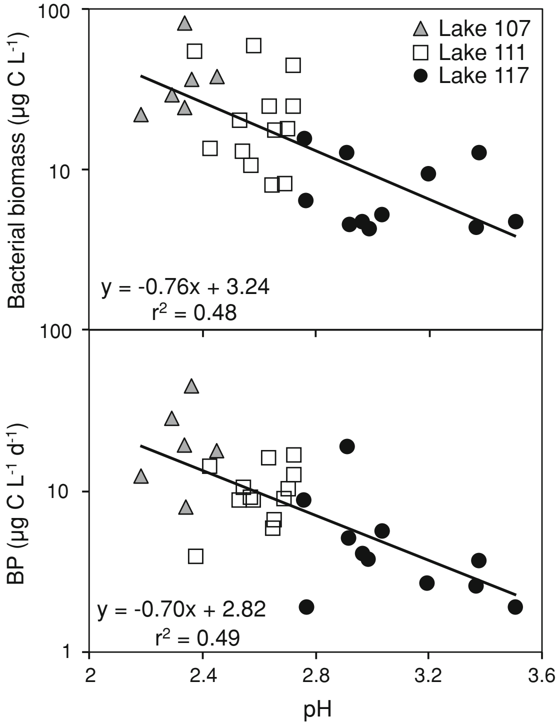
Most of the bacteria found in acidic mine lakes in Lusatia (Germany) were chemo-organo-heterotrophic, i.e. they take up organic compounds and gain energy from respiration. Chemolithotrophic bacteria (i.e. bacteria that use inorganic resources for gaining energy) of the genera *Acidithiobacillus* and *Leptospirillum* were found in very low numbers in the aerobic pelagic zone of the acidic mine lakes (Kamjunke et al. 2005; see also Sect. 3.3.1.3), so their metabolism can be assumed to be of minor importance compared to that of heterotrophic bacteria. Furthermore, no light absorption characteristic for bacterial pigments (bacteriochlorophyll or rhodopsin) was observed and, thus, no bacterial photosynthesis took place (Kamjunke et al. 2005). The bacteria comprised at least four species of the genera *Acidiphilium*, *Acidocella*, and *Acidosphaera* (Kamjunke et al. 2008). In contrast to mine waters in China (Yin et al. 2008), no differences in bacterial composition were observed in German lakes of different pH (Kampe et al. 2010).

Biomass and Production

In the Lusatian mine lakes, bacterial biomass showed values of 4–16 $\mu g\ C\ L^{-1}$ in Lake 117, 8–59 $\mu g\ C\ L^{-1}$ in Lake 111, and 22–82 $\mu g\ C\ L^{-1}$ in Lake 107 (Kamjunke et al. 2005). Bacterial production (BP) ranged between 2–19 $\mu g\ C\ L^{-1}\ d^{-1}$ in Lake 117, 4–17 $\mu g\ C\ L^{-1}\ d^{-1}$ in Lake 111, and 8–45 $\mu g\ C\ L^{-1}\ d^{-1}$ in Lake 107. The mean BP in all three mine lakes (10 $\mu g\ C\ L^{-1}\ d^{-1}$) was in the range of the mean (26 $\mu g\ C\ L^{-1}\ d^{-1}$, median 11.5 $\mu g\ C\ L^{-1}\ d^{-1}$) reported by Cole et al. (1988). The biomass-specific BP amounted to 0.06–1.8 d^{-1} (one value 2.6 d^{-1}, mean 0.78 d^{-1}) in Lake 117, 0.03–2.3 d^{-1} (one value 3.3 d^{-1}, mean 0.73 d^{-1}) in Lake 111, and 0.06–2.0 d^{-1} (mean 0.70 d^{-1}) in Lake 107, and fell in the range observed by Tremaine and Mills (1991) in acidic lakes with a pH of 3.6 (1.1–1.9 d^{-1}). Biomass-specific heterotrophic production (HP) in the mine lakes showed no dependence on pH but was positively related to water temperature ($p < 0.001$). The Q_{10} value (factor of increase within 10°C) amounted to 2.45 and agreed with literature values from non-acidic environments, which usually range between 2 and 3 (Lee et al. 2001; Pomeroy and Wiebe 2001; White et al. 1991).

Total bacterial biomass and production were negatively related to pH, and the highest values were observed in the most acidic, most iron-rich lake (Fig. 3.62; Kamjunke et al. 2005). Bacterial biomass was probably promoted by iron photoreduction. In non-acidic waters, DOC is photochemically degraded (Kieber et al. 1989)

Fig. 3.62 Negative correlation ($p < 0.001$) between the vertical means of bacterial biomass and bacterial production (*BP*) and the pH in three acidic lakes of eastern Germany with different, extremely low pH and high iron concentrations. Modified after Kamjunke et al. (2005)



by UV irradiation and photosynthetic active radiation (PAR; Graneli et al. 1996, 1998; Wetzel et al. 1995). This mechanism differs in iron-rich mine lakes, where UV and short wavelength PAR are absorbed within the uppermost layer (Koschorreck and Tittel 2002) and the photolysis of Fe(III) aquo complexes generates hydroxyl radicals that react with refractory DOC (Brinkmann et al. 2003; Friese et al. 2002; Herzsprung et al. 1998). Light stimulated the formation of ferrous iron, changed the DOC composition (formation of low-molecular-weight organic acids, such as acetate, formate, and pyruvate), and increased the BP in laboratory experiments, suggesting that iron photoreduction caused DOC degradation (Kamjunke et al. 2005). Since the iron concentration in the mine lakes is negatively related to the pH of the waters, this may explain why measurements of BP were the highest in the most acidic and most iron-rich lake and lowest in the least acidic lake.

Carbon Sources

Vertical means of BP were not correlated with DOC concentrations, which ranged between 0.3 and 2.2 mg C L^{-1} in Lake 117, 0.7–2.9 mg C L^{-1} in Lake 111, and 0.1–1.8 mg C L^{-1} in Lake 107 (Kamjunke et al. 2005). The bulk of the DOC in the lake consists of polymeric fulvic acids (Poerschmann et al. 2004) that cannot be used directly by bacteria, whereas qualitative changes in chemical composition

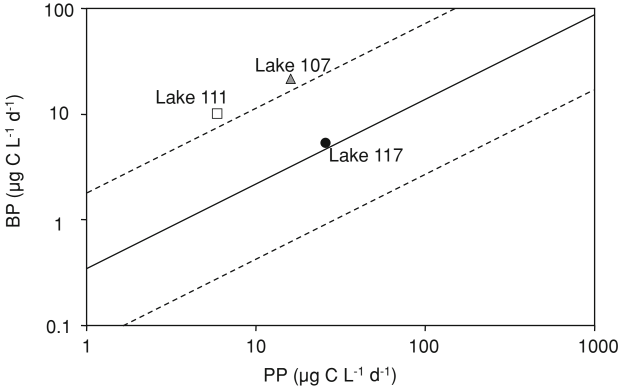


Fig. 3.63 Relationship between bacterial production (*BP*) and primary production (*PP*) of many water bodies. The line shows the regression of Cole et al. (1988; logBP = 0.8 logPP − 0.46) with 90% CI for the values. Data points represent data from acidic mine lakes of eastern Germany (modified after Cole et al. 1988)

of the DOC after degradation allow increased bacterial assimilation and utilization of the organic substrates (Wetzel et al. 1995). Unlike other lakes (Coveny and Wetzel 1995; Kamjunke et al. 1997; Robarts et al. 1994), there was no significant relationship between vertical means of BP and PP in the mine lakes (Kamjunke et al. 2005). This uncoupling is the first indication that planktonic PP was not the bacteria's main carbon source. Comparing average BP and PP of many waters, the data points of the more acidic, iron-rich, Lakes 111 and 107 are situated above the regression line (Fig. 3.63).

The high importance of other carbon sources is supported by high ratios of BP to PP, ranging between 0.08–2.0 in Lake 117, 0.7–10.8 in Lake 111, and 0.7–1.5 in Lake 107. Contrary to results from many other systems, BP was on the same order as PP in the lakes, and exceeded it in two-thirds of all cases. The majority of the values were far above the mean proportion of 20% BP compared to PP, as reported in many other lakes (Cole et al. 1988). Values above 100% have been observed, mainly from humic lakes with high DOC concentrations (above 10 mg C L^{-1}) from allochthonous inputs (Jansson et al. 2000), whereas such values were also observed for mine lakes at low DOC concentrations (Fig. 3.64). Karlsson et al. (2002) also found high BP/PP ratios in clear alpine lakes with low DOC concentrations, and their maximum ratio of 10 matched the maximum of 11 in the mine lakes. The exceptionally high ratios clearly indicate that BP in the lakes was supported by PP and additional carbon sources.

In one particular lake (Lake 111, pH 2.6), bacteria exhibited high growth rate and efficiency on exudates of pelagic and benthic algae. In contrast, they showed a lower growth rate and efficiency with organic carbon from groundwater, and grew at a very high rate but a very low efficiency on leaf leachate (Kamjunke et al. 2006). Given the magnitude of differential source inputs into the lake, benthic

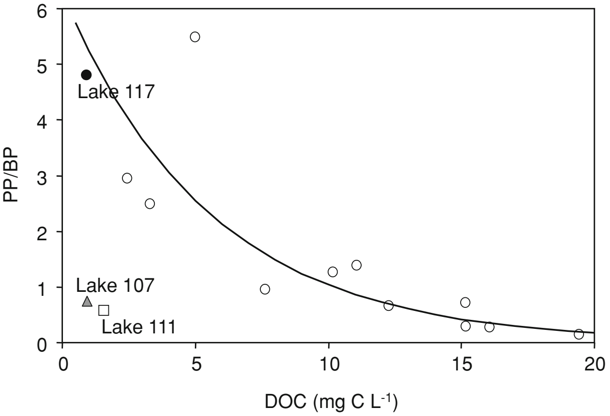


Fig. 3.64 Relationship between the ratio of primary to bacterial production (PP/BP) and concentration of dissolved organic carbon (*DOC*) of many water bodies. The line with small open *circles* shows the regression of Jansson et al. (2000; $PP/BP = 6.28e^{-0.18DOC}$). Large data points represent acidic mine lakes of eastern Germany (modified after Jansson et al. 2000)

primary production was probably the most important carbon source for pelagic bacteria.

Overall, it appears that bacteria play a more important role in the cycling of matter and as a basis for the whole food web in acidic mine lakes than in other lake ecosystems, and that their importance increases in more acidic and iron-rich lakes.

Accumulation of Algae in Subsurface Layers

In mesotrophic circumneutral lakes, algae often build up high biomasses at the thermo- or chemocline, leading to a deep chlorophyll maximum (DCM). These DCMs often comprise cyanobacteria and/or cryptophytes (Adler et al. 2000). A prerequisite for the formation of a DCM is a stable stratified water column. DCMs have also often been observed in mine pits. A case study of the DCM in Lake 111 revealed that the accumulation of the alga *C. acidophila* at depth was based on grazing losses in the upper water layers. *Chlamydomonas* was consumed by the pigmented flagellate *Ochromonas*. This mixotroph combined photosynthesis and prey uptake as substitutable energy resources. The abundance of prey alga reflected the critical food concentration of *Ochromonas*. The alga was reduced to low numbers if light was well available and vice versa, creating low *Chlamydomonas* abundances near the surface and a maximum at depth (Tittel et al. 2003). Such a situation leads to two partly segregated subhabitats with differing trophic interactions and species composition (Kamjunke et al. 2004; Weithoff 2004).

Food Web Structure in Acidic Mine Lakes

The pH of the water is a major factor determining the distribution of zooplankton. For example, crustaceans, which need calcium carbonate for their carapax, suffer severely from low pH, because the dominant inorganic carbon species in such environments is CO_2. Thus, very few crustacean species occur in waters with a pH near 3 (Deneke 2000; Sect. 3.3.1.2). The lack of crustaceans and especially efficient filter-feeders such as *Daphnia* as well as the lack of higher invertebrates and vertebrates has considerable consequences for the structure of the food web and the flow of energy therein. The extreme nature of the habitat limits the length of the food chain to about two trophic levels due to the absence of higher trophic levels organisms (Gaedke and Kamjunke 2006) rather than low productivity, as suggested by Havens (1991b, which was derived from a field survey of rain-acidified lakes in North America). However, since most species are either mixotrophic or omnivorous, no straight food chains occur, though more complex interconnected trophic relations are common. Nevertheless, most of the carbon channelled through the trophic compartments is transferred by only one or two steps. Furthermore, the number of species of typical plankton groups (phytoplankton, heterotrophic protists, and rotifers) is also strongly reduced, leading to truncated pelagic food webs with a limited number of acting species (Gaedke and Kamjunke 2006; Kamjunke et al. 2004; Weithoff et al. 2010; Woelfl 2000, Wollmann et al. 2000). In neutral lakes with low abundances of cladocerans, the dominant bacterivores are phagotrophic flagellates (Jürgens 1994). This pattern was also found in a very acidic lake (Lake 111), where the estimated loss of bacterial production was mainly attributed to the phago-mixotrophic flagellate *Ochromonas* sp. The feeding of *Ochromonas* was size-selective, with highest volume-specific ingestion rates in a size range of 1.5–2 μm in diameter (Schmidtke et al. 2006).

Another key feature of these food webs is the dominance of mixotrophs and the prevailing omnivory of some consumers (e.g. Havens 1991b). As planktonic top predators, Heliozoa have been identified feeding on mixotrophic algae (*Chlamydomonas*) and on consumers such as rotifers (Bell et al. 2006; Woelfl 2000). However, as for rotifers, Heliozoa do not achieve positive growth rates with *Ochromonas* as the single food source (Bell et al. 2006; Weithoff 2004).

Increasing pH values in the range of 4–6 support an increasing number of phytoplankton and zooplankton and the resulting food web resembles the classical food web known from neutral lakes (Belyaeva and Deneke 2007; Havens 1991b; Keller and Yan 1991).

Potential of “Controlled Eutrophication” for Abatement of Acidification

Eutrophication is a classical field in limnology and the undesirable consequences of algal mass development are well known. With respect to acidic lakes and their neutralisation, however, the potential of a deliberate eutrophication has been debated for a long time (see also Chap. 4). The idea is based on the stimulation of lake photosynthesis and organic carbon production (Davison et al. 1995) and differs from approaches in which organic carbon of external origin is supplied (Brugam et al. 1995; Klapper and Schultze 1997). Algae have also been used for the removal of heavy metals from acid mine drainage (see also case study 5.7). This has been reviewed by Das et al. (2009) and is not addressed here.

The growth and biomass production of algae can change the alkalinity directly by uptake and incorporation of inorganic nitrogen and its permanent burial in the sediment (Koschorreck and Tittel 2007). The assimilation of nitrate is associated with a gain in alkalinity, while assimilation of ammonia, which is the dominant form of inorganic nitrogen in acidic pit lakes, leads to a decrease in alkalinity (Wendt-Potthoff and Neu 1998). The photosynthetic uptake of inorganic carbon does not affect the pH, in contrast to circumneutral lakes, since bicarbonate and carbonate ions are practically absent below pH 4 and inorganic carbon is present only as dissolved CO_2 gas. Potentially more important is the indirect contribution of primary production if it serves as a carbon source for iron and sulfate reduction. These are the most significant processes of alkalinity generation in pit lakes (Blodau 2006) and their rates are typically limited by the availability of organic carbon compounds (Peine and Peiffer 1996).

There are examples indicating that internal organic carbon production can actually support iron- and sulfate reduction. In a productive lake having a moderately high phytoplankton biomass, the sediment top layer was characterised by higher organic carbon contents and lower C: P ratios compared to a less productive lake. More reduced sulfur was accumulated in the productive lakes' sediment and the pore water exhibited a neutral pH, in contrast to the lake with low phytoplankton production. The authors concluded that the potential of acidic lakes to be internally neutralised can be based on the supply of autochthonous carbon (Peine and Peiffer 1996). Other studies have also pointed to the significance of the origin and availability of organic substrates. For example, autochthonus carbon contributed 5–14% to total organic carbon in the sediment of three pit lakes but supported 50–75% of respiration (Blodau et al. 2000).

The idea that the addition of mineral nutrients stimulates the internal production of algal carbon and subsequently neutralisation has been applied to experiments at different scales. Laboratory-based mesocosms with a moderate to high base capacity of the water ($k_{B8.2}$ 2–15 mmol L^{-1}) were fertilised with phosphorus. Although dramatic increases of algal biomass could be observed, there were no significant effects on alkalinity or pH (Fyson et al. 1998a, 2006; Totsche et al. 2006). Mesocosms with a diameter of 30 m were mounted in the acidic Lake 111 (pH 2.6) and fed with straw and other substrates (Koschorreck et al. 2007a). Two years later, the leached mineral nutrients still supported a substantial algal biomass and carbon production. However, assuming that 30% of the production were channelled into iron- and sulfate reduction, the internal carbon production was sufficient to compensate for only 14% of ongoing inputs of acidity. The base capacity was very high and equalled 13–15 mmol L^{-1} (Tittel and Kamjunke 2004). The addition of organic waste products to Lake Koyne 113 (Lusatia, Germany) resulted in an increase of total organic carbon, phosphorus, and phytoplankton biomass, up to 6 mm^3 L^{-1} and to 85 µg L^{-1} Chl *a*. However, no change of base capacity (13–15 mmol L^{-1}) was observed (Lessmann et al. 2003), and the pH remained at 2.6 (Spijkerman 2008a). In contrast to these examples from acidic pit lakes, moderate fertilization affected acidity in a rain-acidified softwater lake characterized by a low base capacity (0.01 mmol L^{-1}). The pH responded to phosphorus addition and subsequent phytoplankton growth with a moderate increase, from about 5–6 (Davison et al. 1995).

How much of the autochthonous carbon in fertilised mesocosms and lakes may be channelled into iron and sulfate reduction is not known. From planktonic organic carbon production, we can estimate an upper limit of acidity input that can be compensated for by internal lake processes. In general, acidic conditions do not prevent the development of a high phytoplankton biomass (Woelfl et al. 2000). In the acidic and polymictic Lake Niemegk (Lusatia, Germany), algal biomass peaks reached 22 g C m^{-2} and the production ranged from 0.23–11.5 g C m^{-2} d^{-1} (Zippel 2005), which is similar to biomass yield and production in hyper-eutrophic lakes. Assuming that 30% can be used for alkalinity generation, a theoretical removal of acidity of 2–117 mol m^{-2} a^{-1} can be calculated. The actual rates, however, strongly depend on the conditions at the sediment and are probably much lower (Blodau et al. 2000). This is illustrated by the example of Lake 117, where the actual rate of iron reduction was less than 1% of the potential rate derived from carbon supply (0.8 and 106 mol m^{-2} a^{-1}, respectively). The authors attributed this large difference to a possible limitation of iron availability and to competition with other processes, e.g. aerobic mineralization (Koschorreck et al. 2007b). Furthermore, high rates of gross sulfate reduction do not equal a long-term alkalinity gain, as a substantial proportion of reduced sulfur can be reoxidised and is not buried (Koschorreck et al. 2007a). In conclusion, deliberate eutrophication can be an option, if the standing stock of acidity and the inflow of acidity are low, the latter probably not higher than 0.5–1 mol m^{-2} a^{-1}. Candidates are lakes without a distinct red coloration of water. If neutral conditions are achieved, ongoing acidity inputs can be balanced by internal alkalinity generation of 0.24–1.4 and 1.6–9.5 mol m^{-2} a^{-1} in less productive and productive lakes, respectively (Koschorreck and Tittel 2007).

3.3.2 Littoral, Benthic and Sediment Zone

3.3.2.1 Macrophytes and Neophyte Invasions

Benedikt Beck and Arnulf Melzer

Introduction

The major reasons for macrophyte community changes during the last century have been eutrophication of freshwater ecosystems and acidification, caused by atmospheric deposition, and the consequences that these have had on lake water and sediment chemistry (e.g. Arts 2002; Farmer 1990; Smolders 2002). Indicator systems based on characteristic macrophyte communities have been developed in Germany to assess the trophic status of lakes and running waters (e.g. Kohler and Schneider 2003; Melzer 1999). In addition to natural lakes, a large number of new artificial water bodies have formed in Germany over the last few decades or are in the process of being formed in the old open cast lignite mining pits (Nixdorf et al. 2005; see also Sects. 2.1 and 5.1). Many of these lakes are strongly acidified due to pyrite or marcasite oxidation. As a result, some of them offer living conditions comparable to extreme naturally occurring habitats, like volcanic crater lakes. Nevertheless, the lakes have been and are being colonized by specialized species. The most extensive work in the world on macrophyte colonization of this extreme environment was undertaken in the Lusatian Mining District (LMD) in Germany (Pietsch 1965, 1970, 1973, 1998). Overall, 234 water bodies ranging from acidic to neutral have been investigated since 1963, and a macrophyte community sequence has been developed that characterizes the aging process of the acidic mining lakes (Pietsch 1998). The latest research has focused on macrophyte species in strongly acidic mining lakes (e.g. Chabbi 1999, 2003; Chabbi et al. 2001; Fyson 2000; Küsel et al. 2003; Nixdorf et al. 2001).

There is an increasing demand for knowledge of macrophyte colonization of mining lakes. First, there are commitments to evaluate the ecological state of mining lakes larger than 50 ha to comply with the EU Water Framework Directive (WFD; Nixdorf 2005). Macrophytes are commonly used as an indicator for the ecological state of lakes and running waters (e.g. Meilinger et al. 2005; Schaumburg et al. 2004; Stelzer et al. 2005), but until now, no WFD classification for mining lakes has been developed that takes into account acidified mining lakes. In addition, mass development of indigenous and neophytic macrophytes is a problem in water ecosystems all over the world and threatens the planned usage of large mining lakes. The most prominent example is the invasion of the neophytic macrophyte species *Elodea nuttallii* in the formerly acidic mining lake Goitsche near Bitterfeld (Hilt et al. 2006; Rönicke et al. 2006). Here, the main macrophyte communities, the adaptations of selected species, and the possibility of invasions of unwanted aquatic weeds in mining lakes shall be discussed.

Vegetation of Mining Lakes

In the most acidic mining lakes, pHs down to 1.9 have been reported (Pietsch 1998). Their water is strongly buffered by an iron buffer system (Klapper and Schultze 1995; Nixdorf et al. 2003). At a pH between 4 and 5, the buffer system changes to an aluminum buffer system, which is also characteristic of acidified soft water ecosystems with a comparable pH. At a circumneutral state, a calcium bicarbonate buffer system prevails.

Pietsch (1998) identified four different stages of macrophyte colonization in mining lakes that are mostly concordant with these buffering systems. The so-called Initial and Early Stage referred to mining lakes that have a pH below 4.

The Transitional Stage included mining waters with a pH ranging from 4 to 6. The Climax Stage consisted of weakly acidic to weakly alkaline mining lakes with a pH of 6 to 8.

Young lakes of the Initial Stage were found to lack macrophyte vegetation due to extreme chemical conditions and other adverse factors, like unstable soil substrates (Pietsch 1998). The older Early Stage lakes (ca. 10 years) had somewhat mitigated chemical characteristics but still had a pH less than 4. An overview of macrophyte species occurring in these mining waters is provided (Table 3.16). The main types of vegetation described by Pietsch (1998) were dominant stands of the submerged growing bulbosus rush (*Juncus bulbosus*) and/or emergent reed species. Bog mosses (*Sphagnum* div. spec.), *Potamogeton natans*, and the neophytic *Myriophyllum heterophyllum* were also observed at a pH below 4 (Pietsch 1998; Pietsch and Jentsch 1984), and also commonly occur in Transitional Stage lakes.

In addition to the species mentioned by Pietsch (1998), Samecka-Cymerman and Kempers (2001) found the moss *Drepanocladus aduncus* as the only submerged macrophyte in a Polish mining lake at a pH of 2.8. Other mosses of the genus *Drepanocladus* are known to grow in volcanic crater lakes (e.g. Satake 2000) as well as acidic arctic ponds, at a pH from 2.8 to 3.8 (Havas and Hutchinson 1983; Hawes et al. 2002; see also Sect. 5.7.4).

Despite comparable chemical properties, the mentioned mosses do not seem to be common in acidic mining lakes. The moss *Leptodictyum riparium* has only been reported from a neutral mining lake (Hussner et al. 2005; own observation) even though it is able to survive at a pH down to 1.6 in a volcanic crater lake (Tamura 1936, cited in Havas and Hutchinson 1983). Additionally, it has been found together with a sedge, *Eleocharis acicularis*, in secondary acidified Canadian lakes (Gorham and Gordon 1963).

Flowing waters affected by acid mine drainage (AMD) in North America have often been found to be colonized by *E. acicularis* (e.g. Koryak and Reilly 1984; Kroh and Schein 1981; Rothrock and Wagner 1975). The lowest pH reported from these sites was 2.85. We have observed this species in mining lakes in Germany with a pH around 4 as well as in circumneutral pH mining lakes. Additionally Pietsch (1998) mentions an *E. acicularis* dominated vegetation type (Littorello—Eleocharietum acicularis) typical for fish ponds as one of the Climax Stages of macrophyte colonization in circumneutral mining lakes in the LMD. Other examples of submerged macrophytes in strongly acidic flowing waters affected by AMD are the liverwort *Scapania nemorosa* (Engleman and McDiffett 1996), *Sparganium emersum* (Sand-Jensen and Rasmussen 1978) and *S. americanum* (Rothrock and Wagner 1975).

For Transitional Stage mining lakes, Pietsch (1998) described various *J. bulbosus* associations that show some similarities to the vegetation of natural lakes. Massive growth of *Juncus bulbosus* together with bog mosses (*Sphagnum* div. spec.) was reported from secondarily acidified soft water lakes (e. g. Arts 2002; Melzer 1997; Melzer and Rothmeyer 1983; Melzer et al. 1985; Roelofs et al. 1995; Smolders et al. 2002). Outside of the Lusatian Mining District, this type of vegetation has been found in acidified Bavarian mining lakes near Schwandorf (C. Weilner, personal communication) and in mining waters of the Helmstedt Mining District in Lower

Table 3.16 Submerged and emergent macrophyte species occurring in mining waters with a pH below 4

Species	References
Submerged species	
Drepanocladus aduncus	Samecka-Cymerman and Kempers (2001)
Eleocharis acicularis	Rothrock and Wagner (1975)
Juncus bulbosus	Chabbi (1999), Nixdorf et al. (2001), Pietsch (1998), Wiegleb (1978)
Myriophyllum heterophyllum	Pietsch and Jentsch (1984)
Potamogeton natans	Pietsch (1998)
Sparganium americanum	Rothrock and Wagner (1975)
Sparganium emersum	Sand-Jensen and Rasmussen (1978), Nixdorf (2001)
Scapania nemorosa	Engleman and McDiffett (1996)
Sphagnum div. spec.	Pietsch (1998), Wiegleb (1978)
Emergent species	
Carex rostrata	Mayes et al. (2008), Nixdorf et al. (2001), Pietsch (1998)
Eriophorum angustifolium	Mayes et al. (2008), Nixdorf et al. (2001), Pietsch (1998)
Eleocharis acicularis	Rothrock and Wagner (1975)
Juncus bulbosus	Chabbi (1999), Nixdorf et al. (2001), Pietsch (1998)
Juncus effusus	Mayes et al. (2008), Nixdorf et al. (2001), Pietsch (1998)
Phragmites australis	Mayes et al. (2008), Nixdorf et al. (2001), Pietsch (1998)
Schoenoplectus lacustris	Mayes et al. (2008), Nixdorf et al. (2001), Pietsch (1998)
Typha angustifolia	Mayes et al. (2008), Nixdorf et al. (2001), Pietsch (1998)
Typha latifolia	Mayes et al. (2008), Nixdorf et al. (2001), Pietsch (1998)

Saxony (Wiegleb 1978). Other common species in the Transitional Stage are the fern *Pilularia globulifera*, the pondweeds *Potamogeton natans* and *P. polygonifolius*, and the mixotrophic bladderworts *Utricularia minor* and *U. ochroleuca* (Pietsch 1998). While the first three species are also known from acidic softwater lakes (e.g. Eriksson et al. 1983; Srivastava et al. 1995), the latter are typical for fens, bogs, or heath ponds (Pott 1995). As has been mentioned before, the neophytic species *M. heterophyllum* is also frequent in lakes of the Transitional Stage, developing dense dominant stands. In Germany, mainly manmade waters are colonized (Pietsch and Jentsch 1984).

Overall, Transitional Stage mining waters are rarely found in Germany outside of the LMD due to differing geological conditions. Klapper and Schultze (1995) showed that most mining lakes in the Central German Mining District (CGMD) are either strongly acidified or neutral. In the Lower Rhine Mining District (LRMD), only two small acidified mining lakes exist (Christmann 1998). The same can be assumed for some of the vegetation types of the Climax Stage displayed by Pietsch (1998). As he mentions himself, most of these are typical of the Lusatian region and mainly occur in bog and heath ponds.

Christmann (1998), in contrast, describes mainly typical hardwater macrophyte species in the LRMD. Similarly, we have found macrophyte communities known from neutral hardwater lakes in over 30 mainly neutral mining lakes in the most

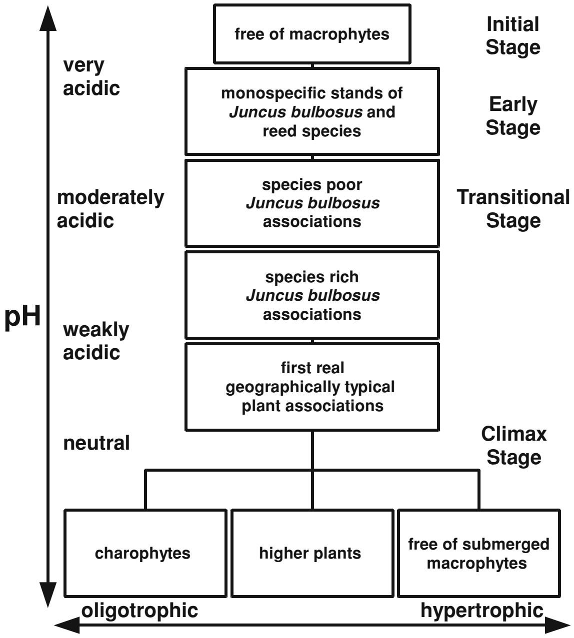


Fig. 3.65 Dominant macrophyte vegetation in German mining lakes (modified and supplemented after Pietsch (1998))

important lignite mining districts in Germany (Fig. 3.65). The species composition is mostly influenced by the trophic state, as also occurs in natural neutral hardwater lakes (Melzer 1999). Lackmann (1998) gives an example from the vegetation of three mining lakes from the LRMD. Charophytes dominate an oligotrophic lake while more eutraphent higher plants occur in the eutrophicated lakes. Pietsch (1998) mentions lakes dominated by *Chara hispida* as a possible climax state in neutral mining lakes, mainly outside of the LMD. Our investigations show that *C. hispida* is only one of several different charophyte species that frequently occur in oligotrophic mining lakes (see Table 3.17). These lakes are unusually transparent, which has allowed macrophyte vegetation down to a depth of 20 m. One intensively investigated example is the Kulkwitzer Lake west of Leipzig (Doege et al. 2006).

We have observed that mainly higher plants from the genera *Myriophyllum* and *Potamogeton* generally dominate mesotrophic to eutrophic mining lakes. Similar to natural lakes, very eutrophic mining lakes may lack submerged vegetation due to turbidity.

Strategies of Macrophyte Survival in Acidic Environments

In acidic environments, aquatic plants are faced with adverse conditions. One important peculiarity of most acidified waters is the low content of dissolved inorganic carbon (DIC) in the water column, which occurs almost totally as free CO_2, in equilibrium with the atmosphere below a pH of 4.5 (Klapper and Schultze 1995;

Table 3.17 Examples of dominant charophyte species in oligotrophic neutral mining lakes in Germany

Dominant charopyhte species	Bla	Bor	Hel	Kul	Mar	Wer
Chara contraria	▲	▲	▲	▲	▲	▲
Chara globularis	▲	▲	▲	▲		
Chara hispida			▲	▲		
Chara polyacantha			▲			
Chara vulgaris		▲			▲	▲
Nitella mucronata				▲		
Nitella opaca	▲	▲	▲	▲		▲
Nitellopsis obtusa			▲	▲		
Maximum macrophyte depth limit, m	16	19	16	19	10	13

Bla: Blausteinsee (LRMD), Bor: Borkener See (BMD), Kul: Kulkwitzer See (CGMD), Mar: Markkleeberger See (CGMD), Wer: Werbener See (CGMD), Hel: Helenesee with Katjasee (LMD); BMD: Borken Mining District (Hessen), unpublished data (Beck 2006–2007)

see also Sects. 3.3.1.1, 3.3.1.4 and 3.3.2.2). Low DIC concentrations can limit macrophyte growth at low pH more than the acidity (e.g. Pagano and Titus 2007; Roelofs et al. 1984; Titus et al. 1990). This is not the case for emergent macrophyte species, such as *Phragmites australis* or *Typha latifolia* (see Table 3.16), and species possessing floating leaves, like *Potamogeton natans* or *P. polygonifolius* (Maberly and Madsen 2002), due to their ability to use atmospheric CO_2. *Juncus bulbosus* has many adaptations that allow it to thrive in low DIC environments (Table 3.18). Wetzel et al. (1984) demonstrated the ability of bulbous rush to recycle CO_2 originating from its own respiration in the lacunar system of the plant. Additionally, the species can rely on higher DIC concentrations in sediment pore water (Roelofs et al. 1984; Wetzel et al. 1985). Root uptake can account for 15–35% of the total CO_2 demand of the plant (Raven et al. 1988), which is extremely high, second only to various isoetid species (Maberly and Madsen 2002). Additionally, the species benefits from bacterial CO_2 production in the rhizosphere as well as in the sediment–water interface (Wetzel et al. 1984, 1985). Comparable results were shown by Chabbi et al. (2001) and Küsel et al. (2003). They assumed greater CO_2 availability due to microbial decomposition of organic root exudates by bacteria inhabiting microspaces in iron plaques around the roots of *J. bulbosus*. The *Sphagnum* species that occur in acidified mining lakes or soft water lakes together with *J. bulbosus* are CO_2-dependent and do not possess roots. Observations of Roelofs (1983) show the highest sediment pore water DIC concentrations beneath *Sphagnum* beds. This indicates a "local CO_2" supply as would be the case near the sediment–water interface. Maberly and Madsen (2002) have suggested that this CO_2 uptake strategy is also used by species of the genus *Utricularia*. *Eleocharis acicularis* may possess a C_4-like carbon fixation (Keeley and Sandquist 1991) that is comparable to the crassulacean acid metabolism often found in isoetid species (Keeley 1998).

Another characteristic of acidified mining lakes is a high concentration of NH_4^+, which results from inhibited nitrification (Nixdorf et al. 2001), which can be toxic to some aquatic plants (e.g. Glänzer et al. 1977; van Katwijk et al. 1997). Many submerged macrophyte species occurring in acidic mining lakes show a preference for ammonium uptake. *J. bulbosus* predominantly uses ammonium as a nitrogen source (Schuurkes et al. 1986) but can also use nitrate, to a lesser extent. Exclusive ammonium use and high tolerances have also been shown for different *Sphagnum* species (Paffen and Roelofs 1991; Schuurkes et al. 1986). It has been assumed that the elevation of ammonium together with DIC were key factors for extensive growth of *J. bulbosus* and *Sphagnum* in acidified softwater lakes (Arts 2002; Farmer 1990; Smolders et al. 2002). In situ experiments showed little nitrate reductase activity by *Potamogeton natans* (Melzer 1980), which implies preferential ammonium use. This is supported by reports of high ammonium concentrations in a typical *P. natans* association in a small stream influenced by acidic water from mining lake Bergwitzsee (Köck 1981). Pietsch and Jentsch (1984) describe habitats for *Myriophyllum heterophyllum* that are surprisingly low in ammonium concentrations unless it colonizes acidified sites with a pH down to 3.7. This may indicate that high ammonium concentrations negatively affect this species.

The high solubility of most metals under low pH conditions and the possibly phytotoxic effect of the resulting high concentrations is another characteristic of acidic mining lakes (Nixdorf 2001). Some macrophytes have been shown to accumulate high concentrations of heavy metals without toxic effects (e.g. Aulio 1986; Farmer 1990). This allows certain reed species to be used in wetlands constructed for remediation of polluted areas (e.g. Mayes et al. 2008). There are two principle ways for plants to avoid heavy metal toxicity; the first is to prevent the uptake of the toxic ions and the other is to dispose of any that enters the plant (Reichman 2002). Iron and manganese root plaque formation, which results from radial oxygen loss by aquatic plants and acts as a physical barrier or site of precipitation, is widely discussed as a heavy metal tolerance mechanism (e.g. Batty et al. 2002; Chabbi 1999, 2003; Ye et al. 2001). Different iron tolerances among fen plants have been shown to be related to iron plaque formation on the roots (Snowden and Wheeler 1993, 1995). Some of the most iron tolerant species of the study, like *Eriophorum angustifolium* or *Juncus effusus*, are found in strongly acidified mining lakes (Table 3.16). However, the role of the plaques is not clarified. Negative effects of root plaque formation have been shown for the acid-tolerant species *Lobelia dortmanna* (e.g. Christensen and Wigand 1998; Christensen et al. 1998). Organic acids exudation also plays a role in metal tolerance of plants by formation of complexes (Reichman 2002) but the function is also unclear and very species specific (Jones 1998). For *J. bulbosus*, organic acid exudation over the roots has been reported (Chabbi et al. 2001; Küsel et al. 2003), which might additionally favor the occurrence of the species in very acidic habitats. Internal mechanisms for metal tolerance have been reviewed by Reichman (2002) and include: compartmentation in vacuoles, complexing with phytochelatins, methallothioneins, organic acids, and inorganic and organic ligands, as well as alterations in cell metabolism. However, as the author mentioned, additional research is needed to reveal species specific mechanisms. For *J. bulbosus*, it has

Table 3.18 Effects of low pH-environment and adaptations of *Juncus bulbosus*

Effect	Adaptation	Reference
Low DIC in water column	Internal CO_2 recycling	Wetzel et al. (1984)
	CO_2 uptake from sediment and water	Wetzel et al. (1985), Roelofs et al. (1984)
	Microbial CO_2 production in iron root plaques	Chabbi (2001), Küsel (2003)
High NH_4^+ concentrations	Almost exclusive ammonium use	Schuurkes et al. (1986)
High concentrations of dissolved metals	Iron and manganese root plaque formation[a]	Chabbi (1999)
	Exudation of organic acids[a]	Chabbi (2001), Küsel (2003)
	Internal barriers	Chabbi (1999), Chabbi (2003)
High turbidity	Extremely low light compensation point	Roelofs et al. (1985)

[a] unclear function

been shown that metals are internally accumulated at the rhizodermis, exodermis, and endodermis (Chabbi 1999, 2003). Aquatic mosses have been found to accumulate metals in or at their cell walls (e.g. Crowder 1991; Engleman and McDiffett 1996; Satake 2000). In this context, cation exchange capacities of the species play an important role (Crowder 1991; Reichman 2002), which is especially high in *Sphagnum* mosses (e.g. Breuer and Melzer 1990a, 1990b; Clymo and Hayward 1982).

Macrophyte Invasions in Mining Lakes

The invasion of aquatic ecosystems by neophytic macrophyte species and their negative consequences to the ecosystem and to public use of the water bodies are known from all over the world (Willby 2007). The economical costs of invasions can be huge. For example, mass development of *Myriophyllum spicatum* has caused annual losses of 30–45 million US $ in the Truckee River watershed in the USA (Charles and Dukes 2007).

The impacts of a neophytic invasion were impressively demonstrated by the mass development of *Elodea nuttallii* in the formerly acidic mining lake Goitsche, near Bitterfeld (Hilt et al. 2006; Rönicke et al. 2006). It occurred in 2004 only two years after the pit was fully flooded with eutrophic river water, which also led to neutralization of the lake (Schultze and Geller 2004). The plants formed dense floating canopies more than 5 m deep, which seriously restricted the use of the lake for swimming, boating, and fishing. Subsequently, the mass development has been less intense although the only countermeasure that has been taken has been mowing stands of the species. Hilt et al. (2006) mentioned annual expenses ranging from 19,000 to 130,000 € spent in mowing *E. nuttallii* in other German lakes. Like most other neophytic aquatic weeds, *E. nuttallii* is distributed easily by fragments of the plants (e.g. Di Nino et al. 2005). In the case of Lake Goitsche, the great flood in August 2002 caused the river Mulde to break through into the lake basin. This probably led to wide distribution of *Elodea* fragments which, along with nutrients provided by the flood water and other inflows, resulted in nuisance macrophyte developments and eutrophication. Nutrient-rich sediments can also promote eutraphent species like *E. nuttallii*, even under oligotrophic conditions (Angelstein 2008).

Typically, charophyte communities dominate nutrient-poor lakes. These are not problematic, even if occurring in masses. Additionally, they are beneficial since they help maintain the oligotrophic state by acting as a nutrient sink (Hilt et al. 2006; Kufel and Kufel 2002; Kufel and Ozimek 1994). In Lake Goitsche, charophytes can compete even with the very aggressive *E. nuttallii* during ongoing oligotrophication of the lake (personal observations).

In contrast to circumneutral mining lakes, the extreme habitat conditions of strongly acidified mining lakes restrict the occurrence of macrophytes to a small group of adapted species. Even so, mass developments of *Myriophyllum heterophyllum* in mining lakes with a pH down to 3.7 have demonstrated that such ecosystems can be invaded by neophytic species (Pietsch and Jentsch 1984). Additionally, some other invasive neophytic macrophytes can colonize acidified lakes. For example *Cabomba caroliniana* (Crow and Hellquist 2000; Hogsden et al. 2007) or *Crassula helmsii* (Klavsen and Maberly 2009) might be problematic in such lakes in the future, though there is no evidence of invasions in Germany yet.

No neophytic macrophyte occurrence has been reported in the most acidified mining lakes. However, the predominant indigenous species in these lakes, *J. bulbosus*, can be considered to be invasive as well. Examples of dense floating mats can be seen in Lake Senftenberg (see Fig. 4 C in Chabbi 1999) and were described by Pietsch (1998). From natural waters, problems with mass occurrences of bulbosus rush have been documented (e.g. Roelofs et al. 1994; Rorslett 1988). Dense stands of the species can produce impressive biomass of more than 1,000 g dry weight m^{-2} (Roelofs et al. 1994). In acidic mining lakes with extensive shallow areas, even extensive stands of reed species like *Phragmites australis* might interfere with planned uses of the lake (see Fig. 3.66).

At near-neutral pH, a great variety of neophytic as well as indigenous macrophyte species are capable of causing a nuisance. Gollasch and Nehring (2006) have provided a list of aquatic neophytes in Germany. Evidence of macrophyte mass developments, mainly in natural lakes, was shown by Hilt et al. (2006), while Table 3.19 lists examples in mining lakes. Rising water temperatures associated with climate change will further increase the number of potential invasive species (Hussner and Lösch 2005; Willby 2007).

Considering the great variety of possible invaders, it has to be realized that "… invasions are more than *just likely*, they are *inevitable*." (McIntosh et al. 2007). Nevertheless, some considerations might mitigate or even prevent macrophyte invasions in future mining lakes. As has been mentioned, flooding water plays an important role. Eutrophic flooding water should be avoided whenever possible.

Fig. 3.66 Examples of dominance stands of *Myriophyllum heterophyllum* (**a**) and *Phragmites australis* (**b**) in German mining lakes (Photos by B. Beck 2006–2007)

Table 3.19 Examples of mass developments of neophytic (N) and indigenous (I) macrophyte species observed in mining lakes from acidic to neutral

Species	pH preference	Example
Ceratophyllum demersum (I)	Circumneutral	Speicher Friedersdorf[a]
Elodea nuttallii(N)	Circumneutral	Goitsche [b, c, a]
Hippuris vulgaris(I)	Circumneutral	Möhlauer See [a]
Myriophyllum heterophyllum(N)	Moderately acidic to circumneutral	Heider Bergsee [d, c, a]
Myriophyllum spicatum(I)	Circumneutral	Speicher Knappenrode [a]
Myriophyllum verticillatum(I)	Circumneutral	Zechau III [a]

[a] own observation; [b] Rönicke et al. (2006); [c] Hilt et al. (2006), [d] Hussner (2005)

Additionally, knowledge about potential invasive species in the watershed of the river could be useful in assessing invasion risk. Another problem to be considered is the planned connection of mining lakes with channels for boating. If one lake is invaded, the invasion risk for connected lakes rises due to propagule dispersion by either boating or water flow (e.g. Jacobs and Macisaac 2009). Finally, the morphology of the lake basins can promote intensive macrophyte growth by offering wide areas of shallow water with an approximate depth of 5 m or less (see Sect. 2.1). The creation of steep shores in critical lake areas could at least prevent floating stands of rooted macrophyte species.

3.3.2.2 Zygnematalean Green Algae (Streptophyta, Zygnematales) in Lakes Impacted by Acidic Precipitation, Experimental Acidification, and Acid Mine Drainage

Andreas Kleeberg

Introduction

The green algal order Zygnematales has long been known to occur in diverse habitats worldwide (West and Starkey 1915). They occur in brackish and limnic waters, including natural acidic freshwaters (Greenwood and Lowe 2006; Hoshaw and McCourt 1988) and even in the Antarctic (Hawes 1989). Zygnematales typically colonize stagnant shallow lakes, ponds, pools, acidic wetlands (Greenwood and Lowe 2006), and the slow-flowing parts of running waters over a large pH range (Hoshaw and McCourt 1988). The dispersion of the Zygnemataceae due to acidification was documented for the first time in Scandinavia (Hendrey et al. 1976) and later in experimentally acidified (pH 4.5–6.2) lakes in North America (e.g. Stokes 1986). Zygnematalean green algae (ZGA) also occur in freshwaters that have been acidified by acid mine drainage (AMD; Bray 2007; Kleeberg et al. 2006).

Previous authors have focused on diverse facets of zygnematalean biology: (1) identification (France et al. 1992), (2) distribution (e.g. Howell et al. 1990; Turner et al. 1995a, b, c), (3) function as pH indicator species (e.g. Greenwood and Lowe 2006; Jackson et al. 1990; Verb and Vis 2005; Vinebrooke 1996; Vinebrooke and Graham 1997), (4) nutrient interactions (e.g. Fairchild and Lowe 1984; Hansson 1989; Graham and Vinebrooke 1998; Müller 1980; Niyogi et al. 1999; Pringle 1987), and (5) ecophysiology (Donahue et al. 2003; Graham et al. 1996; Gross 2000; Klug and Fischer 2000; Sheath et al. 1996). These studies, mostly for North America, further emphasize the importance of Zygnematales in acidic lakes. Several review articles provide useful general coverage of Zygnematales (Hoshaw and McCourt 1988), methodology (Aloi 1990), and the effects of acidification on Zygnematales (Planas 1996).

This chapter aims to summarize scientific knowledge on ZGA in freshwaters that have been impacted by acid rain, experimental acid additions, and acid mine

Table 3.20 Systematic classification of filamentous green algae of Zygnemataceae with the acidophilic genera occurring in acidic waters, with the number of their species and their percentages on species number of the family (Kadłubowska 1984; Hoshaw and McCourt 1988)

Taxon	Species	% total
Conjugatophyceae Streptophyta (Chlorophyta)		
Zygnematales Zygnemataceae		
Spirogyra	386	49.2
Zygnema	139	17.7
Mougeotia	138	17.6
Zygnemopsis	43	5.5
Zygogonium	29	3.7

effluents, and raise issues that require future study on this functional group in acidic mining lakes. For the purposes of this project, it was not appropriate to include coverage of humic (bog/peatland) lakes or acidic hot springs.

General Features of Zygnematales

Zygnematales and Desmidiales are exceptionally diverse and numerous in acidic (humic) lakes and bogs. The Zygnematales include the unicellular saccoderm desmids and closely related unbranched filamentous algae, such as the genus *Zygnema* (for which the order is named). Zygnematales are classified in the phylum Streptophyta, which includes the land plants (Bremer et al. 1987), or in Charophyta (Lewis and McCourt 2004), instead of in Chlorophyta. Modern systematic treatments apply the term Chlorophyta to groups of green algae that do not include the Zygnemataleans. It is important to note that the filamentous zygnemataleans do not form a separate clade from closely related saccoderm unicells. Zygnematales and Desmidiales are monophyletic sister clades that together form a monophyletic group/class, variously named Zygnemophyceae or Zygnematophyceae. The family Zygnemataceae represents unbranched ZGA, which sexually reproduce by conjugation as shared with Desmidiales. 13 genera with 784 species belong to the Zygnemataceae (Hoshaw and McCourt 1988). Only a few specialized genera occurring in acidic waters ($pH < 5$) are considered (Table 3.20).

Distinctive Features of Zygnematalean Green Algae

Conjugation distinguishes the Zygnemataceae from all other filamentous Streptophyta, except for a few species of filamentous desmids; for details, see Kadłubowska (1984) and Hoshaw and McCourt (1988).

ZGA, such as *Mougeotia* spp., *Spirogyra* spp., and *Zygogonium* spp., excrete copious amounts of muscilaginous substances, which prevent colonization by epiphytic algae (Vinebrooke et al. 2001). The metaphytic floating growth forms may also be unreliable and physically inaccessible to most littoral organisms.

Therefore, the blooms and mats, respectively, of ZGA occur because they outcompete other species at conditions of low concentrations of dissolved inorganic carbon (DIC) and grazing pressure (Vinebrooke et al. 2001).

Chloroplast movement is a light-driven phytochrome-mediated process. For example, in response to direct light, the chloroplast of *Mougeotia* spec. rotates about the long axis of the cell to change the amount of surface area exposed to light. In low light, the large flat side of the chloroplast faces the light. In bright light, the narrow edge profile is turned toward the light (Hoshaw and McCourt 1988).

Ecological Importance of Zygnematalean Green Algae

The acidification-induced growth of ZGA in lakes is most probably primarily a water temperature governed seasonal phenomenon, whereat the maximal abundances can fluctuate from lake to lake and from year to year (Morin and Cattaneo 1992; Planas 1996). While diatoms (e.g. Bacillariophyceae) have been used for a long time for pH indication (Hustedt 1939), the ZGA were linked to the acidification of lakes considerably later (Hendrey et al. 1976). In particular, the species of the genus *Zygogonium* (Table 3.20) are acidobiontic (dependent on acidity) indicator species, which exhibit broad acidity tolerance (Vinebrooke et al. 2001).

ZGA have an important influence on nutrient cycles (C, N, and P), and partly on the deposition of nutrients (Turner et al. 1995a, b), and can considerably contribute to the benthic C accumulation. They also influence the biogenic alkalinity generation via the sulfur cycle, by moving the horizon, in which the benthic sulfate reduction occurs, into larger sediment depth where the reoxidation of deposited reduced compounds is prevented (Koschorreck et al. 2007; Turner et al. 1995b). Thus ZGA can be important for the mediation of the internal alkalinity generation of acid mining lakes (Kleeberg et al. 2006; Koschorreck et al. 2007).

The respective zonation of the ZGA can be assigned to specific ecologically defined growth forms—mostly associated with the littoral sediment –according to morphology, chemistry, trophy and light climate of a lake:

- *Periphyton*—microfloral community, which lives on surfaces of submersed objects and substrates, respectively (Roll 1939), which does not include fungi, bacteria and protozoa and other animal components (unequal to the German term ‘Aufwuchs’, Weber 1973).
- *Metaphyton*—amounts of filamentous algae, which are conjunct with benthic substrates. However, these algae can also form loose flocs, mats or clouds, which lie on the bottom or which float above the bottom (Behre 1956; Wetzel 1983). Metaphyton is synonym to the older terms tychoplankton, pseudoplankton (Naumann 1931) and pseudoperiphyton (Sládečková 1960).

The classification of ZGA to peri- or metaphyton is not always clear, since periphytic algae can pass into metaphytic aggregations in response to hydrostatic pressure (Howell et al. 1990), wind-induced water movement (Turner et al. 1987),

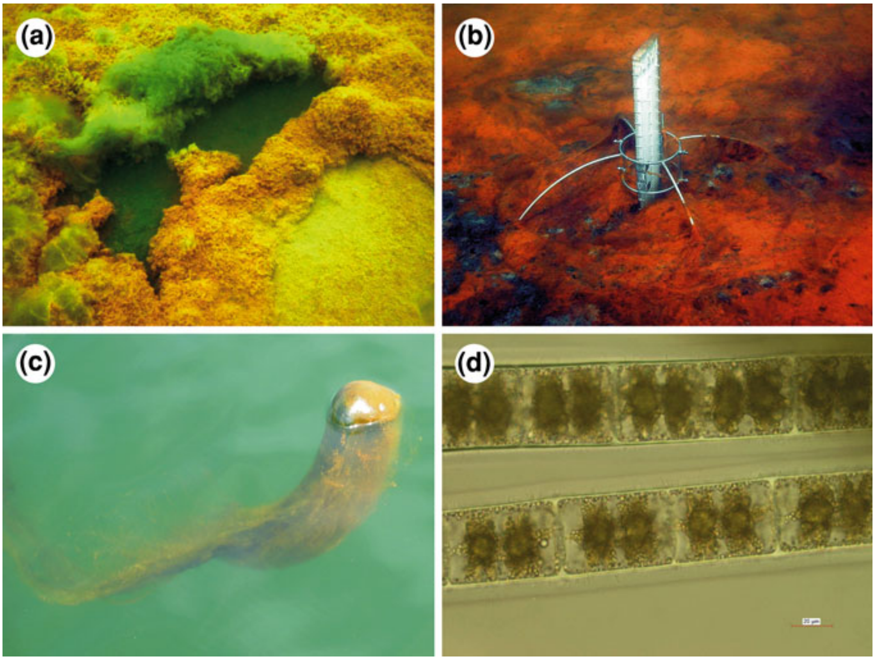


Fig. 3.67 **a** periphytic canopy of *Zygogonium ericetorum* at the sediment surface of acidic (pH ≈ 3) mining lake Grünewalder Lauch, Lusatia, Germany, **b** dense cover of *Z. ericetorum* at the sediment surface after 14 days of incubation of an *in situ* pore water sampler in the same lake (photos by M. Beyer), **c** momentary (jellyfish-like) flotation of *Z. ericetorum* at the water surface due to intensive O_2 production and its related enclosure of O_2 bubbles (photo by B. Grüneberg), and **d** microscopic picture of filaments of *Zygnema* spec. with the stellate and asteroidal chloroplasts, respectively (photo by H. Täuscher)

at changes of species composition along with a decreasing pH (Howell et al. 1990; Turner et al. 1995a). Intensive primary production (PP) at low depths, with simultaneous formation of O_2 bubbles within the densely-packed associations of the filaments (Fig. 3.67), supports the buoyancy of algal canopies (Hillebrand 1983).

Motility may be favored to best use environmental resources, light, CO_2, or to escape unfavorable conditions. Specific cell wall components such as algaenan, or possessing non-cellulosic cell walls may also facilitate growth and tolerance of low pH conditions (Bray 2007).

The pH-dependent Occurrence of Zygnematalean Green Algae

Acid and acidified waters are colonized by acidophilic (limited to growth in acidic conditions) and acid-tolerant (highly tolerant of acidic conditions) species of ZGA. Acidophilic algae, which occur down to pH values of 0.05, are not able to grow at neutral pH. For algae that live in very low pH conditions, several adaptations are necessary. For growth at low pH, a neutral cell pH must be maintained, which is made possible by a relatively impermeable plasma membrane, reduced proton fluxes, and increased proton pump efficiency (e.g. Gross 2000). In addition, the algae have to cope with a restricted supply of CO_2 for photosynthesis since HCO_3^- is absent. Although DIC limits benthic PP in acid lakes (Klug and Fischer 2000), the species of Zygnemataceae are superior to other species (Vinebrooke 1996). Thus, most studies show that acidification increases the benthic algae biomass in both the littoral zones of lakes and in lotic systems (Planas 1996). Consequently, due to the high CO_2-requirements and ambient shortages, ZGA in acidic environments must have a CO_2 concentration mechanism (Gross 2000).

- Acidophilic to acid-tolerant peri- and metaphyton in lakes is composed mainly of the genera given in Table 3.20. At pH 5.5–4.8, acidophilic Zygnemataceae, such as *Spirogyra* spp. and *Mougeotia* spp., occur (Table 3.21).
- Usually, ZGA are found in monospecific aggregations below pH 4.8 (France et al. 1992). Usually a metaphytic coverage hardly exists below a water depth of 3 m. At all depths, the biomass and PP decreases with the lowering of light supply (e.g. Planas 1996; Schindler 1993). If the pH decreases < 4.8, *Spirogyra* spp. and *Mougeotia* spp. (Table 3.21) are displaced by *Zygogonium* spp. (Turner et al. 1995a, b), which are acid-tolerant over a wide span of pH (Table 3.22).
- Peri- and metaphytic aggregations, which are exposed to the conditions of a high acidity, often consist of dense filamentous canopies of *Zygogonium ericetorum* Kütz., 1843. Thus, this species paid attention to for a long time (Hodgetts 1918; West and Starkey 1915). While this acidobiontic indicator species colonized the whole shore area in an anthropogenic, acidified ($pH < 5.6$) lake (Planas 1996), it covered about 88.3% of the bottom in an acidic ($pH \leq 3$) mining lake, Grünewalder Lauch, Lusatia, Germany (Kleeberg et al. 2006).

Factors that Determine the Distribution and Productivity of Zygnematalean Green Algae

Besides the direct physiological effects of the acid on the acid-tolerant ZGA (e.g. Klug and Fischer 2000), their species composition, biomass, and PP are determined by abiotic and biotic factors. The abiotic factors are: (1) pH, i.e. prevailing H^+ and metal concentrations; (2) limiting nutrients; (3) penetration depth of light, water temperature, and movement; (4) interfaces of the metaphytic mats, as well as; (5) substrate availability. The biotic factors include (1) the community of the littoral herbivorous macroinvertebrates and (2) competition for a limiting resource.

Abiotic Factors that Determine Distribution and Productivity

Ecosystematic disturbances that accompany the acidification of lakes, cannot be exclusively attributed to the potential toxicity of the H^+ and metal concentrations, particularly that of Al. The changed biogeochemical cycle of different components

Table 3.21 Occurrence and dominating growth forms of *Mougeotia* spp., Zygnemataceae, at respective pH in natural, acid and circum-neutral as well as artificial freshwater systems (according to Graham et al. 1996, changed and supplemented). AMD—acid mine drainage

Growth form	Occurrence	pH	Source
Benthic and planktonic	Tundra, pond, Kap Bathurst area	8.1–8.2	Sheath et al. (1982)[a]
Floating mats	Eutrophic pond, the Netherlands	7.5–9.9	Hillebrand (1983)
Floating mats	Pond in coastal dunes, the Netherlands	5.5–8.2	Simons (1987)
With the sediment associated filaments	Georgia Bay and North Tunnel, Ontario	6.6–7	Sheath et al. (1988)
Associated with stones	Streams of the Signy Islands, Antarctica	6–7	Hawes (1989)[b]
Aggregates associated with different substrates	Acidified soft water lakes, NE PA, USA	4.4–6.2	Fairshild and Sherman (1993)[c]
Metaphytic mats	Lake 223, experimental lake area, Ontario	5.1–5.6, 5.0–5.2	Schindler et al. (1985); Turner et al. (1987)
Algal mats	Groundwater influenced lake, mid-Wisconsin	4.7–5.6	Webster (1992)[d]
Metaphytic mats	Lake Little Rock, Wisconsin, enclosure	4.7	Klug and Fischer (2000)
Aggregate associated with diverse substrates	Acidified rivers, Scotland	4.4–6.7	Kinross et al. (1993)
Periphyton community	AMD stressed rivers, Westport, New Zealand[e]	3.2 ± 0.1	Bray (2007)
Macroalgal community	AMD impacted Hocking river sites, OH, USA	2.6–8.2	Verb and Vis (2001)
Periphyton assamblage	AMD impacted stream sites, unglaciated western Allegheny Plateau, OH, USA	1.6–4.7	Verb and Vis (2005)
Periphytic patches	Río Tinto, S Spain[f]	1.5–2.5	Sabater et al. (2003)

[a] *Mougeotia* did not occur in ponds with pH 3.6, 2.0, and 1.8; [b] in the cold streams grazers did not occur (see below); [c] for *Mougeotia*, the authors gave a pH optimum of 5.3 ± 0.8; [d] the maximum of biomass was determined at pH 5.2; [e] *Mougeotia* cf. *depressa*, (Hass.), *M*. cf. *laevis* (Kütz.) and *Zygnema* c.f. *cylindrospermum* (West et West); [f] in Río Tinto, at pH 0.8–3, *Zygnemopsis* spec., Zygnemataceae, also occurred (Aguilera et al. 2007)

Table 3.22 Occurrence and dominating growth form of *Zygogonium* spp., Zygnemataceae, and the pH of natural, circumneutral, and acidified freshwater systems reported in the literature

Growth form	Environment	pH	Source
Epilithic, epiphytic	Bowland Lake, Ontario	5.7–6.7	Jackson et al. (1990)
Metaphytic floating and semi-attached	0–2 m littoral of softwater lakes, Ontario, Canada	5.6–6.5	Howell et al. (1990)[a] France et al. (1991)
Periphyton	Low alkalinity lakes, Killarney Provincial Park, Ontario	< 5	Vinebrooke (1996)[b] Vinebrooke and Graham (1997)
Metaphyton	Experimentally acidified Lake 302S, NW Ontario	4.5	Turner et al. (1995a) Turner et al. (1995b)
Periphyton loosely attached, tall	Lake Ruth-Roy (Ontario)	4–4.6	Graham and Vinebrooke (1998)
Loose flocs	littoral of mining lake Koschen, Lusatia, Germany	3.2	Jacob and Kapfer (1999)[c]
Dense mats, peri- and metaphytic form	1.6–10.5 m depth in lake Grünewalder Lauch, Lusatia, Germany	2.9	Kleeberg et al. (2006)
Floating mats	Warm (30–31 °C) water near thermal springs, Yellowstone National Park, Wyoming	2.4–3.1	Lynn and Brock (19s69)

[a] predominant was *Z. tunetanum*; [b] *Z. ericetorum* and *Z. tunetanum*; [c] predominant during cold season was *Bumilleria klebsiana* (Xanthophyceae), and during warm season *Z. ericetorum* (Chlorophyceae)

(Fe, S, C, and N) can influence physical factors such as light climate, stratification, and/or substrate availability.

Effects of pH

Direct physiological effects of the acid on the ZGA, which determines their distribution and PP, are often difficult to assess because changes in pH are accompanied by changes in other potentially important factors such as dissolved inorganic carbon (DIC) and metals (Kleeberg et al. 2006; Klug and Fischer 2000). Appearance of *Mougeotia* and *Zygogonium* spp. with the (experimental) lowering of pH and their disappearance, if the pH was increased, e.g. by liming (Jackson et al. 1990; Turner et al. 1987) is well documented. However, these studies did not clarify whether the increase or decrease of dominating species are directly or indirectly attributed to pH.

Nutrient Limitation and Primary Production

Carbon—is known to be growth-limiting for the pelagic (e.g. Beulker et al. 2003; Nixdorf et al. 2003b) and benthic PP of ZGA (e.g. Mulholland et al. 1986; Turner et al. 1987, 1995a). HCO_3^- is virtually non-existent at $pH < 5$ and the dissolution of CO_2 from the atmosphere is very low. Consequently, at pH 3, for example, the

Table 3.23 Span of pH, of concentrations of total inorganic carbon (TIC), of ammonium (NH_4^+), and of dissolved reactive phosphorus (SRP) of acidic mining lakes of the Lusatian mining region, Germany (Nixdorf et al. 2003a)

Buffer system	pH	TIC (mg L^{-1})	NH_4^+–N (mg L^{-1})	SRP (μg L^{-1})	Number of lakes
Fe buffered	2.2–3.4	<0.2–18.3	0.12–14.2	1–30	15
Al buffered	3.8–4.0	<0.2–0.5	0.40–0.52	1–2	2
CO_3 buffered	6.0–8.0	0.8–36.7	0.02–3.65	1–8	8

atmospheric equilibrium concentration of CO_2 amounts to about 0.1 mg L^{-1} (Nixdorf et al. 2003b). Table 3.23 summarizes the span of nutrient concentrations of mining lakes.

Additions of N, P, and N + P alone in lab experiments did not stimulate the growth of ZGA (Fairchild and Sherman 1990). Moreover, the dense mats and missing water movement could hamper CO_2 diffusion (Turner et al. 1991, 1994). At the same time, the ZGA use the CO_2 originating from benthic mineralization (Wetzel et al. 1985). After additions of N and C, Fairchild and Sherman (1990) found a significantly increased abundance of *Mougeotia*, whereas not after single C additions. Thus, this species seems to be extremely efficient in CO_2 uptake at low pH, but less efficient in the uptake of HCO_3^- (Turner et al. 1987). For *Spirogyra*, it was hypothesized that this species can induce the formation of the carboanhydrase (Simpson and Eaton 1986), which supports the use of HCO_3^-.

Nitrogen—can be taken up by ZGA as nitrate (NO_3^-) or ammonium (NH_4^+), though NH_4^+ is preferentially used as a N source. In both rain-acidified soft water lakes and geogenically acidified mining lakes the concentration of NH_4^+ is relatively high (Table 3.23), in addition to the the NH_4^+ import caused by the inhibition of nitrification (e.g. Nixdorf et al. 2003a; Rudd et al. 1988). Consequently, the N supply for the benthic Zygnemataceae should be adequate, which is substantiated by the enrichment experiments with nutrient combinations by Fairchild and Sherman (1990). In an experimentally acidified lake (pH 4.5), the N:C ratio of ZGA, mainly of the genera *Mougeotia* and *Zygogonium*, was used to indicate the N limitation. With 0.11, i.e. between 0.1 and 0.13, it indicated a 'moderate' N deficiency (Turner et al. 1995a).

- *Phosphorus*—the availability of P is dependent on its import and the concomitant import of P-binding partners, particularly metals such as Fe, Al, Mn, and Ca, and the prevailing O_2, pH, and redox conditions (see also Sect. 3.2.1.3). Thus, in most acidic mining lakes the P concentrations are very low (Table 3.23). The co-precipitation of P by Al and Fe oxyhydroxides is documented for both acid rain-acidified soft water lakes (e.g. Kopáček et al. 2000) and geogenically acidified mining lakes (e.g. Kleeberg and Grüneberg 2005).
- The uptake of P by epilithic or periphytic mats has rarely been studied (Hansson 1989; Riber and Wetzel 1987; Tate et al. 1995). The activity of

Table 3.24 Span of biomass characteristica and net primary production (PP) of various zygnematalean green algae (ZGA) and the pH reported in the literature (dw: dry weight, Chl a: chlorophyll a)

ZGA	pH	Dw (g m^{-2})		Chl a (mg m^{-2})		Net PP (mg C m^{-2} d^{-1})		*n*	Number of References
		min	Max	min	Max	min	Max		
Periphyton	–	0.03	46.00	0.01	2385	0.6	2,510	#	a
Zygnema	6.7	21.7	39.80	20.00	400	31.7	32	4	b
Metaphyton	5.6	0.82	1.79	1.03	2.33	6.9	119	5	c
Zygogonium	4.5	0.30	32.40	–	–	16.8	2,222	7	d
Zygogonium	2.9	0.30	478.5	0.20	1,025	-12.0	851	4	e

[a] Morin and Cattaneo (1992); # 20 journals between 1975 and 1990 have been reviewed, i.e. $n = 187$–1,194; [b] Sheath et al. (1996); Tundra stream, Toolik region, Alaska; [c] Howell et al. (1990); predominately *Mougeotia* and *Zygogonium*; [d] Turner et al. (1995a); predominately *Mougeotia* and *Zygogonium*, data from 1991; [e] Kleeberg et al. (2006); *Z. ericetorum* in acid mining lake Grünewalder Lauch, Germany

indicators for P availability, such as phosphatases (Sabater et al. 2003), are also determined by other factors, such as available phosphate, and hence do not allow definite termination to an existing P limitation. Turner et al. (1995a) used the mass ratio of P:C × 1,000 as an indicator for the determination of P limitation. For a community of *Mougeotia* and *Zygogonium*, this ratio amounted to 5.8, i.e. was considerably smaller than 10, which indicates an extreme P deficiency. It is also known that benthic algae are able to store P if P is available in surplus. Whether the phosphate that is released (possibly quickly) after microbial mineralization is immediately taken up by the algae is unknown. It is also not clear whether the dominating meta- or periphytic growth form of ZGA preferentially uses the water body (Hansson 1990) or the sediment (Wetzel et al. 1985) as the major P source.

- *Primary production*—The determination of photosynthetic rates of the peri- and metaphytic ZGA is, because of their heterogeneous distribution between the growth forms, problematic. The variability of size of the metaphytic aggregates and concentration of algal filaments, which lie in high density within the associations close together and float, respectively, can significantly influence the biomass-specific PP due to the competition for light and nutrients (Mulholland et al. 1986; Turner et al. 1994, 1995a, c). This is reflected in the horizontal distribution of the biomass of ZGA in a lake and the span among different lakes (Table 3.24). The PP of ZGA can also be limited by temperature (see below), and is consequently seasonally very different (Graham et al. 1996; Howell et al. 1990). Moreover, the rate of net PP depends on the fall of slope of the littoral bottom, the amount of ZGA incubated for the measurements, and the amount of heterotrophic organisms associated with the algae (Howell et al. 1990; Kleeberg et al. 2006). The problem of comparing the benthic PP of the different waters becomes visible in the wide span of rates (Table 3.24; see also Sect. 3.3.2.3).

For example, in experiments with cultures of *Mougeotia* for the determination of PP and respiration as a function of pH, the production strongly decreased at $\text{pH} = 3$, but at $\text{pH} < 3$, the algae died (Graham et al. 1996a). 56 combinations of light and temperature with *Mougeotia* resulted in optimal conditions at 25°C and 300–2,300 μmol quanta m^{-2} s^{-1}, the net photosynthesis averaged 40.4 mg O_2 g^{-1} h^{-1} (Graham et al. 1996b).

In determining the PP of ZGA, beside the physical factors of light and temperature, pH-related factors such as the prevailing Al concentration and species have to be considered. Mulholland et al. (1986) determined the chlorophyll-specific rate of PP over a span of pH of 4.5–6.4. The lowest rates at pH 4.5 were not only determined by C and P limitation, but also by the toxicity of Al.

The rates of dark respiration of all benthic algae communities studied in acidified or acid lakes were higher than those of neutral references (Turner et al. 1991). A changed ratio between PP and respiration is generally regarded as an indicator of acid stress (Schindler 1993; Turner et al. 1995c). At $\text{pH} < 5$, the ratio of PP:respiration approached 1 (Schindler 1993).

Deposition and Toxicity of Metals

The most significant effect of AMD conditions on acid-tolerant communities is the deposition of metal oxides (e.g. Bray 2007; Niyogi et al. 1999). In comparison to the poorly buffered soft water lakes acidified by airborne pollutants, the metal concentrations in geogenically acidified mining lakes are much higher. For the latter, the concentrations of Fe vary between 0.09 and 170.2 mg L^{-1} and that of Al between 0.03 and 20.5 mg L^{-1}. In lakes with $\text{pH} < 3.4$, the molar proportion of Fe exceeds those of Al; at $\text{pH} > 3.7$, the relations are converse (Geller et al. 2000).

At $\text{pH} < 6$, Al becomes highly soluble; however, not all forms are toxic (Gensemer and Playle 1999). Inorganic monomeric forms are very toxic; Al fluoride complexes are not. An Al concentration of 50 μg L^{-1} was toxic for phytoplankton (Planas 1996). In acidified synthetic soft water, growth of the green alga *Chlorella pyrenoidosa* was inhibited after 96 h at an Al concentration of 162 μg L^{-1} (Parent and Campell 1994). In comparison, ZGA of the genus *Mougeotia* (Table 3.21) are distinctly tolerant of elevated Al concentrations. *Mougeotia* have been found in lakes at Al concentrations of 26–200 μg L^{-1} at pH 4.5–5.1, and in rivers at 41–1,410 μg L^{-1} at pH 4.4–7.3 (Graham et al. 1996). At higher experimental concentrations, Al caused a rapid decline in the ZGA growth rate and a lower final biomass (Kinross et al. 2000). The physiological mechanisms responsible for Al toxicity are still unknown (Gensemer and Playle 1999). The tolerance of *Mougeotia* to Zn depended on the level of concentrations (6–34,000 μg L^{-1}) in the waters from which they were isolated (Graham et al. 1996). Hence, in experimental cultures, *Mougeotia* tolerated a Zn concentration of 3,400 μg L^{-1}.

In acid mining lakes, the pH of the water is often seen as the primary variable that affects aquatic biota, but pH also acts as a master variable affecting metal hydroxide deposition. The high metal (particularly Fe) sedimentation rates should stress the ZGA in these lakes. For example, *Zygogonium ericetorum* was always associated with Fe hydroxides in the mining lake Grünewalder Lauch, Lusatia, Germany (Kleeberg et al. 2006). In comparison, at pH < 4, periphytic *Ulothrix* sp. (Chlorophyceae) biomass accumulated only when the Fe deposition rate was below ≈ 1 g m^{-2} d^{-1} (Niyogi et al. 1999). Consequently, *Z. ericetorum* growth in Lake Grünewalder Lauch is obviously seriously stressed by high rates (around 0.9 g m^{-2} d^{-1}) of Fe deposition during summer at shallower sites. *Z. ericetorum* can become covered by Fe hydroxides (red–orange colour in Fig. 3.67) if it does not grow faster than the rate of Fe deposition, which is between 1.2 and 2.2 g m^{-2} d^{-1} at deeper sites. Moreover, these Fe hydroxides might also influence the extreme P deficiency of *Z. ericetorum* by their ability to efficiently adsorb phosphate (Kleeberg and Grüneberg 2005). This is supported by the *Zygogonium*-mediated diurnal Fe cycling, where about 34% of the dissolved Fe is reduced at night time and then oxidized and precipitated during the day (Koschorreck et al. 2007).

Physical Parameters that Determine Distribution and Productivity

Light—Oligotrophying factors such as a C limitation, particularly in shallow regions of acidified soft water lakes, can improve the light climate for ZGA and can lead to a shift of the light compensation point (Planas 1996; Turner et al. 1995a). In boreal lakes, Experimental Lake Area, NW Ontario, attached algal composition was mostly determined by photosynthetically active radiation and ultraviolet radiation fluxes. The community on rock surfaces exposed to high solar fluxes contained very high concentrations of a photoprotective scytonemin-like pigment, and was dominated by ZGA (Donahue et al. 2003). On the other hand, light can be a growth-limiting factor for ZGA. At low iron turbidity, as occurs in some acid mining lakes, ZGA development can be suppressed in the relatively clear water by oversaturation of light, and chlorophyll a concentrations (0.2–9 μg L^{-1}) remain at a low, C-limited, mostly oligotrophic level (Nixdorf et al. 2003b), which favors the yield of light at the sediment surface. In contrast, deep chlorophyll a maxima (Beulker et al. 2003; Nixdorf et al. 2003b) could deteriorate the light climate for benthic ZGA.

Water temperature—The species of the Zygnemataceae occur over a wide range of temperature. They can colonize both cold streams of the Antarctic (Table 3.21) and warm thermal springs (Table 3.22). The temperature dependency of growth, photosynthesis, and respiration is only known for a few species. Studies on the influence of light (10–2,338 μmol quanta m^{-2} s^{-1}) and temperature (5–30 °C) on the net PP of *Mougeotia* at pH 4.7 showed that the compensation point (net PP = zero) lies between 10 and 20 μmol quanta m^{-2} s^{-1} at 5 °C; the temperature optimum was at 25 °C (Graham et al. 1996b). Thus, different species within a lake (Table 3.22) can rotate in dependence on temperature (Jacob and Kapfer 1999).

Water movement—The ZGA prefer lentic water zones. Nevertheless, moderate water movement can increase the dispersion of benthic ZGA by modifying the boundary layer around the cells and increasing diffusion. Thus, water movement could increase the efficiency of ZGA in absorbing dissolved C (Planas 1996;

Turner et al. 1987, 1991). Excessive turbulence in lotic water zones, however, can be detrimental for the sediment-associated algae. Lower biomasses and abundances or absence of ZGA in low (littoral) water depth can be ascribed to wind-induced intensive water movements, when water velocity exceeds a threshold at which mechanical abrasion of turbulences surpasses the resistance limit of ZGA (Howell et al. 1990; Kleeberg et al. 2006).

Substratum—ZGA are often very heterogeneous and highly dynamic in their physical characteristics, so substrata are an important variable to consider when comparing the occurrence and the spatial distribution of the Zygnematacea. ZGA live beyond the very steep micro gradient zones within the upper sediment and influence buffering capacity by their presence and activity; they also influence the pH through their direct and indirect influence on alkalinity formation (Cook et al. 1986; Koschorreck et al. 2007). However, up to now, there are no specific studies showing any relationships between ZGA and the composition of the sediments or the effects of the influence of the sediment, e.g. the pH buffering onto the algae community, or the CO_2 supply from microbial mineralization and nutrient availability.

Biotic Factors that Determine Distribution and Productivity

The effects of biotic drivers (influencing factors) cannot always be definitely distinguished from abiotic (physical and chemical) factors, since different species have very different sensitivities to pH.

Grazers—The increase of ZGA biomass with decreasing pH is often ascribed to control by grazers, i.e. decreasing grazing pressure accompanying increased acidification. This hypothesis is supported by the fact that the acid-sensitive taxa of the macrozoobenthos, which need Ca for their shells or exoskeletons (like crustaceans and molluscs) disappear if the pH decreases < 5.5 (median). Around a pH of ≈ 6, the ZGA become dominant. The dominance coincided with the loss of gastropods and amphipods (Turner et al. 1991). However, at lower pH, no larger cell diameter ZGA dominated, which indicates that the grazing of invertebrates is not a determining factor for the composition of the algae community (Kinross et al. 1993). Tadpoles of an acid-tolerant frog, *Rana clamitans*, have suppressed Zygnemataceae associated with loose sediment and thereby stimulated closer sediment-associated species (e.g. *Coleochaete scutata*), i.e. supported a succession towards an algal physiognomy that is resistant to herbivores (Graham and Vinebrooke 1998). Only larger animal species, such as the algae-feeding cyprinids in soft water lakes (pH 5.6–5.9), can exert significant grazing pressure on the littoral metaphyton (France et al. 1991).

The relative effect of acidification and the total biomass of insects and productivity and the relationship between the grazer's abundance and the algae development are also not clear. In many acidified and acid lakes, chironomid larvae (Chironomidae, Diptera) dominate; according to different authors, their abundances and biomass seems to be pH-independent (Müller 1980; Planas 1996). The decrease in the number of different taxa and their biomass could be related to the fact that ZGA can shift from their two-dimensional periphytic into the three-dimensional metaphytic growth form (Planas et al. 1989), and thus become physically inaccessible to most benthic taxa (Vinebrooke et al. 2001), since the metaphytic growth form represents a food item only available to herbivores with flexible life histories and feeding behaviors.

Traditionally, it has been argued that changes in the macroinvertebrate community can determine the composition of the algae (Harvey 1989). This implies that herbivores are selective. Their selectivity, in turn, is related to the physiognomy of the ZGA and their usability (Steinmann 1996). However, only a few observations deal with the food of acid-tolerant insects. Studies of Collier and Winterbourn (1990) showed that a large proportion (> 60%) of the stomach content of fishflies (Ephemeroptera) and chironomids was detritus of a pH-independent origin. Donahue et al. (2003) found for ZGA species of *Spirogyra*, *Mougeotia*, and *Zygogonium* that chironomid density explained only 2% of algal species variance, suggesting that they were not overly important in determining ZGA community structure. Hence, so far, the increase in algal biomass and ZGA community structure cannot be definitely explained by the decrease of top-down regulation.

Competition—Increased ZGA biomass can be a consequence of lowered heterotrophic activity with a ratio growth:decomposition that favors Zygnemataceae (Stokes 1986). The balance between the different heterotrophic and autotrophic populations, representing the periphyton, could change the nutrient cycle and thereby decrease competition for a certain resource (Mulholland et al. 1986; Planas 1996). Whether the bacteria can outcompete the algae for a restricted P resource, as occurs in circumneutral lakes (Jansson 1988), remains an unanswered question.

Summary of Research Needed on Zygnematalean Green Algae in Acid-influenced Habitats

- *Occurrence*—Most studies of ZGA have only considered direct cause-effect relationships between two or a few environmental factors (e.g. pH, presence or absence of a ZGA species, distribution across AMD gradients), without considering other physical, chemical, and biological variables that might influence their presence or absence. Integrative bioassays (e.g. Pringle 1987) could contribute to a better elucidation of connectivity.
- *Long-term studies*—that document the situation before and along with acidification or after neutralization in conjunction with the occurrence and productivity of ZGA are needed. Spatial replications are often overlooked. An open question is why some ZGA species that occur together over a certain span of pH collectively disappear after neutralization, but only some of these species reappear after re-acidification (e.g. Jackson et al. 1990).
- *Ecological importance*—The importance of ZGA as an algae substrate and a food base for invertebrate benthic organisms is still not adequately known. The correspondence of acidification and total biomass of insects and productivity and the relationship between grazer abundance and algae development is also not clear. The increase in algal biomass and ZGA community structure cannot be definitely explained simply by decreased top-down regulation.

- *Productivity and nutrients*—Only a few scientific studies of circumneutral systems have paid attention to the interactions between the pelagic and benthic PP. However, they should be included in studies of mining lakes with $pH < 5$. Either the pelagic or benthic PP have been determined, rarely both. The C and P limitation of ZGA are mostly estimated using C:N:P relations. Lab experiments to estimate the degree of limitation have rarely been performed, and would, in conjunction with other environmental parameters, explain the respective occurrence, species composition, and productivity. It is also not clear whether the dominating meta- or periphytic growth form of ZGA preferentially uses the water body or the sediment as the major P source, and to what extent and by which mechanisms ZGA can mobilize and use P in the presence of a surplus of P-binding partners. How the densely packed filaments of mats influence nutrient exchange as conditions of diffusion change also needs to be studied.
- *Interplay with bacteria*—In most studies, the autotrophic components of the peri- and metaphyton, i.e. the ZGA itself are studied manifold, particularly with respect to chlorophyll a concentration and PP. The heterotrophic components with bacteria and fungi are significantly less considered. There are no specific studies on the relationships between ZGA and the composition of the sediments or the influence of the sediment, e.g. the effects of pH buffering onto the algae community or the CO_2 supply from microbial mineralization. The importance of bacteria is not only restricted to the effects of the nutrient transformations within the mats, since they also play a potential role as competitors for nutrients. Whether the phosphate that is released (possibly quickly) after microbial mineralization is immediately taken up by the ZGA is unknown. Also, whether the bacteria can outcompete algae for a restricted P resource, as shown for circumneutral lakes (Jansson 1988), remains an unanswered question.

Algal physiology—The physiologic adaptations of ZGA, such as the CO_2 concentration mechanism and the mechanisms responsible for Al toxicity, are not completely elucidated over the large span of extent of acidification and the respective water types.

Acid mining lake remediation—Information on the occurrence of acidophilic ZGA, their physiological adaptations, and their ecological functions are very useful pertaining the development of acid mining lakes and strategies for acid removal, i.e. particularly their role in benthic C accumulation, sediment early diagenesis, and biogenic alkalinity generation.

3.3.2.3 Benthic primary production

Matthias Koschorreck

If light reaches the bottom of an acidic pit lake, the sediment surface will be colonized by benthic algae. The sediment surface is a favourable place for primary producers since the concentrations of nutrients as well as dissolved inorganic

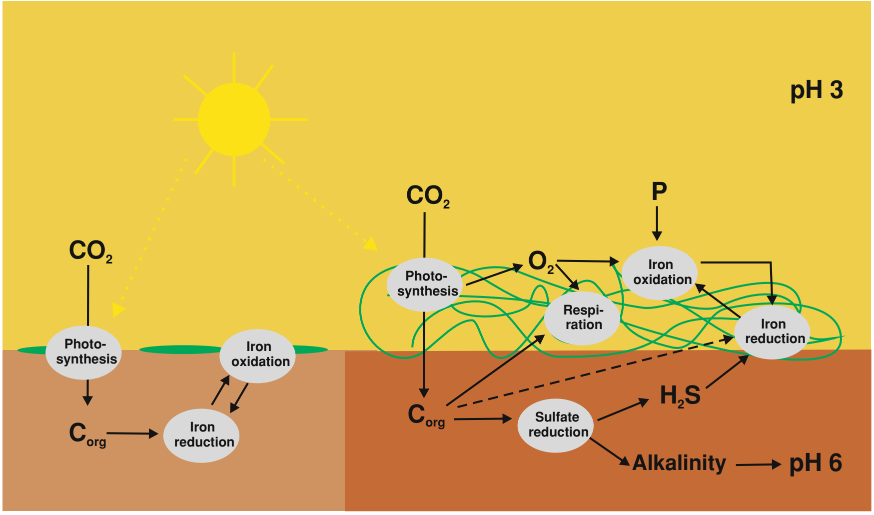


Fig. 3.68 Possible effects of benthic primary production in acidic pit mine lakes. The left part shows a benthic diatom biofilm, the *right* part shows a metaphyton layer covering the sediment

carbon are higher than in the open water (Nixdorf and Kapfer 1998). Although light intensities are often low, benthic algae can carry out photosynthesis directly at the sediment surface. This has important consequences for the biogeochemistry and also the acidity status of the lake (Fig. 3.68).

The sediment surface can be colonized by small unicellular algae, mostly diatoms such as *Eunotia exigua*, *Nitzschia palaeformis*, *Pinnularia acoricola*, or the Euglenophyte *Euglena mutabilis*, which shows highly variable abundance due to patchy growth (Lessmann et al. 1998; Kapfer, 1998). The phytobenthos can also consist of metaphytic filamentous algae, typically *Zygnemataceae* (Fig. 3.69; see also Sect. 3.3.2.2). In Mining Lake (ML) Grünewalder Lauch (ML117), 88% of the lake bottom was covered by several centimetre thick mats of *Zygogonium ericetorum* (Kleeberg et al. 2006; see also Sect. 3.3.2.2), with the highest abundance at water depths between 5 and 6 m and a mean biomass of 92 ± 96 g-dw m^{-2} (where dw indicates dry weight). These *Zygogonium* mats are P limited and seriously stressed by Fe deposition, which results in low annual primary production rates of 0.12 g C m^{-2} $year^{-1}$, which is in the range of literature values for filamentous green algae in lakes of various pH. Compared to the annual pelagic production of 43 g C m^{-2} $year^{-1}$ (Nixdorf et al. 2003), primary production by *Zygogonium* is of minor importance in Lake Grünewalder Lauch. During summer, however, benthic net primary production can be as high as 21.4 mg C m^{-2} d^{-1}. This biomass production is the basis for high rates of microbial sulfate reduction observed in the permanently anoxic sediment below the metaphyton layer (Koschorreck et al. 2007).

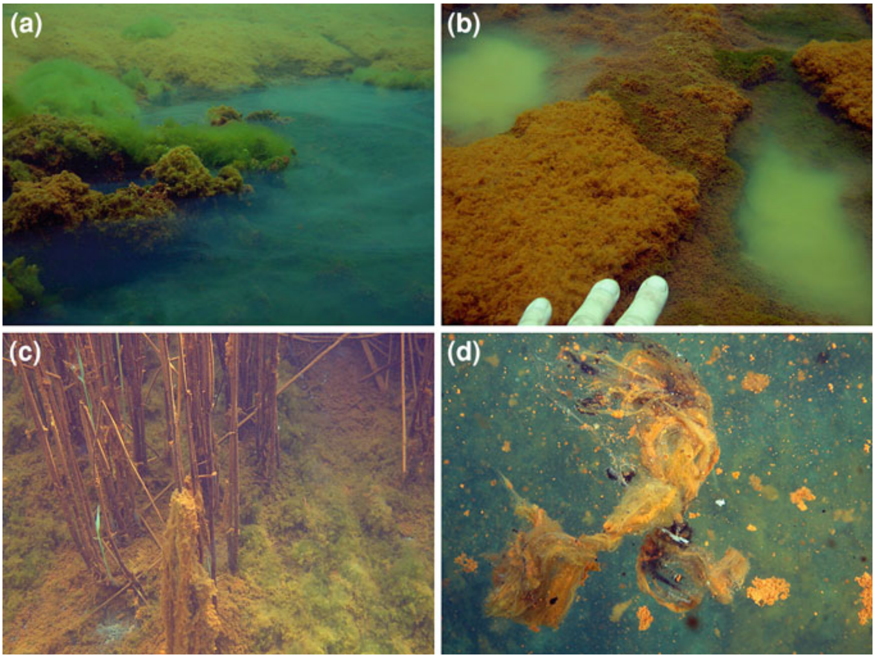


Fig. 3.69 Sediment surface of Mining Lake (ML117) Grünewalder Lauch (Germany) covered by periphytic filamentous algae (a–c) and suspended filamentous algae and iron precipitates (d; photographs: M. Beyer)

Photosynthesis carried out by the filamentous algae triggers diurnal fluctuations of oxygen in the metaphyton layer, which in turn leads to a diurnal redox-cycling of iron. Oxidation and precipitation of iron during the day scavenges phosphorus efficiently (Fig. 3.70).

Phytobenthic chlorophyll concentrations were 60 mg Chla m^{-2} in Lake Plessa 107 (pH 2.3; Lessmann et al. 1999) and in ML111 (pH 2.6; Koschorreck and Tittel 2002), about 10 mg m^{-2} in Lake 108 (pH 2.9), and about 110 mg m^{-2} in Lake Koschen (pH 3.1; Kapfer 1998).

Diatom-dominated benthic biofilms reached primary production rates of 1–5 mg C m^{-2} h^{-1} with specific rates being around 0.2 mg C mg-Chl^{-1} h^{-1}, as measured by the radiocarbon method (Kapfer 1998). Benthic gross and net primary production in ML111, as measured by oxygen microsensors, was 33 and 15 mg C m^{-2} h^{-1} at a light intensity of 15 µE m^{-2} s^{-1}, respectively (Koschorreck and Tittel 2002). The compensation irradiance of the photosynthetic benthic community was 6.8 µE m^{-2} s^{-1}, showing adaptation to low light intensities. The particular light spectrum in iron-rich acidic lakes fits the absorption spectrum of benthic diatoms better than the light in "normal", not coloured lakes. Thus, for a given photosynthetic active radiation (PAR), the benthic algae in ML111 could use 1.5 times more photons than in a non-acidic lake (Koschorreck and Tittel 2002).

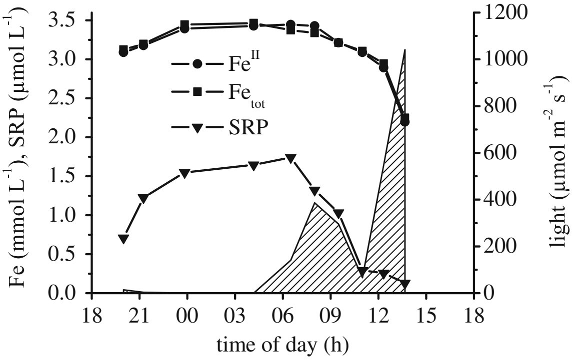


Fig. 3.70 Diurnal concentration fluctuation of dissolved iron and phosphorus in the metaphyton in lake Grünewalder Lauch (modified from Koschorreck et al. 2007). The shaded area indicates the light intensity

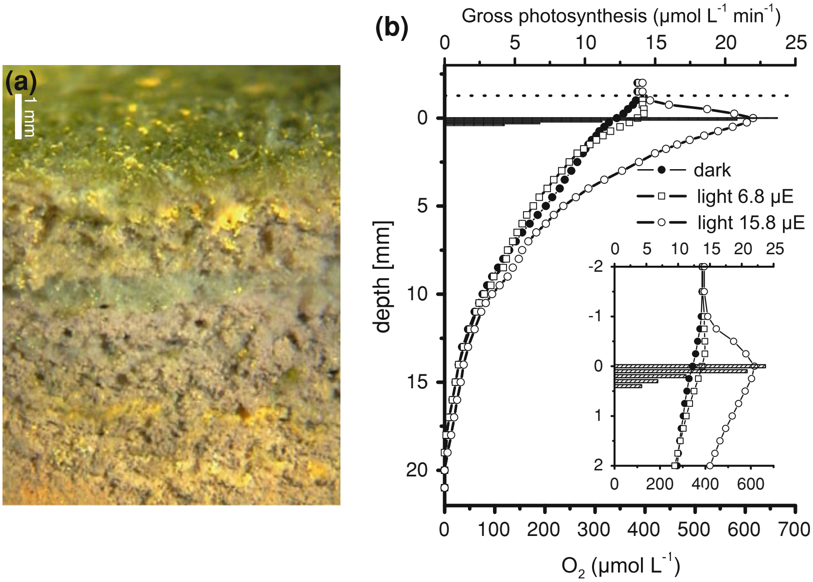


Fig. 3.71 Cross section of the sediment–water interface in ML111 showing a benthic phototrophic biofilm **a** and oxygen distribution in the light and in the dark (*lines*) as well as gross photosynthesis (bars). **b** Graph after Koschorreck and Tittel (2002). The insert shows a magnification of the water sediment interface

Although photosynthesis increased the oxygen concentration in the sediment, the oxygen penetration depth was not affected (Fig. 3.71). Thus, the direct influence of benthic diatom biofilms on the redox status of the sediments is probably of minor importance. Benthic primary production, however, is probably the most important source of organic carbon in shallow, extremely acidic mining lakes. It has been

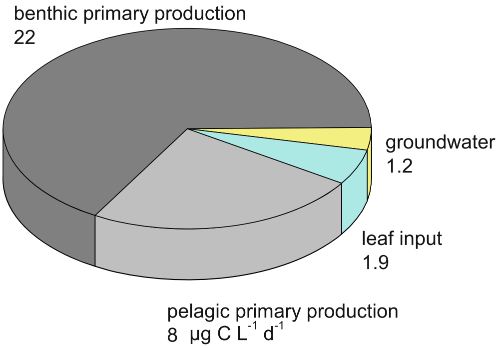


Fig. 3.72 Contribution of different carbon sources in Mining Lake 111 (data from Kamjunke et al. 2006)

estimated that it contributes about 2/3 of the organic carbon in Mining Lake 111 (Fig. 3.72). Thus, with respect to the relative role of pelagic and benthic primary production, acidic pit mine lakes are comparable to "normal" shallow lakes (Ask et al. 2009; Vadeboncoeur et al. 2001).

3.3.2.4 Benthic and Sediment Community and Processes

Katrin Wendt-Potthoff

Zoobenthos

Due to the extreme chemistry, diversity of macrozoobenthos in acidic pit lakes is very restricted. Acid-tolerant predatory corixids are common (Wollmann 2000); however, they are not strictly benthic. Invertebrates that actively shred leaf litter are absent (Mutz et al. 2000). Aquatic insects are the most common group in acid waters, with 48.3% of total taxa being *Diptera*, mostly chironomids (Rodrigues and Scharf 2001). Apparently, chironomid larvae are able to withstand the high mineral acidity, and due to the very low predatory pressure, they can reach high abundances (Table 3.25, Zullo and Stahl 1988). A species that was mistakenly identified as *Tendipes plumosus* and later designated as *Chironomus* sp. was regularly found in 11 of 19 coal pit lakes in Missouri and Kansas, most of which had strongly acidic water and sediments (Harp and Campbell 1967). The authors reported that occurrence of the larvae was more related to the presence of leaf detritus than to pH, indicating that lack of food sources constrained them more severely than water or sediment chemistry. Only in the most acidic lake (Lake A_1, pH 2.3, potential free acidity 819–9,090 mg $CaCO_3$ L^{-1} = 16.4–182 mmol L^{-1}) were pupae unable to emerge. A pit lake of the same pH and acidity ($K_{B4.3}$) of 30.9 mmol L^{-1} in Lusatia had a slightly lower chironomid density, and there was no data on emergence but evidence of predation by corixids (Lessmann et al. 1999, Table 3.25). Harp and Hubbard (1972) studied the benthic fauna of bauxite open-pit lakes in Arkansas, which resemble coal pit lakes with respect to pH, but have a different metal chemistry (iron = 0.2–13.9 mg L^{-1}, aluminum = 5.2–49.7 mg L^{-1}). Their sediments had a similar density of benthic animals as the iron-rich coal pit lake, Lake 111 in Lusatia, which

Table 3.25 Abundance of chironomid larvae in acidic pit lakes

Lake	pH	Individuals (m^{-2})	Comments	Source
A1	2.3–3.2	0–7,435	Pupae were unable to emerge	Harp and Campbell (1967)
A3	3.4–4.1	0–40,124		Harp & Campbell (1967)
Lake 107	2.3	0–430	*C. plumosus* group	Lessmann et al. (1999)
Bauxite pit lakes 1–4	2.9–3.4	511–5,479	Total benthic fauna counts, but almost entirely *Chironomus* sp.	Harp and Hubbard (1972)
Lake 111	2.6	0–4,500	*C. crassimanus*	Lagauzère et al. (2011)
Bradley's acidic pit	2.30–3.85	3,055–14,137 (49,972)[a]	*C.* near *maturus*	Zullo and Stahl (1988)
Bradley's acidic pit	2.30–3.85	0–17,352 (50,105)[a]	*Tanytarsus dendyi*	Zullo and Stahl (1988)

[a] The range given comprises all sampled depths and seasons with *: the range of numbers in transects and the maximum station density indicated with parentheses

appears to be a medium value (Table 3.25). Analysis of the gut contents of *Chironomus crassimanus* larvae from this lake revealed that they mainly fed on filamentous bacteria, fungal hyphae, and photosynthetic microorganisms (Rodrigues 2001).

The seasonal development and reproductive cycle of chironomids in acidic pit lakes have rarely been studied in detail (Zullo and Stahl 1988), and their relevance might have been overlooked by common episodic sampling. It has been demonstrated for natural freshwater environments that the bioturbation and feeding activity of chironomids play an important role in matter transport and sediment biogeochemistry (Nogaro et al. 2008). Therefore, in acidic pit lake sediment where they dominate the sediment macrofauna, effects of their bioturbating activity should be significant. To date, there is only one study dealing with the effects of burrowing chironomids on acidic pit lake sediments (Lagauzère et al. 2011). The authors found a three-fold increase of the diffusive oxygen uptake by the sediment, indicating a stimulation of organic matter mineralization. Iron transformations were also influenced (lower rates of oxidation and reduction, stimulation of mineral transformations, increased abundance of iron-oxidizing bacteria), but the flux of iron across the sediment–water interface was not affected.

Among the meiofauna, mites and nematodes are present in acidic pit lake sediments. Rodrigues and Scharf (2001) detected *Hydrozetes lacustris* in exposed leaf packs in three lakes, with increasing abundance from water pH 2.3 to 3, while nematodes were not found at pH 2.3. A later transect study by Traunspurger (pers. comm.) revealed the presence of both nematodes and water mites in Lake 111 sediment, which did not show a systematic relation to water depth. Nematodes comprised 8 species feeding on bacteria and fungi, with *Prismatolaimus* sp. being dominant.

There is little information available on microzoobenthos of acidic pit lakes. Bell and Weithoff (2008) reported the importance of benthic recruitment of the dominant zooplankton organisms, rotifers and heliozoans, in littoral sediments in Lake 111 in Lusatia. Protozoan and metazoan abundance in the sediment did not exceed 25 individuals cm^{-3}; however, these values were comparable to rotifer densities of other, natural lakes. The testate amoeba, *Arcella vulgaris*, has been found to inhabit even the most acidic ($pH < 2$) part of James Lake, a lake acidified by dumping of waste rock from pyrite mining (Kumar and Patterson 2000).

Microbial Numbers and Biomass

Sedimentation rates have been determined for several acidic pit lakes (Siefert and Mutz 2001: 0.9–4.9 g m^{-2} d^{-1}). A considerable part of the sedimenting material may be ferric iron, as indicated by schwertmannite sedimentation rates of 1–4 g m^{-2} d^{-1} (Peiffer 1999) or iron sedimentation of 1.4 g m^{-2} d^{-1} in Lake 77 (Küsel 2003). This is in contrast to natural lakes of similar depth, where dead biomass is a more important fraction of sedimenting material. Despite this, sediment bacterial counts in acidic pit lakes appear to be similar to those of natural lake sediments. Average bacterial densities in the upper 2 cm of Lake 111 sediment, determined by epifluorescence microscopy, were $0.82 \pm 0.26 \times 10^9$ g-dw^{-1}, which corresponds to $1.01 \pm 0.34 \times 10^9$ cells cm^{-3} or a mean bacterial biomass of 22.48 ± 7.13 μg C cm^{-3} (Bell and Weithoff 2008). Maximum cell counts reached 1.6×10^9 g-dw^{-1} or 1.97×10^9 cm^{-3}. These numbers were approximately three orders of magnitude higher than pelagic counts and did not show pronounced seasonal trends. They were also in the same range as in other freshwater environments (Bell and Weithoff 2008). The sediments of the extremely acidic and metal-rich Berkeley Pit also contained 3×10^9 cells per gram sediment (Cameron et al. 2006). When bacterial counts are converted from phospholipid phosphate values instead of counting cells microscopically, values tend to be considerably higher for surface sediments. On a basis of 11 sampling campaigns from 2001–2004, the upper 2 cm of Lake 111 sediment yielded cell numbers of $3.4 \pm 1.2 \times 10^{11}$, corresponding to 9.5 ± 3.5 mg C g-dw^{-1} bacterial biomass (Wendt-Potthoff, unpublished). These values are roughly two orders of magnitude higher than the counts of Bell and Weithoff (2008). The discrepancy can be explained by the fact that the phospholipid phosphate method does not discriminate between bacteria and other viable microbial biomass such as fungi, microalgae, or protists. Phospholipid-phosphate based values for surface sediments of other pit lakes were similar (Table 3.26), and they did not show a clear relation to pH. This was further tested using a set of 194 sediment samples from different pit lakes (Fig. 3.73a). The data showed no correlation between biomass and pH, but illustrated that there are few sediment samples with intermediate pH values. A similar distribution has already been documented for the water column of such

Table 3.26 Biomass, cell counts and carbon contents in surface sediments (upper 2 cm) of pit lakes based on phospholipid phosphate extraction of duplicate samples

Lake	N	Sediment pH	nmol P ($g\text{-}dw^{-1}$)	Cells ($g\text{-}dw^{-1}$)	Microbial carbon (mg $g\text{-}dw^{-1}$)
Lake 111	11	2.8 ± 0.4	851 ± 310	$3.4 \pm 1.2 \cdot 10^{11}$	9.5 ± 3.4
Lake 117 with filamentous algae	1	6.2	1,066	4.3×10^{11}	11.9
Lake 117 without filamentous algae	1	4.2	1,242	5.0×10^{11}	13.8
Lake 107	1	2.3	93	3.7×10^{10}	1.0
Lake Niemegk	1	2.8	376	1.5×10^{11}	4.2
Lake B	1	7.0	221	8.8×10^{10}	2.5

N is the number of sediment samplings, and results for Lake 111 are given with standard deviation

lakes (Geller et al. 1998). However, microbial biomass was negatively correlated with sediment depth (Fig. 3.73b; Pearson Product Moment correlation: P value 3.26×10^{-9}).

Prokaryotic Diversity in Pit Lake Sediments

Some attempts have been made to obtain a general overview of the prokaryotes present in a pit lake, e.g. clone libraries were generated from pit lake sediment after amplifying the 16S rRNA gene. The prokaryotic diversity in acidic pit lake sediments is obviously higher than that of extremely acidic mine waters, but apparently these communities comprise a considerable number of similar organisms. However, since the detected clones are often only distantly related to known organisms, this approach is more suited to comparing different locations or sampling events than to infer microbial physiology at the studied site. Pham et al. (2007) found mostly Proteobacteria, Actinobacteria, and Firmicutes when applying DGGE profiling to a sediment transect of Lake Kepwari, an oligotrophic pit lake in Western Australia (pH 4.5–5). Bacterial diversity appeared to be higher in samples of intermediate depth (10 and 18 m) than in very shallow or deep water (0 and 29 m). Sulfate-reducing bacteria belonging to the genera *Desulfomonile*, *Desulfococcus*, *Desulfobacterium*, and *Desulfomicrobium* were detected except in the 10 m sample, which in contrast was the only one containing Acidobacteria. However, the number of analyzed bands and clones was low, so this picture is probably incomplete.

A rRNA-based clone library was generated from the sediment of the strongly acidic (water pH 2.7, sediment pH 2.5–3.6) Lake 111 (Meier et al., in revision; Müller 2004). In this study, sulfate reducing bacteria were not detected. Beside a large number of clones retrieved from algae chloroplasts, the largest group of clones was found within the Xanthomonadaceae. These clones are closely related to phylotypes and to cultures retrieved from other acid mine drainage

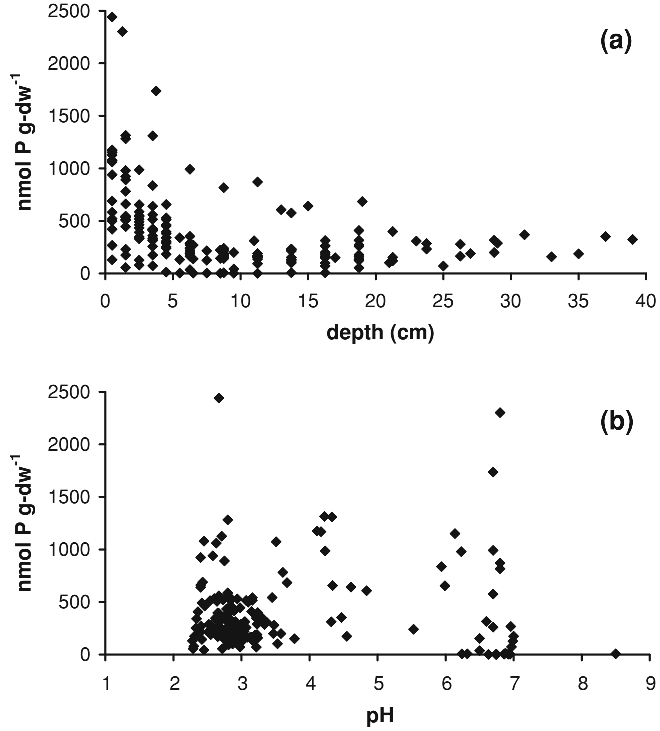


Fig. 3.73 Relationship between **a** sediment depth and microbial biomas and **b** sediment pH and microbial biomass

environments. The next relative genera were *Dokdonella*, *Frateuria*, *Dyella*, *Rhodanobacter*, *Fulvimonas*, and *Luteibacter*, but sequence similarities were $\leq$91%. The second largest group of clones also belonged to the Gammaproteobacteria. Again, they resembled phylotypes retrieved from AMD environments, but sequence similarities to the next cultivated species were $\leq$89%. Other important genera (several percent of the clones) that are also well-known from other acidic habitats were Acidobacteria, Alphaproteobacteria of the *Acidiphilium* group, *Acidimicrobium*, *Sulfobacillus*, *Leptospirillum*, *Chloroflexi*, and *Entotheonella*. The diversity of archaeal clones was low. All of them belonged to the Thermoplasmatales and were related to phylotypes from the Río Tinto and other acid mine drainage sites (sequence similarities 89–99%).

Blöthe et al. (2008) investigated the prokaryotic diversity in the sediments of Lake 77 in Lusatia, Germany. The sediments of this lake possess geochemically different zones, an upper acidic zone I (pH 3), a transition zone II, and a weakly acidic zone III (pH 5.5). Zone I and zone III were studied separately by 16S rRNA based community analysis. Denaturing gradient gel electrophoresis (DGGE) screening revealed 40 and 42 different phylotypes in zones I and III, respectively.

A large fraction of the clones (45 and 43% in zones I and III, respectively) belonged to the phylum *Acidobacteria*, which is remarkably different from Lake 111 (discussed above). Other sequences detected in both zones were affiliated to *Nitrospira*, Cytophagales, Alpha-, Gamma-, and Deltaproteobacteria. Among the Alphaproteobacteria, many belonged to the genus *Acidiphilium*, members of which have also been cultured from pit lake sediments (Küsel et al. 1999). No archaeal sequences were obtained. While sequences related to Firmicutes, *Actinomyces*, and Betaproteobacteria were only found in zone I, sequences related to *Verrucomicrobia* subdivision 5, *Thermus*/*Deinococcus*, *Bacillus*/*Clostridium*, and an uncultured group were only obtained from zone III. These findings are comparable to those of Becerra et al. (2009), who studied an old abandoned mine site in Massachusetts where an AMD-generating zone (GZ; pH 1.7–2.4) and an AMD-attenuating zone (AZ; pH 4.5–6.0) could be distinguished. The authors detected 44 and 45 operational taxonomic units (OTUs) at the GZ and AZ, respectively. *Acidobacteria* were important components of the community in both zones, and Alphaproteobacteria were also present in GZ and AZ. Members of the Nitrospira (*Leptospirillum*) were only detected in the GZ, where they comprised the majority of clones. Similar to the findings of Blöthe et al. (2008), clostridia were only important in the higher pH AZ. However, Becerra et al. (2009) also undertook a rarefaction analysis, which revealed that sampling was inadequate for covering bacterial diversity in both zones and that GZ and AZ could contain 3.1–4.4 and 1.3–1.7 times the number of OTUs found in the clone library.

It can be concluded that results have to be complemented by additional studies, including rarefaction analysis, to really understand diversity in pit lake sediments. Future research should aim at obtaining a better taxonomic resolution of some groups and include comparative rRNA-based analyses of sophisticated culture or microcosm approaches.

Microbially Mediated Sediment Processes

In general, the same sequence of terminal electron-accepting microbial processes from oxic respiration to methanogenesis may be expected in pit lakes sediments as in natural sediments, although it is evident that the absolute or relative intensities of processes differ considerably due to the extreme chemistry.

A special case is the littoral sediment, which is often sandy with a patchy distribution of microphytobenthos (Sect. 3.3.2.3) or colonized by bulbous rush, *Juncus bulbosus* (Chabbi 1999). In the practically unvegetated littoral sediment of Lake 111, relatively deep oxygen penetration (up to 24 mm) has been observed. The accompanying diffusive oxygen fluxes of 3.1 ± 1.6–8.4 ± 0.4 mmol m^{-2} d^{-1} (Koschorreck et al. 2003a, 2004) were an order of magnitude lower than in natural lakes (Wendt-Potthoff and Koschorreck 2002), which indicates a relatively low respiratory activity. The general presence of Fe(II) in acidic pit lake sediments suggests that microbial Fe(II) oxidation should make an important contribution to O_2 consumption near the oxic sediment–water interface. However, no in situ evidence for this process was found by Koschorreck et al. (2003a), and the observed disappearance of dissolved Fe(II) was rather due to jarosite precipitation within the sediment. In contrast, a laboratory incubation of the same sediment revealed a potential biological Fe(II) oxidation rate of 0.65 mmol cm^{-3} h^{-1} (Wendt-Potthoff and Koschorreck 2004). The range of CO_2 production rates in this sediment was 6–42 mmol m^{-2} d^{-1}, with maximum values in the summer months (Koschorreck et al. 2004), which is higher than in the profundal sediment and comparable to natural lakes. This suggests that heterotrophic aerobic activity was responsible for O_2 consumption in the littoral sediment of Lake 111. The same study reported potential iron reduction rates in the range of 6–45 mmol m^{-2} d^{-1}, depending on the season. The depth of maximum activity varied, and potential Fe(III) reduction was regularly detected near the sediment surface. Active zones generally showed elevated most probable number (MPN) counts of acidophilic Fe(III) reducing bacteria. This suggests Fe(III) reduction by oxygen-tolerant organisms such as *Acidiphilium* or *Acidobacterium*, which have been shown to carry out Fe(III) reduction under micro-oxic conditions (Coupland and Johnson 2008; Johnson and Bridge 2002).

Many littoral sites in acidic pit lakes are colonized by *Juncus bulbosus*, e.g. Lake 108 in Lusatia (Chabbi 1999). The plant roots release oxygen into the sediment, which stimulates microbial Fe(II) oxidation and the formation of ferric crusts (plaques) around the roots. Contrary to other plants, the crusts are not directly attached to the root, but a space is left which is colonized by microorganisms (Chabbi 1999). High numbers of Fe(III) reducing bacteria and other organisms have been found to be associated with the roots (Küsel et al. 2003), which apparently live from root exudates. The CO_2 they generate during respiration is beneficial for the plants in an environment with limited inorganic carbon (Koschorreck et al. 2004).

Iron plaques also form on leaf litter sedimenting in the acidic pit lakes. Although this process triggers trapping of fine particulate material and biofilm formation, it leads to incomplete decomposition, making the leaves only a temporary carbon source (Schlief and Mutz 2005). However, compared to streams affected by acid mine drainage, iron plaque formation was weaker on sedimented leaves in a pit lake, which was accompanied by higher fungal biomass and respiration rates (Schlief and Mutz 2005).

Nitrate reduction and manganese reduction are not important in acidic pit lake sediments, since their nitrate and Mn concentrations are low (Schultze et al. 2010). Low nitrate concentrations are common because nitrification is inhibited at low pH.

Iron reduction is the dominant terminal electron accepting process for the oxidation of organic matter, hydrogen, or reduced sulfur in acidic pit lake sediments (Johnson 1995; Küsel and Dorsch 2000; Langner 2001). Signs of microbial Fe(III) reduction are reported from most investigated sediments, even the extremely metal-rich Berkeley pit (Twidwell et al. 2006), but few studies report quantitative in situ rates. Generally, maxima of potential Fe(III) reduction are accompanied by elevated viable counts of Fe(III) reducing microorganisms (e.g. Koschorreck et al. 2007a; Meier et al. 2004; Wendt-Potthoff et al. 2002). Despite this correspondence, viable counts are too low to explain the observed activities, which is easily seen if cell-based rates are calculated (e.g. Meier et al. 2005). More effort is needed to detect and isolate the organisms responsible for Fe(III) reduction in such systems. If available, Fe(III) reduction rates are comparable to or even higher than those found in iron-rich freshwater environments (Table 3.27), although physiologically and phylogentically different organisms are responsible for the observed activities. However, comparison is not trivial, since there is no good standard for quantifying in situ Fe(III) reduction, such as ^{35}S-sulfate used for in situ sulfate reduction measurements. Rates based on Fe(II) fluxes are not necessarily the same as those from anoxic batch incubations with total Fe(II) determined over time.

Despite the generally large sulfate pools and cultivation-based detection of sulfate-reducing bacteria in acidic pit lake sediments, sulfate reduction is only rarely detected. Similar to Fe(III) reduction, there are often reliable signs of this process, but no quantification of the activity. For example, laboratory incubations revealed sulfate reducing activity in the littoral zone of Lake Kepwari, Australia (Read et al. 2009). This is in contrast to the well-studied Lake 111, where sulfate reduction was measured in a deep small basin (Meier et al. 2004), but not in the littoral zone (Koschorreck et al. 2004). However, another acid, nutrient-rich pit lake, Cueva de la Mora in the Iberian Pyrite Belt, had much higher sulfate reduction rates in the mixolimnetic compared to the monimolimnetic zone (Wendt-Potthoff et al. 2012). Examples of spontaneous (without substrate addition or other treatments) sulfate reduction rates in pit lakes are given in Table 3.28. Low pH alone does not preclude sulfate reduction, and H_2S or organic acid concentrations observed in pit lake environments are too low to be inhibitory (Koschorreck 2008). Competition with iron reduction and electron donor limitation are more likely explanations (Blodau and Peiffer 2003; Koschorreck 2008), and this aspect is further discussed in the following subsection.

In contrast to natural freshwater ecosystems, methanogenesis is generally negligible in acidic pit lakes. This is not a consequence of the low pH, as methane formation is an important process in acid peatlands, swamps, and mires (Bergman et al. 1998; Cadillo-Quiroz et al. 2006). Methane formation is inhibited by the high sulfate concentrations in the sediments (in the g L^{-1} range, see Sect. 3.2 on pit lake chemistry). In a lake acidified by volcanism, methanogenesis was found to take place in deeper sediment layers, where the pH value was above 4 and sulfate reduction became sulfate limited (Koschorreck et al. 2008). Low concentrations of methane (10–60 μmol L^{-1}) were detected in the sediments of Lake 166 in Lusatia (Blodau et al. 1998). The Spanish pit lake Cueva de la Mora, which is considerably enriched in carbon and nutrients, also had methane concentrations between 15 and 70 μmol L^{-1} in the monimolimnetic sediments, but incubation assays failed to detect methanogenic activity (Wendt-Potthoff et al. 2012).

Iron and Sulfate Reduction and Potential for Remediation

If sulfate and iron reduction coexist in a given sediment, these reactions might reverse the acidification caused by pyrite oxidation, and to a certain extent, pyrite will be formed again. Generally, the addition of suitable substrates to pit lake

Table 3.27 Fe(III) reduction (FeR) in pit lake (P.L.) sediments and natural freshwater sites; n.a.: not available

Lake	Type, location	Sediment pH	Method	FeR (nmol cm^{-3} d^{-1})	FeR (mmol m^{-2} d^{-1})	Reference
Lake 77, zone I[a]	P.L., Germany	≈3	Batch incubation	204		Küsel and Dorsch (2000)
Lake 77, zone I[a]	P.L., Germany	≈3	Batch incubation	250		Peine et al. (2000)
Lake 77, zone I[b]	P.L., Germany	3	Batch incubation	710		Blöthe et al. (2008)
Lake 77, zone II[b]	P.L., Germany	5.5	Batch incubation	895		Blöthe et al. (2008)
Lake 116 littoral	P.L., Germany	3– >6	Pore water profile/flux	150	6.9	Blodau et al. (1998)
Lake 116 pelagial	P.L., Germany	3– >6	Pore water profile/flux	50	3.8	Blodau et al. (1998)
Lake Niemegk	P.L., Germany	2.6–5	Pore water profile/flux	5,000		Langner (2001)
Cueva de la Mora mixolimnion	P.L., Spain	2.8–3.2	Batch incubation	585–627	6.06	Wendt-Potthoff et al. (2012)
Lake 117	P.L., Germany	6	Pore water profile	150–260	2.6	Koschorreck et al. (2007b)
Lake 111	P.L., Germany	2.7	Batch incubation	670		Wendt-Potthoff (unpublished)
Great Ghost Lake	Oligo-mesotrophic, Taiwan	n.a.	In situ accumulation of Fe(II)		5.07	Wann et al. (1997)
Baldeggersee littoral	Eutrophic lake, Switzerland	n.a.	flux		0.06	Schaller et al. (1997)
Baldeggersee pelagial	Eutrophic lake, Switzerland	n.a.	Flux		0.15	Schaller et al. (1997)
Kalix River estuary	Estuary, Sweden	n.a.	Pore water profile		0.77	Widerlund and Ingri (1996)

[a] probably an underestimate, since only dissolved Fe(II) was measured; [b] incubated at 15°C, although the maximum sediment temperature was 12°C

Table 3.28 Sulfate reduction (SR) in the sediments of acid lakes measured by ^{35}S tracer technique. The lakes are pit lakes except Lake Caviahue, which is a glacial lake acidified by volcanism

Lake	pH of water	pH of sediment	SR (nmol cm^{-3} d^{-1})	SR (mol m^{-2} d^{-1})	References
Reservoir 29	2.7	3.8	16–152		Gyure et al. (1990)
Lake 111 (10 m)	2.6	>4	1.6–7.2		Meier et al. (2004)
Lake 116	3	>6	17–130	1.2–5.2	Blodau et al. (1998)
Lake 76	2.8	>6	70		Blodau et al. (2000)
Lake 77	3	>5	6		Peine et al. (2000)
Lake 117	3.1	6	57–265		Koschorreck et al. (2007b)
Cueva de la Mora (mixolimnion)	2.5	2.8–3.2	4.5–314	13	Wendt-Potthoff et al. (2012)
Cueva de la Mora (monimolimnion)	3.6–4.3	4.3–4.9	0.2–2.3	0.1	Wendt-Potthoff et al. (2012)
Lake Caviahue	2.6	3	33		Koschorreck et al. (2003)

sediments increases both iron and sulfate reduction (e.g. Becerra et al. 2009; Koschorreck et al. 2007a; Küsel and Dorsch 2000; Langner 2001; Meier et al. 2005; Wendt-Potthoff et al. 2002). However, many pit lake sediments do not show sulfate reduction at all, and the estimated times for neutralization in others are very long (several hundreds or more than a thousand years: Blodau and Peiffer 2003; Peine and Peiffer 1998; Wendt-Potthoff et al. 2012). The long times for neutralization are due to a considerable reoxidation of sulfides in lake systems (Koschorreck and Tittel 2007), which is hard to control during any in situ remediation approach (Geller et al. 2009; Chap. 4). Blodau and Peiffer (2003) demonstrated that the neutralization process is constrained by organic matter quality and thermodynamic effects, which together control the relative rates of sulfate and iron reduction. Substantial amounts of iron sulfides were only formed at a simultaneous partial thermodynamic and solubility equilibrium of the involved biogeochemical processes. If this is not reached, the sediments remain in an Fe(III) reducing and sulfide oxidizing state, despite addition of organic matter and nutrients. In addition to organic matter quality and low pH, which thermodynamically favors Fe(III) reduction, the supply of reactive Fe(III) is a key factor. This is demonstrated by many cases in addition to those discussed by Blodau and Peiffer (2003). For example, the deep part of Lake 111, which in contrast to the rest of the lake shows low rates of sulfate reduction (Meier et al. 2004; Table 3.28) has been excluded from lake overturn for several years and has developed a small reduced bottom water body. This might have greatly reduced the supply of Fe(III) to the sediments. Lake Caviahue, a glacial lake acidified by volcanism with active sulfate reduction, not only had substantial production of biomass, which was precipitated by volcanic ash following an eruption, but also has a relatively low iron content compared to acidic pit lakes (Koschorreck et al. 2003b; Table 3.28). As a consequence, it might not be sufficient to add a cheap carbon source or lime to an acidic pit lake to neutralize it, but biological production and inflows of iron, carbon, acidity, and sulfate have to be studied carefully to plan a sustainable treatment, if necessary.

In conclusion, despite restricted colonization by benthic invertebrates and practical absence of some microbial processes typical for freshwater lakes, the sediments of acidic pit lakes show considerable microbial diversity compared to extremely acid mine sites, and biomasses and total microbial activities comparable to natural lakes. Further research is necessary to unravel the true microbial diversity of pit lake sediments and its relation to environmental factors. It will be both of scientific and practical interest to better quantify rates of Fe(III) reduction (also in natural freshwater bodies) and to identify and isolate the organisms responsible for Fe(III) reduction at acid and intermediate pH values. This should include the more systematic study of different habitats in acidic pit lakes, such as littoral and profundal zones, vegetated and unvegetated sediments, and chemoclines in meromictic lakes. If neutralization of an acidic pit lake is attempted, such studies will complement approaches to get reliable estimates on carbon and nutrient supply, inflows of iron, acidity, and sulfate, which are all necessary to plan realistic and sustainable treatment options.

3.4 Modeling of Pit Lakes

Donald S. Dunbar

3.4.1 Introduction

The long-term planning and allocation of financial resources required for effective monitoring and remediation of pit lakes can benefit immensely from defensible predictions of physical and geochemical pit lake properties in advance of lake formation. In this section, we consider numerical computer models that are designed to simulate the evolution and spatial distribution of physical and/or geochemical properties of pit lakes. The discussion is limited to models designed for long-term simulations spanning decades or even centuries. Other types of pit lake models, such as those designed for predicting biological productivity will not be addressed.

Model predictions can provide regulators, mine operators, and other stakeholders with information critical to anticipating and addressing water quality concerns that are likely to arise after cessation of mining and dewatering, such as: filling rates and the timing of overtopping; water column stability, stratification, overturning, and the onset of meromixis, and; the evolution and spatial distribution of pH, sulfate, dissolved metals, and other chemical species.

Flooded open pits, unlike most natural lakes, are typically deep and steep-sided with large values for the relative depth, z_r, given by

$$Z_r(\%) = 100\frac{Z_m}{d}, \tag{3.27}$$

where Z_m is the maximum depth and d is the mean lake diameter (Gammons and Duaime 2006). Defining $d = 2\sqrt{A/\pi}$ for lake surface area A yields

$$Z_r(\%) = 50Z_m\sqrt{\frac{\pi}{A}} \tag{3.28}$$

The small fetch (i.e. length of lake surface exposed to wind-energy) and large depth result in relatively ineffective downward transfer of wind energy, thereby limiting vertical mixing. Natural lakes that exhibit strong stratification and are poorly mixed typically have z_r values greater than 4; by contrast, well-mixed natural lakes have z_r values generally less than 2.

Pit lakes, and their related environmental issues, share common characteristics that provide a unique challenge to computer modelers. The large relative depth has important implications for the downward penetration of thermal and wind energy, and their concomitant effects on vertical mixing and stability. Unlike natural lakes, which typically have a layer of organic matter at the bottom, the bottom of a pit lake–initially at least–consists of bare (and commonly, oxidized) rock. In addition, the time scales for environmental issues related to pit lakes often span decades or even centuries.

3.4.2 Physical Properties of Pit Lakes

3.4.2.1 Water Density

Density in freshwater lakes is largely determined by temperature. The density of pure liquid water attains a maximum of 0.99998 g/cm^3 at 3.94 °C. Therefore, dense lake bottom waters tend to remain near 4 °C while the temperature near the surface varies in response to inflows and atmospheric conditions.

The addition of dissolved salts to freshwater results in an increase in density. Seawater, for example, has a density approximately 2.8% greater than freshwater. Pit lakes contain water that has a wide range of dissolved salts and other geochemical species due to inflows of groundwater, precipitation, and surface inflow that has contacted exposed pit wall surfaces. Thus, both water temperature and salinity influence the density of water in pit lakes. The density of pit lake water is calculated by applying an empirical equation of state relating water temperature and the concentration of dissolved ions (salinity) to water density. Salinity can be accurately determined by measuring the conductivity of the water. The equation of state for water is nonlinear with temperature for a fixed conductivity, and nearly linear with conductivity for a fixed temperature (Fig. 3.74).

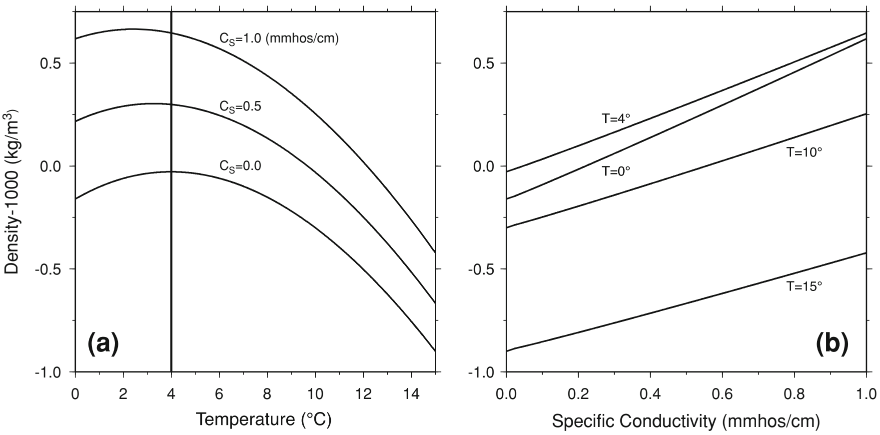


Fig. 3.74 Water density for different values of **a** temperature T, and **b** specific conductivity

3.4.2.2 Vertical Stability

Deep, freshwater lakes typically have at least two layers: a bottom hypolimnion, whose waters are at least seasonally isolated from the atmosphere (and sometimes perennially stagnant), and an upper epilimnion, which is well mixed by the wind. The two layers are separated by a relatively thin thermocline defined by a strong thermal gradient.

The physical stability of a stratified system can be described by the tendency for the upper and lower water layers to mix. The energy required to vertically mix two water masses increases with the density difference between the two layers. Specifically, given two layers of density ρ_1 and ρ_2, of equal volume and thickness, h, the energy required to mix the two volumes completely, ignoring viscous dissipation of energy, is:

$$\frac{gh\Delta\rho}{2} \tag{3.29}$$

Figure 3.75 shows the energy required to raise the center of mass of the original two layers to their geometric center.

Increasing density with depth decreases the tendency of two water masses to mix. Large density contrasts across the density gradient, or pycnocline, suppress mixing and therefore increase the vertical stability of the water column.

Dimictic Lakes

Many natural and pit lakes experience regular, seasonal ice cover, with the timing and duration dependent primarily on latitude and altitude, but also on inter-annual variability of air temperature, wind velocity, and solar radiation. A period of ice

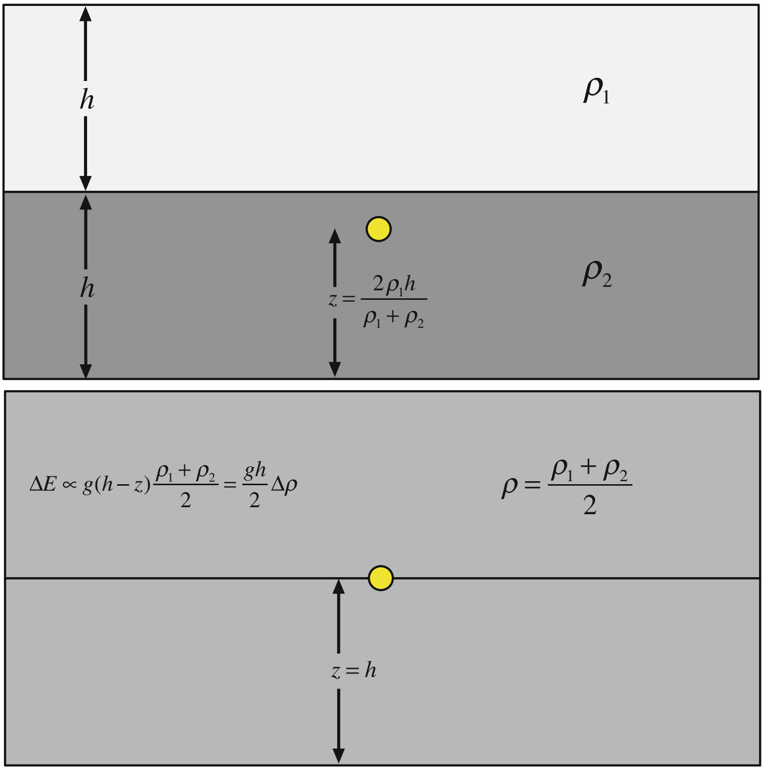


Fig. 3.75 Energy required to completely mix two equal water volumes with different densities. The *yellow dot* marks the location of the centre of mass

cover, and the changes in lake temperature that precede and follow it, profoundly affect the physical properties of lakes. From thermally stratified conditions in late summer, lake surface waters cool and increase in density as fall approaches until a temperature of approximately 4 °C is reached, at which point maximum density is attained and the lake convectively mixes. The degree of mixing depends on the lake depth and vertical density gradient. Some lakes mix fully every year, while others mix fully only occasionally. If meromixis has occurred due to high bottom layer solute concentrations and a stable monimolimnion has formed, then complete mixing is inhibited and is limited to the upper layers of the lake.

If the temperature decreases sufficiently, then ice will begin to form, thickening over the winter months. The lake will again become thermally stratified, with less dense 0 °C water in a surface layer overlying warmer, denser water below. The ice thermally insulates surface waters from the cooler air above and eliminates wind mixing. Snow accumulates on the ice, storing water until it thaws with the arrival of warmer temperatures. With the formation of ice, the level of the lake will often drop as surface inflows decrease or stop altogether. Some solutes may become supersaturated immediately under the ice due to salt expulsion as the ice forms.

During the subsequent spring and summer thaw, the snow and ice melt and their volumes are added to the lake over a relatively short interval together with runoff from the surrounding watershed. This sudden influx of water (freshet) may represent a significant portion of the annual surface water budget.

As surface waters warm and the ice and snow melt, the water density increases as the temperature climbs toward 4 °C. Again, convective mixing occurs, and in the case of most natural lakes, complete overturning. The twice-annual cycle of fall-winter and spring-summer overturning is the defining characteristic of dimictic lakes. Because of their importance in lake dynamics, ice formation and thawing are important processes to include in models of pit lakes where this occurs (Hamblin et al. 1999; Patterson and Hamblin 1988; Rogers et al. 1995).

3.4.3 Geochemical Processes Influencing Pit Lake Chemistry

The density structure of stratified lakes has an important influence on the chemical and biological processes occurring in both the water column and sediments. In particular, the restricted mixing across the pycnocline can result in the depletion of O_2 and the accumulation of other chemical species associated with the breakdown of organic matter in the lake interior. In natural aquatic systems, dissolved oxygen is consumed principally by bacterially-mediated oxidation of organic matter (OM; Fenchel and Blackburn 1979; Stumm and Morgan 1981). OM produced in the surface waters (i.e. plankton, zooplankton) is delivered to the interior of the lake and lake bottom via the settling of organic detritus.

Due to the downward transport of OM, the oxidation reactions associated with its degradation occur throughout the water column. Organic matter is oxidized or remineralized by both aerobic and anaerobic bacteria. These remineralization reactions are redox processes in which electrons are transferred from the reductant (OM) to an electron acceptor (oxidant). In shallow lakes, much of the oxidation of OM occurs at the sediment–water interface, while in deeper lakes, significant OM oxidation can occur in bottom water (Hamilton-Taylor and Davison 1995; Northcote and Johnson 1964). Collectively, these oxidation processes result in depletion of oxygen in the bottom waters. Without deep water mixing and associated replenishment of oxygen, or where the OM flux to bottom waters is high (as in productive or eutrophic lakes), oxygen-consuming reactions can completely deplete oxygen in bottom waters leading to anoxia.

In aerobic environments, oxygen is preferentially used as the final electron acceptor in the oxidation of OM. Once oxygen is depleted, other electron acceptors are employed. Based on decreasing free energy yield, thermodynamics dictates that electron acceptors are used in the order: $O_2 > NO_3^- \approx Mn^{IV}$-oxides $> Fe^{III}$-oxides $> SO_4^{2-}$ (Froelich et al. 1979; Sigg et al. 1991; Stumm and Morgan 1981). Once oxygen has been exhausted as an oxidant, nitrate will be employed as the electron acceptor for OM oxidation, followed by Mn-oxides.

The development of anoxic bottom waters can greatly influence the behavior of trace elements. Of particular importance is the reduction of sulfate, which liberates hydrogen sulfide (H_2S). In most mine pit lake scenarios, sulfate is readily available at concentrations capable of generating significant quantities of hydrogen sulfide. Many trace elements (e.g. Fe, Co, Ni, Zn, Cd, and Pb) react rapidly with free sulfide to precipitate insoluble sulfide minerals (Balistrieri, Murray et al. 1994; Stumm and Morgan 1981). Consequently, the precipitation of metal sulfides, and their subsequent settling to the lake floor, can provide an effective mechanism for removing trace elements from the water column (Achterberg et al. 1997; Green et al. 1989).

The same redox processes outlined above for the water column occur within sediments and submerged mine tailings. Accordingly, lacustrine sediments containing organic matter are often devoid of dissolved oxygen within a few millimeters of the sediment–water interface, even if bottom waters are fully saturated with dissolved oxygen (Martin et al. 2003; Pedersen et al. 1993). This sometimes has important implications for the chemistry of waters seeping out of a perched pit lake where seepage to groundwater is important.

3.4.4 Pit Lake Model Characteristics

3.4.4.1 Basic Properties

Pit lake hydrodynamic models may be classified based on the number of spatial dimensions they include. Generally, the complexity and demands imposed on computer resources (i.e. memory, disk space, and CPU cycles) and the quantity of field data required for model initialization and inputs increases significantly with the number of dimensions.

These considerations, and the very long time periods over which a model may be required to simulate pit lake properties, impose severe constraints on the number of spatial dimensions that may be reasonably included in a model design. Models used to simulate pit lakes over long time periods usually include just one spatial dimension, with temporal variation of water properties occurring only in the vertical, and with water properties in the horizontal dimensions assumed to be isotropic.

The validity of applying a one-dimensional model to a particular pit lake is often done without justifying the assumptions implicit in the model design. The key assumption is that lake properties in the vertical change much more slowly than in the horizontal.

Horizontal gradients occur within pit lakes for a variety of reasons. For example, a strong wind blowing on the lake surface will temporarily create a small surface slope by piling water toward one side of the lake. This tilts the isopycnals, resulting in horizontal thermal and salinity gradients. When the wind stops, both a surface and internal seiche may develop which persist until friction dissipates the energy as heat. In addition, inflows of fresh and treated water can be a source of lateral inhomogeneity. When the sources of the horizontal gradients cease, the time over which the gradients relax and vanish is generally much shorter than the typical time scale over which comparable changes in vertical properties occur.

If necessary, the validity of the one-dimensional assumption may be tested by calculating the Lake Number (Atenucci and Imerito 2002), which takes into account the stability of the water column, and the destabilizing effect of the wind.

$$L_N = \frac{(z_g - z_0)Mg(1 - z_T/z)}{A^{1/2}(1 - z_g/z) \int\limits_{A(z_H)} \rho_0 u_*^2 dA} \tag{3.30}$$

where ρ(z) is the vertical profile of water density; z_g, z_0, z_T and z_H are the center of volume, center of gravity, height of the center of the metalimnion, and height of the water column, respectively (measured upward from the pit bottom); M is the total mass of water; g is the acceleration due to gravity; A is the plan view area of the lake surface; and u is the surface friction velocity. For values of $L_N \gg 1$ the one-dimensional assumption is considered to be valid.

The equations governing the conservation of momentum, mass, and heat are expressed in three spatial dimensions. To reduce this number from three to one vertical dimension, the equations are laterally integrated; thus, models based on this modified set of equations are referred to as laterally integrated models.

3.4.4.2 Turbulence and Mixing

A fundamental difficulty in modeling the physical processes in many hydrodynamic systems, including pit lakes, is the broad range of spatial and temporal scales that are observed in nature. In natural hydrodynamic systems, there is always a cascade of kinetic energy from large spatial scales through to small scales due to nonlinear interactions. At the smallest scales, viscosity becomes important and the energy is finally dissipated as heat. This energy cascade is the signature of turbulent systems and is an important cause of mixing. In practice, it is impossible to model turbulent systems exactly because of the lower bound on spatial resolution in the computational grid used to represent the physical system being modeled.

All processes that occur on scales smaller than the minimum model resolution must be included using a turbulent energy closure scheme (Moin et al. 1991). Ignoring sub-grid scale dissipation of energy creates aliasing–a transfer of small-scale energy to larger spatial scales that produces numerical instabilities and model failure. A common approach to solving this problem is to parameterize the small-scale turbulent processes using an analogue to molecular diffusion. Specifically, mixing at the small-scale end of the turbulent cascade is assumed to be isotropic, and is approximated by a term that includes a turbulent diffusion coefficient. In the vertical component of the momentum equation, this term appears as:

$$\frac{\partial}{\partial z}\left(K(z)\frac{\partial u}{\partial z}\right), \tag{3.31}$$

where $K(z)$ is the vertical turbulent diffusion coefficient and u is the horizontal current velocity. This analogue treats sub-grid scale turbulence in the same way as molecular diffusion, except that the diffusion coefficient is a variable that depends on other properties of the system (Kipfer et al. 2000; Osborn 1980; Weinstock 1978).

Wind is a principle source of kinetic energy for turbulent mixing in pit lakes. Surface wind stress creates vertical current shear, which in turn generates turbulence. The Wedderburn number, an indicator of wind-driven mixing rates in pit lakes, is defined by

$$W = \frac{g' h_m^2}{u_*^2 L} \tag{3.32}$$

where $g' = \Delta\rho/\rho$ is the reduced gravity corresponding to the density jump $\Delta\rho$ across the bottom of the surface mixed layer; h_m is the surface mixed layer thickness; L is the length of the lake; and u_*^2 is the kinematic shear stress due to the wind. For $W \ll 1$ observations and scaling arguments suggest that the mixed layer deepens rapidly due to shear production of turbulent energy (Monismith 1985).

Other mechanisms exist for transporting and releasing energy for mixing within a pit lake. The vertical density structure of a pit lake leads to spectral decomposition of the horizontal velocity field into a set of internal vertical modes that are excited by surface winds, resulting in horizontal currents throughout the water column. Modes are characterized by their number of zero crossing points. Vertical current shear resulting from this modal excitation can generate turbulence and mixing (Hamblin et al. 1999).

Another source of mixing can occur at the interface of a monimolimnion and an overlying, cooler hypolimnion. The differential molecular diffusion rates of heat and salt (heat diffuses at approximately 100 times the rate of dissolved salts) can cause destabilizing heating at the bottom of the hypolimnion, resulting in convective mixing.

3.4.4.3 Pit Shell Morphometry

The pit shell morphometry is a fundamental component of pit lake models. In one-dimensional, laterally integrated models, it is expressed as a curve or function relating elevation, z, above the pit bottom to the corresponding plan view area, $A(z)$, of the pit shell. Shell volume between two elevations can then be calculated from the expression:

$$V(z_1, z_2) = \int_{z_1}^{z_2} A(z)dz \tag{3.33}$$

These data are typically extracted from maps or digital engineering drawings of pit shells.

Hydrologic Balance in Pit Lakes

The hydrologic balance for a pit lake determines the filling rate, final lake elevation, and volume, and is often complex, with many distinct components, including:

- surface and sub-surface inflows of natural runoff, tailings, and treated water
- groundwater inflows/outflows
- precipitation/evaporation/sublimation (ice/snow)
- removal via pumping

Surface and subsurface inflows can consist of water diverted from nearby streams as well as water from treatment plants, tailings, and onsite water collection facilities. Inflows may be seasonal due to variable rates of precipitation, evaporation, and ice/snow melt. At high latitudes, it is common to have a freshet, or peak in the annual inflow corresponding to increased temperatures and subsequent rapid ice and snow melt.

Groundwater flows may be directed into or out of a pit lake, and are often a major component of the water balance. The depth and intensity of these flows over time depend on hydrological gradients in the water table enclosing the pit shell and may be difficult to quantify accurately without extensive field data.

Other types of inflows and outflows occur in pit lakes. For example, the Main Zone pit lake at the Equity Silver Mine site near Houston, BC (Canada) receives a surface discharge of relatively dense slurry (neutralization sludge) that penetrates downward through the lake as a density flow (Crusius et al. 2003). The flow generates shear turbulence that entrains ambient lake water and transports it downward. The entrainment increases the volume and decreases the density of the descending flow, causing it to decelerate. Over the summer months, this mechanism results in large-scale redistribution of water properties and is an important mechanism for surface metal removal (Dunbar 2008). In addition, clean water is pumped into an adjacent stream from a depth of 20 m in the lake.

At the Island Copper Mine saltwater pit lake near Port Hardy, BC (Canada), treated water is injected through a pipe directly into the hypolimnion at a depth of approximately 220 m (Fisher 2003).

3.4.4.4 Energy Balance in Pit Lakes

The primary components in the energy balance for pit lakes are the contributions of wind and surface heat fluxes to the surface momentum flux. Subsurface flows, including groundwater and density inflows from high conductivity discharges, may also affect the heat budget. Less frequently, geothermal sources make a significant contribution (Henderson-Sellers 1986). The net heat flux is given by (Balistrieri et al. 2006):

$$H_{NET} = [H_{SW}(1 - A_{SW})] + [H_{LW}(1 - A_{LW})] - H_{LWB} - H_E \pm H_C \tag{3.34}$$

where the components include incident short (H_{SW}) and long (H_{LW}) wave radiation; long wave outgoing (blackbody) radiation (H_{LWB}); sensible heat (H_C), and latent heat of evaporation (H_E). The fraction of incident radiation absorbed by a pit lake is determined by the reflectivity or albedo (A) of the lake, which varies depending on latitude, lake color, surface roughness due to waves, and the frequency of the incident radiation.

Radiation fluxes are divided between: direct solar short wave radiation (280–2,800 nm); incoming long wave radiation (greater than 2,800 nm) emitted from clouds and water vapor; and outgoing long wave radiation emitted by the pit lake surface. Short wave radiation is usually measured directly, while long wave radiation is more often calculated from cloud cover, air temperature, and humidity. Short wave radiation with a wavelength of less than 700 nm is classified as penetrative, while longer shortwave radiation is non-penetrative. The former exhibits exponential decay with depth while the latter adds energy only at the lake surface.

Approximately 45% of the incident short wave radiation is penetrative (Gates 1966). The penetrative depth is determined by the transmissivity of the pit lake water and follows the Beer-Lambert Law given by:

$$P(z) = P_0 10^{-\mu z}$$

where P_0 is the incident shortwave power, and μ is a coefficient that is dependent on the lake properties.

3.4.5 Model Inputs and Outputs

Pit lake models require input data of various types to perform calculations and generate output. *Initial values* are required for some variables at the beginning of the simulation (e.g. pit morphometry; initial lake depth, temperature, salinity, and geochemical composition), while time-series of *boundary values* are required for input variables that change during a model simulation (e.g. meteorological variables, surface and sub-surface inflows).

The following is a list of input data required for a time-dependent, laterally-averaged (one-dimensional) pit lake model, although specific data requirements will depend on the particular application and model design:

- Initial Values
  - Pit morphometry

    pit area versus elevation
    elevation of pit bottom, spillway, and crest

  - Lake Properties

    surface elevation
    temperature

salinity
pH
concentrations of all chemical species of interest

- Boundary Values
  - Inflows/Outflows

    Surface inflows
    groundwater (elevation dependent inflow/outflow)
    waste treatment plant discharge (inflow)
    pumping (outflow)
  - Inflow Properties

    temperature
    salinity
    pH
    concentrations of all chemical species of interest
  - Meteorological

    air temperature
    relative humidity
    wind speed
    precipitation
    evaporation
    incident short wave radiation
    incident long wave radiation
    cloud cover

Ideally, all time-series data required for a pit lake model simulation are available as measurements from stations at or near the lake. Since this is often not the case, proxy data must be substituted for unknown values. Suitable proxy meteorological data may be available from permanent data collection stations. Environment Canada, for example, maintains an on-line database of historical meteorological data that are easily accessible. These data are often not comprehensive, however, and may need to be supplemented from other sources.

Numerical weather forecast and climate models are often a good source of proxy data. For example, regional values of short and long wave radiation and other variables are available through the Internet from the National Centers for Environmental Predictions (NCEP; Glahn and Ruth 2003).

3.4.6 Model Verification and Sensitivity

In principal, all pit lake models should be verified against measurements to validate their use in a particular application. However, it is often not possible to undertake thorough model verification, either because a complete data set is unavailable, or because of the nature of the model application (e.g. a 200 year simulation of a pit lake for a mine that is in the design phase). Such circumstances may require a certain amount of faith in a model based on an established record of previous successful verifications.

Of equal importance is the need to conduct sensitivity analyses for model inputs (Castendyk and Webster-Brown 2007a, b; Romero and Melack 1996). This entails a systematic variation of key model input variables through values that bracket anticipated ranges. This is particularly important in nonlinear hydrodynamic systems that can exhibit unpredictable, chaotic behavior due to strong nonlinearities (Pattantyús-Ábrahám et al. 2008). In pit lakes where there are numerous inflows, a well designed sensitivity analysis will determine the dependence of lake stratification and stability on inflow properties (Castendyk and Webster-Brown 2007a, b). The thoroughness of a sensitivity analysis for a pit lake model is often constrained by the time required to complete a single model simulation, which may extend to several days or more depending on the model and simulation complexity.

3.4.7 Examples of Pit Lake Models

3.4.7.1 DYRESM

The one-dimensional Dynamic Reservoir Simulation Model, or DYRESM, is one of the most frequently used and cited numerical models for simulating pit lake hydrodynamics. It was developed by the Center for Water Research at the University of Western Australia where it continues to be maintained and made available through the Internet.

DYRESM has been successfully applied to studies of natural and artificial lakes, reservoirs, and pit lakes (Balistrieri et al. 2006; Hamblin et al. 1999; Hamilton and Schladow 1997; Patterson et al. 1984). While the current version of DYRESM available from UWA does not include ice formation, modified versions that include this process have been successfully tested (Patterson and Hamblin 1988). At present DYRESM is limited to modeling pit lake hydrodynamics; however, it can also be run together with the Computational Aquatic Ecosystem Dynamics Model (CAEDYM; Hipsey, et al. 2006). However, CAEDYM does not, at present, simulate the geochemical processes associated with pit lakes.

3.4.7.2 PitMod

PitMod is a proprietary, one-dimensional model developed by Lorax Environmental Services in Vancouver, BC (Canada). It is specifically designed to model pit lake hydrodynamics and geochemistry (Crusius et al. 2002). PitMod incorporates many of the physical processes included in DYRESM as well as including an ice formation algorithm (Rogers et al. 1995). Most significantly, however, PitMod simulates an extensive set of geochemical reactions by coupling to the PHREEQC geochemical speciation model (Parkhurst et al. 1999). This allows PitMod to perform simulations of a century or more in length that include the evolution of both the geochemical and physical properties of a pit lake.

Like DYRESM, the structure of PitMod is based on a set of vertical layers. The values of geochemical variables required by PHREEQC, such as pH and chemical species concentrations, are maintained and adjusted in PitMod based on modeled pit lake physical processes. At each time step, PHREEQC is implemented within all layers to calculate the equilibrium concentrations of geochemical variables.

PitMod is designed to predict the physical and chemical properties of pit lakes, given suitable estimates for environmental input variables. Model results provide details of the chemistry in vertical layers over time.

3.4.7.3 PitMod: Physical Component

The physical component of PitMod simulates the evolution of the pit lake stratification by predicting salinity, temperature, density (calculated from salinity and temperature) and dissolved oxygen concentration. The physical component of the model is a one-dimensional stack of variable thickness layers. Each layer is assumed to be homogeneous in all water properties. The principal physical processes simulated by PitMod include:

- *Solar heating* of the lake surface: thermal energy from the sun is added to surface waters, thereby altering the temperature and density. Heat is transferred to deeper layers through penetrative absorption, diffusion, mixing, and convection. Similarly, the model allows for geothermal heat where it is considered important.
- *Vertical mixing* as a function of the lake density stratification—kinetic energy from the wind causes adjacent water layers to mix to varying degrees, depending on the vertical density structure of the lake.
- *Convective mixing* due to static instabilities in the water column density, i.e. when water in a layer is denser than the water in the underlying layer.
- *Oxygen consumption* in the water column and sediments is a critical parameter in the geochemical state of the pit lake. Oxygen is introduced to the surface waters through interaction with the atmosphere and is distributed through the water column by mixing and diffusion across adjacent layers. Oxidation of organic matter in the water column and sediments consumes oxygen; if the consumption rate of oxygen in a given layer exceeds its rate of replacement, the layer becomes anoxic.

Along with these processes, PitMod can accommodate the introduction of external source water, or the removal of resident water at any depth in the lake.

3.4.7.4 PitMod: Geochemical Component

The geochemical component of PitMod employs PHREEQC, a geochemical model originally produced by the USGS (Parkhurst et al. 1999). PHREEQC is capable of a wide variety of aqueous geochemical calculations, including:

- speciation and saturation index calculations;
- mineral and gas equilibrium;
- surface complexation (adsorption) reactions;
- ion exchange reactions; and,
- redox reactions.

PHREEQC was selected because it is widely and extensively used, has been rigorously validated, and the computer code is freely available on the Internet. In addition, it includes several thermodynamic databases including WATEQ4F and Minteq. Furthermore, PHREEQC's treatment of aqueous solution chemistry is valid from freshwater through to the high ionic strength media often observed in pit lake systems (Parkhurst personal communication 1998).

PHREEQC requires a comprehensive set of chemical input data to characterize the pit lake water. For a typical simulation of mine-impacted waters, this would include pH, temperature, the controlling redox couple, and the concentrations of oxygen, secondary oxidants (e.g. nitrate and sulfate), major cations, major anions, and trace metals.

PitMod integrates the effect of all inputs on the physical and geochemical properties of the pit lake by solving the set of governing hydrodynamic equations followed by calls to PHREEQC routines that calculate equilibrium concentrations of all chemical species within each model layer. PHREEQC predictions are based on thermodynamic principles and a database that includes hundreds of chemical species. Figure 3.76 shows the sequence of steps in a typical application of PitMod.

The output of PHREEQC includes the equilibrium concentration and speciation of all aqueous components, as well as the equilibrium concentrations of all minerals. Water quality is predicted for each model layer as a function of time, yielding vertical profiles of each parameter. PHREEQC predicts whether a metal will remain dissolved, precipitate from solution, react with an existing mineral by ion exchange, or adsorb to a particle. An important case occurs in anoxic waters, where PHREEQC can predict, for a given metal and dissolved sulfide content, whether or not the metal sulfide will precipitate.

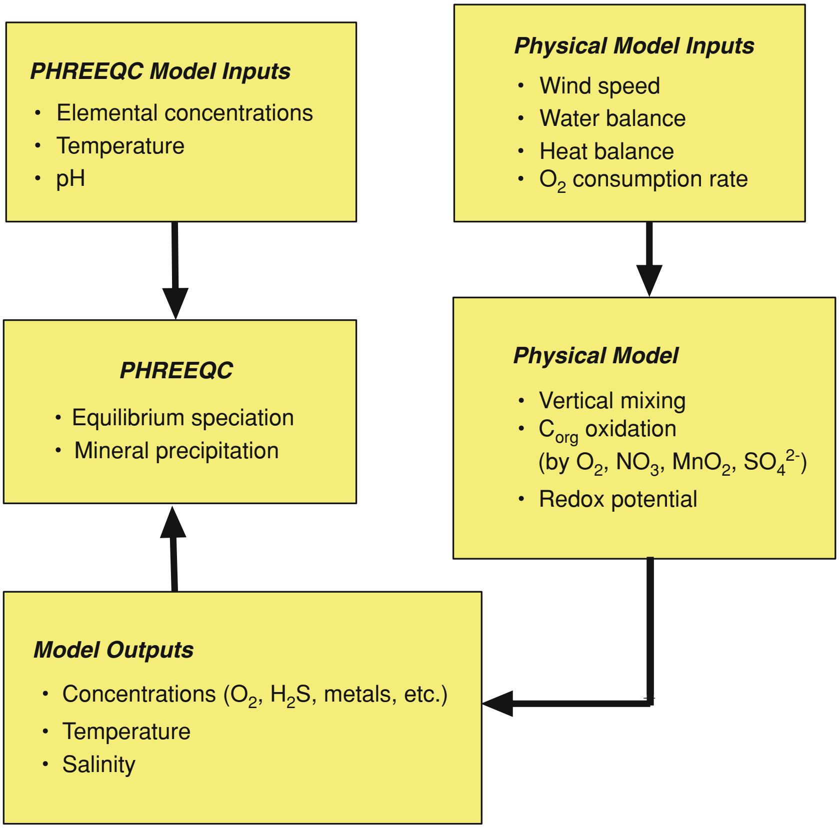


Fig. 3.76 Components of PitMod, a coupled physical-geochemical pit lake model

3.4.8 *Case Studies*

3.4.8.1 The Equity Silver Mine

The Equity mine site is located in south-central British Columbia, Canada (54°11.59′N, 126°15.90′W). The two Equity pits produced silver, copper, and gold from 1981 to 1994. Subsequently, both pits flooded with groundwater and surface runoff. In addition, the larger Main Zone pit receives seasonal surface discharge of relatively dense treatment slurry (ARD neutralization sludge) as well as runoff from the slightly higher Waterline pit lake (Table 3.29).

Water quality in the Main Zone pit lake is characterized by elevated trace metal concentrations in the epilimnion (particularly zinc) during late spring and summer, and significantly lower values in the hypolimnion. The water level in the Main Zone pit is managed by pumping water from a depth of 20 m to a nearby stream.

Table 3.29 Properties of the Main Zone (MZ) and Waterline (WL) pit lakes

Pit Lake	Surface Elev, m	Depth, m	Area, m^2	Volume, $10^6\ m^3$
MZ	1,255	130	175,812	9.80
WL	1,270	45	37,979	0.70
MZ:WL		2.9:1	4.6:1	14:1

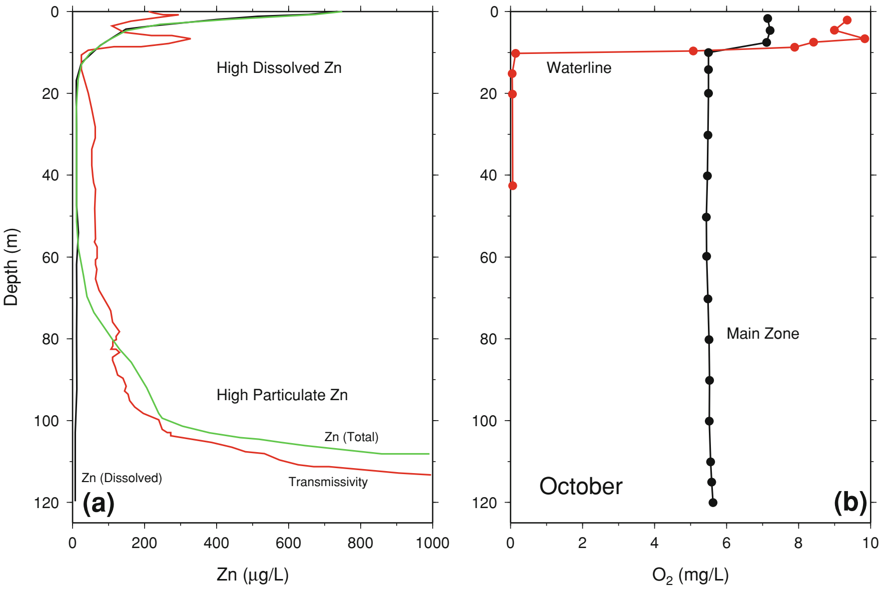


Fig. 3.77 Vertical profiles from the Equity Mine of **a** dissolved Zn, total Zn, and transmissivity in the Main Zone pit lake **b** dissolved oxygen in the Waterline and Main Zone pit lakes during October 2001

The neutralization sludge slurry discharged to the surface of the Main Zone pit lake contains high concentrations of zinc particulates and low concentrations of dissolved zinc. The slurry flow penetrates downward as a density current along the pit wall to the bottom layer of the lake. This is evident in the high particulate zinc concentrations found below 100 m in conjunction with high turbidity (Fig. 3.77a). In addition, the slurry is well oxygenated and delivers dissolved oxygen to the hypolimnion (Fig. 3.77b). In contrast, the Waterline pit lake oxygen remains permanently stratified, despite Waterline being much shallower (Fig. 3.77b).

Typically, both pit lakes are covered by up to 1 m of ice from November through May. During late spring and early summer, drainage into the lakes is greatly enhanced by melting snow and ice. In addition, the flow of surface water from Waterline into Main Zone increases. The latter flow, combined with runoff down the pit walls, increases the flux of trace metals into the Main Zone surface waters. The value for [Zn] measured at 1 m depth during June 2001 was 800 µg/L.

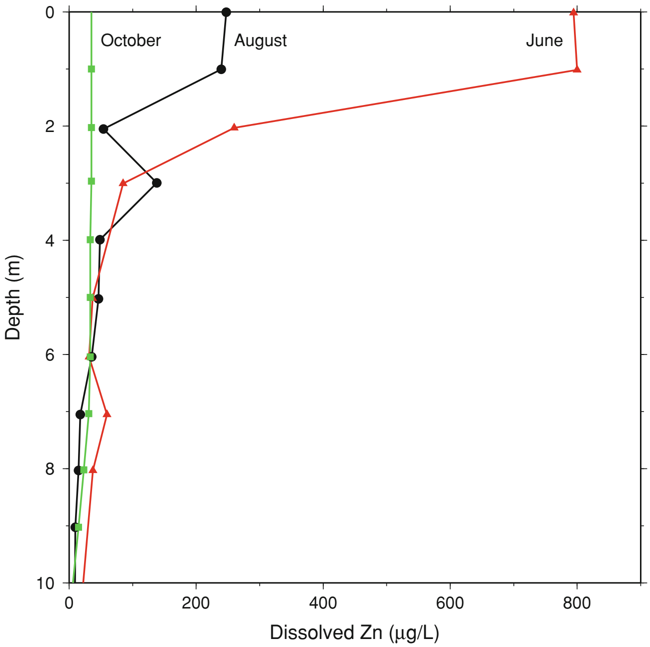


Fig. 3.78 Vertical profiles from the Equity Mine of dissolved Zn in the Main Zone pit lake during June, August, and October 2001

This value subsequently decreased to 250 µg/L in August, and to 40 µg/L by October 2001 (Fig. 3.78).

Experiments carried out within limnocorrals located in the Main Zone pit lake show that algae can facilitate removal of dissolved zinc through both surface adsorption and biological uptake (Martin et al. 2003). High rates of removal were observed after fertilization of limnocorral surface waters stimulated algal growth. The Main Zone pit lake is oligotrophic, however, and naturally occurring algal concentrations are insufficient to account for the observed rates of zinc removal observed between June and October 2001.

PitMod was used to help explain temporal changes in zinc concentration during 2001 within the Main Zone pit lake. The model showed that surface discharge of neutralization sludge slurry, and subsequent density flow down the pit wall, is responsible for the observed zinc concentrations.

Density flows occur in pit lakes when a relatively dense liquid or slurry enters less dense receiving waters and travels downward along the pit walls in response to gravity. The behavior of the density flow depends on its volume flux and excess density. As the flow accelerates toward the lake bottom, the velocity gradient between the quiescent lake water and the outside surface of the density flow generates shear turbulence. This results in mixing between the two water masses and a transfer of momentum from the density flow to the lake water.

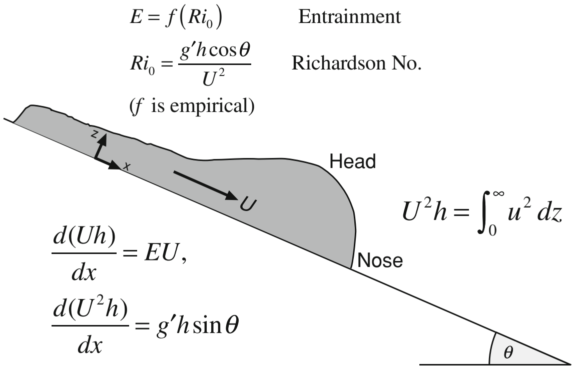


Fig. 3.79 Schematic and equations governing the properties of pit lake density flows

Table 3.30 Mean water balance for the Main Zone pit lake during the period simulated by the model from June 29, 2001 to August 28, 2002

Slurry contact pond surface	30.0 L/s	63.4%
Waterline inflow	9.6 L/s	20.4%
Surface inflow	4.7 L/s	9.9%
Net precip/evap	3.0 L/s	6.3%
Total	47.3 L/s	100%

The vertical component of this momentum causes some of the lake water to be entrained, and to move downward with the slurry. At the same time, mixing of slurry with some of the lake water increases the volume of the density flow and decreases its relative density, causing it to decelerate. Depending on the volume flux and density of the slurry, and the density and depth of the lake, the density flow will either reach the lake bottom or separate from the pit wall near a level of neutral buoyancy above the lake bottom. A schematic of a density flow together with the governing equations are shown in Fig. 3.79.

From late June, 2001 through late August, 2002 a comprehensive set of physical and water quality measurements were made in the Main Zone and Waterline pit lakes as part of a three year Canadian National Science and Engineering Research Council (NSERC) and industry funded study. Additional data were used to construct a detailed water balance for the lake during the same period, including: lake surface level; precipitation and evaporation; and pumping and slurry discharge rates (Table 3.30). These provided data inputs for a 425 day PitMod simulation of the evolution of water properties in the Main Zone pit lake. For this simulation, all geochemical processes were ignored and the PHREEQC module was not required. All changes in modeled concentrations were therefore the result of physical processes only.

Time-series of zinc and copper concentrations were extracted from the model output, corresponding to depths of 1, 5, and 100 m in the Main Zone pit lake and then compared with field measurements at the same depths. The data reveal two occurrences of elevated zinc and copper concentrations at a depth of 1 m in June

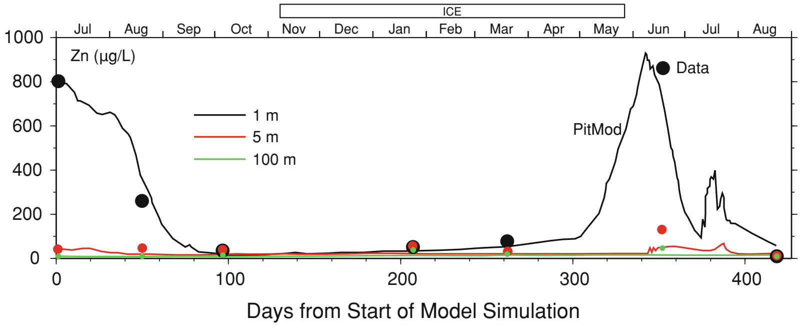


Fig. 3.80 Comparison of modeled and measured dissolved Zn concentrations from the Equity Mine at depths of 1, 5, and 100 m in the Main Zone pit lake

of both 2001 and 2002. In both cases, subsequent measurements revealed a large decrease over the following two to three months.

The model time-series for zinc agree well with the measured zinc concentrations (Fig. 3.80). In the absence of any geochemical or biological mechanism in the model, the results support the hypothesis that the entrainment and subsequent downward transport of surface waters by the relatively dense slurry is responsible for the rapid removal of dissolved trace metals from the surface waters of the Main Zone pit lake. These results indicate that surface water entrainment may be an important mechanism for the removal of trace metals in other pit lakes that receive similar inflows of relatively dense slurries.

3.4.8.2 A High Latitude Pit Lake

This example focuses on both the physical and geochemical evolution of a pit lake located at high latitude. Three scenarios were modeled using PitMod. The scenarios differ only in the depths that two inflows are discharged to the pit lake–one from a contact pond (CP), and the other an overflow from an existing pit lake. The three scenarios are: CP and overflow both enter at the surface; CP discharged at depth; overflow enters at the surface, and CP and overflow both discharged at depth

The relevant physical and hydrodynamic processes simulated by PitMod under these conditions include:

- solar heating of the lake surface by short- and long-wave radiation;
- cooling by emission of long-wave radiation
- sensible heat and latent heat of evaporation
- wind mixing;
- convective mixing due to vertical density instabilities; and
- oxygen (oxidant) consumption in the water column and sediments.

The relevant geochemical processes modeled by the PHREEQC component of PitMod include:

- speciation and saturation index calculations;
- mineral and gas equilibrium;
- surface complexation (adsorption) reactions;
- ion exchange reactions; and
- redox reactions.

PitMod requires the following input for these three simulations:

- pit shell morphometry;
- daily or hourly meteorological data, including: wind speed and direction; precipitation; evaporation; relative humidity; short- and long-wave radiation; cloud cover (%).
- water balance with daily values of inflows and outflows;
- areas of exposed pit-wall geology and predicted chemistry from different rock units; and
- flow volumes and water chemistry of inflows and outflows, including both surface runoff, waste rock seepage chemistry, consolidation water from reclaimed tailings and groundwater (Table 3.31).

PitMod accommodates various types of data depending on their availability. Where data are missing or unavailable, surrogates are specified based on experience at similar pit lakes or from other data sources. Specifically, regional data for short and long wave radiation were obtained from the National Centers for Environmental Prediction (NCEP) global model database managed by NOAA (National Oceanic and Atmospheric Administration).

In the PitMod simulations, the pit lake receives inflows from tailings consolidation, water surface runoff from the surrounding watershed, seepages from a waste rock facility, highwall runoff, direct precipitation to the surface of the lake, and groundwater. These inflows are introduced into the pit lake at elevations and times appropriate for each scenario, and are allowed to mix and evolve according to the model equations governing lake physics and geochemistry.

To estimate the contributions from pit wall runoff, the surface area of each exposed rock unit was digitized and input to PitMod as a surface area vs. depth profile. The chemistry from each unit (Table 3.32) was then added to the pit lake during the filling process until the corresponding pit wall area was submerged by the lake, at which point it was no longer considered reactive. Therefore, the loading of dissolved material to the lake from each rock unit decreases as the lake fills (Table 3.31, Table 3.32).

To account for exposure and repeated flushing and rinsing of salts and metals from the pit wall rocks, concentrations for certain parameters were permitted to decay over time. The concentrations provided in Table 3.32 are the initial levels prescribed.

Table 3.31 Summary of water quality of major inflows for selected species; all units in mg/L, except for Cd and Hg, which are in μg/L, and pH

	Waste rock seep 1	Waste rock seep 2	Tailings surface water	Consolidation water	Ground water	Runoff
pH	7.7	7.46	7.7	5.5	7.5	6.4
As	25.7	25.6	1.33	15.7	0.205	0.010
Sb	2.40	2.40	0.104	1.16	0.0037	0.001
Cd	0.5	0.5	0.55	0.93	0.25	0.1
Cu	0.0249	0.113	0.412	0.674	0.001	0.050
Fe	0.0021	0.0025	0.051	107	2.23	0.030
Pb	0.0142	7.37	0.00147	0.0825	0.0045	0.003
Mn	8.76	84	56.0	45.6	0.463	0.500
Hg	0.077	0.08	0.92	1.44	0.006	0.3
Se	0.140	2.65	0.134	0.220	0.005	0.0025
Tl	0.001	0.001	0.00153	0.00258	0.0001	0.001
Zn	0.11	386	0.048	0.079	0.012	0.050
Sulfate	1,995	38,850	13,700	15,900	20	60

Table 3.32 Water quality of inflows from various pit wall geologic units; all units in mg/L, except for Cd and Hg, which are μg/L, and pH

	Unit 1	Unit 2	Unit 3	Unit 4	Unit 5	Unit 6	Unit 7	Unit 8	Unit 9
pH	7.8	8.0	7.8	7.8	7.7	7.8	4.47	4.5	6.4
As	0.269	0.563	0.900	0.900	6.13	16.8	0.341	0.327	0.01
Sb	0.697	0.362	0.250	0.250	0.130	2.4	0.0012	0.0012	0.001
Cd	0.5	0.5	0.5	0.5	0.5	0.5	0.3	0.44	0.5
Cu	0.004	0.007	0.017	0.017	0.016	0.017	0.024	0.031	0.02
Fe	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.44	0.03
Pb	0.017	0.017	0.017	0.017	0.015	0.023	0.00077	0.00098	0.005
Mn	0.39	0.314	1.22	1.22	0.181	4.8	0.121	0.155	0.5
Hg	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.0006	0.3
Se	0.172	0.164	0.170	0.170	0.118	0.171	0.0023	0.003	0.0025
Tl	0.001	0.001	0.001	0.001	0.001	0.001	0.0001	0.0001	0.001
Zn	0.097	0.083	0.085	0.085	0.062	0.163	0.135	0.172	0.05
Sulfate	81	138	772	772	1345	1010	32	41	60

3.4.8.3 Scenario 1: CP and Overflow Discharged at Surface

PitMod predicts that the pit lake will fill in approximately 42 years. Throughout this period, a salinity gradient develops due to the presence of highly saline tailings pond water and progressive submergence of exposed pit walls relative to exposed lake surface area (the lake has a very small catchment, only marginally larger than the area of the open pit itself). In other words, as precipitation falls on the pit catchment, it will contact either the pit wall (picking up salinity) or the lake surface (adding no salinity to the lake).

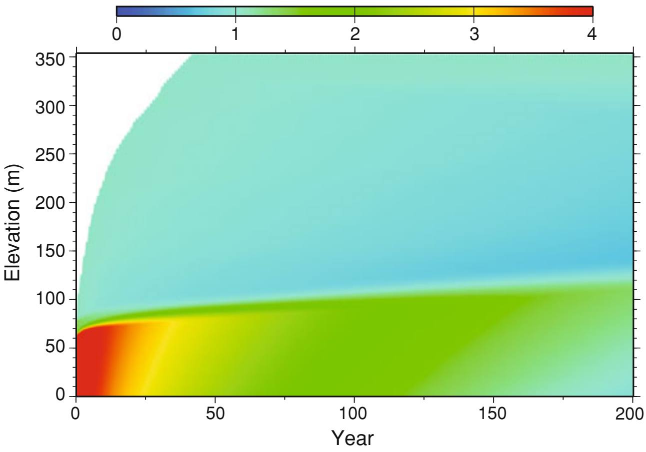


Fig. 3.81 Scenario 1: predicted salinity from a 200 year PitMod simulation (g/L)

The initial pit lake surface area is very small, so virtually 100% of the precipitation will contact exposed rock units on the pit walls, thereby contributing a maximum amount of salts to the emerging pit lake. As the lake grows and the surface area increases, a progressively larger fraction of the precipitation will fall directly on the lake surface. The result is higher salinity water at depth within the pit lake and comparatively fresher water near the surface (Fig. 3.81). The enhanced vertical salinity gradient will increase the stability of the water column.

When the pit lake is partially full, it will begin to behave in a relatively consistent fashion from year to year. Starting in the early spring under ice-cover, the water column will develop a vertical structure in which surface water immediately below the ice has a temperature slightly greater than 0 °C. The temperature then increases with depth to a value near 4 °C—the temperature of maximum water density. The upper layers of the modeled water column display a complex structure resulting from the residual signatures of past mixing events. This structure is ubiquitous in high latitude pit lakes and has also been seen at Equity Silver pit lakes (Lorax 2005).

Typically, ice on high latitude lakes begins to melt and pull away from the pit lakeshore in May or June, and as the air temperature warms during April and May, fresh melt-water is steadily added to the surface waters at the water–ice interface, decreasing surface water salinity (Bergmann and Welch 1985). As the ice melts the surface layer salinity decreases, the temperature increases, and the water column passes through isothermal conditions (Fig. 3.82). The increased salinity difference across the halocline results in greater physical stability of the upper water column with a corresponding resistance to wind mixing and turnover. As a result, even though the lake surface water warms through the temperature of maximum density, the salinity decrease combined with the salinity gradient formed through the lake filling process prevents the surface water from becoming

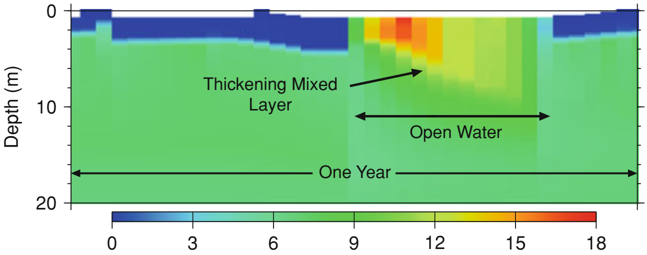


Fig. 3.82 Scenario 1: predicted temperature in the upper 20 m during year 55 of a 200 year PitMod simulation

denser than the water below. Therefore, the lake water column does not experience a spring turnover.

Mixing will only occur to a depth of 5–20 m (depending on wind strength and the magnitude of the salinity gradient). Physical stratification will persist and strengthen through the summer as surface water temperature continues to increase. With the onset of fall, the temperature differential between surface and intermediate water will decrease and wind mixing will begin to erode the density structure of the upper water column, deepening the pycnocline and increasing the salinity of the surface layer as more saline water is mixed into the surface layer from below (Fig. 3.82).

As a result, the water column will be less stable in fall than in spring–a phenomenon observed at the Equity Silver Waterline pit lake in central British Columbia, and at other high latitude lakes. Although the fall turnover should extend to greater depths than in spring, it will likely only affect the upper water column as more saline, and therefore denser, intermediate and deep water hinder deeper mixing.

Fall turnover in similarly stratified pit lakes penetrates to depths of 10–50 m depending on the placement and strength of the halocline. The depth of fall turnover varies from year to year, depending on the quantity of freshwater entering the lake surface during spring, the magnitude of the existing salinity gradient, and the wind speed and duration. PitMod predicts that the wind-mixed layer will occasionally extend to a depth of 20 m.

In the late fall and early winter thermal stratification will strengthen, with cooler water overlying denser 4 °C deep water. Ice will form in late fall and the water column will then become insulated from surface wind energy, remaining quiescent until spring, when the cycle will start again.

Given this impediment to whole-lake mixing, the pit lake deep waters will evolve towards reducing conditions over time. As is typical of lakes with small catchments and low nutrient inputs (deep lakes in particular), it is likely that the pit lake will be poorly productive (oligotrophic) and as a result, the in situ oxygen demand will be very low. Nevertheless, the imposed barriers to mixing combined with deep, isolated waters indicate that the dissolved oxygen will be fully consumed in regions of the lake before it has completed its filling, provided that CP and overflow inputs are not injected at depth, as in Scenarios 2 and 3. Once

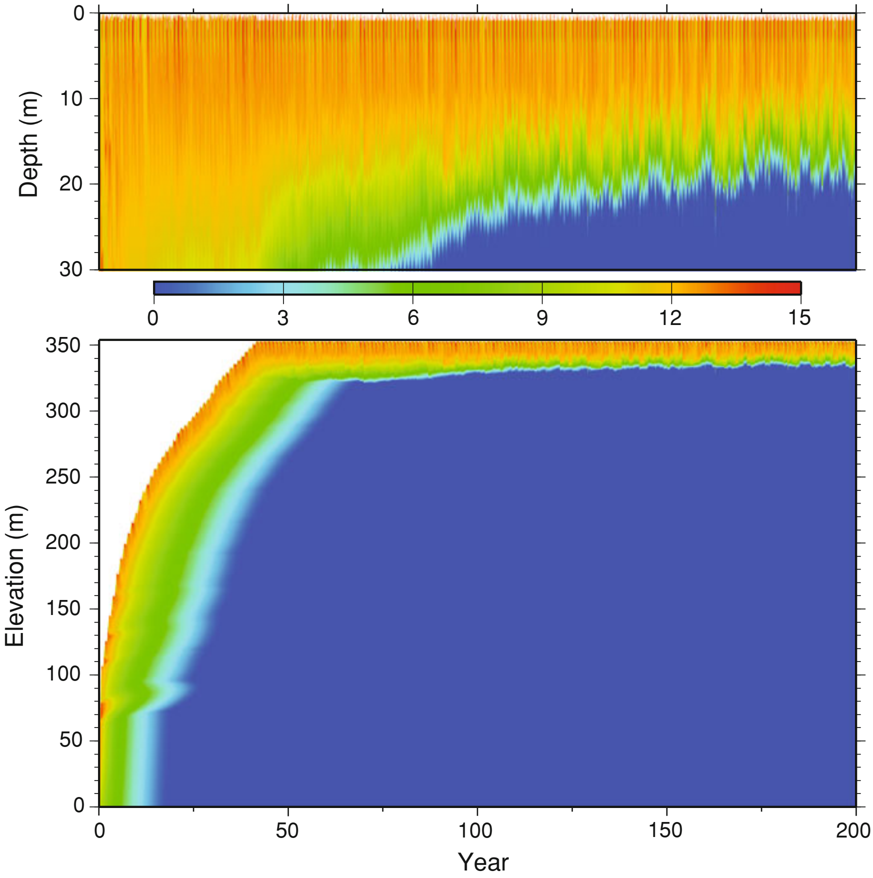


Fig. 3.83 Scenario 1: predicted dissolved oxygen concentration from a 200 year PitMod simulation (mg/L)

dissolved oxygen has been removed, secondary oxidants will be employed and the deep lake will experience sulfate reduction, sulfide formation, and the precipitation of a variety of solid-phase sulfide minerals.

Figure 3.83 shows the predicted dissolved oxygen concentration during Scenario 1 (discharge of CP and overflow at surface). As the pit fills with water in the early stages, the water column will remain reasonably well oxygenated until approximately year 10, when the lake is roughly 200 m deep. At this time, dissolved oxygen in the bottom layers will become depleted due to the absence of complete turnover. Salinity gradients within the interior of the lake will be sufficiently large to limit wind mixing and seasonal turnover to the upper 20 m, resulting in stagnation in the bottom portion of the pit lake (Fig. 3.83).

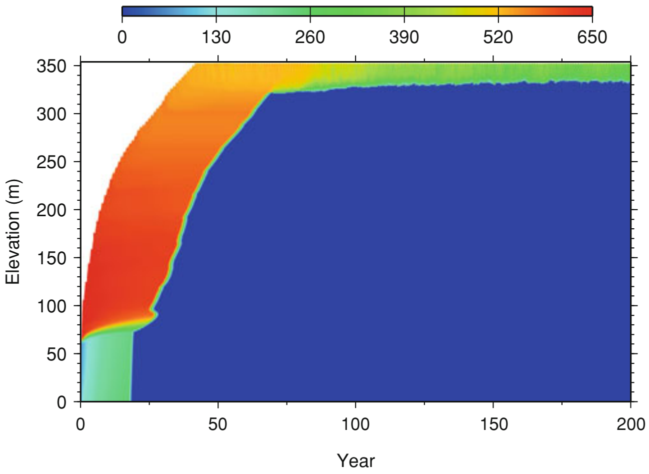


Fig. 3.84 Scenario 1: predicted dissolved nitrate concentration from a 200 year PitMod simulation (μg/L)

The depletion of oxygen in the interior of the pit lake will result in the utilization of secondary oxidants; specifically, nitrate (Fig. 3.84), Fe-oxides (Fig. 3.85), Mn-oxides, and sulfate. The evolution of nitrate–the first of the secondary oxidants to be consumed–resembles that of dissolved oxygen in that the nitrate concentration will begin to decrease with time once oxygen has been depleted (Fig. 3.84). Within 15 years of the start of pit filling, the interior of the water column will start to lose nitrate through denitrification.

Iron shows evidence of its use as a secondary oxidant in deep water beginning at approximately year 18, when the concentration of dissolved Fe will increase to 50 μg/L. This addition of dissolved Fe to bottom water is due to the reductive dissolution of Fe-oxides, which liberates dissolved ferrous Fe (Fe^{2+}) to solution. However, the increase in the inventory of dissolved Fe^{2+} is transitory due to the precipitation of Fe as Fe-monosulfides (FeS), which commences following sulfate reduction. The commencement of sulfate reduction can be seen in Fig. 3.86, which shows the presence of detectable sulfide at 20 Year.

Once most of the trace metals have been precipitated as insoluble sulfide minerals, dissolved sulfide concentrations will increase, particularly within the interior of the pit lake where there is no source of dissolved oxygen (Fig. 3.86).

With the onset of sulfate reduction in the interior of the pit lake, trace element concentrations will decrease due to their insolubility in the presence of free sulfide (Fig. 3.86). This behavior is illustrated in Fig. 3.87, where dissolved As within the lake interior decreases due to the formation of As sulfide once sulfate reduction starts and most of the dissolved Fe is consumed. Dissolved As will disappear in the interior of the lake, but not in surface waters where oxic conditions will persist.

The As concentration within the pit lake surface mixed layer will decrease with time to a quasi-steady-state value fluctuating between 70 and 130 μg/L (Figs. 3.87 and 3.88). This slow decrease with time corresponds to the progressive decrease in

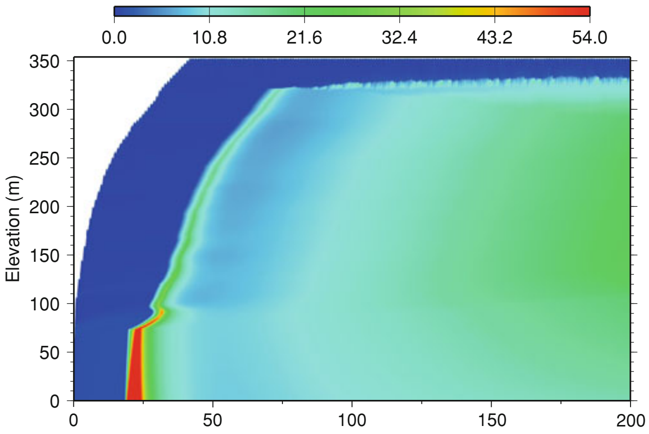


Fig. 3.85 Scenario 1: predicted dissolved Fe concentration from a 200 year PitMod simulation (µg/L)

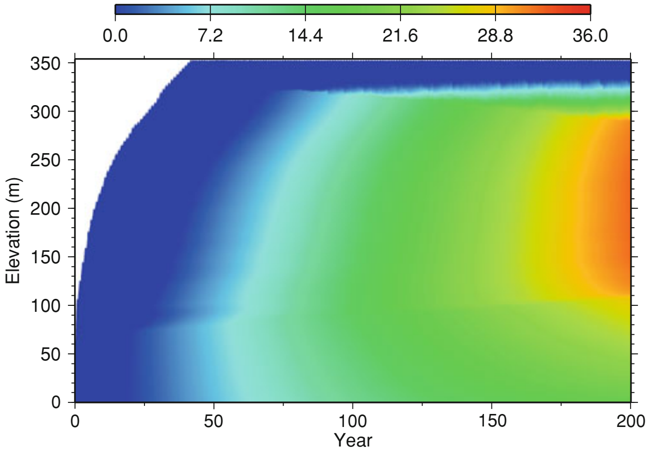


Fig. 3.86 Scenario 1: predicted dissolved HS concentration from a 200 year PitMod simulation (mg/L)

As loading from the highwall as it is submerged by the rising lake surface, and with ongoing removal of As through sorption to Fe- and Mn-oxyhydroxides, which will settle in the water column to the pit lake bottom. In comparison, the surface water sulfate concentration for Scenario 1 will vary little with time (≈700 mg/L), as it will behave conservatively in the upper, oxic water column where sulfate reduction will not occur (Fig. 3.89).

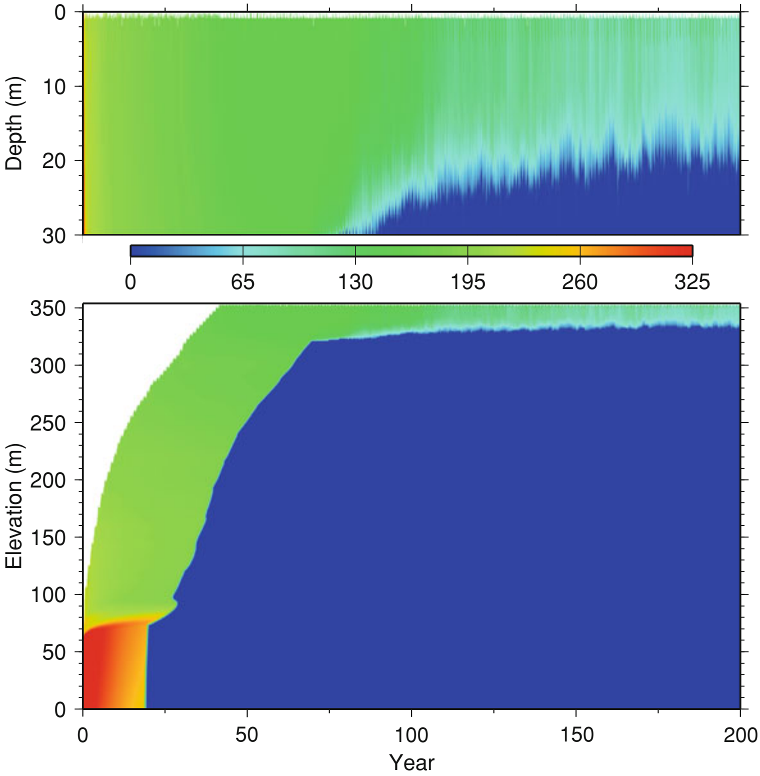


Fig. 3.87 Scenario 1: predicted dissolved As concentration from a 200 year PitMod simulation (μg/L)

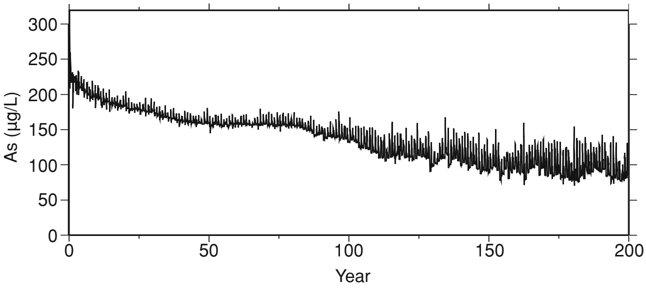


Fig. 3.88 Scenario 1: predicted dissolved As concentration in the surface layer from a 200 year PitMod simulation

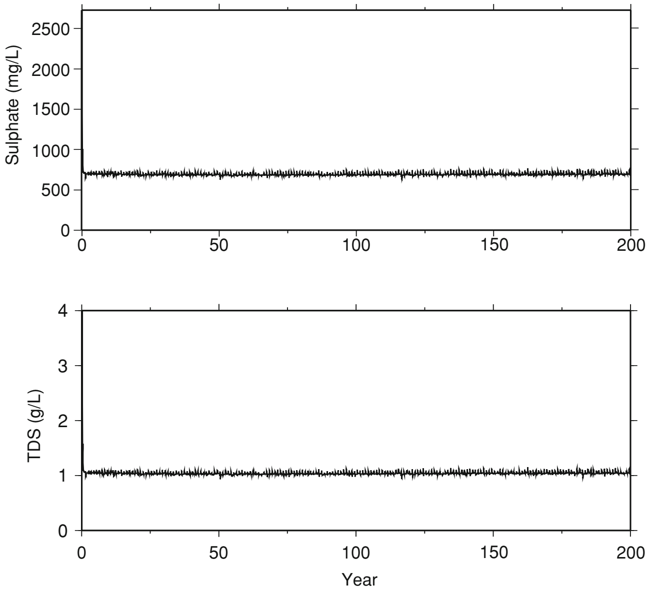


Fig. 3.89 Scenario 1: predicted dissolved sulphate and total dissolved solids concentrations in the surface layer from a 200 year PitMod simulation

3.4.8.4 Scenario 2: Discharge of CP Water at Depth

Scenario 2 differs from Scenario 1 in that CP water is diverted to 10.5 m above the lake bottom instead of being discharged to the lake surface. On a seasonal or annual basis, the behavior of the upper water column of the pit lake in Scenario 2 should be similar to Scenario 1. However, the surface inflow from the CP will be considerably less saline than the tailings water, thereby weakening the stratification in the lake as it fills. Initially, this will result in the lake having a relatively uniform, well-mixed vertical structure. Then, as the lake fills and approaches near steady-state salinity stratification, a more stable structure will develop wherein deep lake mixing will occur through the introduction of CP water at a seasonally dependent temperature.

The effect of water loss from surface overflow on the properties of the pit lake will depend on how much the overflow water differs in density from resident pit lake surface waters. The overflow water is predicted to be only slightly more saline than the pit lake surface water and is therefore expected to sink within the mixed surface layer of the lake to depths of a few tens of meters.

PitMod salinity values for Scenario 2 are presented in Fig. 3.90. As previously suggested, a strongly stratified salinity structure will evolve very early in the filling process as a relatively fresh surface layer forms above a more saline bottom layer. This will be partly due to the introduction of saline contact pond water to the bottom of the pit lake, together with mixing of highly saline tailings pond water

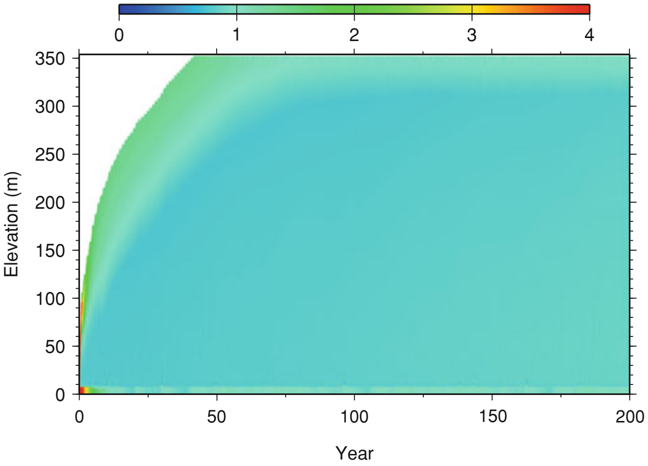


Fig. 3.90 Scenario 2: predicted salinity from a 200 year PitMod simulation (parts per thousand)

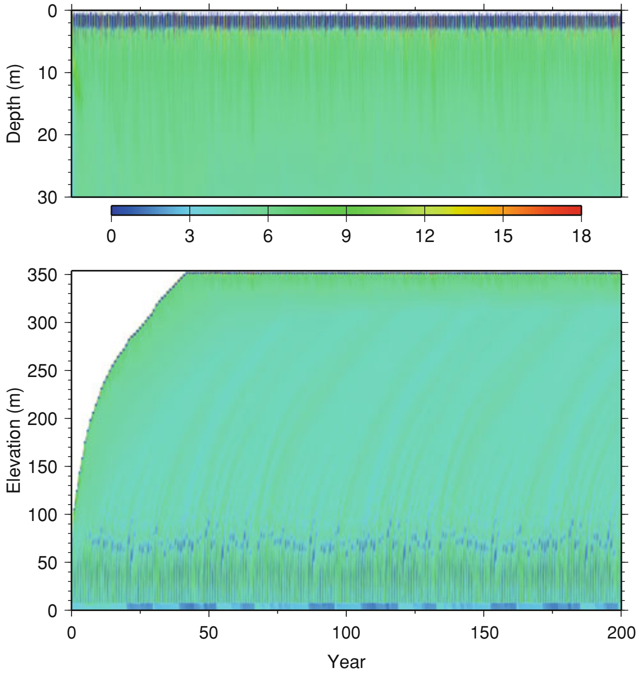


Fig. 3.91 Scenario 2: predicted temperature from a 200 year PitMod simulation (°C)

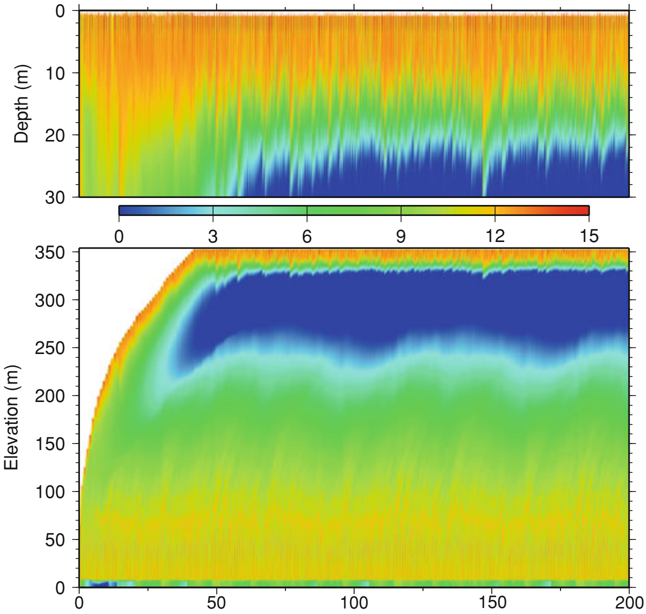


Fig. 3.92 Scenario 2: predicted dissolved oxygen concentration from a 200 year PitMod simulation (mg/L)

into the pit lake surface waters. The predicted influence of this source on the deep waters is visible in the thermal structure of the lake (Fig. 3.91). Seasonal variations are visible as temporal striations within the bottom water caused by seasonal incursions of warm and cold water. Warm water, introduced during the summer, is less dense than the ambient water and therefore tends to mix upward in the water column, while cold fall and spring water is denser and remains near the lake floor.

The seasonal wind-mixed epilimnion will be restricted to the upper few meters; however, fall turnover will penetrate more deeply than in Scenario 1, resulting in a 20–30 m thick inter-annual mixed layer. This will have important implications for the seasonal introduction of dissolved oxygen into the pit lake surface layer and to the addition at the surface of water with disparate chemical qualities originating from below the mixed layer.

An interesting and potentially important consideration involves the decreasing penetration depth of the inter-annual turnover once the pit lake is full and overflowing occurs (Fig. 3.92). When surface water overflows, and is lost from the lake, it causes a thinning of the mixed layer; that is, fresh surface water is removed from the lake, allowing relatively saline water to move upward toward the lake surface. This is important if discharge water from the pit lake is to be removed from depth, rather than directly from the surface since the chemical gradients within the pit lake tend to be greater in the upper water column.

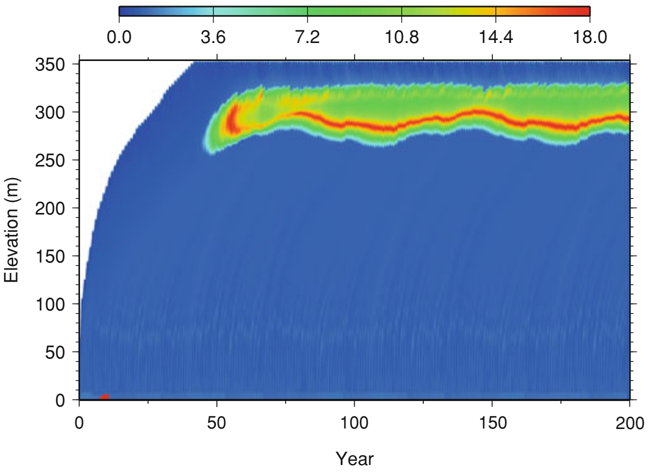


Fig. 3.93 Scenario 2: predicted dissolved Fe concentration from a 200 year PitMod simulation (μg/L)

Perhaps the most important implication of the Scenario 2 configuration is the impact of the introduction of oxygenated CP water on the geochemical properties of the deep water. In particular, the stable stratification of the water column early in the lake filling process will have an important effect on the oxygen (and secondary oxidant) distribution within the water column (Fig. 3.92). As for Scenario 1, lake productivity was set to oligotrophic conditions in Scenario 2 (i.e. very low productivity; hence, very low oxygen demand); nevertheless, the interior of the pit lake, approximately 220–330 m above the lake floor, evolves to suboxic conditions within 30 years of filling (Fig. 3.92).

The surface mixed layer will remain well oxygenated through direct contact with the atmosphere while bottom water is oxygenated by the introduction of CP water, resulting in an upward migration of water through the lake interior such that lake water 'age' is inversely related to depth (i.e. deep water is youngest, shallow water is oldest). Accordingly, the oxygen concentration of the lake interior will decrease away from the lake floor with time as oxygen is consumed (Fig. 3.92).

As expected, the model predicts a very low dissolved Fe concentration in the surface layer due to the precipitation of particulate oxyhydroxides under oxygenated conditions (Fig. 3.93). This mechanism is also responsible for removing As from the wind-mixed surface layer over time. Similarly, dissolved Fe will remain at low concentrations in the deepest lake waters due to the presence of dissolved oxygen. Within the intermediate water column, dissolved Fe will be remobilized through reductive dissolution, resulting in localized elevated concentrations, and will be removed via sulfide precipitation as the lake water ages within a relatively narrow range of depths.

The corresponding concentration of free sulfide will progressively increase with the age of the lake water until the water contacts the oxygenated wind-mixed surface layer. Sulfide concentration will increase in the water column once oxygen

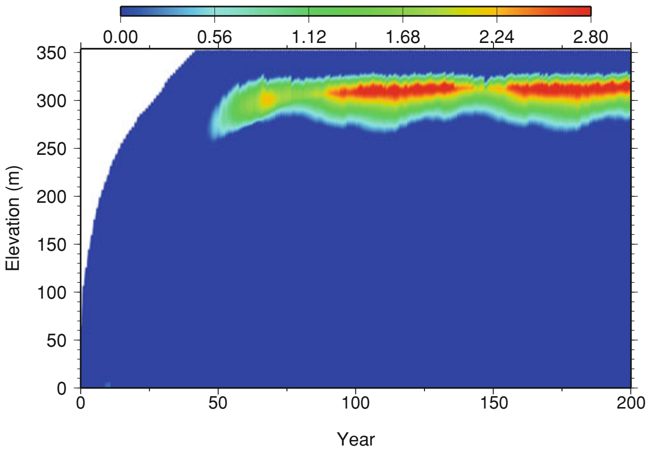


Fig. 3.94 Scenario 2: predicted free sulphide concentration from a 200 year PitMod simulation (mg/L)

has been depleted and the majority of trace metals are consumed within the lake interior (metal sulfide precipitation is the primary sink for free sulfide). Accordingly, sulfide concentration will progressively increase with time and distance from the source of oxygen at lake bottom, reaching a maximum immediately below the wind-mixed surface layer.

Interestingly, dissolved sulfide will increase to relatively high values within the lake interior despite the oligotrophic conditions, due to the relatively long residence time of water within the pit lake basin. Even though the driving force for the creation of free sulfide is weak (i.e. low primary productivity), the concentration will increase as the water of the lake interior has a long residence time before it is exposed to oxygen at the lake surface (Fig. 3.94).

The impact of the pit lake structure on As is illustrated in Fig. 3.95. Arsenic will be introduced into the pit lake primarily in the tailings pond water, and secondarily through highwall runoff and overflow into the lake. In comparison, the CP will add comparatively low concentrations of As to the pit lake. Because of the discharge configuration, the tailings pond water will enter the young lake, followed by the CP water, which will be added to the denser tailings pond water, inducing convective mixing. The addition of highwall and overflow waters to the lake surface will result in the highest modeled surface layer As concentrations (Fig. 3.95).

The contribution of As from the highwall will diminish as the lake level rises. Combined with limited removal through co-precipitation with Fe-oxyhydroxides, this will progressively decrease the concentration of dissolved As in the surface layer (Fig. 3.95).

Loss of As (and other trace elements) in the lake interior will result from sulfide precipitation; however, the proximity and resulting entrainment of low As concentration water immediately below the wind-mixed layer due to sulfide precipitation will promote further decreases in As concentration within the lake surface

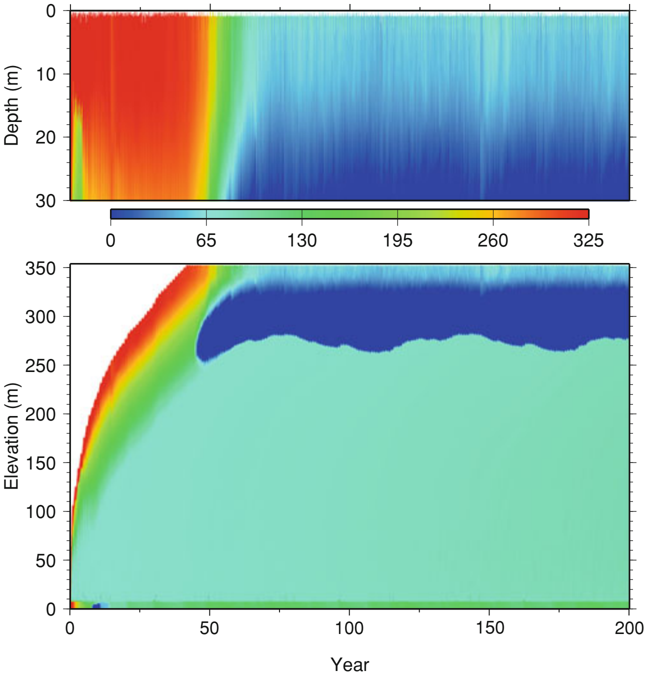


Fig. 3.95 Scenario 2: predicted dissolved As concentration from a 200 year PitMod simulation (μg/L)

(Fig. 3.96). The As concentration in the surface water will decrease with time, from concentrations exceeding 300 μg/L to values of 50–100 μg/L (Fig. 3.96).

In a similar way, the sulfate concentration will decrease over the same period as the less saline CP water is entrained from depth commensurate with the loss of freshwater from the surface layer. The primary water quality issue for this scenario stems from the contributions of total dissolved solids (TDS) and sulfate to the receiving environment, rather than from trace metals (Fig. 3.97).

3.4.8.5 Scenario 3: All Inflows Directed to Depth

Scenario 3 differs from the first two Scenarios in that both overflow and CP inflow to the pit lake are 10.5 m above the pit lake bottom. In this regard, Scenario 3 is similar to Scenario 2 with the addition of overflow water added at this depth.

The effect of discharging overflow water to depth is apparent in the difference in salinity concentrations between Scenarios 2 and 3 (Figs. 3.90 and 3.98). While much of the water column for Scenarios 2 and 3 is of nearly uniform salinity from the start of lake filling, the absence of overflow discharge to the surface layer in Scenario 3 results in an initially fresher surface mixed layer. Salinity eventually will increase as deeper water is gradually transported upward into the surface

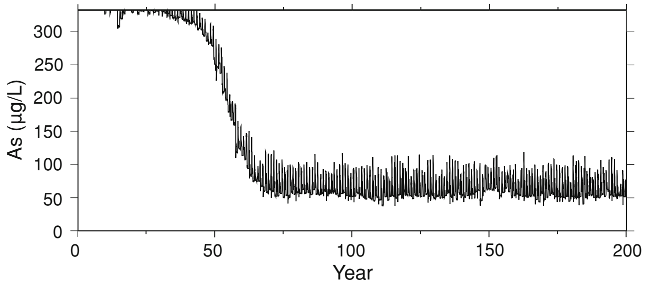


Fig. 3.96 Scenario 2: predicted dissolved As concentration in the surface layer from a 200 year PitMod simulation

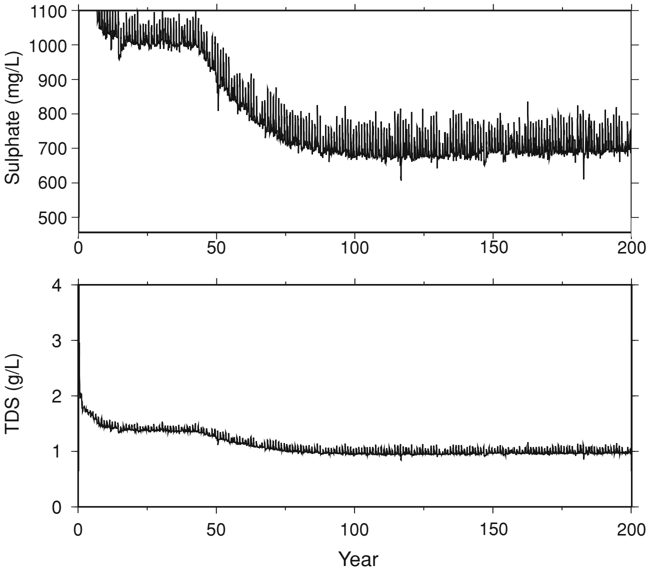


Fig. 3.97 Scenario 2: predicted dissolved sulphate and total dissolved solids concentrations in the surface layer from a 200 year PitMod simulation

layer. As in Scenario 2, the tailings water at the bottom of the lake will be mixed into the water column through the introduction of overflow and CP water at depth (Fig. 3.98).

The modeled temperature further illustrates the impact of redirecting surface waters to the pit lake bottom during the open water season (Fig. 3.99). All of the temperature variation will occur in the surface mixed layer through direct contact with the atmosphere and ice, and in the deepest regions of the lake where overflow and CP waters will be introduced.

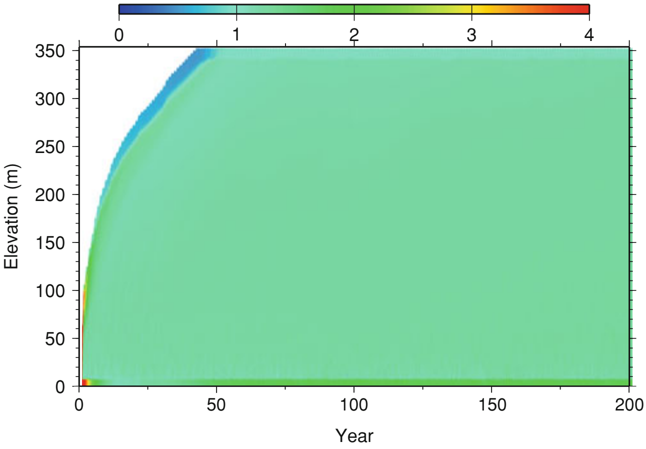


Fig. 3.98 Scenario 3: predicted salinity from a 200 year PitMod simulation (parts per thousand)

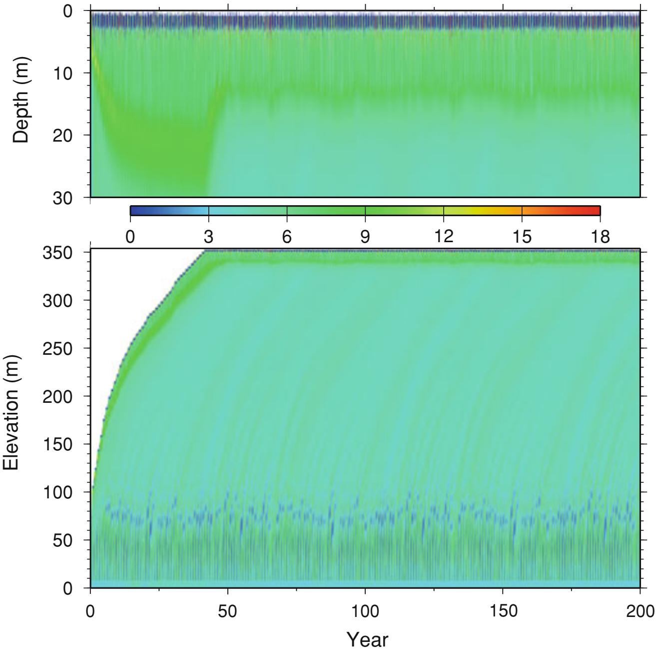


Fig. 3.99 Scenario 3: predicted temperature from a 200 year PitMod simulation (°C)

Dissolved oxygen will be saturated in the surface mixed layer and at depth but will vanish in the intermediate water after the lake has aged 10–20 years (Fig. 3.100). The reason for this distribution of dissolved oxygen is the same as in Scenario 2; that is, as oxygenated water is introduced at depth and migrates slowly

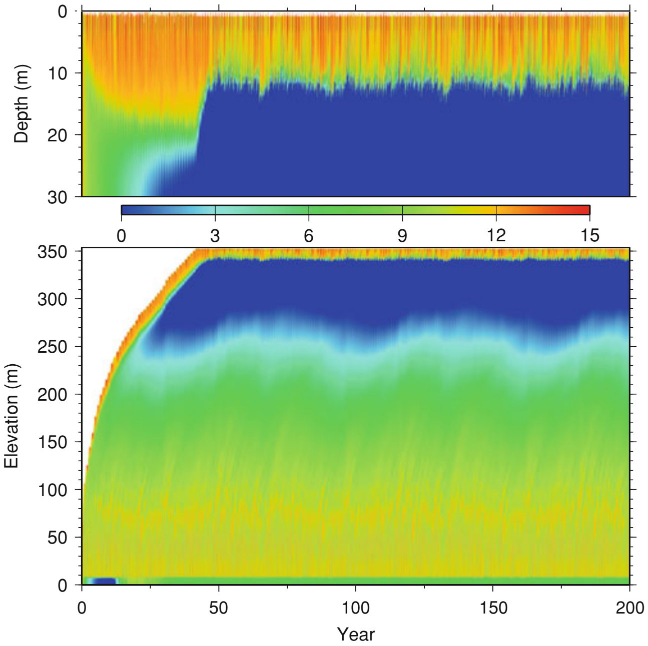


Fig. 3.100 Scenario 3: predicted dissolved oxygen concentration from a 200 year PitMod simulation (mg/L)

upward towards the lake surface, it ages and loses dissolved oxygen even though the oxygen demand in the water column is assumed to be low.

Dissolved Fe in Scenario 3 will behave similarly to Scenario 2, in that the Fe concentration will be very low in the surface and bottom layers due to the presence of dissolved oxygen and the associated stability of Fe oxyhydroxides. However, as the redox potential decreases with time in the water introduced at depth, Fe(III) reduction will eventually occur, resulting in the local maximum in dissolved Fe concentration indicated by the red zone in Fig. 3.101. This Fe maximum will be constrained above by sulfide precipitation combined with dissolved oxygen in the wind-mixed layer, and below by the presence of dissolved oxygen.

Arsenic concentration in Scenario 3 will also resemble Scenario 2 except that the As in the surface layer will decrease to a greater extent (Fig. 3.102). This likely will occur for two reasons: first, the addition of inflow at depth through the discharge of overflow water to the pit floor will enhance the upward migration and entrainment of clean intermediate water into the surface layer, causing As removal from intermediate water through sulfide precipitation. Second, and more importantly, the absence of overflow water, which contains significant concentrations of As, in the surface layer will result in cleaner surface layer water. The modeled surface As concentration will decrease rapidly after the lake over-tops, and within 10 years it should drop to a steady-state concentration of approximately 30 μg/L (Fig. 3.103).

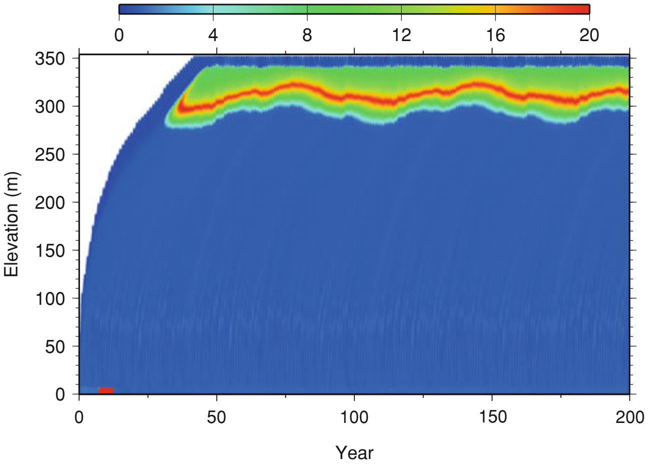


Fig. 3.101 Scenario 3: predicted dissolved Fe concentration from a 200 year PitMod simulation (μg/L)

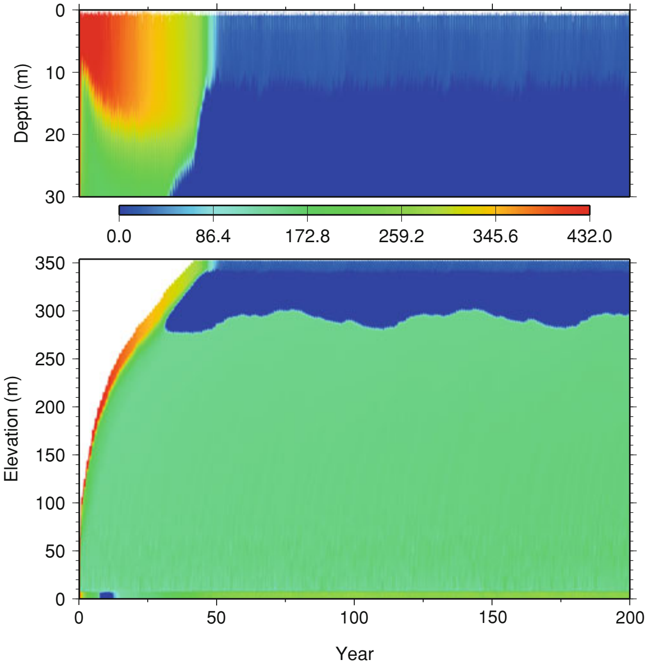


Fig. 3.102 Scenario 3: predicted dissolved As concentration from a 200 year PitMod simulation (μg/L)

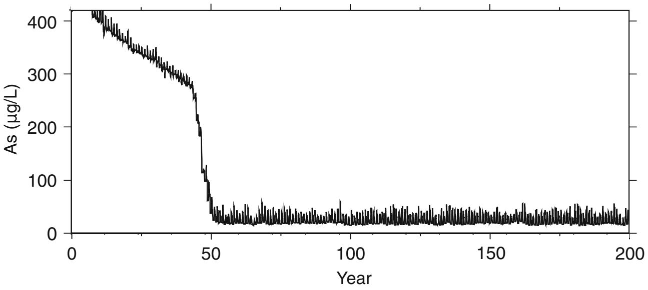


Fig. 3.103 Scenario 3: predicted dissolved As concentration in the surface layer from a 200 year PitMod simulation

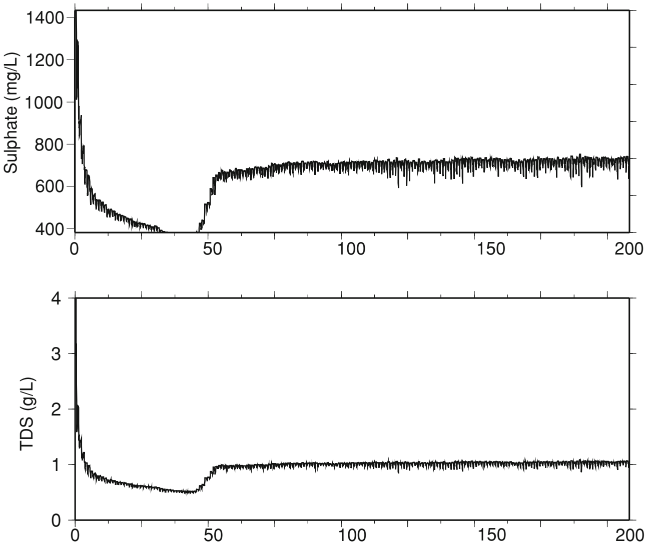


Fig. 3.104 Scenario 3: predicted dissolved sulphate and total dissolved solids concentrations in the surface layer from a 200 year PitMod simulation

In Scenario 3, sulfate concentration will progressively increase from a low at year 42 to a steady-state concentration of approximately 700 mg/L. TDS will remain relatively constant at 1,000 mg/L (Fig. 3.104).

3.4.9 Conclusions

Pit lakes exhibit a variety of physical and geochemical properties covering a broad spectrum of spatial and temporal scales. Obtaining accurate assessments of future environmental and economic impacts from pit lakes requires reliable predictions of pit lake water quality. Computer models are an indispensable tool for predicting the spatial distribution and evolution of pit lake properties. However, the gaps in our understanding of many of the important physical and geochemical processes observed in pit lakes ensure that models will always be limited in their ability to mimic nature.

DYRESM and PitMod are examples of models that determine pit lake properties by solving systems of mathematical equations, including mass and energy balances. In addition, PitMod includes surface ice formation and the capabilities provided by the PHREEQC equilibrium chemistry model to predict geochemical properties.

For any pit lake model, the accuracy of its predictions depends strongly on the quality of corresponding input data. More often than not, there are large gaps and deficiencies in data sets used to run model simulations, necessitating the use of proxy data, interpolation, or estimation.

With increases in the speed and capacity of computers showing no sign of abating, and with our increasing understanding of the physical and geochemical processes that determine pit lake properties, it appears certain that the performance of models will continue to improve and their predictions will become increasingly reliable.

Chapter 4
Remediation and Management of Acidified Pit Lakes and Outflowing Waters

4.1 Goals and Conditions of Remediation and Management

Walter Geller and Martin Schultze

4.1.1 Introduction

Pit lakes are a common feature in a mining-dominated landscape composed of active and closed mine sites, along with large dump areas and surface and groundwater that are adversely affected by acid drainage. The water quality in the pit lakes change over time as surface and groundwater flow in and out of them. The generally accepted goal is to have a landscape with a balanced and healthy system of lakes, rivers, and groundwater. According to our experience with long-lasting AMD, it is essential to decide which flows or pools should be restored, at what location, and in which sequence in time. The available money for remediation is limited, and so it is important that the approaches that are selected produce the best and most sustainable benefits.

AMD appears characteristically in two physicochemical types. The first type is aerobic, with a low pH and high acidity. The second type appears in anoxic groundwater, has higher pH values, and a hidden, potential acidity that only becomes apparent if the water is aerated, converting the second type of AMD to the first type. This conversion occurs where anoxic groundwater enters an oxygenated water body, such as a pit lake.

The remediation approaches for AMD-affected pit lakes aim to: (1) neutralize the water to pH values between 6 and 8, (2) eliminate toxic metals, e.g. Ni, Cu, Cd, and decrease dissolved aluminum and iron, and (3) decrease the concentration of sulfate below the human threshold for taste and health (250–500 mg L^{-1}), and below the levels for corrosion and ecological problems. Dissolved iron is generally not toxic to humans, but it tastes bad and causes ochre precipitation, thereby degrading ecosystems in the receiving waters.

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4.1.2 Hydrological Lake Types

Webster et al. (2006) and Kratz et al. (1997, 2006) classified natural lakes in the northern highlands of Wisconsin according to their hydrological position (Fig. 4.1). They distinguished "drainage lakes," which have inflows and outflows of surface water and groundwater, from "seepage lakes," which lack surface-water connections. They then subdivided seepage lakes by their specific groundwater regime. "Recharge lakes" are situated above the groundwater table receive only rainwater, interflow, and local runoff and recharge the groundwater system. "Flow-through lakes" receive both rain and groundwater, and have an outflow as groundwater. "Discharge lakes" have groundwater inflows, but no outflow because of higher evaporation than precipitation. A comparable classification system has been proposed for the pit lakes in Australia (see Kumar et al., Sect. 5.4).

Water chemistry of acidic pit lakes is initially dominated by AMD-contaminated groundwater. AMD contamination of groundwater can come from surrounding dumps, underground mining operations, from the weathering of sulfidic materials. Pit lakes start as empty voids after mine closure in the hydrological position of discharge lakes, receiving influent groundwater from the rising groundwater table and interflow and surface runoff of the surrounding area. When artificially filled with river or lake water they have the hydrological function of recharge lakes as long as the surrounding groundwater table is lower.

4.1.3 Flow of Acidity in the Post-mining Landscape

Knowing the position in the flow system and in the landscape is crucial in deciding the optimal method and placement of restoration measures. The flow and dilution of AMD within the transport path is shown in Fig. 4.2 The first criterion is the extent, quality, and anticipated lifetime of the primary source of AMD, usually the dumped materials (e.g. overburden, waste rock, tailings; level A). Here, the concentrations of adverse components in the water are high but the volumes are relatively low. At the end of the path (level E), within the receiving river or lake, the AMD-components are diluted. The pit lake example in Fig. 4.2 (level C) is a "drainage lake" with an outflow at the surface (flow 6) and with a through-flow of groundwater (flows 3 and 4). Other pit lakes may show other flow regimes.

The AMD load on the whole system lasts throughout the lifetime of the primary source. This time can be estimated at the central German lignite mine dumps by records of AMD contaminant concentrations. The concentrations typically decrease until they plateau after about 50 years of exposure to elution by rainfall (Hoth et al. 2005). However, elution time will be different in other locations. For example, Nordstrom (2009) estimated thousands of years of

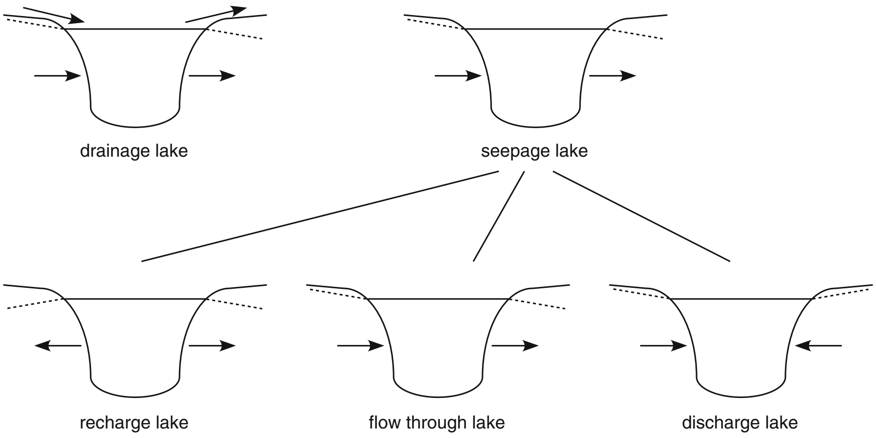

Fig. 4.1 Schemes of the hydrological lake types as defined by Webster et al. (2006) and Kratz et al. (1997, 2006). More types may be possible but did not occur in the respective study region. *Dotted lines* indicate the groundwater level. *Arrows above* the groundwater level indicate surficial in- or out-flows, i.e. streams or rivers. *Arrows below* the groundwater level indicate subsurficial in- or out-flows, i.e. groundwater. Overland flow, interflow, precipitation and evaporation are not shown

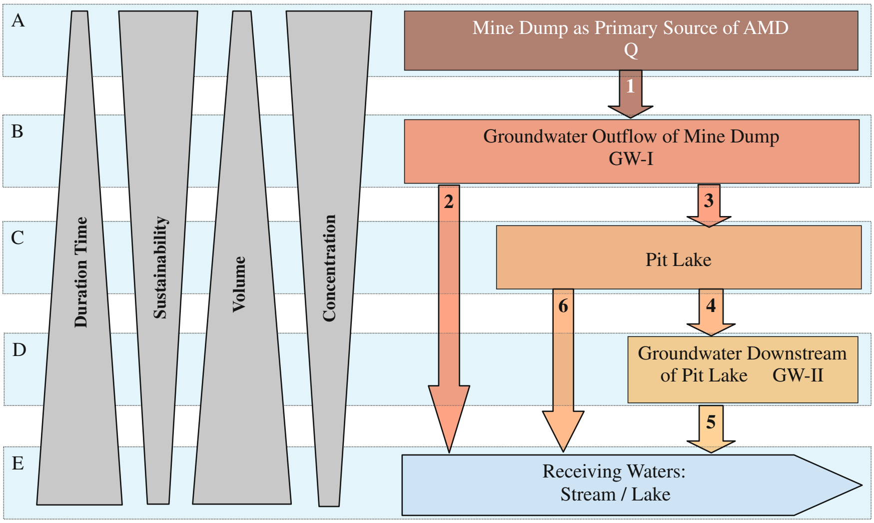

Fig. 4.2 Flows and pools of acidity in post-mining landscape. *A*–*E*: Hydrological levels from primary source of AMD (dump) to the receiving water body. The flows (1–6) and the pools are differently accessible for treatment. Vertical gradients from levels *A* to *E*: concentration and volume of water body to treat, and criteria to assess treatment success, sustainability and duration time of the load. For example: on level (*E*) a big volume of water with low concentration has to be treated. The respective sustainability of treatment is low, and the necessary duration of treatment in the flow path is longer than the AMD-emissions from the primary source. The pit lake example (level *C*) is a "drainage lake" with an outflow at the surface (flow 6) and with a through-flow of ground water (3 and 4)

elution time will be required for the former Iron Mountain underground workings in California.

Given the expected lifetime of acid sources, cost-benefit comparisons can be made of treatments of pools vs. flows, and of singular treatments of or near the source vs. permanent treatment at the end of the line of transport and dilution. The options are limited by the available treatment technologies for solid phases of dumps, for slowly flowing groundwater with high concentrations of pollutants, for standing water in lakes, or for fast-flowing water in streams after dilution of the initial acid concentrations on the other side. The costs have to be compared to singular in-lake treatments with permanent neutralization of water flows into receiving rivers over the necessary duration. Beyond costs, the other important criterion is the sustainability of any beneficial measure, which might also be defined as the cumulative long-term avoidance of adverse effects. Generally, the treatment is best placed at the source, where the concentrations of contaminants are high and the water volumes are small. Suitable technologies to treat dumps or groundwater, however, are not readily available. Most applied approaches at field scale, therefore, are directed with in situ treatment of the more accessible surface inflows to receiving streams or to lakes. The disadvantages of this approach are the low concentration but large volumes to be treated.

4.2 Hydrological Management and Chemical In-Lake Treatments

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4.2.1 Acidic Pit Lakes Filled and Flow-Through with Fresh Water

After the artificial lowering of the groundwater table needed during active surface mining is terminated, the open mine voids fill with rising acidic groundwater to form pit lakes. The magnitude of acid input may be limited by rapidly filling the pits with external freshwater from nearby rivers or from nearby active mines. The fresh water displaces the inflowing acidic groundwater and thereby minimizes the degree of the pit lake's acidification during the time of void filling. Depending on the continued inflow of acidity, the pit lakes can be kept neutral but might acidify again after a few years. At pit lakes that continue to have a flow-through of neutral river water, the steady inflow of acidity load is equilibrated (e.g. Lake Senftenberg, Germany; Werner et al. 2001). In the lignite mining districts of eastern and central Germany, numerous pit lakes are interconnected in hydrologic network system that enables central control and distribution of available water resources (case study 5.1).

Table 4.1 Acidified lakes that were successfully treated by liming and/or used for AMD treatment: volume is provided in millions of cubic meters (10^6 m^3) and acidity in mmol/L

Pit lake	Vol.	Acidity	Chemical	pH change	Source
Lake Orta, Italy	1,240	0.77	$CaCO_3$	3.9–6.8	Calderoni and Tartari 2000
Lake Koschen, Germany	82	1.6	$CaCO_3$	3.0–3.3	http://www.lmbv.de
Lake Burghammer, Germany	36	2.88	$CaCO_3$/ $Ca(OH)_2$	2.9–8	Pust et al. 2010
Lake Lohsa, Germany	44	2.9	$Ca(OH)_2$	2.7–5.4	http://www.lmbv.de
Lake Bockwitz, Germany	19	8.1	Na_2CO_3	2.7–5.4	Roenicke et al. 2010
Lake Anchor Hill, USA	0.2		CaO, NaOH	3–7	Lewis et al. 2003
Lake Rävlidmyran, Sweden	0.53		$Ca(OH)_2$	3.7–7.5	Lu 2004
Island Copper Mine, Canada	241		Fertilizer	Cu, Zn removal	Fisher and Lawrence 2006

4.2.2 Chemical Treatment of Acidified Lakes

Pit lakes with extremely acidic water can be neutralized by large-scale liming. This technology was developed to treat lakes acidified by acid rain. The 143 m deep, pre-alpine soft water of Lake Orta, Italy, was polluted by acidic industrial wastewater, and its water volume of 1.24 km^3 was finally neutralized with a suspension of 14,800 t of powdered limestone (Calderoni and Tartari 2000). The world's largest liming program was conducted in Sweden starting in 1982 in watersheds affected by acid rain; 200,000 t of lime were spread every year over severely affected land and water. By 1991, 6,000–7,500 lakes with their drainages had been treated, and about half of the acidified area had been restored (Henrikson and Brodin 1995; Svenson et al. 1995). The acidification resulting from acid rain is substantially different from that of acid mine drainage. Through the liming of the drainage basins the natural buffer capacity of the lakes can be restored. The acidification by acid drainage is not only at least one to two orders of magnitude greater than through acid rain, but the establishment of a sustainably buffered pit lake water is often an essential problem. Nevertheless, several lignite pit lakes in eastern Germany (Merkel et al. 2010), and ore mining lakes in Sweden (Rävlidmyran; Lu 2004) and at the Gilt Edge Mine Superfund Site (Anchor Hill, USA; Lewis et al. 2003) have been chemically treated (Table 4.1).

The first German pit lake to be treated (using alkaline fly ash) was Lake Steinberg (District Oberpfalz) in 1985. However, after immediate neutralization, the lake re-acidified to pH 4 in 1986 and subsequently stabilized at pH 3.5 (Hemm et al. 2002). Influent acidity from the lake's catchment area caused the re-acidification. Lake Zieselsmaar (Rhenish District) acidified due to groundwater rise and has been limed every year (Hemm et al. 2002). Lake Horstteich (Lusatian district) with 600,000 m^3 volume, a pH of 2.8, and an acidity of 3.9 mol/m^3 was treated in three steps. First 94 t of NaOH were added, followed with 54 t of a mixture of suspended dolomite ($CaCO_3/MgCO_3$) with lastly an addition of dolomitic quick lime (CaO/MgO). This lake similar to lake Zieselsmaar receives groundwater and is likely to re-acidify within 4–5 years (Rabe and Uhlmann 2006).

4.2.2.1 Alkaline Substances to Neutralize AMD Water

Several alkaline substances can be used to neutralize acidic waters and soils. The traditional substances are limestone, which is primarily calcite ($CaCO_3$), or dolomite ($CaMg(CO_3)_2$). Calcite can be burned to form quick lime (CaO), which in turn can be converted to hydrated lime after reaction with water ($Ca(OH)_2$). Sodium hydroxide (NaOH) and soda ash (Na_2CO_3) are very soluble in water and highly reactive. However, to protect the ecosystem of lakes, aggressive and highly alkaline chemicals like sodium hydroxide or quicklime should be avoided, with slurry suspensions of limestone or dolomite preferable instead. Below, examples are shown where the mentioned alkaline substances have been used in large-scale applications (Table 4.1).

Some by-products are also useful as alkaline substrates to treat acidic soils and water. Most mined lignite and substantial portions of mined coal are used in nearby power plants, and the process of generating electricity creates large quantities of coal combustion by-products (CCB), mainly fly ash. In many regions, such as in Lusatia, limestone is added during combustion to capture sulfur from the flue gas. The resultant fly ash, therefore, is alkaline, with typical CaO contents of about 10% (Drebenstedt 1994; Loop et al. 2003). Fly ash from the three major power plants in Lusatia/Germany (annually ca. 3×10^6 t) have been distributed since 1993 on dump areas, and deposited in four pit lakes (Drebenstedt 1995). Since the addition of fly ash showed positive effects on acidic soils and water, it is increasingly being used for basic amelioration of dump soils (Drebenstedt and Schollbach 1995; Wang et al. 2006). Although it is not as alkaline as sodium hydroxide, and lime, this fly ash still has a high pH and requires special care when applied in secondary treatments. Also, some fly ash contains high concentrations of potentially toxic contaminants, which may limit their use; all fly ash should be tested in leach tests that simulate the deposition environment before it is used in this manner.

Liming While Flooding in Sleeper Lake

Dowling et al. (2004) gave a report on development of the Sleeper Mine pit lake in Nevada, at an open pit gold mine that closed in the 1990s. Prior to flooding of the pit void, the inventories of acid generating, un-oxidized bedrock, and neutralizing rock, alluvium, and overburden were comprehensively investigated (Atkin and Schrand 2000). Based on the acid–base analysis, the lake was expected to become slightly acidic after being flooded with alkaline groundwater. The water, however,

Fig. 4.3 Distribution of lime in Lake Koschen by floating pipeline and circular sprinklers (Photo: Egbert Gassert 2004)

could be kept circum-neutral by applying lime during the 2 years of flooding. During the first year, the lake stratified, with the pH ranging from 4 to 9 between the epilimnion and the deep water layers. After fall and winter turnover of the water column, the pH stabilized between 7 and 8. By monitoring the chemistry of the lake, long-term addition of lime (up to 4 t/d, on average) could be flexibly adapted to actual developments. The incoming flood-water was utilized to distribute the added lime slurry.

Lime in Lake Koschen (Lake Geierswalde)

A combination of a suction excavator and a floating pipeline was successfully used at Lake Koschen (Lusatian District, Germany) to redistribute large amounts of lime slurry left over from a former treatment plant that had operated at the site. The material consisted of 85% calcite and hydrated lime (Benthaus and Uhlmann 2006). A 1,200 m long pipeline float was used, along with ten circular area irrigation sprinklers (Fig. 4.3). About 500,000 m^3 of a 1.9% lime suspension (corresponding to 10,000 t of lime) were excavated from the lake sediments, re-suspended, and re-distributed during 5 months in 2004–2005. The treatment reduced the acidity of the lake water from 1.6 to 0.9 mmol/L, indicating that the redistributed lime suspension had a neutralization efficiency of over 90%.

Fig. 4.4 Lake Bockwitz (central German lignite district) being treated with soda ash. The soda is delivered by tanker trucks (*lower left corner*), suspended in lake water and distributed through a 1.2 km long floating pipeline ending in the lake center (*upper right corner*; Photo: P. Radke/ LMBV)

Soda Ash in Lake Bockwitz

Lake Bockwitz (Central German district), with a water volume of 19×10^6 m^3, a pH of 2.8, and 8.1 mmol L^{-1} of acidity, was successfully neutralized with soda ash (Na_2CO_3) over 4 years (Roenicke et al. 2010). A total of 14,595 t of soda ash were added stepwise to neutralize the lake from 2004–2007; 975 t were added in 2008 to maintain neutral conditions. The powdered soda ash was blown into the lake via a floating pipeline (Fig. 4.4). Calcite formed close to the addition site in 2004 due to a locally elevated pH, the concentration of carbonate (provided by the soda ash), and the concentration of calcium in the lake water. The calcite settled to the lake bottom and was buried without exploiting its neutralization potential. Consequently, the rate of soda addition was lowered from 147 t/d in 2004–2025 to 65 t/d in 2005 and to 25 t/d in the following years (2006–2008) to prevent further losses due to calcite precipitation. Formation of calcite has not been observed since 2005 (Neumann et al. 2007). Lake Bockwitz is the largest German pit lake to have been completely neutralized by the addition of alkaline substances, but it still requires frequent addition of soda ash to prevent re-acidification.

A balance calculation showed that 65% of the added alkalinity was consumed neutralizing the water body, and 10% was consumed treating the ongoing influent acidity from surrounding dumps and underground, while 20% went to the sediment, and 5–10% was lost. Figure 4.4 shows the iron-rich waters entering the lake from the east and south-east, indicating influent acidity. This acidic input must be counterbalanced by regularly repeated in-lake treatment or by remediation of the acid-producing sites (Neumann et al. 2007, 2008).

Iron Hydroxide Low-Density Sludge

Since outflows of acidic water into receiving rivers or lakes have to be neutralized, treatment byproducts, especially low-density iron hydroxide sludge, accumulate. These often contain considerable quantities of excess lime. The seven major mine water treatment plants in the Lusatian lignite district in Germany produce more than 10,000 m^3/d of low-density sludge (LMBV). The available neutralizing potential of the sludge from the different treatment plants depends on the chemistry of the treated water and the amount of lime used for the treatment. The calcite content of dewatered sludge was found to range from 5 to 30% (Gröschke 2007; Uhlmann et al. 2007). The low-density iron hydroxide sludge can be handled like fly ash slurry and pumped through large pipes for deposition into empty or partially filled pit voids. Alternatively, the sludge can be used for lake neutralization. In the case of Lake Spreetal (Lusatian District), the sludge contributed about 30% to the reduction of the acidification of the lake water from 1998 to 2006 (pH 3.2 in 1998, pH 4.8 at the end of 2006). Filling with treated mine water contributed the remaining 70% to the improvement reached by the end of 2006 (Uhlmann et al. 2007).

Fly Ash, Limestone and Hydrated Lime in Lake Burghammer

About 26×10^6 m^3 of suspended fly ash has been deposited in the 31×10^6 m^3 Burghammer pit lake (Lusatian District, Germany), creating a large alkaline reserve at the lake bottom (Koch et al. 2007, 2008). The use of this ash for lake neutralization was tested successfully by resuspending and redistributing a small portion of the formerly deposited ash on the lake surface (Koch et al. 2008; Koch et al. 2008). In a pilot-scale field experiment, a swimming suction excavator and an airlift pump lifted the alkaline sediment from the lake bottom (4–8 m deep). The suspension was then mixed with lake water and distributed through a floating 150 m long pipeline. The pumping rates in the field test reached 100 m^3/h with the suction excavator, and 13 m^3/h with the airlift pump. Neutralization of the whole lake would need a much larger version of the excavator or airlift pump to treat 3,600 m^3/h over 20 months. To treat all of Lake Burghammer, alkalinities between 0.22×10^6 and 0.65×10^6 t of fly ash sediment would be needed, corresponding to about 1% of the deposit.

In 2009, the lake was treated and neutralized with 10,000 t of powdered limestone to raise the pH from 2.9 to 5.2. Then, 1,000 t of hydrated lime was added to increase the pH to 8. The suspensions were distributed by a truck-transportable liming ship that has been used to treat rain-acidified lakes in Sweden

Fig. 4.5 Distribution of lime suspension in Lake Burghammer using a Swedish liming ship (Photo: P. Radke/LMBV)

(Fig. 4.5). The efficiency of the chemical neutralization process reached 77–80% for $CaCO_3$ and 65–67% for $Ca(OH)_2$ (Pust et al. 2010).

CO_2 Addition

The resuspension of ash deposits was successfully combined with the addition of CO_2 in Lake Burghammer (Lusatian District; Koch et al. 2008; Koch et al. 2008). The addition of CO_2 considerably improved the reactivity of the ash and resulted in a higher bicarbonate gain in the lake water. The addition of CO_2 also improved the effectiveness of adding low-density sludge from the treatment plant in one of the lakes to be treated in the Lusatian District (Unger 2007; Unger-Lindig et al. 2010). Additional CO_2 also improved the alkalinity gains of applying lime and sodium hydroxide in lab-scale experiments (Schipek and Merkel 2010); field experiments are underway (Merkel et al. 2010; Rohr and Uhlmann 2010). Other projects are considering the option of combining chemical treatment of acidic pit lakes with CO_2 sequestration (Merkel et al. 2005).

4.2.2.2 In-Lake Distribution, Particle Size, and Reactivity of Suspended Chemicals

Major difficulties with full-scale treatment of pit lakes were encountered due initially choosing too simple techniques to distribute the chemicals to the water body. Discharging alkaline material from the shore is ineffective at large lakes as the insufficient distribution prevents a complete reaction of the added agents with the water (e.g. Aubé 2009). In the worst case, underwater dumps in non-reactive layers of concentrated lime, fly ash or soda ash formed at the lake bottom. Improved distribution systems appeared by pumping a diluted suspension of the neutralizing materials or a slurry through floating hoses or pipelines (e.g. Lake Bockwitz). The chemicals can be added to and mixed with the lake water effectively by circular, large-area sprinklers (Lake Koschen) or with sophisticated high-speed jet-distribution systems (Kranawettreiser 1996; Thürmer 1999), which are currently being tested in field-scale experiments (Preuß 2010).

The efficiency of chemical lake treatment depends on both the kind of neutralization material added, its reactivity, the acidity of the pit lake, the type and size of particles and their time they remain in the water column. Generally particles, depending on their density, need a minimum size before they settle to the bottom (Buffle et al. 1992). Investigations of natural turbidity inflow into Lake Constance showed that 4 μm-particles remained in the water, whereas particles of 20–40 μm sank rapidly and can be considered as a coarse fraction (Eder et al. 2008; Lang and Paul 2008).

Merkel and Schipek (2008) used a combination of different alkaline chemicals in laboratory experiments, powdered limestone ($CaCO_3$) to reach pH 5 in the initially acidic water, and then switched to the more reactive quick lime (CaO) to obtain a final pH of 7.2–7.6. Thus, most of the lake acidity can be treated with the cheaper limestone, while the more reactive and more expensive burnt lime is needed only for the last step of fine-tuning the pH. The reactivity of the first reaction decreases with increasing pH, while the second reaction is nearly independent of pH in this range.

4.2.2.3 Sustainability of Chemical Lake Treatment

The long-term success of chemical treatment depends on the exchange rate of lake water with groundwater and other inflow from surrounding acidic dumps and rock. If the sum of the influent alkalinity and the autochthonous alkalinity produced by the lake's biota is greater than the rate of influent acidity, the initial treatment should be sustained. The biological production of alkalinity is the sum of the processes that eliminate nitrate and sulfate from the system. In natural lakes, this ranges from 0.5 to 5 mmol m^{-2} d^{-1}, based on median values for oligotrophic and eutrophic lakes, respectively (Koschorreck and Tittel 2007). These rates might be achieved in neutralized pit lakes once the lake ecosystems are established, which takes time.

4.2.2.4 Primary and Secondary Chemical Treatments

From an ecological point of view, there is no concern with the initial chemical treatment of extremely acidic lake water. After some years, the neutralized lake may develop a limnic ecosystem, planktonic organisms and gradually littoral macrophytes, benthic invertebrates and fish populate the lake. When re-acidification occurs a second chemical treatment might become necessary. Since the sensitivity of the lake has changed, any secondary treatment should be done in a way to avoid a fish-kill and other adverse effects on the ecosystem. Aggressive and highly alkaline chemicals like sodium hydroxide or quicklime should be avoided. Slurry suspensions of limestone or dolomite, which have been successfully used in liming campaigns at rain-acidified soft water lakes, are preferable and have also been successfully used in continuing treatments of re-acidifying pit lakes.

4.2.3 Decontamination by Copper Recovery: A Special Case

Berkeley Pit Lake in Montana is nearly full but water elevation is maintained below the planned final level to avoid contamination of an aquifer as the pit water has severely elevated copper and other toxic metal(loid)s concentrations (e.g. case study 5.5). An ex-situ process of copper recovery is expected to eliminate most of the toxicity by exchanging copper with iron. Water from the monimolimnion is pumped to the surface and passed over scrap iron to precipitate copper in its elemental form. This treatment approach combines ex-situ and in-lake decontamination of the water with recovery of a valuable metal (case study 5.5).

4.3 Biological In-lake Treatment

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The natural processes of sulfate reduction and neutralization occur in lakes where they have a suitably low redox potential (ORP), in sediments and hypolimnic water. Organic substances can be added as a carbon and energy source, and as electron donors to support this bacterially driven process. Sulfate and metal reduction and metal sulfide precipitation works well in laboratory and mesocosm experiments. At larger scales (Fig. 4.6), wind-driven turbulence of the water brings about oxygen input leading to re-oxidation of iron at the sediment–water interface (e.g. Blodau and Peiffer 2003; Stumm and Sulzberger 1992).

There are reports of high rates of biological sulfate reduction and production of alkalinity in the deep water of stratified pit lakes during the warmer months (Brugam and Stahl 2000). These effects, however, usually disappear with the autumnal mixing of the water column. The input of atmospheric oxygen leads to re-oxidation of the reduced sulfur and iron species, i.e. the process is not sustainable in holomictic lakes. Respective field experiments in mesocosms, in enclosures, and in pilot scale tests were conducted at Berkeley Pit Lake in Montana (case study 5.5), at Garrick East Pit Lake in Australia (see below in this chapter and case study 5.4), and in lignite mining lakes in Germany (Friese et al.

Fig. 4.6 Field experiments with enclosures of different sizes in Mine Lake 111 (Lusatian district, Germany). The smallest enclosures (about 20 m^3) worked successfully, but the large enclosures (4,500 m^3) failed to neutralize the water column because the iron sulfide formed during lake stratification were re-oxidized during the cold season with holomixis of the water (Photo: P. Radke/LMBV)

2010; Frömmichen et al. 2004; Fyson et al. 2006; Geller et al. 2009a; Koschorreck et al. 2007, 2010; Totsche et al. 2006; Nixdorf and Deneke 2004).

4.3.1 Stimulation of Sulfate Reduction in Lake Water and Lake Sediment

The first field tests involving stimulation of sulfate reduction in a pit lake were reported by Brugam et al. (1995) and Brugam and Stahl (2000). Tests were conducted first in an enclosure and subsequently scaled up to treat a small lake in Illinois. Neither test resulted in sustainable neutralization. The small increase in pH and alkalinity in the deeper part of the enclosures and hypolimnion was lost within a few months due to oxygen supplied to the reductive zones via water exchange or overturn in autumn, respectively.

A subsequent full-scale test was conducted in Mining Lake 113 (Lusatian District) using floating bags filled with waste paper. It did not result in any measurable increase in pH or decrease of acidity (Lessmann et al. 2003). Another approach, based on the addition of Carbokalk (a byproduct of sugar production) and straw over the lake sediment had promising success in the laboratory (Frömmichen et al. 2004), but experiments in 4,500 m^3 enclosures (Mining Lake 111, Lusatian District; Fig. 4.6) failed (Geller et al. 2009a). The major reason for this failure was again the re-oxidation of the iron- and sulfate-reduction compounds by ferric iron in the lake sediment or by oxygen and ferric iron in the lake water during overturn in autumn and spring (Koschorreck et al. 2007). During the treatment with carbokalk and straw, a reactive layer with reducing conditions and acitivity of sulfate reducing bacteria was formed in the upper sediment layers. Microprofiles of pH-values in the sediment through the following years showed that new acidic sediment containing ferric iron was burying the neutral, active zone below at a rate of 5 mm per year (Geller et al. 2009a).

Diverse laboratory experiments indicate that controlled eutrophication might be an interesting approach to stimulate sulfate reduction in pit lakes via production of high amounts of algal biomass (Nixdorf and Deneke 2004; Fyson et al. 2006). However, the amount of biomass required for sulfate reduction was found to be impractical in the field (Tucci 2006; Totsche et al. 2006).

4.3.1.1 Anchor Hill Pit Lake

According to Lewis et al. (2003), Anchor Hill Lake, with a water volume of 265,000 m^3 was neutralized by treatment with quick lime, requiring 265 t of lime to neutralize the initial acidity (20.9 mmol/L). Since the pH of the aluminum-dominated water remained low, between about 5.0 and 5.5, the lake was also supplied with organic substances in addition to the chemical treatment. Altogether, 221 t of molasses, 76.7 t of methanol, and 88 t of wood chips were added to support microbiological activity and thereby further reduce acidity and metal concentrations. During the next warm season, denitrification took place, later followed by sulfate reduction. The process was supported by meromictic conditions that were induced by the large amount of chemicals added to the water column. The whole lake experiment can be considered successful, since batches of 150,000 m^3 of treated, neutral water could be and were released to a receiving river. The use of the whole lake as a discontinuously working reactor required initial chemical neutralization with follow-up biological treatment to remove the high levels of metals and sulfate. Altogether, the approach demanded large inputs of organic substance, in the range of one kg molasses and methanol per m^3 of water (Doshi 2006; Lewis et al. 2003; Park and Bless 2008; Park et al. 2006). Similar to the problems encountered in the German limed lakes, the effective distribution of the neutralization agents proved difficult. Attempts to distribute 50% sodium hydroxide by spreading it over the ice cover failed since the concentrated chemical was not properly diluted to react with the bulk of the lake water.

Fig. 4.7 Field macrocosms experiment at Garrick East Pit Lake (sewage and green waste treated macrocosm in the foreground, control at the back). Data: East Garrick Mine Lake: pH 2.4, sulfate 4.3–6.6 g L^{-1}, iron 600–650 mg L^{-1}, aluminum 62–110 mg L^{-1} (Photo: M. Lund)

4.3.1.2 Australian Pit Lakes: Garrick East and Ewington

Biological treatment has been tested at a pilot scale in two Australian pit lakes in different climatic zones (see also case study 5.4), in the Collinsville mining district with subtropical, semi-arid climate and in the Collie district with temperate climatic conditions (Lund et al. 2006). At both Lake Ewington and Garrick East Lake (McCullough et al. 2008a, b), sections with volumes of 1,800 m^3 and 70,000 m^3, respectively were separated from the main lake. The experimental 1,800 m^3 macrocosm at Lake Ewington was further subdivided into three sections (600 m^3), which were treated with superphosphate fertilizer (to increase P concentrations by 10–15 mg m^{-3}) and 20 kg of mulch/m^3 of water, superphosphate alone, and mulch alone. The initial pH of 3.3–4.6 increased above 6 for 2 months, but then returned to levels similar to the controls in the following months. The low sulfate concentrations in the water (less than 30 mg/L), low labile organic carbon, and the low P dosing all worked to reduce the effectiveness of the treatment.

For the field-scale experiment at Lake Garrick East (Fig. 4.7), the 70,000 m^3 lake section was supplied for 6 months with dried and liquid sewage sludge, and with green waste, altogether 5.7 kg of total organic carbon (TOC)/m^3 in the form of mixed fresh and degraded organic substances. After organic dosing, the pH increased while the lake was stratified and sulfate reduction started in the hypolimnion. There was, however, a sudden decline in pH when a cyclonic rainfall event briefly overturned the lake. The ORP and pH quickly returned to pre-rainfall levels once stratification resumed. Unlike in the other examples, this lake showed a resilience to mixing, possibly due to the three dimensional nature of the green waste protecting the sediment from the full effects of the mixing event.

4.3.1.3 Conclusions on Biological Treatment of Holomictic Pit Lakes

The biological remediation lake experiments that were successful—at least over the available observation times—needed 1.1 kg/m^3 of molasses and methanol (Anchor Hill Lake) to 5.7 kg TOC/m^3 (Garrick East) of organic material. Success at Anchor Hill Pit Lake was observed after the lake changed from a holomictic lake to meromixis. The respective experimental lakes should be monitored over some years to prove the long-term success of the biological treatment. In Lake Rävlidmyran, 570 g/m^3 of sewage sludge was applied, estimated (after McCullough et al. 2008) to equal ca. 6 g TOC/m^3, but subsequent monitoring over one year showed no effect (Lu 2004). Since over-dosage can cause the formation of free H_2S (Anchor Hill Pit Lake), the necessary amount of organics should be added in steps.

4.3.2 Meromictic Lakes Used for Subhydric Deposition and as Large-scale Reactors

Meromictic lakes have a permanent deep-water body and therefore lend themselves to treatment sustainability. Meromixis usually has important consequences on water quality: (1) anoxic conditions in the permanent deep-water body (monimolimnion), (2) enrichment of microbial decay products in the monimolimnion, and therein, (3) occurrence of H_2S and precipitation of metal sulfides. Unwanted substances can be enriched in the monimolimnion due to the very low rate of exchange with the water layers above.

According to Lewis et al. (2003), “the Anchor Hill pit lake appears to have become a meromictic lake, with a chemocline located at a depth of about nine metres” and “The present stratification raises the question as to whether the stratification might be used to advantage. In light of EPA’s interest in potentially using the pit as a pretreatment vessel upstream of the site water treatment plant, or even an alternative to the treatment plant itself.”

The 330 m deep pit lake in the former Island Copper Mine (Vancouver Island, Canada) has been filled with seawater. By adding an overlay of fresh water, the lake was made meromictic and the formation of an acid pit lake was prevented.

The whole pit lake is run as an AMD treatment plant to remove precipitated and adsorbed metals with sedimenting plankton. The deep-water body is used for subhydric deposition (Fisher and Lawrence 2006; Pelletier et al. 2009). A daily average flow of about 11,840 m^3d^{-1} of AMD has been treated by the system. Highly acidic AMD is fed directly into the monimolimnion whereas AMD with low acidity and metal load is directed into the freshwater layer at the lake surface. Similarly sustainable treatment might be applied in other meromictic pit lakes.

4.3.3 Sulfate Reduction in Floating In-Lake Reactors

Microbial sulfate reduction in floating reactors was tested in Mining Lake 111 (Lusatian District, Germany) using methanol as a carbon source for the microorganisms (Luther et al. 2003). After several improvements of the reactors, considerable success was reached in 2007 (Preuß et al. 2007). However, the final reaction rates (0.12 mmol SO_4^{2-} L^{-1} h^{-1} at a flow rate of 200 L/h) were not high enough for further development and full-scale neutralization of a complete lake (Koschorreck et al. 2010; Wendt-Potthoff et al. 2010).

4.3.4 Ecological Engineering of AMD Affected Lakes

Passive treatment may be successful in pit lakes and AMD-affected natural lakes where the loads of acidity and of toxic metals can be balanced by internal limnological processes and by reduction of incoming AMD. There are several natural processes that can be used to produce alkalinity and to sequester metals. Supporting such long-term processes is referred to as "ecological engineering" and promises to avoid expensive in-lake chemical and ex-situ treatments. Ecological engineering approaches are described in detail in three case studies by Kalin and Wheeler (case study 5.7).

Metals and arsenic can be removed by chemical precipitation, but also by accumulation onto algal biomass and subsequent burial in the sediment (Martin et al. 2003; McNee et al. 2003). Further examples are given in case study 5.7 by Kalin and Wheeler. In mesocosm experiments at Cluff Lake (Saskatchewan, Canada), algal growth was stimulated by P-fertilization; this was followed by significant declines in concentrations of toxic metals (Dessouki et al. 2005). This approach requires safe burial of the metals and arsenic in the sediment. In eutrophic lakes, with reductive conditions in the sediment, buried metals may be re-dissolved. Martin and Pedersen (2004) reported mobilization of arsenic after the lake became eutrophic and the sediment became unstable.

Therefore, meromictic pit lakes may be preferable sites for this approach, as used at Island Copper Mine pit lake (Vancouver Island, Canada; Fisher and Lawrence 2006; Pelletier et al. 2009). Weekly dispersion of liquid ammonia, polyphosphate, and urea ammonium nitrate (totaling 300 mg N/m^2 and 50 mg P/m^2 per week) has kept the concentrations of zinc, copper, and cadmium below the required thresholds in the mixolimnion and the outflow of the lake since the start of year-round fertilization in 2001 (Pelletier et al. 2009).

Kalin and Wheeler (case study 5.7) used combined ecological engineering approaches in weakly affected oligotrophic lakes. Metal adsorption was observed by mats of filamentous algae on suspended substrates (cut brush) in shallow parts of the lake and on aquatic moss growing on the sediment. The development of such benthic algae, epiphytic bacteria, and moss is supported by fertilization (phosphate mining wastes) and by offering additional surface areas for growth, i.e. brush cuttings. The living cover of moss over the sediment consumes oxygen, thereby reducing re-oxidation of iron hydroxides.

4.3.5 Carbon Dioxide Accumulation in Meromictic Pit Lakes

Degassing and CO_2-eruptions have been documented for the volcanic crater lakes Nyos and Monoun (Kling et al. 1994, 2005), leading to 1,800 lives lost by asphyxiation. Whether pit lakes are potentially susceptible to limnic eruptions needs be considered, as highlighted by Murphy (1997). High values of CO_2 are occurring at depth in the Berkeley Pit (Jonas 2000; case study 5.5), originating possibly from influx of alkaline groundwater from underground mine workings (Gammons and Duaime 2006). Sánchez-España reported 300—1,300 mg/L CO_2 in the monimolimnon of the 35 m deep meromictic Cueva de la Mora in the Iberian Pyrite Belt (case study 5.3). The high value corresponds to about 15% of saturation as pure CO_2 gas. If this deep water were in contact with the atmosphere, the partial pressure of CO_2 in air (0.04%) would limit such CO_2 saturation of the water. The 35 m deep water of the Cueva de la Mora would be oversaturated by two orders of magnitude if it rose to the surface and contacted air. It follows that the potential of a gas eruption exists if, for example, energy input was provided by an earthquake or landslide (see example in Sect. 4.2.1, Fig. 4.2), disturbing the deeper strata of a meromictic pit lake.

Murphy (1997) concluded that "it may be unwise to attempt to neutralize stratified acid pit lakes by dumping large quantities of carbonate rock on the lake bottom". He recommends monitoring dissolved CO_2 in pit lakes. New probes and sensors for in situ measurements of CO_2 gas are available (Johnson et al. 2010), and de-gassing methods for supersaturated deep strata in meromictic pit lakes were described by Kling et al. (1994, 2005). However, chemical treatment with highly reactive $Ca(OH)_2$ or alkaline low-density sludge, complemented with CO_2 gas to create carbonate alkalinity and to neutralize acidic pit lakes may have to be used with caution (Koch et al. 2007; Unger-Lindig 2010; Werner et al. 2006).

4.4 Treatments of In- and Out-Flows

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Treating influent water is a way to protect a pit lake and to improve its water quality. Treating out-flowing water prevents damage only to receiving waters (streams, rivers, lakes, and groundwater). Such an approach may be appropriate if remediation of the pit lake is not possible or if an implemented remediation measure requires time to produce an acceptable water quality in the pit lake.

Recent reviews and guidelines for technologies to treat acidic and contaminated mine waters, including management on the catchment scale, have been provided by the ERMITE Consortium (2004) and the U.S. Environmental Agency (Miller 2006).

4.4.1 Water Management in a Mining District

In the Lusatian lignite mining district (Germany), water distribution is managed by an integrated system among the rivers Neiße (tributary of the Odra River), Schwarze Elster, and Spree (tributaries of the River Elbe; Fig. 4.8). The management system comprises a network of 5 active mines, 3 reservoirs, more than 47 pit lakes, and 5 mine water treatment plants (Fig. 4.10). In 2008, the five chemical plants treated 324 Mio. m^3 of contaminated water before its release into receiving rivers. The hydrological lake positions are changing with flooding of the voids and with long-term recharge of the formerly lowered groundwater bodies across the district area.

4.4.2 Treatment of Acidified Streams

Some special approaches have been developed to treat streams and small rivers. Limestone sand and pebbles added to streambeds intermittently (Brown 2005; Menendez et al. 2000; Zurbuch et al. 1997) or dosing feeders that add alkalinity continuously to the stream are used (EPA 2004; Jenkins and Skousen 1993; Mills 1996; Sheeham et al. 2005; Skousen and Jenkins 1993; Skousen et al. 1998; Zurbuch 1996; Zurbuch et al. 1996, 1997).

4.4.3 Suitability of Passive and Active Treatments

Both active and passive treatments (AT and PT) are able to remove contaminants and neutralize acidity. The processes for treatment are based on: (1) neutralization with alkaline substances, (2) physical treatment with membranes, ion exchange, or

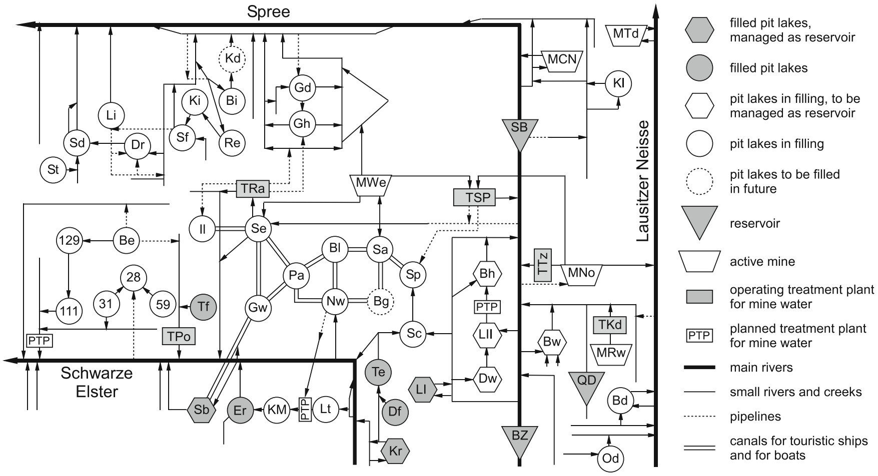


Fig. 4.8 Water management system and water transfer in the Lusatian lignite-mining district among the river systems of Schwarze Elster, Spree, and Neiße. The scheme shows the system in the Lusatian district south of Berlin, Germany with an area of ca. 100 × 100 km (modified after unpublished scheme from LMBV) Pit lakes: Lakes named by numbers: 28, 29, 31, 59, 111, 129, 130, and 131, *Bd* Berzdorf, *Be* Bergheide, *Bg* Bergen, *Bh* Burghammer, *Bi* Bischdorf, *Bl* Bluno, *Bw* Bärwalde, *DF* Lakes D and F, *Dr* Drehna, *Dw* Dreiweibern, *Er* Erika, *Gd* Gräbendorf, *Gh* Greifenhain, *Gw* Geierswalde (Koschen), *Il* Ilse, *Kd* Kahnsdorf, *Ki* Kittlitz, *Kl* Klinge, *KM* Kortitzmühle, *Kr* Knappenrode, *Li* Lichtenau, *LI* Lohsa I, *LII* Lohsa II, *Lt* Lugteich, *Nw* Neuwiese, *Od* Olbersdorf, *Pa* Partwitz, *Re* Redlitz, *Sa* Sabrodt, *Sb* Senftenberg, *Sc* Scheibe, *Sd* Schlabendorf, *Se* Sedlitz, *Sf* Schönfeld, *Sp* Spreetal, *St* Stiebsdorf, *Te* group of ponds near Hoyerswerda, *TF* group of ponds near Brieske; Reservoirs: *BZ* Bautzen, *QD* Quitzdorf, *SB* Spremberg; Active mines: *MCN* Cottbus Nord, *MNo* Nochten, *MRw* Reichwalde, *MTd* Taubendorf, *MWe* Welzow; Mine water treatment plants: *TKd* Kringelsdorf, *TPo* Pößnitz, *TRa* Rainitza, *TSP* Schwarze Pumpe, *TTz* Tzschelln

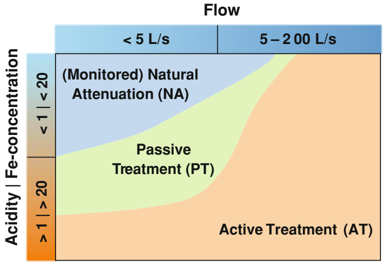


Fig. 4.9 Suitability of (monitored) natural attenuation (*NA*), passive treatment (*PT*) and active treatment (*AT*) options for remediation of polluted mine waters, expressed as functions of the magnitude of flow (L s^{-1}) and intensity of contamination of mine water discharges: Acidity (meq L^{-1}), Fe (mg L^{-1}; modified from ERMITE 2004; Younger 2002)

electrolysis, and (3) biological reduction and removal of ferric iron, toxic metals, and sulfate. The suitability of chemical and/or biological processes in PT or AT depends on the magnitude of flow and the concentrations to be treated (Fig. 4.9).

Fig. 4.10 Chemical treatment plant (Grubenwasserreinigungsanlage GWRA. Photo: P. Radke/ LMBV) Rainitza, treating acidic filling water of the future Lake Ilse/Pit Meuro in the Lausatian lignite district, eastern Germany. The final capacity will be 3 m^3/s

Small flows of moderate AMD or larger flows of mild AMD can be handled with passive treatment, whereas large flow volumes with highly concentrated acidity loads need AT plants. Flows of more than 5 $L\ s^{-1}$ and concentrations higher than 1 $mmol\ L^{-1}$ of acidity are generally too high for the relatively low-cost PT option (ERMITE 2004; PIRAMID 2003; Younger 2002).

Seasonal variability of both flow rates and acidity of influent and effluent water may also limit treatment options due to technical problems and/or cost. If, for example, water flow is very high during the wet season but very low or even missing during the rest of the year, the large treatment facilities necessary for high flow in the wet season may not be cost-effective during the dry season or may fail under low flow conditions.

4.4.4 Active Treatment

4.4.4.1 Chemical Treatment Plants

Chemical neutralization of AMD is the simplest type of treatment (Fig. 4.10). For high flows and high concentrations, the addition of lime after oxidation of all components is the most conventional and often cheapest form of treatment. It can be applied at all scales of flow and acidity and may be considered as the standard for comparisons with alternative technical approaches (McGinness 1999). The AMD-waters are neutralized with hydraulic residence times (HRT) from 10 min to 8 h. Liming can decrease sulfate concentrations below the solubility limits of gypsum.

Table 4.2 Chemical processes to treat acidic mine water in active treatment plants and respective examples

Chemical treatment plants	Processes and chemicals	Inflow vs. outflow characteristics
$CaCO_3$ neutralization[a] navigation site coalmine, Witbank, South Africa	Limestone ($CaCO_3$) powder	In: pH 1.8; 8.34 g L^{-1} SO_4^{2-}; 2.5 g L^{-1} Fe; Out: pH 6.6; 1.97 g L^{-1} SO_4^{2-}; <0.056 g L^{-1} Fe
Conventional treatment plant Tzschelln, Spree River, Vattenfall Mine Nochten, Germany[b]	Aeration; lime ($Ca(OH)_2$)	Treated flow: 86.400 m^3 d^{-1}; In: pH 4–5; Fe 700 mg L^{-1}; Out: pH 6.5–8.5; Fe < 1 mg L^{-1}
High-density-sludge (HDS) process[c, d]; navigation site coal mine	Limestone ($CaCO_3$), lime ($Ca(OH)_2$), CO_2 gas	In: pH 2.1; about 3 g L^{-1} SO_4^{2-}; Out: pH 8.5, about 1.1 g L^{-1} SO_4^{2-}
HDS process[e]; Wheal Jane pilot treatment plant, Cornwall, UK	Oxidation and chemical neutralisation (lime), unipure process	Treated flow: 864 m^3 d^{-1}’; In: pH 3.8; Fe 160 mg L^{-1}; Out: pH 9; Fe 1.3 mg L^{-1}
SAVIM (ettringite) process, cost effective sulfate removal (CESR)[f], 20 European plants	Lime ($Ca(OH)_2$, $Al(OH)_3$, CO_2 gas	In: ca. 0.6–3.35 g L^{-1} SO_4^{2-}; Out: basic quality: 0.5 g L^{-1} SO_4^{2-}; potable water: 0.2 g L^{-1} SO_4^{2-}; industrial water: 0.05 g L^{-1} SO_4^{2-}
Barium sulfide process[f, g] pilot scale study, Crown Mines; CSIR, South Africa	Lime pre-treatment; BaS treatment and SO_4^{2-} removal as $BaSO_4$; H_2S stripping by CO_2 gas	Lime treatment: SO_4^{2-} lowered from 2.8 to 1.25 g/L; precipitation of metal hydroxides; BaS treatment: pH 1.6 to 7.2; SO_4^{2-} 200 mg/L

More details are presented in Geller et al. (2009b). *Data sources* (a) Maree et al. (2004a); (b) Merkel et al. (eds.). Wissenschaftliche Mitteilungen, vol 25/2004, 28/2005, 31/2006, 35/2007. Techn. Univ. Bergakademie Freiberg; (c) Nengovhela et al. 2004 (d) Maree et al. (2004b); (e) Younger et al. (2002, 2005), Coulton et al. (2003); (f) INAP (2003) <http://www.inap.com.au> (g) Maree et al. (2004c)

Table 4.3 Active treatment of acidic mine water in full-scale bioreactors using solid, liquid and gaseous organic substrates

Bioreactor treatment plants	Flow, m^3/d	Hydraulic retention time, d	Substrate	pH in/out	SO_4^{2-}, g/L in/out	
On-site bioreactor	5,760	4–5	manure, straw	3.6/8.9	3/2.39	(a)
Thiopaque, South Africa	192–384	0.2–0.4	ethanol	7.2/7.7	2.2/0.2	(b)
Thiopaque, Budelco	8,400		ethanol		1/<0.2	(c)
Thiopaque, Budelco	7,200	1–3	acetate, synthesis gas	7.0–7.5/-	5–10/ 0.6–1.2	(d)

More details are presented in Geller et al. (2009b). *Data sources* (a) Nordwick et al. (2006), Zaluski et al. (2003); (b) Maree et al. (2004d); (c) Picavet et al. (2003); (d) Boonstra et al. (1999), Van Houten et al. (2006)

Additional steps, using barium or aluminum (ettringite process), are able to lower sulfate concentrations to the quality levels of potable and industrial water (Table 4.2).

Using lime, $Ca(OH)_2$, NaOH, or $Mg(OH)_2$, the pH rises to very high levels (10–12), facilitating rapid precipitation of nickel, zinc and other heavy metals. Generally, the highly alkaline water has to be adjusted, in a final step, to neutrality, which can be accomplished by the addition of $CO_2(g)$ or other acidic substances. Calcium carbonate powder could be used as an alternative to lime for neutralization of acid water at a reagent cost saving of 56% in a South African coal mine (Maree et al. 2004a). The water management system of the lignite mining district in Lusatia/Germany presently includes five full-scale treatment plants. One (conventional) chemical plant is designed to neutralize 170,000 m^3/d of acidic water, using 64 t of $Ca(OH)_2$ per day (Fig. 4.10). The produced iron oxyhydroxide sludge contains significant amounts of hydrated lime and might be used for in-lake treatments of acidic lakes.

The density of the large volumes of metal hydroxide sludge formed is usually low, but can be increased by recycling limestone sludge from the final step back to the first treatment step (high density sludge (HDS) technology). The full-scale chemical HDS-plant at the Wheal Jane Mine was designed to treat about 20,000 m^3/d (Coulton et al. 2003; Whitehead et al. 2005). The HDS-technology was successfully tested at the Butte mines area (Montana, USA) and could treat the Horseshoe Bend seep water and the future outflows of two pit lakes (Continental and Berkeley Pit), with a final design for a maximum flow of 26,500 m^3/d (Zick et al. 2004). Starting about 2017, the plant will use 120 t/d of CaO. Chemical treatments produce either large volumes of low density waste sludge (range: 1–5% of the treated water) or smaller volumes of higher density sludge. Before final deposition, the low density sludge may have to be dewatered, requiring additional equipment.

4.4.4.2 Biological Active Treatment Plants

Biologically based treatment plants are an alternative or complement to chemical treatment. Using the sulfate reducing process, they eliminate high sulfate concentrations, in addition to removing acidity and metals. Examples of full-scale bioreactors for active treatment of acidic mine waters are compared in Table 4.3. Biological reactors are designed to neutralize acidic mine water and to decrease high sulfate concentrations below legal limits. Usually a pre-treatment chemical neutralization step is included.

The end products are metal sulfides with a higher density than iron ochre sludges. The waste products have to be finally disposed of where they are protected against ingressing oxygen and remain permanently undisturbed. Otherwise, the treatment waste products may be reoxidized and the removed acidity would be remobilized, so that AMD is produced again.

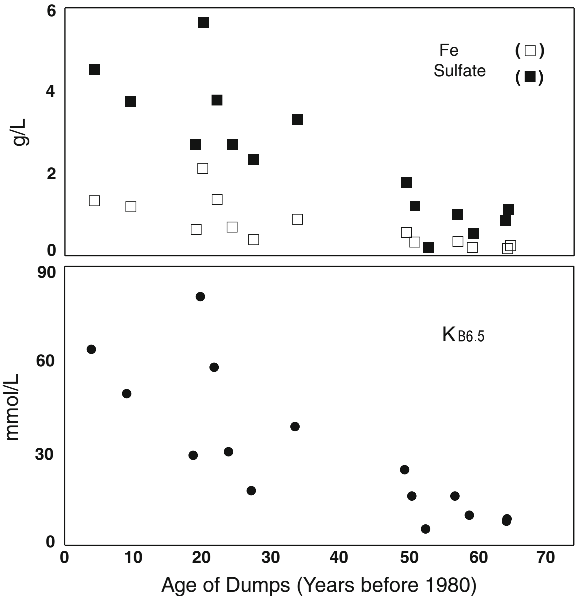
4.4.5 Passive Treatment Options

4.4.5.1 Natural Attenuation in Dumps and Lakes

The simplest method of treatment is counting on natural attenuation (NA) of the contaminants. This was the sole approach for many decades for groundwater and pit lakes. The lack of low-priced alternative options, environmental standards, and pressure by potential lake users encouraged this option to dominate. The natural processes that cause neutralization are complex and include:

(1) Washout and flushing of lakes and the locations from where the acidifying substances originate. The natural cycle is accompanied by eventual, permanent washout of any water-soluble substances. The same holds true for pyrite and its oxidation products.
(2) Neutralization by inflow of bicarbonate from naturally neutral streams and groundwater. Initially acidic water bodies may become neutral and buffered according to the geology and biogeochemistry of their watershed. Water from areas not impacted by mining often contains bicarbonate, depending on its flow path. Such water entering impacted areas—aquifers or lakes—acts as a carrier of alkalinity. Given enough time, the bicarbonate content of such natural water neutralizes the receiving water bodies and replaces the initially acid water.
(3) Sulfate reduction and even methane formation occurs, based on chemical and isotopic analysis of the water and gas phases in the overburden dumps in East Germany (Hoth et al. 2005, 2008; Storch et al. 2007). Hoth et al. (2008) observed that the acidity (calculated as base neutralization capacity $BNC_{6.5}$), dissolved total iron, and sulfate in the groundwater decreased with the age of the overburden dumps (Fig. 4.11). They reported that these processes depend

Fig. 4.11 Total Iron (Fe) and sulfate and amount of base necessary to reach pH 6.5 (after aeration and precipitation of $Fe(OH)_3$; $BNC_{6.5}$) in ground water of lignite mine dumps from the twenties to the seventies of the last century (modified after Hoth et al. 2008)



on total organic carbon (TOC) levels >1% in the overburden material. The TOC mainly consists of small remnant particles of lignite. Although lignite is usually assumed to consist of refractory substances, some microbial communities are able to use it as a substrate (Detmers et al. 2001). The biological activity, preferring the light isotopes of sulfur, enriched the heavy ^{34}S-isotope in the pore waters (Knöller et al. 2004). Since lignite was the main carbon source for sulfate reduction in the above example, natural attenuation of AMD in metal-mining regions is much less likely.

(4) Natural sulfate reduction in acidic German pit lakes was reported by Peine and Peiffer (1996). They estimated long-term neutralization rates of 4–107 mmol m^{-2} yr^{-1}, averaged over the age of the lakes. These rates of alkalinity formation correspond to those observed in rain-acidified lakes, but are somewhat lower than the average rates for neutral lakes of low productivity (182.5 mmol $m^{-2}\cdot year^{-1}$; Koschorreck and Tittel 2007). The observed net rates of alkalinity formation by sulfate reduction were low compared to the amount of acidity requiring neutralization. Therefore, the contribution to neutralization is small. However, the contribution of sulfate reduction to the maintenance of neutral conditions may be relevant if the inflow of acidity with groundwater is small or if the pit lake is productive. The potential compensation of acidity load by internal lake processes was estimated to average 1.88 mol m^{-2} yr^{-1} in productive natural lakes (Koschorreck and Tittel 2007).

4.4.5.2 Natural Attenuation in the Hyporheic Zone of Streams

Few investigations have considered the attenuation processes that occur in the hyporheic zone of rivers where mine-contaminated groundwater first contacts surface water (Gandy et al. 2007). Mining-polluted groundwater may originate from acidic lakes or flow directly from dumps into streams or rivers. The hyporheic zone below and laterally adjacent to the river is the transitional zone between surface water and groundwater. The 'surface hyporheic' zone is the upper stratum dominated by the river water (oxic and chemically identical). The deeper 'interactive hyporheic' zone is a mixing zone that comprises 10–98% river water. Here, oxygen may be completely consumed by microorganisms, and the pore water may become anoxic (reductive and chemically dominated by groundwater). Gandy et al. (2006) report on immobilized metals (Mn and Fe) after oxidation in the interactive and surface hyporheic zone, where the metal hydroxides precipitate, which prevents them from reaching the surface water. With increasingly reductive conditions, however, the immobilized metal hydroxides can be reduced and again dissolved (Benner et al. 1995; Fuller and Harvey 2000; Younger et al. 1993). In the cases reported by Gandy et al. (2007), the reductive conditions obviously supported the reduction of iron and manganese, but did not reach the lower negative Eh range for sulfate reduction, and, therefore, no precipitation of iron sulfides was observed. The interactive and surface layers of the hyporheic zone can be considered as a reactive barrier between AMD groundwater and affected surface waters.

4.4.5.3 Passive Treatment at the Sediment-Water Interface

With known flow paths of water leaving the lake and entering the groundwater body, pilot-scale experiments have been conducted to improve the quality of the water as it passes through the upper layers of lake sediment. In Lake Lohsa II, in the Lusatian district (Germany), the lake basin morphology was to be adapted to stabilize the slopes. Therefore, sediment was translocated within the lake using a swimming suction excavator. The suspended sediment was transported through a pipeline and simultaneously conditioned with added lime (CaO and natural $CaCO_3$). The new sediment was deposited across the test areas in 0.1–1 m thick layers, and the lime products were preferentially placed into the uppermost layers. The aim of still ongoing experiments was to construct a "reactive carpet" for passive long-term treatment of the acidic outflow into the groundwater body.

4.4.5.4 Passive Treatment and Enhanced Natural Attenuation

Natural attenuation may be enhanced (ENA) by additions of alkaline substances to the dump material (see Sect. 4.6) or of organic substances, or both, at the outflow

Table 4.4 Typical combinations of passive technologies to treat AMD and respective results of removals rates and efficiencies

	ALD + aerobic wetland	ALD + RAPS	Aerobic + compost wetland	ALD + aerobic wetland + compost wetland
Technical design	Review of 13 sites (Brodie 1993)	Jones branch, USA (Karathanasis and Johnson 2003)	Lick Run, USA (Mitch and Wise 1998)	Wheal Jane, U.K. (Whitehead et al. 2005)
Flow (m^3 d^{-1})	1,000 ± 1,556	53	164 ± 27	17–34
Area (m^2)	1417 ± 285	1,022	3,869	2,850
Inflow				
pH	5.3 ± 1	3.4	2.8	3.9
Acidity (meq L^{-1})	nd	45	17	nd
Fe (mg L^{-1})	50 ± 54	787	170	144
$SO_4^{2-,}$ (g L^{-1})	nd	3	1.7	1.7
Removal efficiency (%)				
Acidity	nd	95	56	nd
Fe	83 ± 28	95	84	99.5
$SO_4{}^{2-}$	nd	55	23	30
Removal rate				
Acidity eq m^{-2} d^{-1}	nd	2.2	0.4	nd
Fe (g m^{-2} d^{-1})	6.2 ± 11.7	39	6.1	1.3
$SO_4^{2-,}$ (g m^{-2} d^{-1})	nd	87	16.4	4.5

ALD anoxic limestone drains, *RAPS* reducing and alkalinity producing systems, *nd* not determined (modified from Geller et al. 2009b)

interface of dumps (Hoth et al. 2008). Passive treatment is the deliberate improvement of water quality using only naturally available energy sources, in systems requiring only infrequent maintenance to operate effectively over the entire system design life (PIRAMID 2003). Both passive systems and the ENA-approach are simple and cheap, but not readily controlled.

Passive treatment systems (Table 4.4) are designed to remedy AMD-waters with flows of 5–5,000 m^3/d, using surface areas of ponds, wetlands, or subsurface passages, at a scale of 100–2,000 m^2. Water flows through passive systems with hydraulic residence times (HRT) of 1 day to 1 month. The resulting treatment efficiencies are usually high for the elimination of iron, but are often low for sulfate. Compared with single systems, combined successive steps of chemical and biological treatment gave better results in some well-documented cases (Table 4.4).

Passive systems, by definition, would need no technical energy supply to run using different natural processes to cleanse AMD outflows, even in remote areas. There are several reviews, handbooks, reports, and guidelines about, or with chapters on passive systems for treatment of AMD. These include:

- USA: Handbooks of the *Acid Drainage Technology Initiative* (ADTI) on Technologies for Avoidance and Remediation of Acid Mine Drainage (Skousen et al. 1998) and on Mine Pit Lakes (Castendyk and Eary 2009), a review chapter on the *Treatment of Mine Drainage by Anoxic Limestone Drains and Constructed Wetlands* (Kleinman et al. 1998), an overview paper of the U.S. Dept of Energy, *The Passive Treatment of Coal Mine Drainage* (Watzlaf et al. 2004), and a technology transfer document of the U.S. Environmental Protection Agency, *Management and Treatment of Water from Hard Rock Mines* (Miller et al. 2006).
- Canada: *Review of Passive Systems for Treatment of Acid Mine Drainage* of the Mine Environment Neutral Drainage Program (MEND 1999). Critical review on passive bioreactors by Neculita et al. (2007).
- European Union: final reports and guidelines of projects of the European Union on *Environmental Regulation of Mine Waters in the European Union* (ERMITE-Consortium 2004), and on *Passive* In situ *Remediation of Acidic Mine/Industrial Drainage* (PIRAMID Consortium 2003).

The overview by Watzlaf et al. (2004) gives a comprehensive introduction on the development of the different technologies for passive treatment of neutral and acidic mine waters, from the first field observations in the late 1970s that natural wetlands could remediate contaminated mine water, to the current state of combined sequential, passive, chemical, and biological treatments. Experience in proper designs for and the limitations of these passive treatment technologies are presented in the above mentioned publications.

4.4.5.5 Passive Chemical Treatments and Aerobic Wetlands

Low-acidity waters can be improved by passive treatments like open or anoxic limestone channels or drains. Open limestone channels (OLC) are limited to very low loads of metals or to flow rates high enough to prevent rapid formation of reactivity-lowering precipitates on the limestone. Anoxic limestone drains (ALD) are typically airtight covered trenches filled with limestone. ALDs prevent the formation of iron precipitates by keeping the iron in the ferrous state due to the anoxic conditions. The CO_2 resulting from reaction of limestone with acidity enhances further dissolution of limestone:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$$

Therefore, ALDs usually produce neutral water with very high bicarbonate alkalinity. Dissolved aluminum may gradually decrease performance due to precipitation of aluminum hydroxide and aluminum hydroxy sulfate compounds.

In aerobic wetlands, dissolved metals are oxidized and precipitated as metal hydroxides or oxides. Aerobic wetlands are constructed to optimize the ingress of oxygen through shallow depth, cascades, or other methods. The processes of oxidation and precipitation of metals consume alkalinity but lower the contaminant concentrations. The emergent wetland plants increase the settling rate of the precipitates.

The efficiencies of passive chemical treatments were evaluated from a data base of the UK Coal Authority, comprising about 30 sites and measured data series from 11 schemes, and used to develop a model to optimize design criteria (Sapsford and Watson 2011). The model predicts the removal efficiency of iron, depending on the pH, dissolved oxygen, temperature, flow rate, and hydraulic residence time of the treatment scheme. The measured removal efficiencies versus the theoretical ones, calculated by the model, indicate that this methodology can be used to compare different treatments. Schemes that reached the theoretical limits are considered as optimally designed. Other schemes where the theoretical limit was not reached have the potential for further improvements.

4.4.5.6 Passive Biological Treatment in Anaerobic Wetlands

Constructed wetlands have been used for the passive biological treatment of urban wastewaters since the 1950s. These engineered wetlands are designed as aerobic surface flow or largely anearobic subsurface flow (horizontal and vertical) systems. "The subsurface systems have been commonly used in Europe while free water surface systems have been more popular in North America and Australia" (Vymazal 2011). They were further developed and "accepted as certified technologies following official guidelines", and are used in "tens of thousands applications in all parts of the world". Their primary aim is to treat urban sewage water by removing organic substances and the nutrients P and N.

Special wetland designs have been developed to remove metals, sulfate, and acidity from mine water (e.g. Watzlaf et al. 2004). Surface flow compost wetlands are filled with organic material like mushroom compost, sawdust, or composted manure, often mixed with limestone. The mineralization of the organic material provides anoxic conditions in the substrate, so that both chemical neutralization by the limestone and microbial sulfate reduction occur. To force the water through the reductive material, vertical flow systems have been developed, called reducing and alkalinity-producing systems (RAPS) or successive alkaline producing systems (SAPS). These systems are surface inflow wetlands that are sealed from groundwater and filled with layers of alkaline substances and organic material. The outflow of the water is through drainage tubes at the bottom of the wetland. Underground reactors are RAPS-like systems that have no open water on top and are covered.

In an early survey on constructed wetlands, Wieder (1989) found that the efficiencies for the removal of H^+, acidity, Fe, Al, Mn, and SO_4^{2-} from acidic coal drainage were variable and not correlated with design criteria (wetland area, thickness of organic substrate layers, flow rates, and metal loadings). The conclusion was that "the effectiveness of wetland treatment of AMD is … presently not predictable" (Wieder 1989). Some years later, Sobolewski (1997) complained in a review of case studies about insufficient documentation of wetlands constructed to ameliorate water quality and concluded that "the limitations of constructed wetlands are found not in the wetlands, but in information about them."

With further research and experiences, constructed wetlands are now being better designed to reach their optimal efficiencies within the given limits (PIRAMID-Consortium 2003; Watzlaf et al. 2004). Some examples of combined passive treatment systems and their respective efficiencies in removing acidity, iron, and sulfate are presented in Table 4.4.

Neculita et al. (2007) concluded in a review on passive AMD bioreactors: "Passive on-site bioreactors … are well suited for remediation of abandoned, remote mine sites or for sites located in cold areas. … Passive bioreactors can still operate at temperatures as low as 2–6°C and pH 3.0…. The efficiencies of passive bioreactors … (are) mainly controlled by the composition of the reactive mixture. The most important component is the organic carbon source." Chang et al. (2000) showed in an experimental study that different solid waste materials are suitable for passive bioreactors, and that cellulose was the main component consumed in the reactors. Sulfate-reducing bacteria cannot use cellulose; instead, other anaerobes degrade the cellulose and create simpler nutrients that the sulfate-reducing bacteria can use.

Even though formation of metal sulfides is the preferred metal removal process, many metal removal mechanisms, including adsorption and precipitation of metal carbonates and hydroxides, occur in passive bioreactors. Furthermore, these mechanisms change during the life span of a passive bioreactor (Neculita et al. 2007). There is a basic need to develop process models, as Sapsford and Watson (2011) did for constructed aerobic wetlands, to predict the respective optimal efficiencies for the more complex biological treatments in anoxic compost wetlands and RAPS/SAPS. These models should incorporate changes caused by aging of the reactor.

4.4.6 Assessments of Passive versus Active Treatment

Through pilot- and field-scale studies, critical factors for a long-term operation have been identified, including exhaustion of organic carbon, plugging, compacting, and overloading (Neculita et al. 2007). Some of these reduce system efficiency by changing the flow pattern, causing selective flow short-cuts and shorter hydraulic retention times. Wetland systems were initially designed for lifetimes of 20 years or more, but long-term experience is limited (Ziemkiewicz et al. 2003). Eger and Wagner (2003) concluded that early estimates of long lifetimes may be substantially overestimated.

A research paper of the library of the U.K. House of Commons (McGinness 1999) gave comprehensive descriptions and assessments of AMD treatment technologies for the Parliament. The report on passive treatment success and removal efficiencies for the main AMD contaminants (basically iron, aluminum, and sulfur) largely relied on data from recently established constructed wetlands. However, a final assessment can only be made based on the long-term cumulative treatment effectiveness. Factors such as decreasing treatment efficiencies in aging

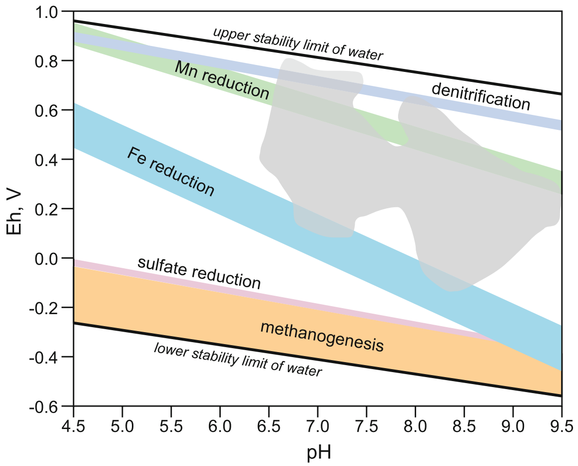


Fig. 4.12 Eh–pH diagram showing the ranges of microbiological reduction of nitrate, Fe, Mn, sulfate, and of methanogenesis. The *grey*-marked polygon area indicates the measured conditions in three biological cells (anaerobic compost bioreactors) of the Wheal Jane experimental passive treatment plant (modified and combined after Gammons et al. 2009 and Whitehead et al. 2005). Similar ranges were measured by Kalin et al. (2006)

wetlands, lifetime limits, the fate of waste products, and the areas needed over the entire time during which water has to be treated. Facing the experiences with the largest experimental passive AMD-treatment plant in Europe (Wheal Jane), Whitehead et al. (2005) noticed that the redox conditions in the anoxic bioreactor cells were suitable for precipitating iron, but did not reach the range for sulfate reduction (Fig. 4.12).

After McGinness (1999), "there have been several modifications of the original wetland solution, with each adding more and more active elements to the passive solution." "The design of the wetland system … is often highly engineered. … The problem here is that such highly engineered systems are likely to require much higher maintenance costs and are unlikely to develop into self containing ecosystems over time" (McGinness et al. 1994).

In a long-term field and laboratory study over a 10 year period with a compost wetland, the initially high sulfate removal rate decreased to 10% of the recommended design rate after 5.5 years (Eger and Wagner 2003). The flow rate through the system had to be reduced to 10% of the original flow to keep the desired water quality. For anaerobic systems Eger and Wagner (2003) concluded that "the estimated lifetime based on total carbon generally exceeds 25 years, but effective treatment is likely to last less than 5 years unless the substrate is replaced or supplemental carbon is added to the system." In a modeling study by Tarutis and Unz (1994), the aging of organic substrate was considered. Since easily available small-chain components are readily used, leaving a remainder that is more difficult to break down, they recommended adding supplemental organic substrates every 3 years.

These weak points can be avoided in well-designed anoxic biological cells (Kleinmann 1998; PIRAMID 2003; Watzlaf et al. 2004), so that the respective wetlands are able to decrease contaminant concentrations to the desired levels (Table 4.4). Considering the outflow treatment of acidic lakes, and the large volumes and high concentrations of acidity, sulfate, iron, and other metals present in many of these, the costs to build a sufficiently large passive treatment plant, and planning for its long-term maintenance, may, in many cases, exceed the costs of an active chemical treatment plant (McGinness 1999).

Neither passive wetland areas nor active treatment plants are self-contained and sustainable since the produced waste products have to be removed and deposited elsewhere (settling pond, tailings dam, protected anoxic final dump). Where the passive cells will be used as final deposits after having reached the end of their lifetime, new treatment cells will have to be built, thereby increasing the total area needed (e.g. Johnson and Hallberg 2002, 2005).

4.5 Conclusions and Lessons Learned

Walter Geller and Martin Schultze

The most consistent way to treat pits filled with AMD is in treatment plants with lime, or by large-scale chemical treatment of the lake. Examples are lignite pit lakes with 19–82 10^6 m^3 of water volume with 1.6–8.1 mmol/L acidity (Table 4.1). Other forms of chemical and biological treatments are known, but they have not been efficient in most field applications, though the combination of chemical and biological treatment appears promising. Alternatively, filling and flushing with river water or water from mines still in operation are efficient options for the neutralization of pit lakes if enough neutral, fresh water is available.

Initial difficulties with full-scale treatment of pit lakes came from using very simple techniques to discharge and dilute the chemicals and organic nutrients into the water body. It was not effective to discharge tons of material directly from the shore of large lakes since incomplete distribution and dilution prevented an effective reaction with most of the water that had to be treated. In the worst case, the discharge procedures ended in underwater dumps of soda ash, hydrated lime, or fly ash (German pit lakes) or in non-reactive layers of concentrated molasses or sodium hydroxide at the lake bottom (first attempts at Anchor Hill Pit Lake, USA). Improved approaches have subsequently been successful in mixing the reagents with the lake water and distributing the diluted suspension or slurry through floating hoses, pipelines, and large-area sprinklers.

Although chemical treatment has largely been successful in neutralizing acidic water bodies, there is a problem with the sustainability of the approach if there are continuing inflows of acidity from adjacent dumps, tailings, or former underground workings. From an ecological point of view, there is no concern with the first, initial chemical treatment of an extremely acidic pit lake. After its neutralization, however, the lake will develop a limnic ecosystem. With re-acidification after some years, a secondary chemical treatment might be necessary, but this should avoid adverse effects on the ecosystem, as fish-kills. Therefore, aggressive and highly alkaline chemicals, like sodium hydroxide or quicklime, should be not be used.

There are major difficulties with full-scale biological treatment of lakes. Simply scaling-up successful smaller scale tests, from microcosms and mesocosms to whole lakes, does not work. Sulfate reduction with metal sulfide elimination works well in the lab and in pilot-scale experiments in lakes, but large-scale field tests in lakes revealed increasing problems with greater size (Geller et al. 2009a; Koschorreck et al. 2007). Natural seasonal mixing of the water column disturbs the anaerobic processes of sulfate reduction and formation of metal sulfides, and allows oxygen transport into the deep water. In iron-rich water, there is an additional problem as ferrous iron is turbulently transported from the sediment into the water, followed by its oxidation, its precipitation, and sedimentation back to the lake bottom. The cycle transports electrons from oxygen of the upper layers into the lower, anoxic zone (Peine et al. 2000), thus supplying ‘oxygen equivalents’ into the oxygen-free zone. Large-scale enclosure tests have shown that an acidic lake can produce the same alkalinity as natural lakes (Geller et al. 2009a; Koschorreck and Tittel 2007). The rate, however, is too slow to neutralize strongly acidic lakes (Koschorreck et al. 2007). These biological remediation approaches are more likely to succeed in meromictic lakes with deep-water that does not overturn seasonally.

Another finding from experiments with large macrocosms and whole lakes is the tremendous amount of organic materials needed to reach anoxic conditions in the seasonal hypolimnion or the permanent monimolimnion of lakes, and generate sulfate reduction. First expectations, that biological remediation only had to be started to support a self-sustaining process of primary production, sedimentation of decaying organisms, and ongoing biological remediation, proved to be far too optimistic. Those biological remediation experiments that were successful—at least over the available observation times—needed 1–10 kg/m^3 of organic substance. Since over-dosage was shown to cause the formation of free H_2S, the necessary amount of organics should be added in steps. “The potential to exchange one form of pollution (organic matter) for another (sulfuric acid) suggests that organic matter additions [must] be done carefully” (Brugam and Stahl 2000).

Treatment of acidic and metal-contaminated flows out of mines or pit lakes must attain legal limits to discharge the water into uncontaminated receiving rivers and lakes. Conventional treatment involves adding lime or other alkaline substances to the acidic water to neutralize the acidity and precipitate iron and other metals. Full-scale chemical plants can treat volumes of 10,000–100,000 m^3 per day. Simple treatment produces large volumes of low-density iron-hydroxide sludge, which must be properly disposed of. More sophisticated plants produce a higher density sludge (HDS technology), thereby minimizing the amount of waste. Unwanted high concentrations of sulfate can be decreased by an order of magnitude in large-scale bioreactor treatments with flows of 1,000–10,000 m^3 per day. Usually, chemical pre-treatment is needed to neutralize the acidic water.

Natural attenuation by sulfate reduction was observed in dumps over ca. 50 years (Hoth et al. 2005, 2008). Sulfate reduction was even observed to be occurring in the field at low-pH conditions, as well in natural sediments (Koschorreck et al. 2003), lignite mine dumps (Storch et al. 2007), and passive bioreator cells (Neculita et al. 2007). However, natural attenuation alone can rarely remediate groundwater and pit lakes without additional remedial measures.

Both active and passive systems are able to successfully remove contaminants from mine waters, within their given limits (Fig. 4.9). Passive treatment has been demonstrated to effectively remediate AMD using relatively low-cost, low-maintenance systems, even at remote closed mines. There are reports of flows of 5–5,000 m^3 per day being treated, needing areas of 100–2,000 m^2 for the limestone drains, constructed wetlands, and polishing ponds. The production of alkalinity in anaerobic limestone drains (ALD) can reach 3–6 mmol/L with 15 h of contact time (Watzlaf et al. 2004). Combined ALD-RAPS-systems achieved removal rates of 2.2 mol m^{-2} d^{-1} of acidity, 39 g Fe m^{-2} d^{-1}, and 87 g sulfate m^{-2} d^{-1} (Table 4.4). Critical assessments, however, showed decreasing effectiveness of aging passive systems and missing final development to a sustained state. The waste substances retained within the reactive cells of passive systems or in settling ponds of active treatment plants represent a pending long-term problem until they are suitably buried in a manner that will avoid potential remobilization.

4.6 Avoidance and Source Treatment

Frank Wisotzky

There are three different general approaches to avoid mine-generated acidic groundwater and pit lakes (Table 4.5):

1. Prevention or mitigation of pyrite oxidation.
2. Decreasing acidity and mineralization.
3. Mitigation of the transport of polluted groundwater and surface water.

Prevention or mitigation of pyrite oxidation can be realized by changing mining activities e.g. dump construction and typically involves decreasing oxygen transport to pyritic materials or decreasing the time that pyritic materials are exposed to atmospheric oxygen. A layer that can diminish oxygen transport can be placed on top of pyritic waste rock. This is possible with different unsaturated cover materials, often called dry covers (Miller et al. 2006). The pyritic material can also be placed underwater because of the lower diffusion coefficient in water (2.1×10^{-5} cm^2 s^{-1}) than in the gas phase (2.0×10^{-1} cm^2 s^{-1}); this is called a wet or water cover (Table 4.5). Besides covering the pyritic material, chemicals can be added to protect the pyrite from oxygen; this is called encapsulation (Evangelou 1995). In practice, this generally involves the addition of alkaline substances like crushed limestone or $Ca(OH)_2$. This leads to high pH values around the sulfide minerals, which causes

Table 4.5 Different approaches, mechanisms and measures to improve the water quality or diminish the acid water problem

Approach	Main mechanism		Measure	Literature (examples)
Prevention or mitigation of pyrite oxidation	Prevention or mitigation of O_2−transport or reduction of the time of exposition	Macroscopic effects	Change of mining activities (dump construction)	Boehm and Von Schwarzenberg 2000; Obermann and Wisotzky 1998
			Dry covers	Gustafsson et al. 1999; Nicholson et al. 1989; O'Kane et al. 2002
			Wet covers/water covers	Amyot and Vezina 1997; Dave et al. 1997; Ellis and Robertson 1999; O'Kane et al. 2002
		Microscopic effects	Coatings, encapsulation	Evangelou 1995; Kringel 1998
	Neutralization with alkaline acting substances	Microscopic effects	Addition of alkaline acting substances	Duel 1974; Fischer et al. 1987; Kringel 1998; Wisotzky 2003
	Inhibition of oxidizing bacteria	Microscopic effects	Addition of bactericides	Kleinmann et al. 1981; Kringel 1998; Tuttle and Dugan 1976
Decrease of acidity and mineralization	Neutralization with alkaline acting substances	in situ	Addition of alkaline substances	Lenk and Wisotzky 2008; PIRAMID 2003; Stewart et al. 2001; Wisotzky 2003; Wisotzky and Obermann 2001
		ex situ	Addition of alkaline substances (water treatment)	Kleinmann et al. 1998; Sengupta 1993
	Neutralization with reducing substances	in situ	Addition of degradable organic substances	Koschorreck and Tittel 2007; PIRAMID 2003; Stottmeister et al. 1999; Wendt-Potthoff and Neu 1998; Wisotzky and Kringel 1998
		ex situ	Addition of degradable organic substances (water treatment)	Hellier 1999; Kleinmann et al. 1998; Sengupta 1993
Reduced transport of polluted groundwater	Diminishing water flow	Decreasing surface water inflow	Sealing to decrease the amount of seepage	Sengupta 1993
		Diminishing groundwater inflow	Wells to decrease discharge	Boehm and Von Schwarzenberg 2000; Brand 1996; Obermann and Wisotzky 1998

precipitation of ferric hydroxides, which, to some extent, diminishes the rate of pyrite oxidation. Addition of large amounts of alkaline substances is generally necessary to significantly increase the pH-value in pyrite oxidation zones. Another alternative is to add bactericides to inhibit pyrite oxidizing bacteria (Table 4.5).

A second approach is to try to decrease acidity and mineralization without changing the extent of pyrite oxidation as the primary source. This can be realized by the addition of alkaline substances directly to the waste rock before dumping (Fig. 4.13); this is sometimes called blending. For example, the overburden of the Garzweiler Mine (Rhineland lignite mining area, Germany) has been limed in this manner since 1999 to neutralize the formed acidity (Fig. 4.13). On average, the limed overburden in this mine has a pyritic sulfur content of 0.225 wt%. On average, 0.065 wt% crushed limestone was added between 1999 and 2004 (Lenk and Wisotzky 2008) to prevent acidic pH-values in the groundwater from this dump. The limestone addition was oriented to the recently released acidity (for details, see Lenk and Wisotzky 2008), not to the total acid production capacity of the overburden (Morin and Hutt 1997), which is much higher. If the total acid production capacity was to be neutralized, the addition of 0.7 wt% limestone would be necessary.

A third approach is to mitigate the transport of acidic mine water to the surrounding environment (Table 4.5). Reducing the amount of water entering the dumps by sealing, which is comparable to the technology of building a landfill, can limit water draining from sites, but this is only practical for low amounts of overburden material and is not an option for huge mining sites. However, diverting water from running on to a site and reducing infiltration by intercepting rainwater are relatively inexpensive measures that can be useful. At sites where groundwater discharges into the mine, groundwater can be pumped to the surface either before it is exposed to the pyritic material or from within the mine site; in the latter case, the pumped water must be treated before it is discharged. Where possible, it is best to avoid water treatment, since it will generally be required for a long time after mine closure.

Experimental dumps or waste rock piles are sometimes used to assess the likely effects that various mitigative or ameliorative actions might have on eventual water quality (Marcoline et al. 2006; Wisotzky 2001). For example, to gauge the expected groundwater quality in the Garzweiler lignite mine dump (Rhineland lignite mining area, Germany), five different experimental dumps were created in 9 m^3 (in volume) containers (Wisotzky 2003; Fig. 4.14). About 12 tons of oxidized and unoxidized overburden were mixed to match the average oxidized pyritic sulfur content (0.032 wt%) of the dump material at the mine. The containers were sealed with a welded cap and were flooded with deep groundwater to simulate groundwater rebound. One container without alkaline additives was kept as a reference or control. Three other containers were treated with a crushed limestone addition of 0.15 wt% at three different grain sizes (fine, finest, and pellets). The finest limestone had an average grain size of 0.1 mm, the fine limestone had an average grain size of 0.3 mm, and the pellets had an average grain size of 0.7 mm (Wisotzky 2003). The pellets came from a water softening

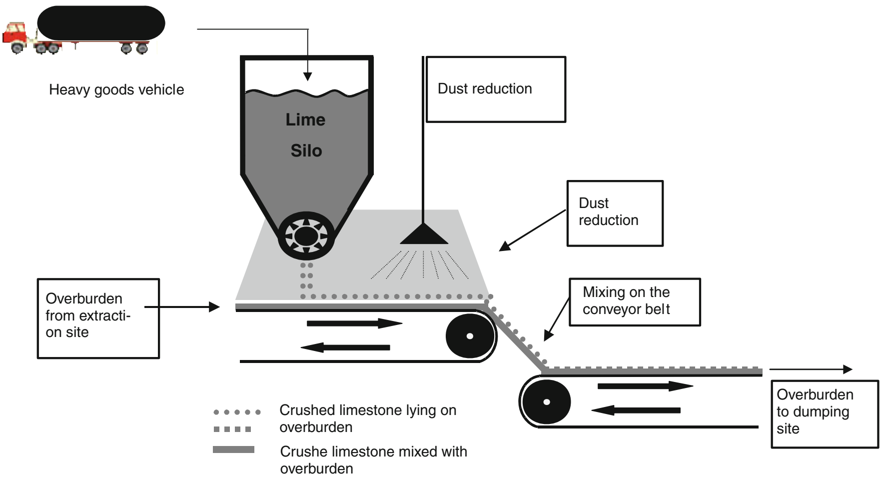


Fig. 4.13 Addition of crushed limestone to overburden at the Garzweiler Mine in the Rhineland lignite mining area (Germany)

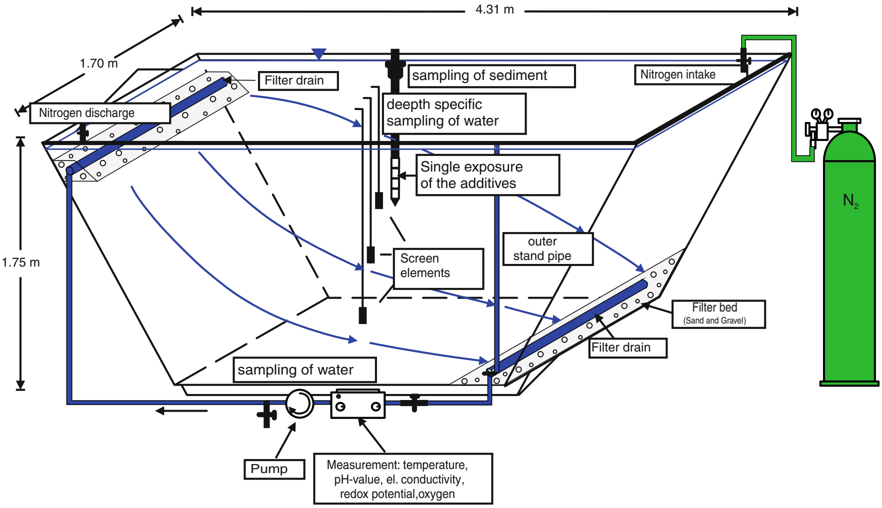


Fig. 4.14 Setup of container experiments to simulate the groundwater quality in the dump of the mine Garzweiler of the Rhineland lignite mining area (modified after Wisotzky 2003)

plant. The final container received a mixture of fine limestone and fly ash from a lignite burning power plant (0.2 wt%). All containers with alkaline additions are referred to as treated containers. To simulate groundwater movement, the water was pumped around before water samples were collected (Fig. 4.14).

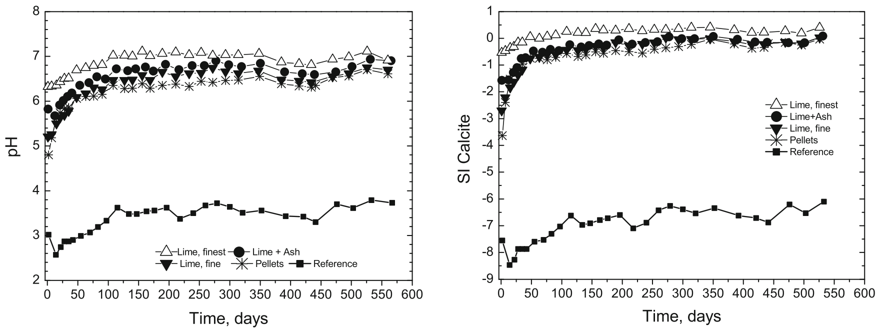


Fig. 4.15 Changes over time in measured pH (*left*) and calculated saturation index values with respect to calcite (*Right*) in the water of the experimental dumps of the Garzweiler Mine (modified after Wisotzky 2003)

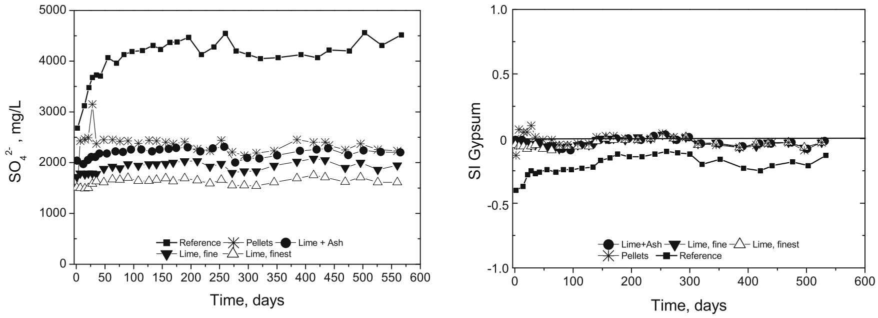


Fig. 4.16 Changes over time in measured sulphate concentrations (*left*) and calculated saturation index values with respect to gypsum (*right*) in the water of the experimental dumps of the Garzweiler Mine

Water samples were regularly collected from the containers and analysed for major elements and some trace metals for about 550 days. The pH in the reference container reached values between 3 and 4 after a few weeks. This is the expected pH in the groundwater of the dump without counteractive measures.

The pH in the treated containers reached values between 6.4 and 7 (Fig. 4.15), demonstrating the success of the treatment approach. The highest pH values were reached in the container with the finest limestone, followed by fine limestone, and pellet addition, reflecting the effect of grain size. The limestone and ash container displayed comparable pH values of ca 6.8. The saturation index (SI) values were calculated with the computer program PRHEEQC (Parkhurst and Appelo 1999) using the measured concentrations. The SI with respect to calcite was below −6 in the reference container (Fig 4.15). This strong undersaturation decreased in the treated containers. After 550 days, the SI reached values of ca. 0 with respect to calcite in the treated containers. The highest values were observed in the container with the finest grained limestone.

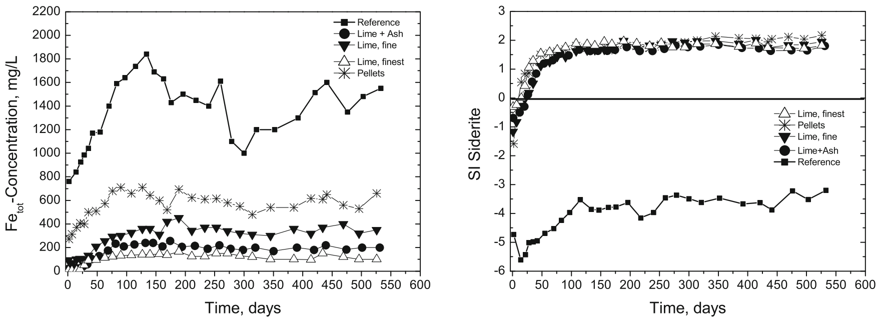


Fig. 4.17 *Left* Changes over time in measured iron concentrations and calculated saturation index values with respect to siderite; *right* in the water of the experimental dumps of the mine Garzweiler

Sulfate concentrations between 4,000 and 4,500 mg/L were recorded after 50 days in the reference container water (Fig. 4.16, left). The analysed sulfate concentrations in the treated containers displayed much lower concentrations. The reference container had SI values with respect to gypsum below 0, reflecting no possible precipitation of gypsum (Fig. 4.16, right; Eq. 4.1).

$$CaCO_3(s) + H^+ + SO_4^{2-} + 2H_2O \Leftrightarrow CaSO_4 * 2H_2O(s) + HCO_3 \qquad (4.1)$$

The dissolution of calcite in the treated containers increased calcium and bicarbonate concentrations (Eq. 4.1), which led to precipitation of gypsum in the treated containers and SI values with respect to gypsum of ca 0 (Fig. 4.16, right). The finest limestone addition resulted in sulfate concentrations of ca 1600 mg/L. Higher sulfate concentrations were observed in the fine limestone (ca 2,000 mg/L) and the pellet container (ca 2,200 mg/L). The higher sulfate concentrations in equilibrium with gypsum are possible because of higher dissolved iron concentration (Fig. 4.17, left) in the latter containers. At the end of the container experiments, ca 100 mg/L of iron was observed in the finest limestone container. Higher iron concentrations were observed in the fine limestone container (ca 350 mg/L) and in the pellet container (ca 600 mg/L; Fig. 4.17, left). The iron concentration is important because a secondary decrease of the pH is expected when groundwater flows into the pit lake and is aerated. In all of the treated containers, a strong supersaturation of the water with respect to siderite was observed (Fig. 4.17, right). A decrease in the dissolved iron concentrations would be expected if equilibrium with respect to siderite was achieved.

There was also a strong reduction in other dissolved contaminants (Al, Ni, Co, Zn, Cr, Cu, As, Pb) in the treated containers (Wisotzky 2003), indicating that the addition of lime and fly ash to overburden material can effectively decrease acidity, sulfate, iron and metals concentrations in groundwater, and illustrating the value of preventing or mitigating pyrite oxidation. Where this is not possible, then efforts should be made to decrease acidity and mineral dissolution as close to the source as possible. Mitigation of the transport of polluted groundwater and surface water is the third option to limit the extent of the problem. Often, it is best to combine some or all of these strategies.

Chapter 5
Case Studies and Regional Surveys

5.1 Pit Lakes in Germany: Hydrography, Water Chemistry, and Management

Martin Schultze, Mike Hemm, Walter Geller and Friedrich-Carl Benthaus

5.1.1 Origin and Regional Distribution

The pit lakes discussed in this chapter generally result from lignite mining. Germany has the largest lignite production worldwide (175×10^6 t year^{-1} in 2008). Power generation based on lignite contributes about 23.6% of the nation's annual production of electricity. The combined annual lignite production of the Federal Republic of Germany and former German Democratic Republic reached its maximum (433×10^6 t year^{-1}) in 1985 (DEBRIV 2009). The opening of the former German Democratic Republic to the world market removed the necessity of using lignite as the main base for its energy supply.

Figure 5.1 shows the location of lignite mining districts in Germany. Only four of the districts are still in operation: Rhenish District (95.8×10^6 t year^{-1} in 2008), District of Helmstedt (2.1×10^6 t year^{-1} in 2008), Central German District (19.4×10^6 t year^{-1} in 2008), and Lusatian District (57.9×10^6 t year^{-1} in 2008; DEBRIV 2009). All lignite deposits in Germany are of Tertiary age. The lignite seams are embedded and overlain only by unconsolidated rock like gravel, sand, loam, and clay. Since geological conditions have a strong influence on the morphometry and development of pit lakes, some basic geological information shall be provided for the three main lignite-mining districts of Germany here.

In the Lusatian and Central German districts, the mined lignite seams are typically 5–12 m thick. The overburden ranges from less than 10 to about 90 m.

Re-activation of old faults, and the uplift and subsidence of blocks greatly disturbed the Lusatian district lignite deposits (Fig. 5.2, upper panel), and the

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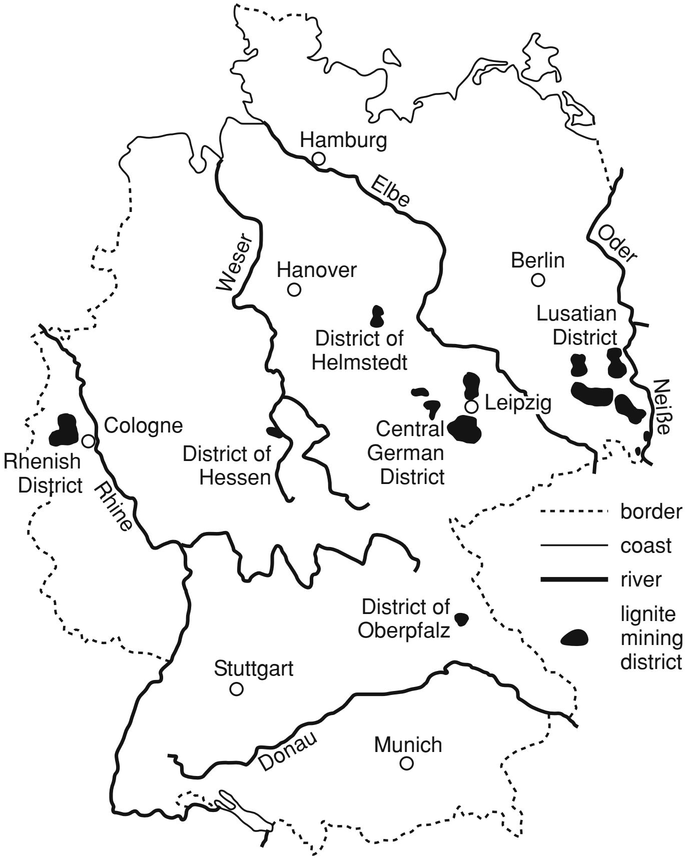


Fig. 5.1 Location of lignite mining districts in Germany

Pleistocene glaciations added to their deformation, as the seams were squeezed, folded, segmented, and sometimes made nearly vertical by the movement and pressure of the glaciers (Fig. 5.2, upper panel). Meltwater associated to glaciations also cut deep valleys, and caused regional erosion (Fig. 5.2, upper panel).

In the Central German lignite-mining district, glacigenic disturbances, although much less important than in the Lusatian district, also occurred (middle panel of Fig. 5.2). The most important aspect was dissolution of salt deposits (mainly rock salt, anhydrite, and gypsum of Permian and Triassic age) below the Tertiary deposits. In some cases, the dissolution occurred syngenetically to the formation of the lignite, resulting in exceptionally thick seams (20–30 m, in the case of the Geiseltal deposit, even 100 m; Fig. 5.2, middle panel). In many cases, the dissolution occurred postgenetically, resulting in local depressions of the seams (Fig. 5.2, middle panel). The dissolution of the salt deposits led to intrusions of saline water into the lignite. The resulting salt content makes affected lignite deposits nearly unusable due to fast corrosion of power plants combustion

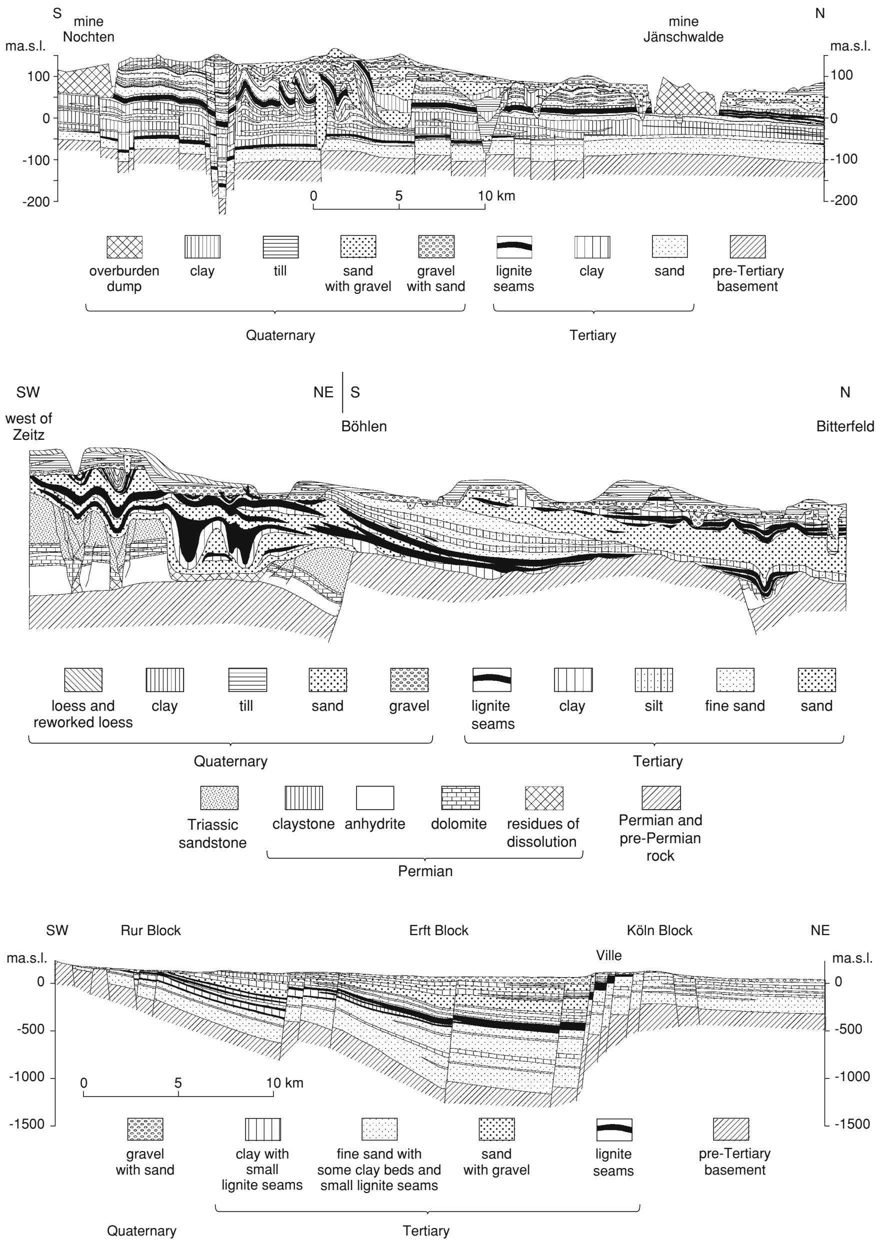


Fig. 5.2 Regional cross sections of the three main lignite-mining districts in Germany. *Upper panel* Lusatian district, *middle panel* Central German District (half-schematic, therefore without scales), *lower panel* Rhenish District (note different scales; modified after Seifert et al. 1993; Eissmann 2002; Briechle et al. 1998)

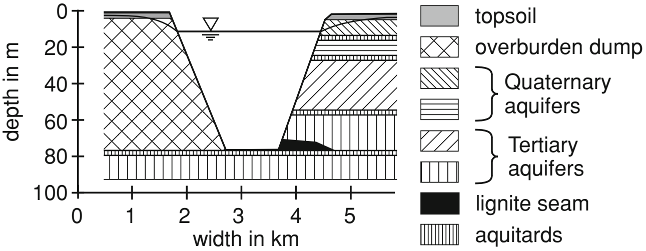


Fig. 5.3 Typical schematic cross section of a German pit lake and its environment

chambers, and the high salt content of the waters from mine dewatering, lignite processing wastewater, and the fly ash.

In the Rhenish lignite mining district (lower panel of Fig. 5.2), the thickness of the lignite seams ranges between a few meters and more than hundred meters. Block faulting and fast subsidence after lignite deposition resulted in a widely ranging depth of the lignite seams (Fig. 5.2, lower panel). Due to a seam thickness of up to 100 m, economic mining of the deeper seams is possible. The Hambach open cast mine goes down to about 500 m below the surrounding landscape.

For more details on the geology of the main German lignite mining districts, see Seifert et al. (1993) for the Lusatian district, Eissmann (2002) for the Central German district, and Briechle et al. (1998), Gliese and Hager (1978), Hager (1993), and Schäfer et al. (2004) for the Rhenish district.

Due to the different conditions of lignite formation (e.g. varying extent of marine influence), the sulfur content of the lignite deposits varies: 0.15–0.5% are typical for the Rhenish district, 0.3–1.4% for the Lusatian district, and 1.5–2.1% for the Central German district, respectively (DEBRIV 2009).

Figure 5.3 shows the typical hydrogeology of German pit lakes. The generalized depiction is derived from Lake Markkleeberg (Central German district) and is basically applicable for all German pit lakes. The pit lakes are in hydraulic contact with overburden dumps and with natural aquifers. The overburden dumps often have a lower hydraulic conductivity than the natural aquifers of the same thickness because the dump is a mixture of the material of the former aquifers and aquitards. Therefore, the exchange of water between undisturbed, natural underground and the pit lake is usually stronger than between pit lake and overburden dump. Another important hydrogeological aspect constituted by the pit lakes is the opening of connections among formerly separated aquifers.

Pit lakes occur in all German lignite-mining districts. The total number with surface areas >1 ha is >500, and about 100 lakes have areas >50 ha (Hemm and Jöhnk 2004; Nixdorf et al. 2001). Most of them (373) are located in the Lusatian and Central German lignite-mining districts. There are three main reasons for that: (1) The Lusatian and the Central German districts are the two largest with respect to their area; (2) The deep position of the major parts of the seams of the Rhenish district requires very large and modern equipment for profitable exploitation, while their thickness allows for long operation of single mines. This restricted the formation of pit lakes to the Ville block in the Rhenish district until now; (3) The Lusatian and the Central German districts are located in East Germany, i.e. the former German Democratic Republic, where lignite exploitation had been extremely intensive. After 1990, when lignite production was strongly reduced, the closure of 30 mines created 120 new voids and pit lakes (Krüger et al. 2002) with a cumulative volume of 4.5×10^9 m^3. Until the end of 2008, 71% of this volume was filled. The entire mine closure and associated remediation had cost 8×10^9 € during the period 1990–2008, and further expenses of about 0.5×10^9 € are planned until 2012. The grand challenge of the necessary remediation stimulated a comprehensive research program on all aspects of pit lakes, including their limnology, remediation, and management (Gläßer and Kabisch 2004).

The creation of pit lakes in Germany began during the end of the 19th century. The first pit lakes were small (surface area <1 ha, maximal depth <10 m) because of the simple techniques used for mining and because the early mines were located in regions where the lignite seams reached the surface or where the overburden cover was thin (see also Sect. 2.1). Often, dewatering requirements resulted in economic problems and fast mine closure after a few years of operation. Technical progress resulted in larger excavation machinery and safer dewatering, altogether allowing for larger mines, and the pit lakes became larger as well (see Fig. 2.5 in Sect. 2.1).

Until the 1970s, pit lake filling was nearly exclusively based on groundwater rebound. Due to the natural limitations of groundwater recharge, the filling of pit lakes took many years or even decades. Such long filling periods were accompanied by strong side wall erosion and safety risks. Slope inclination had to be shallow to limit these risks, but this increased remediation costs. Faster filling by diversion of river water addressed these problems. The first pit lakes filled by diversion of river water were Lake Senftenberg and Lake Muldestausee. River water has been the most important water source for pit lakes created after 1990. From 1990 to 2008, ca. 2×10^9 m^3 of river water were diverted into mine voids to create pit lakes in the Lusatian and Central German districts, filling 62.3% of the final pit lake volume.

Water from dewatering operations of active mines became another important water source. In the southern part of the Central German district, a system of pipelines was constructed to transport mine water from operating mines to the majority of the rising pit lakes in the 1990s (Jolas 1998; Fig. 5.4), and no diversion of river water was necessary in this region. Lake Cospuden was the first pit lake that was filled exclusively in this way. This filling strategy was also used in other parts of the Central German and Lusatian districts. About 700×10^6 m^3 of mine water was used for the filling of pit lakes in eastern Germany from 1990 to 2008, corresponding to 21.9% of pit lake volume filled in that period.

Groundwater rebound, direct precipitation, and local surface runoff contributed the remaining 15.8% of the volume to fill pit lakes in eastern Germany from 1990 to 2008. Keeping the water level of the pit lakes higher than that of the groundwater was important for the stabilization of the sidewalls of the lakes. This meant that substantial portions of the fill water from the rivers and operating mines left the rising pit lakes into the surrounding groundwater. This also means that the

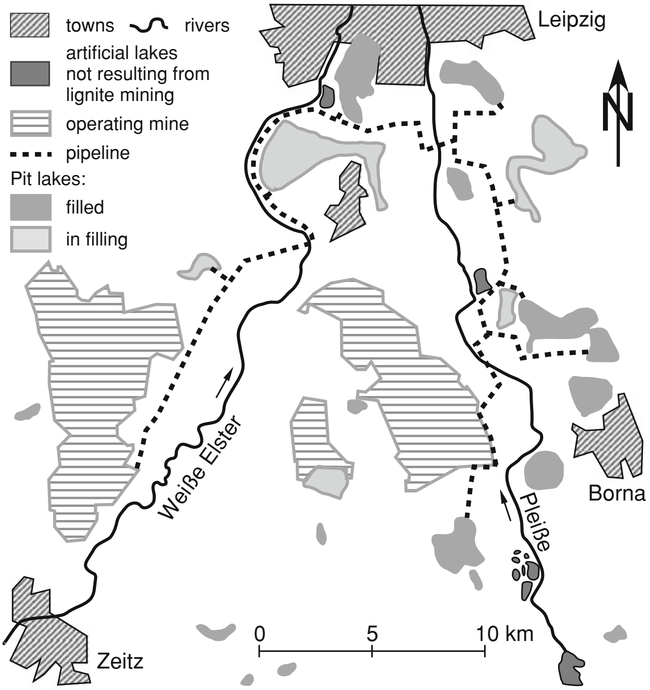


Fig. 5.4 Pipeline system constructed for filling of pit lakes with water from mines still operating in the southern part of the Central German district since 1997

actual contribution of direct groundwater inflow, precipitation, and local runoff was probably somewhat larger than the 15.8% mentioned above. One reason is that pit lakes connect different aquifers, as mentioned above. It is not uncommon that deeper aquifers rebound fast and deliver considerable water into pit lakes whereas aquifers located closer to the surface still have to be refilled. To fill the deep pit voids of the Rhenish district, water from the Rhine River shall be diverted (Briechle et al. 1998).

The Lusatian lignite-mining district belongs to one of the driest regions of Germany (annual mean precipitation for the Lusatian district was 530–650 mm for 1961–1990, compared to 797 mm for all of Germany; BMUNR 2003). The rivers crossing the Lusatian district (Neiße, Spree, and Schwarze Elster) do not have high mountainous regions in their catchments. Therefore, water management for these rivers was already complicated during the period of high lignite production in the 1970 and 1980s. At the beginning of the 1980s, the first model-based management systems were developed for the catchment of the River Spree (Kaden et al. 1985). The reduction of lignite production, and consequently dewatering, as well as the water demand for refilling the dewatered aquifers and the creation of pit lakes caused further problems, and new, improved water management approaches had to be developed (Conradt et al. 2007; Grünewald 2001; Koch et al. 2005; Schlaeger et al. 2003). Permanently operating model systems ensure optimal use of the available water, respecting existing demands and rights of water use in the mining district and downstream. These include the demands of power plants, agriculture, the water supply of Berlin, and also of ecological requirements of the river ecosystems and connected wetlands. Water transfers between the three mentioned river systems were established to fulfill all requirements. Fig. 4.8 in Sect. 4.4 shows a scheme of the network of pit lakes, reservoirs, rivers, operating mines and mine water treatment plants to be managed in the Lusatian District. Since river Neiße constitutes the border between Poland and Germany, this water management system has an international dimension.

In the future, the management requirements will be modified to consider the likely effects of climate change. The diversion of water from the River Elbe is being discussed as a way to deal with the expected scarcity of water (Koch et al. 2009; see also case study 5.9).

5.1.2 Data Sources

Data for the following description of the morphometry and chemistry of German pit lakes were collected from many sources. Morphometric data were extracted from Nixdorf et al. 2001, the web sites of the Lausitzer und Mitteldeutsche Bergbau-Verwaltungsgesellschaft (LMBV, the company established by Germany to remediate the former lignite mines in eastern Germany; www.lmbv.de), and Mitteldeutscher Seenkatalog (a community of governmental and non-governmental institutions concerned with and interested in the sustainable development of lakes in Central Germany; www.mitteldeutscheseen.de). Water quality data were from spring 2007 monitoring programs (period of overturn) conducted by the LMBV, and the Landestalsperrenverwaltung des Freistaates Sachsen (authority for the management of reservoirs and lakes in Saxony). Additional data were obtained from web-published results of lake monitoring in the federal state of Saxony-Anhalt in 2007 (www.sachsen-anhalt.de/LPSA/index.php?id=27953), and from Nixdorf et al. (2001). Less data were available from small and/or old lakes. Therefore, the small and/or old pit lakes are generally underrepresented in the following description of German pit lakes. However, the data from Nixdorf et al. (2001) were used to fill this gap as far as possible. Data from Nixdorf et al. (2001) is considered to be representative for those pit lakes since older pit lakes show mainly seasonal variations in water quality but nearly no inter-annual trends.

5.1.3 Morphometry and Stratification

Figure 5.5 shows the frequency distribution of the major morphometric data of the German pit lakes: volume (V), surface area (A), maximal depth (z_{max}), mean depth

(z_m; quotient of volume and surface area), and shore development (quotient of the real shore length and the circumference of the circle with an area equal to that of the lake). Geological and technological factors span a wide spectrum. Since future pit lakes are included in the dataset with their final morphometry, the planned deep lakes in the Rhenish district appear as the largest and deepest ones: Lake Hambach ($V = 5{,}300 \times 10^6$ m^3, A = 4,040 ha, $z_{max} = 310$ m) and Lake Garzweiler ($V = 1{,}180 \times 10^6$ m^3, A = 1,750 ha, $z_{max} = 170$ m). These two pit voids will be filled after 2050. The largest lake in the Central German District is Lake Geiseltal ($V = 423 \times 10^6$ m^3, A = 1,853 ha, $z_{max} = 78$ m), which will be filled in 2010. Most of the pit lakes (374, i.e. >75%) have surface areas less than 100 ha. The ones with the smallest surface areas (<10 ha) in Fig. 5.5 still represent 49% of the pit lakes. About 59% of the pit lakes have a volume smaller than 10^7 m^3. Finally, about 51% of the maximum depths, based on available data, are less than 15 m. This size distribution reflects the fact that most of the German pit lakes are old, from mining with small equipment (see also Sect. 2.1). Table 5.1 lists the basic morphometric data (volume, surface area, and maximum depth) and the locations for the German pit lakes explicitly mentioned in this chapter.

The relatively small values of shore development indicate that the pit lakes' basins are relatively monotonous and circular, i.e. without small bays or peninsulas. Creation of structural diversity and shore elements would require complicated management of overburden dumping and slope stabilization, and would increase costs. Recently, the shorelines have been constructed more diversely in lakes intended for nature conservation, and compromises were made relative to remediation costs to provide some additional habitat diversity.

The majority of the German pit lakes are monomictic. Only the smaller lakes of the Lusatian district show ice covers each year, and are dimictic. Meromixis also occurs in German pit lakes, usually caused by influent higher-density groundwater. In the Central German district, this is often associated with intrusion of saline groundwater from salt deposits deeper underground. This also indicates that dissolution of salt deposits, which influenced the formation of the lignite seams in the Tertiary, as already discussed, is still going on. Examples are Lake Hufeisensee (Stottmeister et al. 1999), Lake Wallendorf, and Lake Rassnitz (Böhrer et al. 1998; Schultze and Boehrer 2008).

In other cases, the higher density of the groundwater results from pyrite oxidation and its consequences. Examples are Lake Zieselsmaar (Nixdorf et al. 2001), Lake Goitsche (Boehrer et al. 2003), and Lake Lugteich (Rücker et al. 1999). The so-called iron-meromixis (Hongve 1997; Kjensmo 1967, see also Sect. 3.1) appears in Lake Waldsee (Boehrer et al. 2009), a very small pit lake in the Lusatian district. Although not decisive, the respective mechanism also contributes to the stability of meromixis in other pit lakes which accumulate iron in their monimolimnion.

In Lake Vollert Süd, meromixis resulted from the filling of the lake with waste water from coke production, which contains very high concentrations of organic

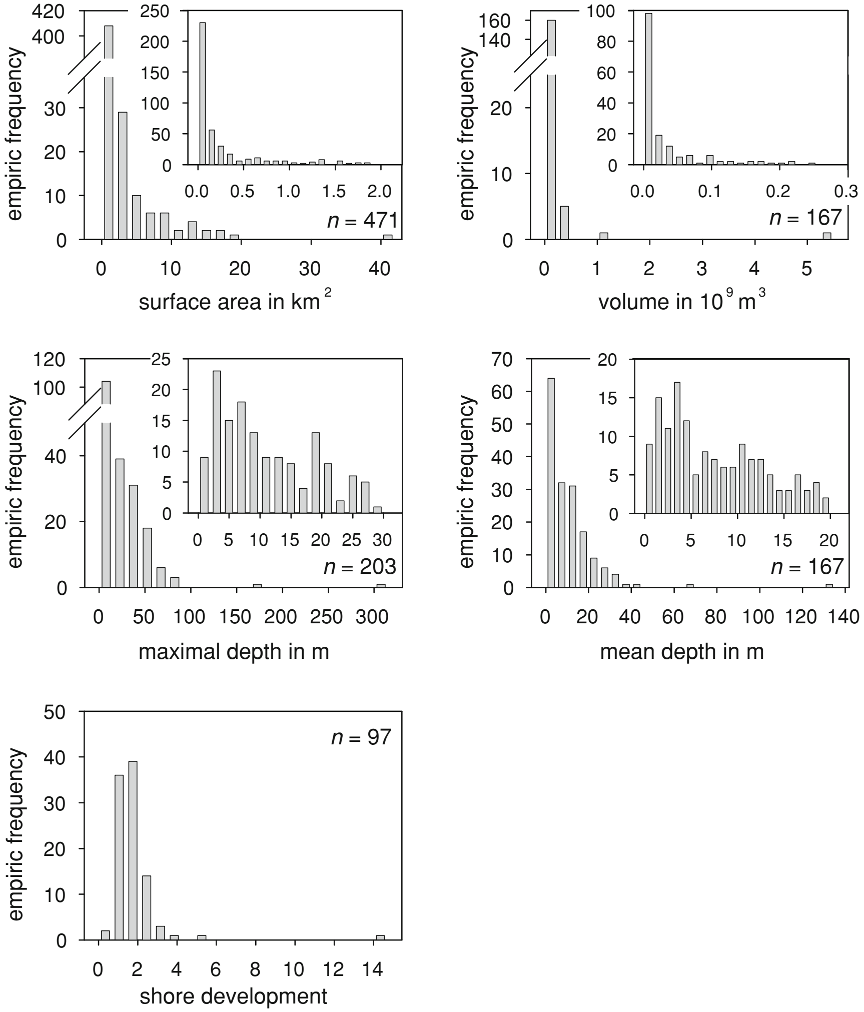


Fig. 5.5 Frequency distribution of morphometric data of German pit lakes

contaminants (260–690 mg/L DOC), mainly poly-aromatic, humic-like substances and phenolic compounds, which restricted the Secchi-depth to 3 cm (Stottmeister et al. 1998, 1999). The applied remediation technology used a sequence of flocculation with iron, neutralization, and fertilization; the meromixis was stabilized by accumulation of the organic contaminants in the monimolimnion and sediment (Stottmeister et al. 2010).

Table 5.1 Location and morphometric data of German pit lakes mentioned in the chapter (alphabetical order)

Lake	District	Status	Location		Volume (10^6 m^3)	Area (ha)	Max. Depth (m)
			Lat. N	Long. E			
Bärwalde	Lusatian	In filling	51°22′30″	14°32′50″	173	1,299	59.5
Bergwitz	Central German	Filled	51°47′10″	12°34′30″	18	220	35
Bockwitz	Central German	Filled	51°08′10″	12°32′30″	18.7	170	19
Borna	Central German	Filled	51°06′40″	12°27′00″	97	265	38
Burghammer	Lusatian	Filled	51°28′00″	14°22′20″	36	445	21.5
Cospuden	Central German	Filled	51°16′20″	12°20′10″	109	436	54
Garzweiler	Rhenish	Operating mine	50°53′00″	6°33′00″	1,180	1,750	170
Geierswalde	Lusatian	In filling	51°30′20″	14°06′40″	92	620	35
Geiseltal	Central German	In filling	51°19′20″	11°51′00″	423	1,853	78
Goitsche	Central German	Filled	51°37′00″	12°23′20″	213	1,331	49
Golpa IV	Central German	Filled	51°42′00″	12°21′50″	0.74	19	6
Großkayna	Central German	in filling	51°17′00″	11°56′20″	27	255	22
Hain-Haubitz	Central German	Filled	51°10′10″	12°27′30″	98	560	49
Hambach	Rhenish	Operating mine	51°04′00″	6°23′00″	5,300	4,040	310
Harthsee	Central German	Filled	51°05′10″	12°32′50″	5	85	14
Horstteich	Lusatian	Filled	51°47′00″	13°42′30″	0.65	10	Nd
Hufeisensee	Central German	Filled	51°27′50″	12°01′40″	6.15	69	30
Ilse	Lusatian	In filling	51°33′50″	14°00′40″	153	771	56
Kulkwitz	Central German	Filled	51°18′40″	12°14′50″	27	159	32
Lohsa I	Lusatian	Filled	51°23′00″	14°22′00″	5.8	342	12.5
Lohsa II	Lusatian	In filling	51°26′00″	14°26′20″	97	1,081	46.5
Lugteich	Lusatian	In filling	51°28′10″	14°10′20″	3	96	10
Markkleeberg	Central German	Filled	51°16′00″	12°24′40″	61	252	62
Muldestausee	Central German	Filled	51°38′10″	12°24′50″	110	605	30
Runstedt	Central German	Filled	51°18′00″	11°56′10″	54	233	33

(continued)

Table 5.1 (continued)

Lake	District	Status	Location		Volume (10^6 m^3)	Area (ha)	Max. Depth (m)
			Lat. N	Long. E			
Rassnitz	Central German	Filled	51°22′40″	12°05′50″	66	315	36
Senftenberg	Lusatian	Filled	51°30′20″	14°00′20″	98	1,300	23
Spreetal	Lusatian	In filling	51°29′30″	14°20′00″	97	314	58
Steinberg	Oberpfalz	Filled	49°16′50″	12°09′40″	40	184	47
Vollert Süd	Central German	Filled	51°06′20″	12°03′30″	2	9	27
Waldsee	Lusatian	Filled	51°37′14″	14°34′17″	0.0065	0.24	4.7
Wallendorf	Central German	Filled	51°22′40″	12°03′20″	36	343	27
Zieselsmaar	Rhenish	Filled	50°51′00″	6°48′00″	0.28	5.8	10
Zwenkau	Central German	In filling	51°14′10″	12°17′40″	172	970	50

5.1.4 Water Chemistry

In this section, diverse frequency distributions are presented for physico-chemical water quality measures and the concentrations of several substances to characterize the water chemistry of German pit lakes. The same datasets were used to prepare scatter plots that relate the concentrations to pH-values in Sect. 3.2.1.1. The data mainly stem from water samples taken close to the lake surface during spring overturn. Therefore, they can be considered as fairly representative of the entire water body. This does not apply for meromictic lakes since the presented data only describe the conditions of the respective mixolimnia. The water chemistry of the monimolimnia strongly deviates from that of the mixolimnia and will be discussed separately.

In spring 2007, about 57% of the German pit lakes were acidic ($pH < 6$; Fig. 5.6). A large number of the old, small pit lakes have been acidic for decades. These small lakes are not important for water management, and there is little pressure for the implementation of neutralization measures. A considerable portion of the larger pit lakes, created after 1990, were still being filled and neutralized in 2007 (see also the sub-section 5.1.5 on remediation and management, below). The frequency distribution of the pH values (Fig. 5.6) shows two buffering systems in the lakes; iron buffers the acidic lakes and bicarbonate buffers the neutral pit lakes. Buffering by aluminum occurs only exceptionally.

The electrical conductivity (Fig. 5.6) indicates high concentrations of dissolved salts in the lake waters. The main salt is gypsum (Fig. 5.7). The highest values of electrical conductivity in Fig. 5.6 (Lake Rassnitz and Lake Wallendorf) result from the intrusion of saline groundwater with sodium chloride as the dominant salt (Fig. 5.7).

Acidity and alkalinity, as presented in Fig. 5.6, were measured by titration with NaOH-solution to pH 8.2 or with HCl-solution to pH 4.3, respectively. Approximately 63% of the lakes had acidities less than 2.5 mmol/L. This was within the range of acidic waters commonly produced by coal and lignite mining (median 3.2 mmol/L), but rather low compared to waters from metal mines (median 40 mmol/L; Geller and Schultze 2009). The frequency distribution for alkalinity includes a column for a value of zero mmol/L for pit lakes with $pH < 4.3$, which comprise about 54% of the 222 lakes (Fig. 5.6). The alkalinity of the neutral lakes was rather low, with about 35% with <1 mmol/L. This is probably the result of scarce carbonates in the Quaternary and Tertiary sands that constitute a large portion of the overburden and consumption of carbonates by acidity from pyrite oxidation.

Sulfate is by far the most abundant anion in the German pit lakes (Fig. 5.7), exceeding the typical natural levels in the respective regions due to pyrite oxidation. This also applies for pit lakes that never were acidic due to the local geological conditions. Most of the German pit lakes had sulfate concentrations below the saturation concentration of jarosite, schwertmannite, and gypsum. This probably resulted from dilution by water not affected by pyrite oxidation. The high

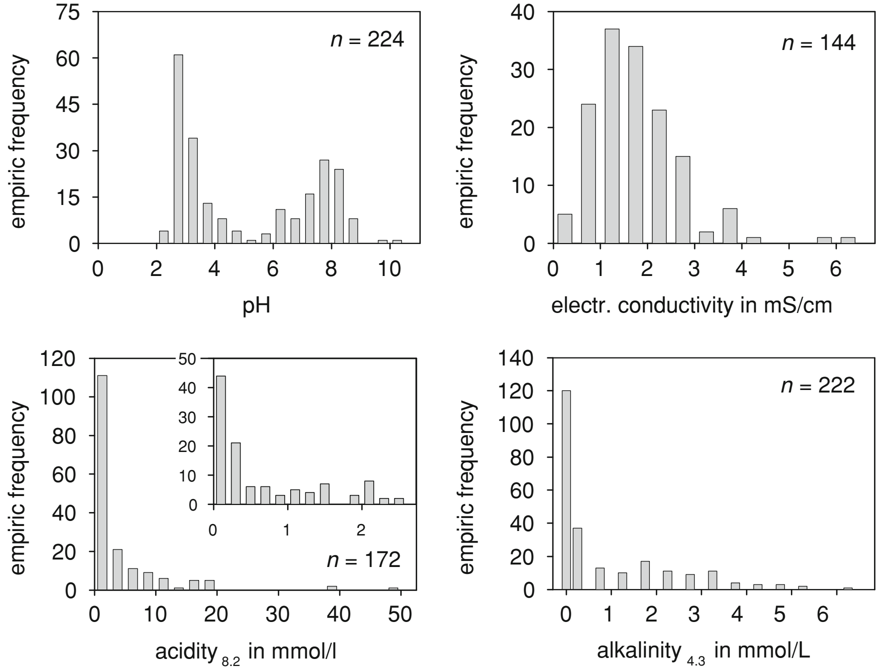


Fig. 5.6 Frequency distributions of the main physico-chemical characteristics in German pit lakes

concentrations of several grams per liter shown in Fig. 5.7 occurred in the acidic pit lakes, but are considerably less than the concentrations of sulfate found in the groundwater of pyrite-bearing natural strata or overburden dumps. In the groundwater of the so-called amber silt at the bottom of Lake Goitsche, sulfate concentrations were 7–31 g/L when the lake first began to fill (Trettin et al. 2007).

The concentrations of chloride and sodium in German pit lakes (Fig. 5.7) are similar to that of natural waters in the respective regions. The very high concentrations in Fig. 5.7 (Lake Rassnitz and Lake Wallendorf) were caused by the intrusion of saline groundwater into these lakes and the partial mixing of the saline water with the mixolimnion. Potassium concentrations (Fig. 5.7) are considerably lower than that of sodium but geological sources are identical. High concentrations are the result of ash deposition.

The concentrations of magnesium (Fig. 5.7) are also comparable to that of natural waters in the German lignite mining districts. The maximum concentrations were the result of acidification and local geological conditions.

Among the alkaline and earth-alkaline metals, calcium concentrations (Fig. 5.7) were affected most clearly by pyrite oxidation, the resulting acidification, and by the buffering of the acidity in the affected soils and aquifers. Therefore, the

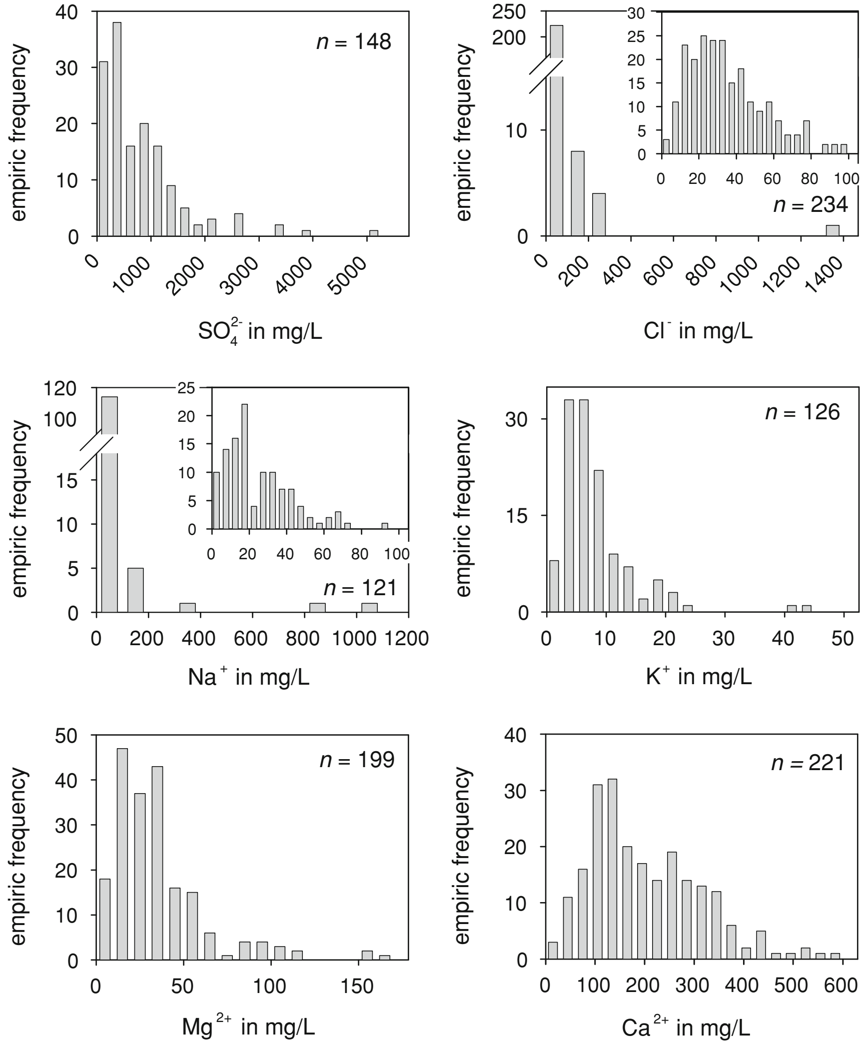


Fig. 5.7 Frequency distributions of the concentrations of the major ions in German pit lakes

concentrations of calcium were elevated compared to natural waters in the German lignite mining districts.

After sulfate, iron is usually the element that is most influenced by pyrite oxidation and acidification in lignite mine water. Trettin et al. (2007) found up to 11 g/L of dissolved iron in the groundwater of the amber silt at the bottom of Lake Goitsche. Mansel et al. (2007) reported up to 3 g/L of iron for groundwater in the overburden dump of the former Witznitz mine (Central German district). Compared to such groundwater, the concentrations of iron, although elevated,

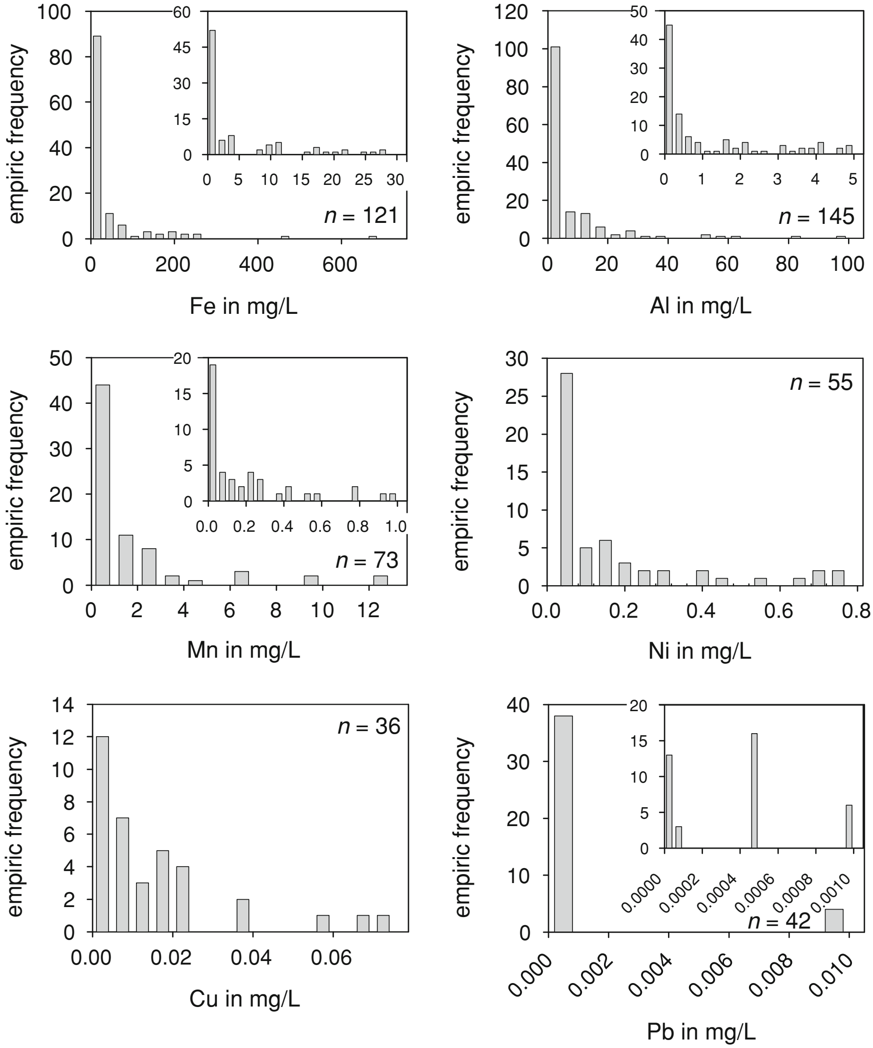


Fig. 5.8 Frequency distributions of the metal concentrations in German pit lakes

were rather low in German pit lakes (Fig. 5.8). Approximately 42% of available data values were less than 1.5 mg/L, representing the neutral pit lakes with pH > 6 and a considerable portion of the acidic pit lakes (see Fig. 3.19b in Sect. 3.2.1.1). The two highest concentrations (476 mg/L and 676 mg/L) occurred in two separated basins of Lake Ilse which was just at beginning to fill in spring 2007. Concentrations in the range of 150–250 mg/L were frequently reported from strongly acidified German pit lakes in the past. However, Fig. 5.8 shows the situation of spring 2007, including the results of neutralization measures implemented

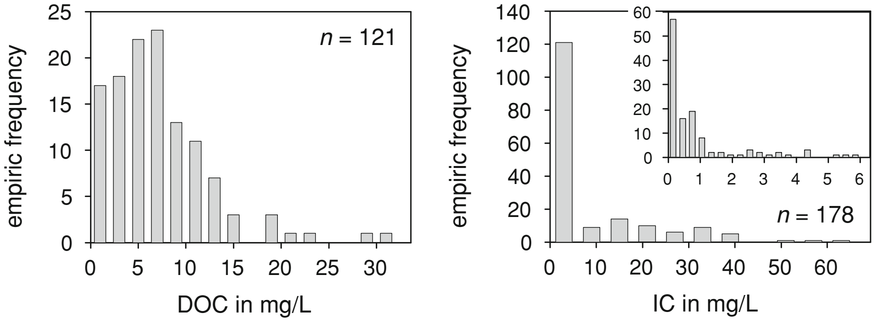


Fig. 5.9 Frequency distributions of the concentrations of dissolved organic carbon (*DOC*) and inorganic carbon (*IC*) in German pit lakes

during the last 15 years. The iron concentrations were in good agreement with the results found for acidity (Fig. 5.6).

Approximately 41% of the concentrations of aluminum (Fig. 5.8) were less than 0.5 mg/L, representing the neutral pit lakes as well as a portion of the acid pit lakes (see Fig. 3.19 in Sect. 3.2.1.1). Thus, the picture is similar to that of iron but with much lower concentrations. The concentrations of manganese, nickel, copper, and lead (Fig. 5.8, and Fig. 3.19b in Sect. 3.2.1.1) showed similar patterns of stepwise lowered concentration levels.

The concentrations of dissolved organic carbon (DOC) in German pit lakes (Fig. 5.9) slightly exceed the level observed in natural lakes of comparable trophic state. Thurman (1986) reported 2–4 mg/L DOC for mesotrophic lakes and 3–34 mg/L DOC for eutrophic lakes, respectively. Almost all German pit lakes were oligotrophic or mesotrophic according to their phosphorus and chlorophyll concentrations (Fig. 5.10). The high DOC concentrations are probably derived from lignite as a carbon source in the overburden dumps and in the unmined underground.

In most German pit lakes, the concentration of inorganic carbon is low (Fig. 5.9), reflecting the low levels of alkalinity in German pit lakes. Concentrations less than 0.5 mg/L occurred in 41% of the pit lakes, approximating the concentration of dissolved CO_2 in pure water in equilibrium with the atmosphere. Primary producers can be carbon limited in this range.

About 50% of the concentrations of ammonia in German pit lakes (Fig. 5.10) were less than 0.5 mg/L NH_4^+-N in spring 2007, i.e. in the range of natural lakes and well below the level of 1.5 mg NH_4^+/L that is considered potentially toxic to fish. High concentrations (>5 mg/L) occurred exclusively under acidic conditions, whereas moderate concentrations (0.5–5 mg/L) were found mainly in acidic pit lakes (Fig. 3.19c in Sect. 3.2.1.1, see also Sect. 3.3.2.2). The elevated concentrations of ammonia under acidic conditions were probably caused by elution of ammonia from lignite. Krejci-Graf (1984) reported nitrogen concentrations in lignite in the range of 0.3–1.4%. Since nitrification is inhibited in acidic environments (Prosser 1986), the ammonia persists in the well-oxygenated lake water of the German pit

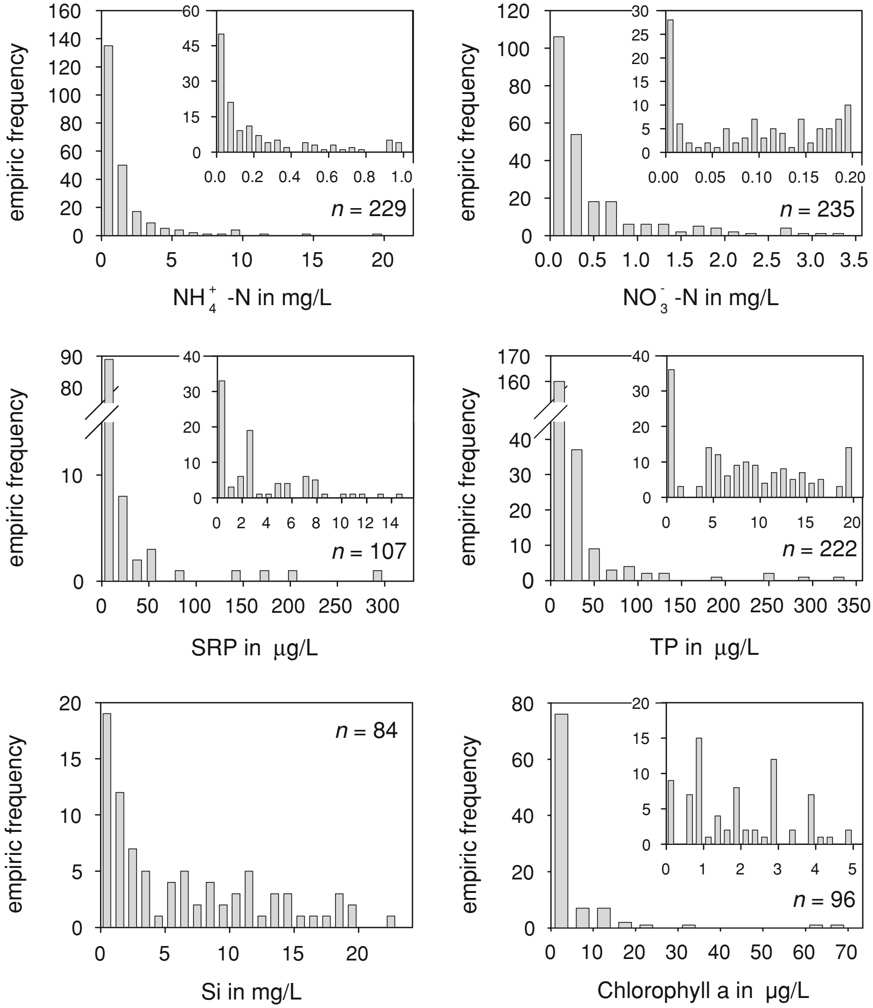


Fig. 5.10 Frequency distributions of the concentrations of nutrients and chlorophyll a in German pit lakes (*SRP*—soluble reactive phosphorus, *TP*—total phosphorus)

lakes. Experiences from chemical neutralization of German pit lakes indicate that the oxidation of ammonia may take more than a year after neutralization (Roenicke et al. 2010). Probably, the community of nitrifying bacteria needs some time to establish and to adapt. Further inhibition may result from persistent acidic conditions in the sediment, e.g. due to inflow of acidifying groundwater.

The nitrate concentrations were low in the German pit lakes in spring 2007 (Fig. 5.10). About 82% of the concentrations were less than 1 mg/L NO_3^--N. The reasons were the inhibited nitrification under acidic conditions and the limited sources of nitrate in the catchments. Since large portions of the catchment areas were forested, diffuse input of nitrate from agriculture were of minor relevance. In the overburden dumps, the remaining pyrite might also have acted as a nitrate reducing agent along the flow path of the groundwater (Kölle et al. 1985).

The concentrations of soluble reactive phosphorus (SRP) were low (Fig. 5.10), with 50% of the concentrations <3 μg/L, and 85% < 15 μg/L. The high availability of iron, and to a lesser degree, aluminum, can permanently fix phosphorus to the sediment (Duffek and Langner 2002; Herzsprung et al. 2010; Kleeberg and Grüneberg 2005; see also Sect. 3.2.1.3). Relatively high concentrations were restricted to strongly acidic conditions. Extremely high concentrations were caused by the presence of phosphorite in some cases temporaryly. E.g. Woelfl et al. (2000) reported the temporary occurrence of 3.5 mg/L SRP in a small side basin of Lake Cospuden during the filling of the lake.

The situation for total phosphorus (TP) was similar to that of SRP (Fig. 5.10), with slightly higher concentrations, since TP included particles containing iron hydroxide with adsorbed phosphorus. This was probably most important in neutral pit lakes.

The concentrations of silica were higher in pit lakes (Fig. 5.10) than in natural lakes. This was the consequence of feldspar and clay mineral dissolution due to acidification. The highest concentrations occurred under acid conditions (Fig. 3.19c in Sect. 3.2.1.1). Since only about 8% of the concentrations were <0.5 mg/L, the concentrations of silica did not limit the growth of diatoms.

Approximately 79% of the concentrations of chlorophyll a were below 0.5 μg/L (Fig. 5.10). Accordingly, most German pit lakes could be classified as oligo- or mesotrophic, based on OECD (1982) standards. This is in good agreement with the observed phosphorus concentrations (Fig. 5.10). Only 4% had chlorophyll concentrations >20 μg/L. Thus, eutrophication is not an issue in German pit lakes, in contrast to the situation in natural lakes (Fig. 5.11).

The water chemistry of the monimolimnia of the meromictic German pit lakes is generally characterized by anaerobic conditions. Other chemical characteristics are less uniform (Table 5.2), reflecting concentration gradients within a particular monimolimnia and, even more important, different meromixis origins.

Meromixis caused by salt water intrusion from deeper underground results in high concentrations of sodium chloride (only chloride is shown in Table 5.2) and electrical conductivity. Lake Hufeisen, Lake Wallendorf, and Lake Rassnitz are examples of this mechanism of meromixis formation. The sulfate concentration in such monimolimnia may be also high, with two potential origins: pyrite oxidation and dissolution of anhydrite deposits associated with the salt deposits deeper underground. The pH of such monimolimnia is usually neutral since the saline groundwater often has to pass through fractured carbonate rock on top of the dissolving salt layers.

A second mechanism of meromixis formation is due to the inflow of groundwater from overburden dumps or other sites of intense pyrite oxidation and associated dissolution reactions. The elevated density of this water prevents fast mixing with the mixolimnion. If the rate of groundwater inflow is high enough, losses by partial mixing at the chemocline can be compensated, maintaining meromixis. Lake Waldsee, Lake Lugteich, and Lake Goitsche are examples (Table 5.2). The water of the monimolimnia of these lakes is slightly acidic.

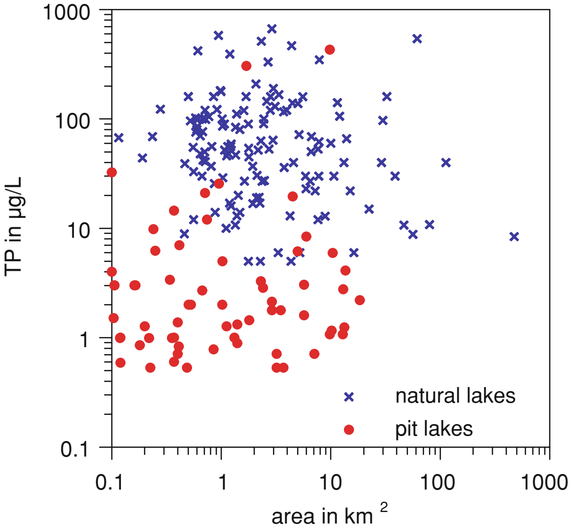


Fig. 5.11 Comparison of the level of eutrophication in pit lakes and in natural lakes in Germany, indicated by the concentrations of total phosphorus (*TP*; modified from Hemm and Jöhnk 2004)

The electrical conductivity and the concentration of chloride are much lower than in the lakes discussed above, which receive saline groundwater.

The anaerobic conditions and the relatively high concentrations of DOC in all six examples result in elevated concentrations of reduced species in the monimolimnetic water. Iron was enriched in five of the monimolimnia, while Lake Hufeisen was enriched in hydrogen sulfide. The water of the monimolimnion of Lake Hufeisen has always had a black opalescence due to fine particles of iron sulfide. The concentration of H_2S/S^{2-} represents only dissolved sulfide in Table 5.2. Therefore, elevated concentrations of sulfide and iron are excluding each other. The concentrations of ammonia were also elevated, due to dissolution of ammonia from lignite or from decomposition of fresh organic material settling into the monimolimnion. Due to the anaerobic conditions, nitrification was not possible.

The enrichment of phosphorus in the monimolimnia was not high, except for Lake Hufeisen. Probably, the phosphorus settling into the monimolimnion was bound to iron, maybe as vivianite. In addition, ferric iron precipitates that adsorbed phosphorus resist reductive dissolution better than precipitates without phosphorus (Golterman 2001). The excess sulfide and the more complete reduction of ferric iron, as well as the binding of ferrous iron to sulfide, are probably the reason for the elevated phosphorus concentrations in Lake Hufeisen.

5.1.5 Remediation and Management

Abatement of acidification is the major goal of pit lake remediation and management in Germany. A second problem for about half of the Lusatian pit lakes (LMBV data) may be ammonia levels above 1.5 mg/L, the permissible limit for

Table 5.2 Chemical characteristics of monimolimnetic water in German pit lakes (*EC*: electrical conductivity, *nd*: no data, *<dl*: below detection limit)

Lake	pH	EC mS/cm	Cl^- mg/L	SO_4^{2-}	H_2S/S^{2-}	Fe	TP	NH_4^+-N	DOC
Hufeisen	6.5–7.0	28–36	7,980–8,850	70–340	188–580	<dl	1.9–5.0	85–305	33–52
Wallendorf	7.0–7.5	30–71	48,860	2,460	<dl	128	0.055	15	32
Rassnitz	7.0–7.6	10–26	17,200	1,610	<dl	109	0.24	12	16
Waldsee	6.6–6.7	1.0–1.1	4.5–5.7	138–205	<dl	138–168	nd	4.2–8.6	54–73
Lugteich	4.5–5.8	2.9–3.3	8.9–11.0	2,050–2,330	<dl	449–607	0.10–0.18	7.3–17.1	38–76
Goitsche	6.5–6.8	1.7–2.0	33–38	1,230–1,400	<dl	220–335	0.05–0.16	7.0–11.0	22–31

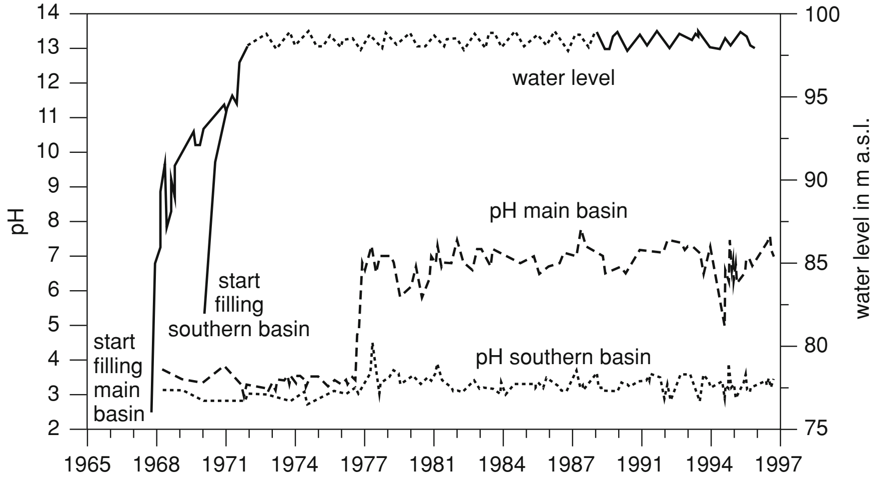


Fig. 5.12 Development of water level and pH in Lake Senftenberg (from Werner 1999; for details see text)

effluent water discharging into river systems. Other threats to water quality, like eutrophication or contamination by waste deposits, are less relevant in German pit lakes.

About 50–70% of German pit lakes would be acidic without measures against acidification. Local geological conditions, like abundance of pyrite, its oxidation products, and carbonates in the pit lakes catchment areas are the main factors influencing the extent and duration of acidification of particular pit lakes. There are pit lakes that have been acidic for more than five decades without any trend to neutralization, while other pit lakes became neutral within a few years. For example, Lake Harthsee became neutral within five years of being filled with groundwater, while neutralization of Lake Bergwitz took about 30 years (Jordan and Weder 1995). Recharge of the lake water by neutral and alkaline ground and surface water are the most likely processes causing neutralization under such conditions. The natural rates of sulfate reduction in pit lakes (e.g. Peine and Peiffer 1998) and in overburden dumps (Hoth et al. 2005) are too low to substantially contribute to pit lake neutralization.

Lake Senftenberg was the first German example where diversion of river water was successful in neutralizing a pit lake. The lake consists of two sub-basins separated by a large island with shallow sills at its ends. The river water diverted from River Schwarze Elster is flowing through and neutralizing the northern main basin (Fig. 5.12). The small southern basin behind the island receives acidifying groundwater, but no river water (Schöpke et al. 2006; Werner et al. 2001). The most detailed investigations of neutralization by diverted river water were conducted at Lake Goitsche (Boehrer et al. 2003; Dreher 2007; Duffek and Langner 2002; Herzsprung et al. 2010; Kringel et al. 2000; Schultze et al. 2002; Trettin et al. 2007), where both acidity and alkalinity were mobilized by erosion and elution of material from the bottom and sidewalls of the mine voids. A phase of erosive alkalinity mobilization from carbonate-bearing soils of the upper part of the side walls followed an initial phase of acidity mobilization from the bottom of the pit and the lower parts of the sidewalls. Before filling was completed, the alkalinity imported with river water and being generated from the side walls had neutralized all of the acidity (Boehrer et al. 2003; Schultze et al. 2002). Other pit lakes in the Lusatian district are currently being filled, and thereby neutralized, by diversion of river water.

Water from dewatering of mines is also used for filling and neutralization of pit lakes. In the Central German district, the mine water used for filling and neutralization of pit lakes is neutral and well buffered, requiring no pre-treatment. This is a considerable economic advantage, since discharge of mine water into rivers usually requires the removal of iron. In addition, the low phosphorus content of the water is usually an advantage for the new pit lakes. Neutralization with water from operating mines was first successfully used in Lake Cospuden, and later in Lake Markkleeberg. In other pit lakes, however, although the use of such water contributed considerably to neutralization, the neutralization was not complete (Lake Hain-Haubitz and Lake Zwenkau in the Central German district, and Lake Ilse in the Lusatian district). Also, unlike the water from dewatering operations in the Central German district, which could be used without any treatment, much of the water in the Lusatian district needed pre-treatment before it could be used to fill mine pits.

The addition of alkaline substances is a traditional mine water treatment approach, and is also used in German pit lakes. The first example for such treatment was Lake Steinberg. Ashes were used for neutralization, resulting in neutral lake water in 1985. In 1986, however, Lake Steinberg became acidic again (pH 4, further drop to pH 3.5 from 1987 to 1988) due to acidifying groundwater (Hemm et al. 2002). Another example of pit lake neutralization using alkaline substances is Lake Zieselsmaar, which has been neutralized every year by liming to allow its use for bathing and swimming. The annually repeated liming is necessary because of influent acidifying groundwater (Hemm et al. 2002). The groundwater inflow will probably go on being acidic since the lake is located at the foot of a large overburden dump. Lake Horstteich was neutralized successfully with sodium hydroxide solution and dolomite in 2005 (Rabe and Uhlmann 2006). In 2004 and 2005, Lake Geierswalde was partially neutralized by excavation and spreading of waste lime, which had been deposited years before in the mine void and in the rising pit lake (Benthaus and Uhlmann 2006). The deposition of mine water treatment plant sludge into the rising Lake Spreetal Nordost contributed about 30% to the partial neutralization of the water in the lake in 2006 (Uhlmann et al. 2007). Lake Bockwitz was neutralized using soda ash (14.595×10^6 kg) from 2004 to 2007. Another 0.874×10^6 kg of soda ash was necessary to keep the lake neutral in 2008 (Roenicke et al. 2010). Influent acidifying groundwater and acidic water entering Lake Bockwitz from upstream acidic pit lakes requires continued application of soda ash.

Because of the much higher acidity of the German pit lakes, compared to rain-acidified lakes in Scandinavia and in North America, it was decided in the 1990s that the alkaline addition techniques that worked in Scandinavia (e.g. Henrikson and Brodin 1995; Olem 1991) would not be cost effective. Treatment approaches based on microbial sulfate reduction were believed to be better. However, in recent years, it has become clear that microbial approaches are also not sustainable due to re-oxidation of the produced sulfide (Geller et al. 2009) or insufficient rates of alkalinity production (Preuß et al. 2007; Wagner et al. 2008). In addition, it also became clear that the diversion of river water and the use of water from mine dewatering would not neutralize all acidic pit lakes fast enough. Therefore, techniques developed to neutralize lakes in Sweden were tested in the Lusatian district pit lakes. However, using boats and small ships to spread the alkaline substances proved to be too expensive and not effective enough. Limestone and hydrated lime have been used since 2007, with various distribution systems, in a couple of German pit lakes in addition to the ones mentioned above. Although not really sustainable, this strategy appears to be the only available one that allows the lakes to reach neutrality before initially-acidic pit lakes are allowed to release water into the receiving river system downstream.

Several pit lakes became acidic again after they were neutralized, by re-acidification with influent groundwater, and this kind of re-acidification is a considerable threat to water quality. It requires repeated or continued lake treatment, as in Lake Bockwitz. Another option is permanent flushing of the respective pit lakes by river water. Lake Senftenberg is kept neutral this way. Only in 1995, maintenance of the pipeline connecting the Schwarze Elster River and Lake Senftenberg required temporary interruption of the river water diversion. This resulted in a slightly lower mean water level in the lake for 1995 and, consequently, a temporary drop of the pH in the main basin of the lake (Fig. 5.12). This indicates how successful management of water quantity and water quality requires good knowledge of the entire system (groundwater—pit lake—river; Werner et al. 2001).

For future pit lakes that will be created in currently operating mines, prevention of acidification will be increasingly relevant. The continuous addition of limestone to the pyritic overburden during its dumping started in the Garzweiler Mine (Rhenish district) in 1999 (Eyll-Vetter 2007). For more details on this approach, see Sect. 4.6.

For some pit lakes, remediation was necessary because of contamination with waste materials or other contaminants. Lake Hufeisensee is in contact with a waste deposit at its southern end. A dry cover placed on top of the deposit minimized the inflow of contaminated groundwater from the waste deposit into the lake. Since most of the hazardous substances have been trapped in the monimolimnion of the lake and its sediment (Stottmeister et al. 1999), the use of the lake for recreation has not been at risk. For Lake Goitsche, the inflow of contaminated groundwater (e.g. up to 160 mg/L of chlorinated hydrocarbons; Heidrich et al. 2004) was prevented, since the flow direction of the groundwater changed after the lake was filled (Wycisk et al. 2005). Lake Runstedt receives groundwater with high concentrations of ammonia (>300 mg/L NH_4^+-N) from waste deposited at the bottom of the mine pit. Three hypolimnetic aerators are used to provide enough oxygen for nitrification to occur at the bottom of the lake. The inflow of the contaminated groundwater is expected to continue for more than a century (Schroeter 1997). Supporting nitrification in the pit lake was found to be considerably cheaper and more cost effective than groundwater treatment or removal of the waste deposit before filling the lake. The remediation of Lake Vollert-Süd was already described in the section on stratification since the remediation approach used and stabilized the meromixis in this lake.

Eutrophication of pit lakes is not an important issue in Germany. Even in lakes that are filled and flushed with river water, the high concentration of iron in the lake sediments prevents eutrophication (Herzsprung et al. 2010; Kleeberg and Grüneberg 2005; Lessmann et al. 2003; Schultze et al. 2005; Sect. 3.2.1.3). The only exception is Lake Golpa IV, which has been used to store power plant cooling water for decades, and recharged with water from the Mulde River. Until the beginning of the 1990s, the water of the Mulde River had about 0.6 mg/L of dissolved phosphorus. The accumulation of sediments rich in phosphorus and organic material has created a high internal load of phosphorus (Hupfer et al. 1998).

5.1.6 Use of the Pit Lakes

Pit lakes have diverse uses in Germany. In all of the German lignite-mining districts, the new pit lakes became important sites for recreation. Many lakes are used for swimming, wind surfing, sailing, and water skiing (Fig. 5.13). Scuba diving is also popular in many pit lakes due to their high water clarity associated with the usually low concentrations of phosphorus and limited growth of plankton.

Lake Kulkwitz, located at the western margin of the city of Leipzig (0.5×10^6 inhabitants) became an important recreational site immediately after its filling in the 1970s. The same is true for Lake Cospuden at the southern margin of Leipzig since 2000. The location of both lakes close to the city promoted their use for recreation. Lake Senftenberg, which is about 50 km from Dresden (0.5×10^6 inhabitants) became an important recreational destination in the 1980s. The case of Lake Zieselsmaar, which was mentioned in the section on remediation, indicates the importance of pit lakes for local and regional recreation, which in this case, justifies the annually-repeated neutralization of the lake.

Based on such experiences, the new lake districts currently forming in the Lusatian and Central German mining districts will be developed as tourist destinations. Canals will allow boats to travel from lake to lake. Tourism is expected to be a considerable economic benefit for both regions in the future (Hunger et al. 2005; IBA 2010; Linke and Schiffer 2002; see also case study 5.9). However, reaching this goal may take one or two decades because filling and neutralization of the pit lakes is not yet completed, and establishment of the new tourist attractions may also take time.

Fig. 5.13 Examples for recreational use of pit lakes in Germany: Beach at Lake Markkleeberg (*upper left panel*), Sailing at Lake Baerwalde (in the background power plant Boxberg; *lower left panel*), Boating and wind surfing at Lake Goitsche (*upper* and *lower right panels*; photos provided by LMBV)

A lot of lakes are incorporated into nature conservation areas. The aquatic community is usually not the primary goal of protection. The pit lakes are rather seen as valuable components of the entire post-mining landscape, e.g. providing a habitat for terrestrial species, which need wetlands in certain periods of their life cycle, such as many insects. The lakes partially compensate for the loss of natural wetlands caused by the increasing degree of land use for agriculture and other purposes over the last few centuries. In addition, establishing nature conservation areas in the new post-mining landscape is often much easier than at natural lakes. In the case of natural lakes, established uses would have to be prohibited and economically compensated whereas in the case of new pit lakes, certain uses simply have not been permitted. Under such conditions, a completely self-organized natural succession without any human management is possible. This may include limited stabilization of slopes, allowing for repeated small landslides. Such small landslides produce fresh steep slopes, which were common along rivers under natural conditions but are widely lost in Germany due to river regulation. However, totally free succession requires special protection against human disturbances. Therefore, some NGOs have bought large areas of the new post-mining landscapes in the eastern part of Germany during the last 15 years.

Water storage and flood protection is also an important use of pit lakes. As already mentioned, water management in the Lusatian district requires water storage. Therefore, some of the pit lakes are used as reservoirs. Examples are Lake Bärwalde, Lake Burghammer, and the lakes Lohsa I and Lohsa II, all located in the drainage basin of the River Spree (see Fig. 4.8 in Sect. 4.4). One of the reasons for the necessity of water storage is the water supply for Berlin (3.4×10^6 inhabitants). About 20–30% of the water supply of Berlin depends directly on water from the Spree, and to ensure sufficient water in the future, diversions of water from the Neisse, Odra, and Elbe Rivers are being discussed (Koch et al. 2009; see also case study 5.9).

Flood protection is the primary use of Lake Borna and Lake Zwenkau in the Central German district. The pit lakes replace the former retention capacity of the flood plain sections removed during lignite mining.

The German legislation requires basic care and protection of the fish communities in lakes by the owners of the lakes. This is part of the fishing right. The owners can transfer their fishing rights to commercial fishermen or to associations of anglers. Commercial fishing in pit lakes is often based only on the natural production of the lakes. However, fish farming is also done in some German pit lakes.

A number of pit lakes are just part of the landscape. They have no special use and are not intensely used. Therefore, there are no special requirements regarding water quality, and the neutralization of these lakes is not a high priority. In some cases, even the protection of the acidic state is discussed since the aquatic communities of acidic pit lakes are unique. However, lakes that discharge into river systems usually have to be neutralized to protect the receiving streams and rivers, and to meet the water quality standards of the EU Water Frame Work Directive and related national legislation.

Often more than one kind of use is established in a particular pit lake. For example, Lake Borna and Lake Zwenkau are not only used for flood protection, but also for recreation. Since Lake Goitsche and Lake Geiseltal are large enough, they combine recreation and nature conservation, which are apparently contradictory. Boating or sailing is generally prohibited in protected areas of these lakes.

5.1.7 Conclusions

Pit lakes resulting from open cast lignite mining are a substantial portion of the totality of lakes in Germany. Moreover, pit lakes represent about one-third of the lakes that have a volume greater than 100×10^6 m^3 (Geller et al. 2000). In addition, the German lignite mining districts are located mainly in regions which are poor in natural lakes. Therefore, the pit lakes are regionally important in Germany.

As known from many other countries, acidification is the most important concern with respect to water quality. The filling and flushing of pit lakes with river water and the filling with water from operating mines was found to be a successful approach for the abatement of acidification in German pit lakes. The problem of continuous re-acidification, as it is given in many lakes, will largely be approached by chemical in-lake treatment. Actual developments of arising technologies are aiming to a more powerful distribution of alkaline substances within the lake's water body to achieve a more effective use of the applied lime, soda or other alkaline chemicals on the one side, and to avoid damaging the lake ecosystem on the other side.

5.2 Lakes in Large Scale Open-Pits in Poland

Roman Żurek

The Polish Environmental Ministry has reported 9,050 sites that contain useful minerals (mostly sand and gravel, loamy materials, and stone) and that are destined for surface mining (PIG 2007). Over time, slow but constant exploitation significantly transforms both the landscape and local communities. Hundreds of small sand pits, gravel pits, and quarries are locally important, while larger brown coal (lignite) and sulfur opencast mines have regional and national significance.

Brown coal seams are located in central and western Poland (Fig. 5.14). Sulfur-bearing limestone is found in southeastern Poland and continues into western Ukraine (Fig. 5.15). Production of brown coal continues, whereas sulfur opencast mining is virtually finished both in Poland and Ukraine. Output of sulfur was abandoned due to very low prices between 1980 and 2000. However, the only remaining Polish borehole sulfur mine is very profitable in the current economic situation, offering 95% net profit! Despite this, old dormant mines have not been restarted and are still being decommissioned. Coal and sulfur mines create similar technical and environmental problems. Examples of three groups of post-mining lakes will be discussed below: lakes created during the second half of the 20th century during surface mining of brown coal; later, collapse lakes and old inundated pits from the beginning of the 20th century; and finally, lakes at sulfur opencast mines.

5.2.1 Contemporary Brown Coal Strip Mining from the Second Half of the 20th Century

5.2.1.1 Economic Background

Poland possesses huge resources of brown coal, which are still strategic resources of energy. There are 77 known lignite deposits (Table 5.3; Dyląg and Bereda 2008; Przeniosło 2005) and the documented beds contain 29,815 × 10^6 t of coal

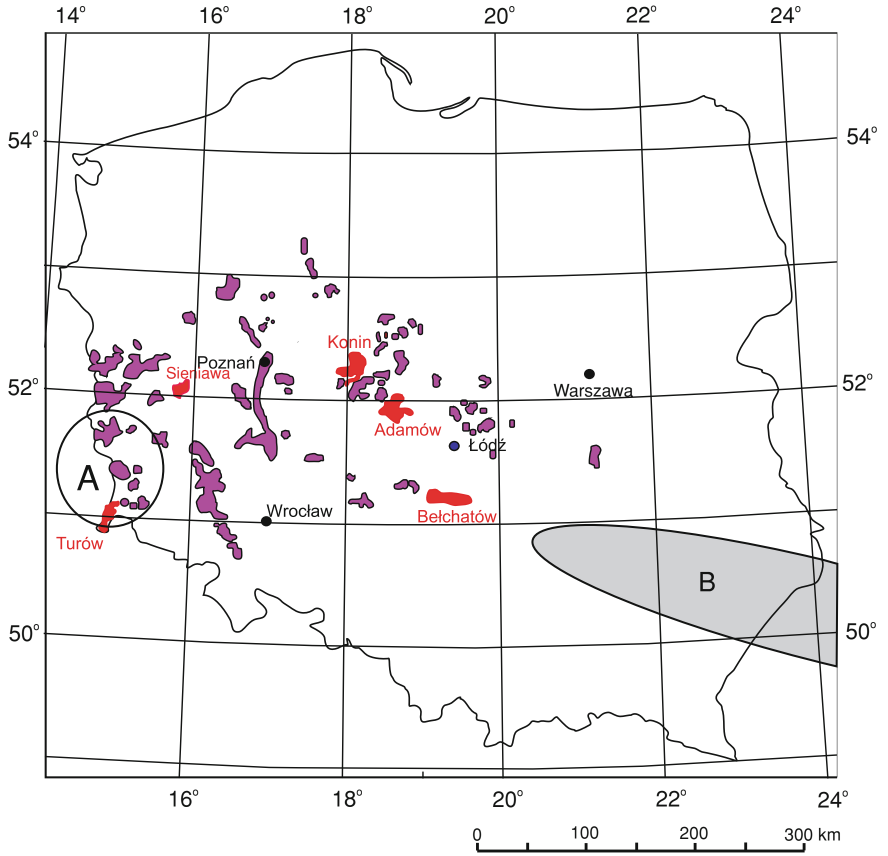


Fig. 5.14 Main deposits of brown coal in Poland. Red—mines and exploited beds. Magenta—geologically documented deposits. *A* anthropogenic transboundary lakeland in Muskau Arch (Muzhakov Arc). *B* region of sulfur deposit, see Fig. 5.15

(Piwocki et al. 2004). Most of these deposits are located in the western, central, and southern parts of Poland. Geographically, these regions are known as the Polish Lowland (Niż Polski) and the Carpathian Foredeep (Zapadlisko Przedkarpackie). The geological balance of resources of brown coal in 2007 was 13,629 × 10^6 t, including 0.8 × 10^6 t of bituminous coal, 2513 × 10^6 t of briquette coal, and 1,496 × 10^6 t of sub-bituminous coal (Table 5.3; Dyląg and Bereda 2008). The annual production of brown coal in Poland is stable, at 60 × 10^6 t. Almost all of it is burned in power plants (Table 5.3). These reserves (40 × 10^9 t) are enough to guarantee coal production for 512 years at today's level of output (Kasiński 2006); Kasiński et al. 2006; Piwocki et al. 2004).

Exploiting these resources is necessary for the Nation's energy security. Alternative energy sources cannot provide enough energy. For example, the power generated from all Polish rivers can supply no more than 15% of national demand

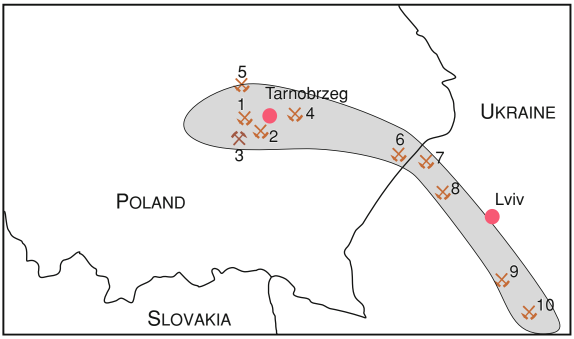


Fig. 5.15 Location of sulfur mining in Poland and Ukraine. Flooded: *1* Piaseczno; *2* Machów; *8* Yavoriv; *9* Rozdol; *10* Podorozhne. Underground melting: *3* Osiek; *4* Jeziórko; *5* Grzybów; *6* Basznia (Bashnia); *7* Nemyriv. Compare Fig. 5.14

and even this amount cannot be realised because of nature conservation concerns. The remaining technologies, such as nuclear power, wind power, photovoltaic cells, and geothermal energy, provide only minor amounts or remain in the planning stage—only biomass has a 6% quota in energy production.

Utilization of these renewable energy resources is relatively low, considering that the relevant Directive of the European Parliament (Directive 2009/28/EC) established mandatory EC energy consumption national targets for 2020: a 20% share of power to be derived from renewable sources and a 10% share of fuel requirements for transport from renewable sources. Due to the low cost of generating electricity from thermal power stations, implementation of this directive in Poland is slow and sluggish. The state's energy model cannot be changed in a few years. It is expected to take between 10 and 20 years to resolve this problem. Poland is in deadlock and must build nuclear power plants to diminish CO_2 emissions from electricity production, as required by the Kyoto protocol and European directives. The Polish government has now decided to develop nuclear power engineering, and build two or three nuclear power plants by 2020. Alternative energy sources are being slowly developed simultaneously while thermal power stations continue to produce electricity.

5.2.1.2 Social Problems

Exploitation of brown coal deposits can cause social, legal, environmental, and organizational problems. Each field of lignite has limited resources, so mines must start exploiting new sites. A good example of the possible problems being faced is the Konin mine, which tried to launch a new lignite mine only a few kilometers from Gopło Lake. This plan was met with strong resistance by 5,000 local inhabitants, who petitioned the Polish Prime Minister to stop the mine. These protests engaged NGOs, local mayors, and members of parliament, who in turn interpellated the Ministry of the Environment. Furthermore, Gopło Lake is listed as a Polish Nature 2,000 area because of its historical significance. People are

Table 5.3 Geologically documented deposit resources of brown coal in Poland (Dyląg and Bereda 2008; PIG 2008) and annual lignite production and burning in the power industry in Poland (Pietraszewski 2008; GUS 2007, 2008); values in millions of tons

	2001	2002	2003	2004	2005	2006	2007	2008
Number of beds	77	76	76	76	76	76	77	77
Managed beds	9	10	10	10	10	11	11	12(13[a])
Total identified economic reserves, 10^6 t	13,924	13,860	13,685	13,635	13,724	13,661	13,629	13,63
Potentially economic reserves, 10^6 t	4,876	4,683	4,611	4,616	4,592		4,494.9	4,148.2
Economic reserves, 10^6 t	1,757	1,697	1,635	1,586	1,527		1,414.4	1,371.3
Production							57.5	59,4
Power industry							57.3	57.8

[a] acc. to Statistical Yearbook, 1 bed in construction is included to this category

afraid of this lake drying out and field steppization (desertification), and do not believe the assurances of mine management.

Another conflict resulted from plans to build a new thermal power station and strip mine near Legnica, a town in southwest Poland. Despite the withdrawal of a potential investor from this project because of high social costs, the idea is still alive. However, newspaper headlines such as “Fear against mine”, “Mine-phantom fright at Legnica”, and “Coal under Legnica—troublesome treasure” show the mood of the public.

5.2.2 *Genesis and Places of Occurrence*

Brown coal formed from the Paleocene to the Miocene periods. The most important beds are associated with the late tectonic movements of the central-Poland aulacogen on contact with the east European Precambrian platform and the younger Paleozoic platform. The surface area of the most important lignite beds (lower and middle Miocene) exceeds 70,000 km^2. If we take into account the surface area of the Tertiary beds, the lignite-bearing area in the Polish Lowland amounts to almost 100,000 km^2 (Fig. 5.14). The brown coal in central Poland is 20 million years old, dating from before the period of upheaval of the Carpathian Mountains. These beds are very thick: up to 30 m at Legnica and up to 100 m at the Lubstów mine, Bełchatów. Coal is usually covered by 8–60 m of overburden, though sometimes it is 100–180 m. The proportion of overburden to coal most beneficial for managing the beds ranges from 4.3 to 9.0; the mean thickness of the coal seams ranges from 4.6 to 46.2 m (Kasiński et al. 2006).

Excavation of brown coal has a long tradition in Poland. Lignite was mined by the classic underground method from the end of the Second World War until 1974. Gradually, surface mining took over and today it is the sole method used. Poland has five large open pits exploiting lignite for the power industry: Turów, Sieniawa, Adamów, Konin, and Bełchatów. Due to the deficit of the ground after coal excavation, almost all opencast mines are or will become pit lakes. Below is a schedule with a short history of each of the mines and the new lakes created by them.

Turów Mine. Lignite was found near Turoszów in 1740. Between 1836 and 1869, almost 70 shafts were excavated. The owners of these mines organized the joint stock company Hercules in 1904, and three years later began strip mining. In 1925, the cap rock was dumped north of the mine. After the Second World War, in 1947, a Polish organization took the mine over from the Russian military administration, and KWB (KWB = mine of brown coal) Turów came into existence. In 2005, its lignite resources were 429.7×10^6 t.

Presently, the pit named Turów I is under exploitation and is dry. The planned maximal depth will be 240 m and the future pit dimension will be 20.85 km^2. Reclamation of the spoil heap began after 36 years of dumping, in 1961. Overburden was dumped inside the Turów II pit from 1984 and from 1992 in the Turów I pit. Underground excavations and passages were completed in 2004. Two years later, in 2006, reclamation of the outer dump heap was finished. The planned termination of exploitation is in 2040. By 2055, the mine will be reclaimed (Uberman 2006). Forming the reservoir bowl/basin will involve the displacement of 220×10^6 m^3 of overburden.

Sieniawa Mine. This mine is located at 52° 22′N, 15° 21′E. Underground exploitation began in 1873. After being damaged during the Second World War, the mine was restored and in 1950, output resumed. Opencast mining began in 1997 and output has been from opencast only since 2002. The seam is exploited above an aquifer. The deposits are strongly dislocated by numerous glaciations. The final depth of the excavation (pit) will be 40 m, and the area of the future reservoir will be 12.5 ha. At present, the opencast is dry. There is a 1.5 ha reservoir near the opencast mine, in the swallet above the old mine gallery.

Bełchatów Mine. The first lignite from KWB Bełchatów was extracted in 1980. This strip mine has two coalfields; Bełchatów and Szczerców. The depth of both opencasts will be 280 m. Excavation should total 1×10^9 t of coal from the first mine and 734×10^6 t from the second. The deepest part will be filled with overburden to a depth of 80 m above sea level (asl), so that the greatest depth of the lakes will be 100 m. Flooding will commence in 2,049. The volume of the reservoirs will be 1.5×10^9 m^3 in the Bełchatów field and 1.25×10^9 m^3 in the Szczerców field. The combined surface area of these reservoirs will be 32.5 km^2. The mine water will be treated in three settling ponds with a total area of 51.6 ha of wetland and a common flow capacity of 405 m^3 min^{-1}.

The overburden cover at Bełchatów contains many minerals that are important for industry and science. The main minerals of value in the overburden are Ca-beidellite at 49–69%, quartz at 20–45%, and kaolinite at 5–16% (Ratajczak et al. 1992). The beidellite silts have interesting properties. Beidellite silt is a natural sorbent with a high specific surface (51.6 m^2 g^{-1}) and ion exchange capacity for cations: 25 mval/100 g for Cr, 46–72 mval/100 g for Pb, 17–31 mval/100 g for Cd, and 13.5–26 mval/100 g for Cu (Bajda 2003; Bajda and Ratajczak 2005). Blending this silt with fly ash makes a self-consolidating mixture

(Wyszomirski et al. 1999). These silts, placed to the bottom of the reservoir, will interact with water to improve water quality.

The rare mineral para-alumohydrocalcite ($CaAl_2(CO_3)_2(OH)_4 \cdot 6H_2O$), which was accepted in 1978 by the International Mineral Association as a new mineral, was found at Szczerców, in the company of chalk and other carbonaceous rocks (Wagner 2006). Its molecule resembles the more common alumohydrocalcite (gismondite, $CaAl_2(CO_3)_2(OH)_4 \cdot 3H_2O$).

Adamów Mine. Adamów has three lignite mines: Adamów, Koźmin, and Władysławów. The first lignite was extracted in 1964 and in 1996, a 1.8 m long 300 kg iron meteorite was pulled out of the coal deposit with a chain-and-bucket excavator.

After production is completed, the nine reservoirs will be able to retain 1.6×10^6 m^3 of excess water, to prevent regional flooding during storm events. The first reservoir was constructed on the inner dumping ground of the Adamów opencast; it was filled in June 2004 (Szwed 2008). Its water table is 105.50–106.50 masl, its surface area is 129.1 ha at 105.5 masl and its volume is $5.915–7.263 \times 10^6$ m^3. It was filled with the drainage waters from the Adamów opencast. In the opencast Adamów mine in 2023, the pit will be turned into a reservoir. Its bottom will be 50–70 masl, and the water table will be at 101 masl. The reservoir will be able to store 161.7×10^6 m^3 of water and will have a surface area of 462 ha. The expected filling time is 15 years.

The Koźmin opencast will have four reservoirs; three small ones on the inner dumping ground (Janiszew, Koźmin, and Głowy) and one in the main opencast pit after exploitation of the Koźmin coal bed ends around 2020. This reservoir will be the deepest and largest in this region (116.1 ha and 42 m deep). Its function will be exclusively environmental.

The Władysławów opencast mine will be reclaimed as a reservoir in 2015, after excavation is finished. It will have a depth of 29 m, the water table will be at 104.00 masl, the bowl surface area will be 68.1 ha, with a water table area of 61.5 ha, and its volume will be 11.7×10^6 m^3. The reservoir will be filled by infiltrating water and the expected filling time is 10–12 years.

Konin Mine. The first lignite from the Konin mine was extracted in 1947. The Konin Mine has a much smaller resource than the others. It is a multi-level opencast mine—the beds are Jóźwin II (with a resource of 51.5×10^6 t), Drzewce (32.5×10^6 t), Kazimierz Północ (164×10^6 t), and Lubstów (12.1×10^6 t). The Lubstów opencast mine was exploited up to 2009, whereas Kazimierz Północ will be exploited until 2011. The deposit at Drzewce has three fields; Bilczew, Drzewce A, and Drzewce B. In 2009, extraction will begin at the Tomisławice opencast mine and in 2010, at Piaski (Grudziński et al. 2007). More details are provided in Table 5.4. The Konin mine has six water reservoirs with a total surface of 716 ha. A seventh lake is planned. These lakes are used for fishing, recreation, water retention, and providing water to firefighters.

Table 5.4 Basic data of Polish reservoirs in strip pits after brown coal mining

Mine, location	State of pit	Depth, pit/lake (max)m	Volume, pit/lake, m^3	Water surface, km^2	Exploitation period, yr	State of affairs in January 2009
'Turów' PGE Kopalnia Węgla Brunatnego Turów S.A., at Bogatynia. First coal mined in 1947						
Turów Mine at Bogatynia; 50°54'35"N, 14°54'E	Dry	225, later 240/ then 105 or 80	1.61×10^9/ $1.28 \cdot 10^9$	>17.4 or 19	1904–2026; 2045[1]; 2035[2]; 2040[3]	To be filled with water from River Nysa Łużycka + precipitation. Present pit 24 km^2; future pit size 20.85 km^2.
Bełchatów PGE Kopalnia Węgla Brunatnego Bełchatów S.A. at Rogowiec; first mined in 1977						
					1980–2019	3 fields: Bełchatów, Szczerców, and Kamieńsk contain 2×10^9 t; 38.5×10^6 t mined annually.
Bełchatów 51°14'30"N, 19°18'E[2]	dry	280, later 205	1.323×10^9	17	Up to 2019	Flooding in 2026–58. Problem: lack of water for flooding. Time to flood: 18–60 yrs. Mean depth 78.2 m. Future depth, volume, and surface depend on final scenario.
Szczerców	dry	179, later 280, then 165	1.752×10^9	22	Planned 2008–2038	15 km^2 area will be flooded in 2049-62; rest of mine will be used for ash disposal, and then filled with overburden to a depth of 165 m. Mean depth 79.6 m. Final reclamation as lake.

(continued)

Table 5.4 continued

Mine,location	State of pit	Depth, pit/lake (max)m	Volume, pit/lake, m^3	Water surface, km^2	Exploitation period, yr	State of affairs in January 2009
Kopalnia Węgla Brunatnego "Konin" S.A. at Kleczew; first mined in 1947						
Pątnów I Flooded 52°20'25"N, 18°17'E	Filled	65/50	135×10^6 83.4×10^6	3.46	1962–2001	1962–1998 stripping of cap rock; mining ended 2001. Filled with ash from Pątnów power plant and water from Jóźwin opencast. Flooding ended 2006. Reservoir = 0.4x0.6 km. Function: retention, recreation, agriculture, and fishing. Mean depth 24 m.
Settling pond	Filled	–/10		0.19	–	Flooded with mine water; location: 52°19'13"N, 18°14'15"E
Pątnów	Filled	–/10		0.04–0.05		Reservoir on dumping ground used by sugar factory. Location; 52°19'03"N, 18°16'24"E
Piaski	Planned				2017–2040	Planned. Common exploitation by Konin and Adamów mines.
Kazimierz Północ, on north field Pątnów III	Exploited to 2011	–/50	$–/97 \times 10^6$	4.76	1965–2011	Exploitation ended 2009[6]; 2 reservoirs after 2020. Flooding time 10 yr by mine water + catchment. Function: retention and recreation.

(continued)

Table 5.4 continued

Mine,location	State of pit	Depth, pit/lake (max)m	Volume, pit/ lake, m^3	Water surface, km^2	Exploitation period, yr	State of affairs in January 2009
Kazimierz Południe	South side filled in 2003	–/3 and 8	–/2.01×10^6	0.65	1965–1997	North field still active with 35 ha ponds for fishing; south side (65 ha) filled, with shallow part (3 m) for recreation and deeper for fishing. Location: 52°20'15"N, 18°06'40"E
Józwin IIB on field Pątnów IV (* Jóźwin IIB—1999)	Planned Exploited		147×10^6	4.4	1971–2021 (2019[1])	In field Pątnów II, later in Pątnów III to 2003 and since 1999 in field Jóźwin IIB. Flooding time 10 yr by mine water + catchment. Mean depth 35 m.[1]
Jóźwin IIA	Settling pond	–/20	/130×10^6	6.45	to 2009	Jóźwin II/ Second lake 0.09 km^2, depth 5 m[5]
Drzewce 3 fields: Bilczew and Drzewce A/ B	Exploited	60/30	207×10^6/ $12.5 \cdot 10^6$	1.25	2005–2018	Since 2005, stripping cap rocks. Mine has Tertiary coal. Flooding time with catchment water will be 15 yr.
Field Piaski	Planned				2017–2040	New strip mine; exploitation 2017–2040
Morzysław	Flooded	–/15	0.02×10^6	0.025	1946–1953	Reservoir since 1953; function: retention; water from catchment, mean depth 0.8 m

(continued)

Table 5.4 continued

Mine,location	State of pit	Depth, pit/lake (max)m	Volume, pit/lake, m^3	Water surface, km^2	Exploitation period, yr	State of affairs in January 2009
Niesłusz	Flooded	27/24	0.148×10^6	0.185	1953–1961	Lake Zatorze from 1961. Function retention and recreation; water from catchment.
Gosławice 52°19’N, 18°16’30”E	Flooded	55/27	0.29×10^6	0.225 to 0.32	1958–1974	Lake Czarna Woda has 2 parts: clear part contains municipal and industrial waste waters; dirty part was a settling pond for briquetting plant until 2000. Function: retention, recreation. Flooding time 6 yr
Gosławice						Ash heap of power plant Pątnów; pH 11.6-12.7; size 1,600 × 1,000 m; Filled with rainwater; 52°16’12”N, 18°14’53”E.
Lubstów on Field Lubstów	Exploited	158/63	200×10^6/ 137×10^6	4.75–5.7	1982–2009	Water table 4.75 km^2. Area of pit 5.693 km^2. Water table at 83 m asl. Flooding time 7–11 yr with river water, or 46 yr by infiltration + precipitation. Flooding began 1 year before mining finished. 52°21’45”N, 18°28’E

(continued)

Table 5.4 continued

Mine,location	State of pit	Depth, pit/lake (max)m	Volume, pit/lake, m^3	Water surface, km^2	Exploitation period, yr	State of affairs in January 2009
Tomisławice	Planned, exploited		Unknown	>2.0	2010–2026	[5]
Mąkoszyn Grochowiska	Prospective		Unknown		2013–2035	[5]
Ościsłowo	Prospective		Unknown		2019–2040	[5]
Kopalnia Węgla Brunatnego ‘Adamów’ S. A. at Turek; first coal 1964						
Adamów Main reservoir	Dry, active	110 later 31–51	80×10^6/ 162×10^6	4.62	1964–2023	After production (2023), the pit will fill in about 15 yr. Bowl area 502.5 ha. Ground level 95–110 m asl. 51°59’N, 18°37’E
Adamów	Filled	?	$5.92–7.26 \times 10^6$	1.29		Filled by waters from Adamów opencast by 2004. 52°00’37”N, 18°39’E. [6]
Kożmin reservoir *Janiszew*	Filled	–/10	$–/3.5–4.05 \times 10^6$	0.56–0.60	1991–1997	Reservoir on inner dumping ground. Bottom at 86 m asl. Flooded in 15–180 days since Feb. 2008 with drainage water from Adamów.
Kożmin reservoir *Koźmin*	In process	–/10	$–/5.56–6.1 \times 10^6$	1.06–1.09		Reservoir to be filled with water from Koźmin and Adamów. Flooding to start in 2012. Function: natural. 52°04’30”N, 18°39’E

(continued)

Table 5.4 continued

Mine,location	State of pit	Depth, pit/lake (max)m	Volume, pit/lake, m^3	Water surface, km^2	Exploitation period, yr	State of affairs in January 2009
Kożmin reservoir Głowy	Dry, planned	–/31–38	–/17.3–17.7 × 10^6	0.635–0.645		Flooding start 2014. Water draining from Koźmin at 30 m^3/min. Time to fill 2 yr. Function recreation.
Koźmin, final reservoir *Końcowy*	Dry, planned	–/41.3–41.7	–/34.1 × 10^6	1.16	1999–2020	From 2023, will be filled with groundwater and after 2 years from Jeziorsko dam / reservoir. Function natural.
Władysławów 52°07'N, 18°28'30"E	Dry	40/29	20.45–23.30 × 10^6/ 11.7 × 10^6	0.61$^{(6)}$; 0.87–1.03$^{(9)}$	1977–2014	Reservoir to be filled by infiltrating water. Mean depth 21.5 m. Expected to fill in 10–12 yrs; area, volume will depend on water table.[6,9]
Bogdałów	Filled	50/10	–/0.6 × 10^6	0.095		Filled in 1994; function: recreation; 52°02'48"N, 18°36'E
Przykona 52°16'12"N, 18°15'E	Filled	–/5.5	–/5.915–7.26 × 10^6 mean 6.5 × 10^6	mean 1.35		Construction began 1996. Filled in 1.5 yr in Oct. 2001 with dewatering water. Reservoir is on inner dumping ground of Adamów opencast and on reconstructed Teleszyna riverbed is for recreation.[7,8] Minimum area 129.10 ha

(continued)

Table 5.4 continued

Mine,location	State of pit	Depth, pit/lake (max)m	Volume, pit/lake, m^3	Water surface, km^2	Exploitation period, yr	State of affairs in January 2009
Kopalnia Węgla Brunatnego 'Sieniawa' Spółka z o.o., at Łagów. First coal 1873						
52°22'N, 15°21'E	Dry	40, later 60/–		0.05–0.06	1873–1942 and 1950-> 2002–2027	Will be filled by infiltration and precipitation

[1] Kasztelewicz et al. (2004)
[2] Kasiński (2006)
[3] Mine office
[4] Kasztelewicz and Jagodziński (2006)
[5] Grudziński et al. (2007)
[6] Szwed (2008)
[7] Małachowska (2006)
[8] Rychter and Małachowska (2008)
[9] Ostręga et al. (2010)

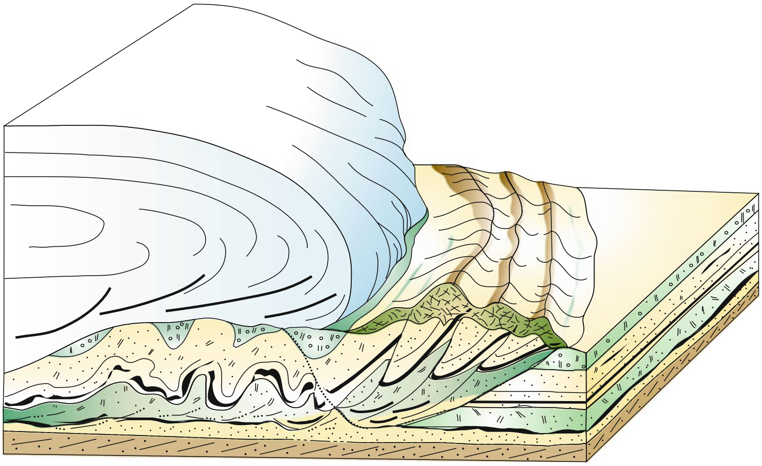


Fig. 5.16 Glaciotectonic deformation of the Neogene deposits reached down to 270–290 m and in a 490–720 m wide belt in front of the ice lobe (from Rascher et al. 2000, image provided by M. Kupetz; see also Kupetz 1997; Koźma and Kupetz 2008)

5.2.3 Historic Brown Coal Mining in the Muzhakov Arc

Mining in the Muzhakov Arc (Muskauer Faltenbogen) began in 1825 at Muskau with alum silt excavation. The first lignite mine, Julius, was established at Wolfshain (Brandenburg) in 1843 at the Muskau field. The presence of valuable minerals above and below the coal beds (alum silt, ceramic silt, quartz glass-making sands) also favored coal mining. The entire area of the Muzhakov Arc along both sides of the Polish-German border has an area of 340 km^2. Lignite was mined on both sides of the border (Fig. 5.14), creating a large lake area.

The lignite in the Muzhakov Arc (German: Muskauer Faltenbogen, Polish: Mużakowski Łuk) are glaciotectonic beds. This means that they were formed under the mechanical pressure of a slow-moving continental glacier. Their shape is usually elongated and semicircular, like a deformed horseshoe (Fig. 5.16). The formation of the terminal moraine began 450,000 years ago in the San 2 glacial period (German = Elster-Eiszeit). The River Nysa dissected this moraine later during the Warta and Wisła glacial period (German = Saale- and Weichseleiszeit). An older arrangement of moraines was overlain by a younger moraine pattern from the Warta glacial period (Kupetz 1997, 2006; Nowel 2006). Using criteria elaborated by the German Geological Survey, Kasiński et al. (2004) registered 34 geotopes (of 95 possible geotopes) in the geopark that has been created in the Polish part of the Muzhakov Arc.

The coal deposits are steeply angled; therefore, most extraction was realized by underground mining. The opencast method was used only in the lignite outcrop zones. The dense system of abandoned extraction galleries, dip-headings, and dip-roads is now disintegrating. The effects of subsidence can be seen as numerous slumps on the surface.

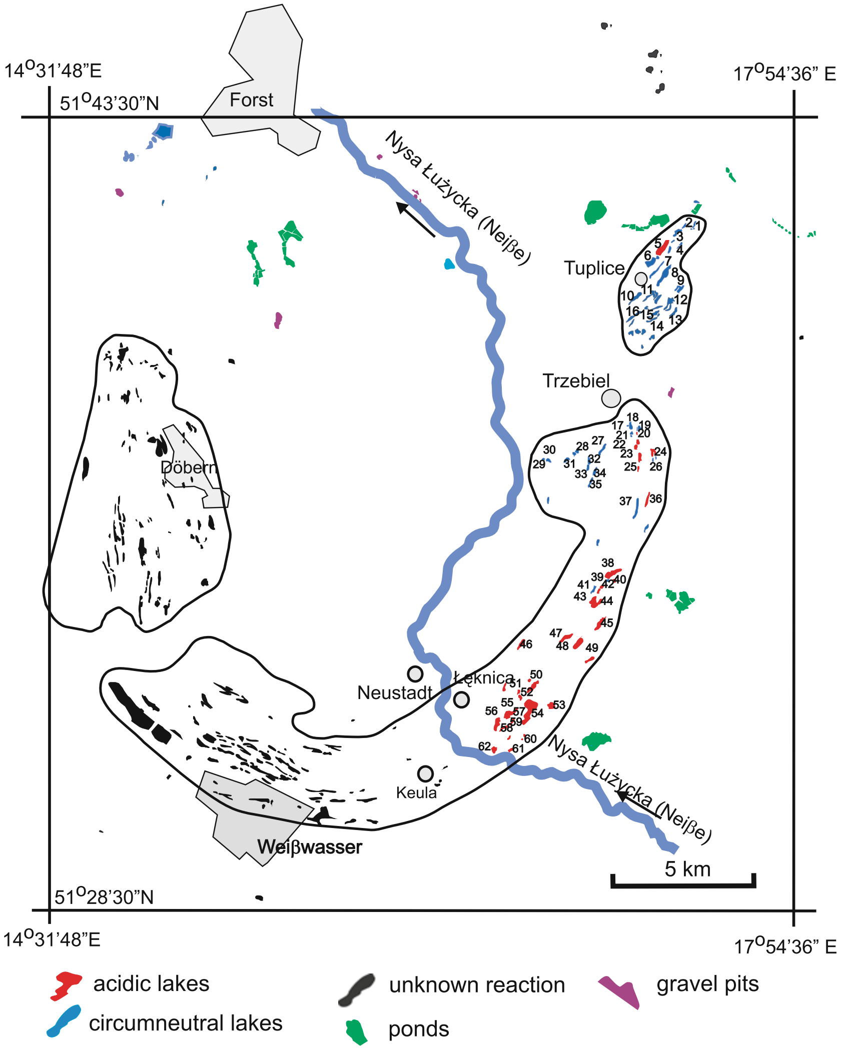


Fig. 5.17 Location of the anthropogenic lakeland and the acidity of the Polish reservoirs. Polish-German border on River Nysa Łużycka

The post-mining area on the Polish side of the border, at Łęknica, is about 430 ha in area and contains over 100 artificial lakes (Fig. 5.17), with an aggregate surface area that exceeds 150 ha. These lakes are unnamed; therefore, Jędrczak (1992) numbered 63 of them. About 40 lakes are not even numbered and have never been monitored. The morphometrical parameters of the largest impoundments are given in Table 5.5.

Table 5.5 The basic morphometric parameters of selected reservoirs (after Jędrczak 1992)

Number	Ordinate of water table (masl)	Surface (ha)	Depth (m)	Volume (10^6 m^3)
8			3	
11			4	
16			3	
17			5.5	
25	138.8	1.85	12.2	
37			4	
38	130.9	7.1	18	0.637
41			6	
43	132.4	6.95	14	
45	142.8	5.04	13	
46	137.8	3.85	10	
47	144.9	4.55	6	
48	142.8	5.34	16	0.470
49	143.5	2.4	7	
50	137.0	4.40	12	
53	133.5	4.10	10	0.213
54	132.0	20.2	24	1.950
55	134.0	6.25	9	0.219
56	134.0	8.45	16	
60	115.0	2.55	5	
62	110.6	3.25	12	

Three of these lakes are meromictic. Special attention was given to the youngest reservoir, No 54, in 1993, when it was 19 years old. When reservoir No 54 was 13 years old, its redox potential was at least 0.40 V. At that time, two other older reservoirs had a potential of 0.30 and 0.212 V (Solski and Jędrczak 1991), indicating that some sulfate reduction was likely occurring. In the opinion of Jędrczak et al. (1998), the lowering of the redox potential in reservoir No 54–0.398 V in 1998 and to 0.39 V four years later indicated slow aging. During the 11 years between consecutive investigations (1981–1992), Al concentrations diminished from 47/86 mg L^{-1} (mixo-/monimolimnion) to 15/2.1 mg L^{-1} above the bottom. During this same period, Fe concentrations in the mixolimnion equalized at 60–200 mg L^{-1}, but gradually increased in the monimolimnion from 800–900 mg to 1,500 mg L^{-1}. NH_4 concentrations increased in the monimolimnion from about 7 mg N L^{-1} above the bottom (in 1981) to 88.9 (in 1992). The concentration of sulfate in the mixolimnion was practically constant for both the seven- and 24 year-old reservoirs (1,400–1,500 mg SO_4 L^{-1}), whereas in the monimolimnion, it increased from 2,000 to almost 4,000 mg L^{-1}, forming a typical chemocline at a depth of 10–13 m (Jędrczak et al. 1998).

5.2.3.1 Water Chemistry

Almost half of the reservoirs in the Muzhakov Arc on the Polish side are acidic. Jędrczak (1992) found 30 acidic reservoirs, applying a threshold of $pH = 4.3$ to distinguish acid reservoirs and the 'remaining' ($pH > 4.3$). Previously, Jędrczak divided these reservoirs according to another criterion: acid, pH 2.6–3.7, Eh 606–755 mV; and 'other' reservoirs: pH 5.2–7.4, Eh 380–600 mV (Solski and Jędrczak 1990). Later, Jachimko (1998) analyzed 24 reservoirs and distinguished three categories of impoundments: acid, with $pH < 4$ and a redox potential of > 600 mV; transitional, with pH 4–5.5; and 'the rest', pits of $pH > 5.5$ and a redox potential of <633 mV.

Almost all of the investigations carried out on these reservoirs concern water chemistry. Data were first collected by Mendaluk and Wróbel (1977). Later, Matejczuk (1986) investigated 16 reservoirs near Łęknica. The next investigations were carried out in 1987–1993 and included 63 reservoirs (Solski and Jędrczak 1990, 1991a, 1991b; Jędrczak 1992). Again, 24 reservoirs were examined in detail in 1993. Subsequently, in 1998, Jachimko (1998) and Jędrczak et al. (1998) repeated their investigations on ten acidic reservoirs. Today, the only lake being monitored is the largest reservoir, No 54, which was monitored in 2006–2007 by Jachimko (2007a, b) and Asani and Kołodziejczyk (2006).

In Matejczuk's (1986) opinion, all of the impoundments had an acid phase in their evolution and, over time, they naturally became less acidic, often becoming alkaline. The chemical characteristics considered included: the proportion of Mg and Ca, Cl, and SO_4, the sum of Ca + Mg versus the sum of Cl + SO_4, and the amount of Mn and Fe. Usually, an impoundment with a low pH has a high concentration of Mn and Fe ions and a small amount of organics. Both acidic and neutral reservoirs occupy characteristic positions on graphs. Synthetic chemical characteristics are presented on a Piper's graph (Fig. 5.18; Jędrczak 1992).

Acidic lakes are high in sulfate, calcium, and magnesium, and contain little or no dissolved organic matter, nitrate, bicarbonate, and Cl (Fig. 5.17a). Considering the cations, three sub-groups can be distinguished:

- Water dominated by Mg ions (reservoirs 20, 22–24, 36, 38, 47, 48, and 58–62)
- Water dominated by Ca ions (49–54, and 57)
- Waters without a dominant cation (40, 42–46, 55, and 56; Fig. 5.18a).

The acidic reservoirs typically contain a high amount of iron (above 10 mg L^{-1}) though, some (20, 23, and 36) had low concentrations, below 1 mg L^{-1}. Ferruginous water was found in reservoirs 24–26, 40, 42, 43, 46–51, 56, 58, 60, and 61. The water in the acidic reservoirs is generally moderate to high in hardness, and sometimes very hard (95–495 mg $CaCO_3$ L^{-1}).

The 'remaining' reservoirs (Fig. 5.18b) had low concentrations of Fe (0.02–1.70 mg L^{-1}), higher pH (5.4–8.9), and higher concentrations of easily oxidized organic matter (Mn–COD 5.5–35 mg O_2 L^{-1}). Concentrations of N_{NO3} and N_{NH4} were lower than in the acidic reservoirs (<1.2 mg L^{-1} N_{NO3} and < 1.75 mg L^{-1} N_{NH4}). In contrast to the acidic reservoirs, there was

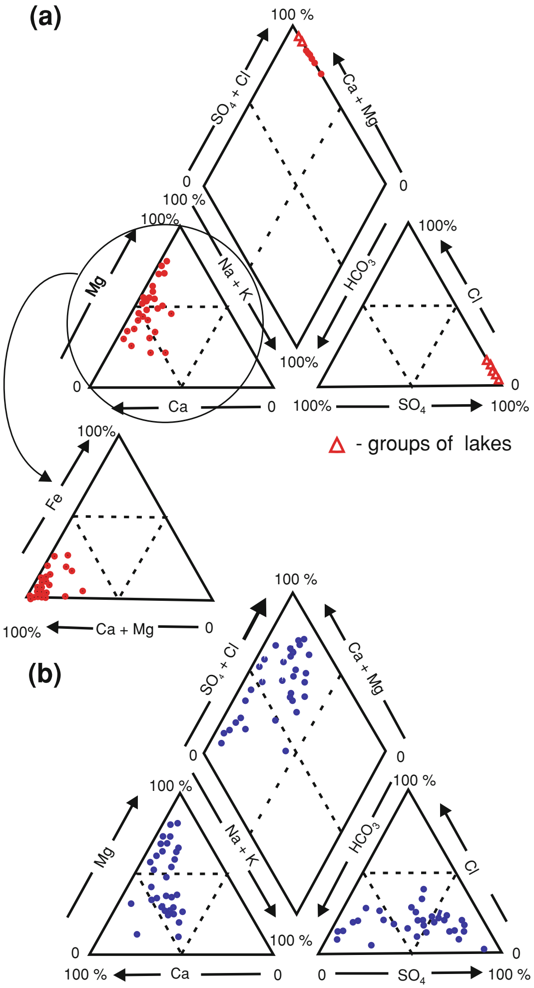


Fig. 5.18 **a** Ionic characteristic of acid reservoirs in basic configuration, in incise configuration taking into account Fe ions; **b** ionic characteristic of 'remaining' reservoirs with pH > 4.3. (modified from Jędrczak 1992). Numbers of reservoirs as in Fig. 5.17

bicarbonate (13–55 mg L^{-1}), Cl^- (13–55 mg L^{-1}), and SO_4 (9–181 mg L^{-1}). This group can also be subdivided as either:

- Ca/Mg sulfate, or
- Ca or Mg bicarbonate

Most of the 'remaining' reservoirs belong to the first group: 2, 3, 5–16, 18, 19, 27, 33–35, 39, and 41. Generally, the impoundments with sulfate-type water had Mg as the dominating cation (11, 18, 19, 27, and 33–35), whereas Ca only dominated in one impoundment (14). The remaining waters had no dominating cation. Similarly, Mg cations also predominated in bicarbonate-type water (17, 21, and 28–32). The Ca cation was dominant in only one reservoir (37). The remaining reservoirs, 1 and 4, had no dominant cation.

5.2.3.2 Biology of Lakes in the Muzhakov Arc

The biology of these lakes has only been investigated by a few investigators (Koprowska 1995; Matejczuk 1986; Najbar 1998, 2000). Their observations indicate a simplified ecosystem in acid lakes (pH 2.4–4.0), a richer ecosystem in transitional lakes (with pH 4.18 and 5.6), and a normal ecosystem at neutral or alkaline pH. This aspect is discussed elsewhere in this book (Sect. 3.3).

5.2.4 Lakes in Sulfur Opencasts

5.2.4.1 Piaseczno [Piasetschno]

The present area of the Piaseczno mine is 63 ha, with a depth of 22 m. The reservoir, once formed, will be 160 ha in area and 42 m deep, with a volume of 27×10^6 m^3. Only the outcrops above the water table (between 122 and 146 masl) were isolated by a 3–5 m layer of clay and silt; outcrops below the water table (down to 100 masl) remain unisolated. The predicted time for autogenous filling is 6–7 years (Fig. 5.19).

The pit was inundated by tertiary and quaternary water in different proportions. As the water level increased, the fraction of tertiary water decreased. Tertiary water is relatively strongly mineralized, with a mean solute concentration of 2,170 mg L^{-1}. The water from both the tertiary and quaternary aquifer can be classified as the sulfate–chloride-sodium-calcium (SO_4–Cl–Na–Ca) type in the Altovski-Shvec classification (Macioszczyk 1987). Sulfur-bearing limestone and sedimentary rocks are rich in calcium, carbonate, and sulfate and have elevated concentrations of Na, Cl, Br, I, and relatively low heavy metal content. The discrimination technique distinguished three chemically different layers (Żurek 2006): the upper layer, ± equal to the photic zone; the transitional layer in the dark hypolimnion; and the monimolimnetic layer below the chemocline. The Piper's diagram (Fig. 5.20) confirms these three layers.

Until now, the water level has been kept at 122 masl, which means that the maximum water depth is only 22 m. Site reclamation should be finished by 2013, and the new reservoir, with an area of 160 ha and a maximum depth of 40 m depth, will be suitable for recreation.

5.2.4.2 Machów

The sulfur was exploited at Machów between 1969 and 1992. The mine was then backfilled with shale and silt from the inner dumping ground. Below the isolating layer is 3.74×10^6 t of industrial waste. During extraction, the opencast mine reached a depth of 70–110 m, but it was later backfilled with shale and silt from the inner dumping ground to a depth of 45 m. Flooding began in spring 2005, using water from the Vistula River, and was completed in April 2009. The

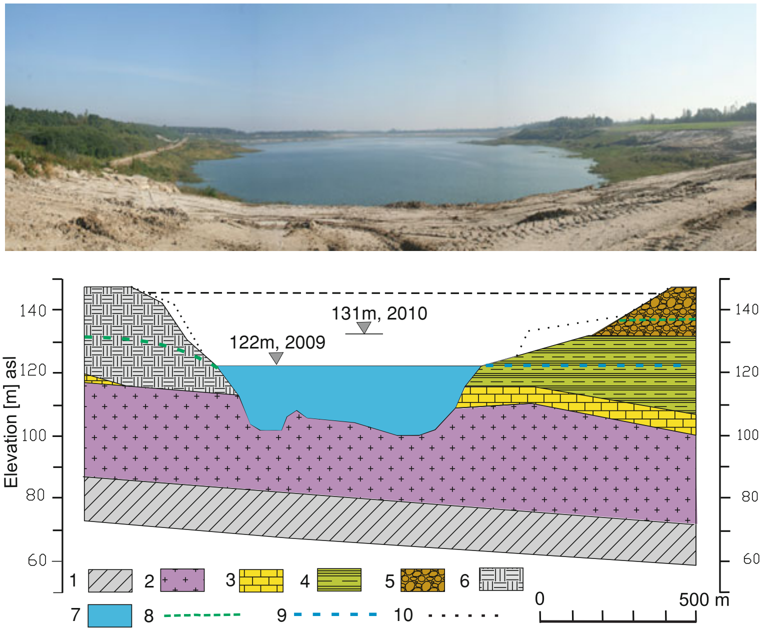


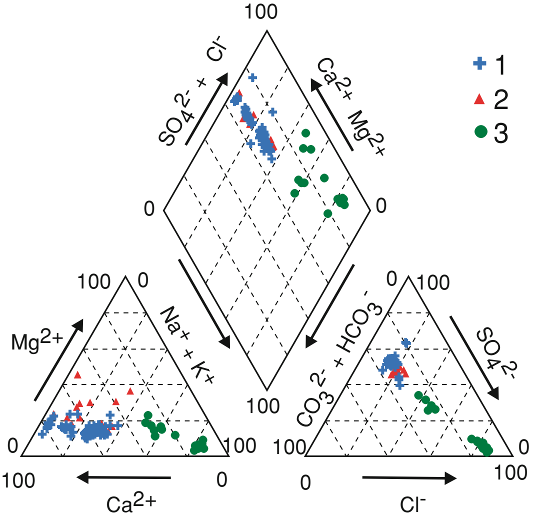
Fig. 5.19 Geological cross-section of the Piaseczno opencast mine: *1* Cambrian shale; *2* Tortonian, sands and sandstones; *3* Torton, chemical series, sulfur-bearing limestone, barren limestone and gypsum; *4* Sarmatian, Krakoviec clays; *5* Quaternary, sand and gravels; *6* inner waste bank—sands, gravels, clays, silts; *7* Present water level of Piaseczno reservoir; *8* Water table of Quaternary aquifer; *9* Potential surface of Tertiary aquifer; *10* Old bowl profile. *Above* view 2010 (modified after Żurek 2009)

reservoir has an area of 460 ha and a volume of 112 × 10^6 m^3; the open cast area is 560 ha. The external dumping ground has an area of 880 ha and a height of 60 m. There are seven small lakes with a surface area of 0.1–3.5 ha and a depth of 1.5–14 m; the inner dumping ground has an area of 720 ha (Fig. 5.21). Reclamation is virtually complete (Fig. 5.22a).

5.2.5 Remediation and Reclamation

Coal excavation generates a deficit in pit volume. In the past, some mines were simply abandoned, but abandonment without reclamation is no longer acceptable. So, mine closure only signals the beginning of a long, arduous, and expensive process of remediation aimed at restoring the ecological value of post-mining areas. Many reservoirs and surrounding post-mining areas are being designed to be attractive places for holidays, which can be particularly significant in regions lacking natural resources, while others are still being reforested, or changed into wetlands, meadows, or farmland.

Fig. 5.20 Diagram of water chemistry for three layers. *1* samples from depth 0, 2.5, 5, 7.5 m; *2* samples from 10 to 15 m; *3* samples from 20 m (from Żurek 2009)



A good example is the Bełchatów mine, from which 100 × 10^6 m^3 of overburden is stripped and 170 × 10^6 m^3 of water is pumped annually. The Bełchatów mine covers 3,240 ha with an external dumping ground that is 195 m high. An area of 1,480 ha has been reforested and transferred to the State Forest. A new hill made of overburden rock (with a volume of 1,354 × 10^9 m^3) makes the region attractive, with a hill-side chairlift for skiers, as well as restaurants and hotels. Overburden has been dumped into the open-pits since 1993. Of the 1,300 ha that will be reclaimed in the future, 5,500 ha will be reforested. The final open-pits, each with a depth of 280 m, will be partially filled with overburden material from temporary dumping grounds. The mine water is being passively treated in three settling ponds/wetland areas with a total area of 51.6 ha of wetland and a common flow capacity of 405 m^3 min^{-1}. The ponds represent a diversified environment that is rich in water plants and fauna. However, in addition to its aesthetic value, place has been set aside for recreation.

The Konin mine, now an artificial lake of 110 ha with special islands, peninsulas, beaches, and other recreational terrains, is popular for sports and recreation, with a ski slope, amphitheatre, golf course, and motocross track as well as the lake. Previously, such lakes were transferred for free to local authorities, such as the 242 ha reservoir created at the Adamów mine, after reclamation was finished. However, in 2009, the Konin mine's owner sold a reclaimed 330 ha lake in the Patnów pit to a private investor. The government has a right of pre-emption, but in this instance, no government agencies took advantage of it. The mine's owner is liable to be charged 170,000 Euros in land-tax annually.

Seventeen years after the Machów open cast sulfur excavation was abandoned, the mine was reclaimed and, in 2009, it was filled with water. At present, the land is being developed. Alongside the Machów reservoir, a water sports base (beaches,

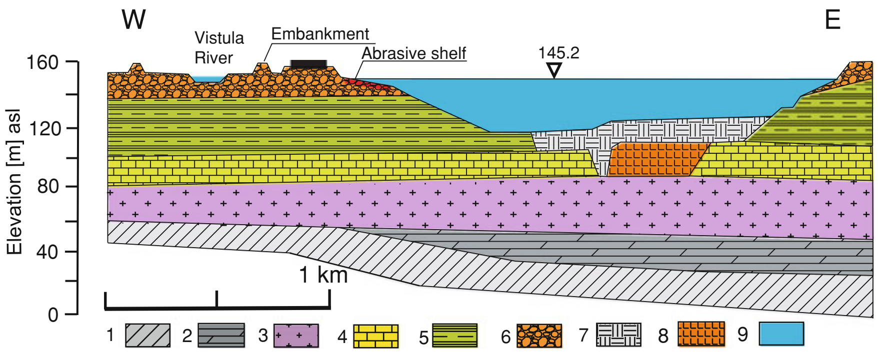


Fig. 5.21 Geological cross-section of the Machów opencast mine. *1* Cambrian shale; *2* sandy siltstones (Lower Badenian); *3* Tortonian, sands and sandstones; *4* Torton, chemical series, sulphur-bearing limestone, barren limestone and gypsum; *5* Sarmatian, Krakoviec clays; *6* Quaternary, sand and gravels; *7* Insulating layer; *8* Post-refining waste; *9* Water (modified after Jakubek 2004)

boat-house, landing-stage for sailing boats) and a 2.7 ha recreation base, with 42 separate building sites, and areas (28 sites) for sale are planned. On the neighboring area to the south, a motel with 50 beds (the capacity of a typical touring bus) is planned, as well as a 1.7 ha camping area equipped with sanitary facilities, a self-service kitchen, parking area, and a seasonal grocery. The neighboring sulfur mine at Piaseczno has finished profiling escarpments, and after the pit fills with water, it will also be managed for recreational purposes (Fig. 5.22b).

5.2.5.1 Approaches and Techniques Used

In the 1970 and 1980s, post-mining lands were reclaimed for agricultural use and as woodland. As ground deficits increased, the idea of creating lakes gained advocates. The practice of lake creation began in Poland during the 1980 and 1990s and new plans for reclamation are constantly being introduced. However, each new reservoir generates different problems.

In general, slopes are formed with a gradient between 1:4 and 1:5. When scarps are above 20 m high, they should be divided every 15 m by the creation of a shelf, separating scarps of the same height and slant. Each shelf of the lower scarp should have small counterscarps (width 5 m, slant 1:20).

The Turów external dump area is drained by a system of open drainage ditches, which directs water to settling ponds located on the floor. From there, water flows by stone or concrete pipes to lower levels and through sedimentary-retention reservoirs into natural waterways. This system operates on each of the six catchments in the dump area. The whole system comprises 190 km of drainage ditches, 140 sedimentary reservoirs, and 11 km of slope drains. The slope drains are made from polyethylene pipes or stone gabions because these materials are more resistant to subsidence than steel pipes and do not corrode. Stone gabions are

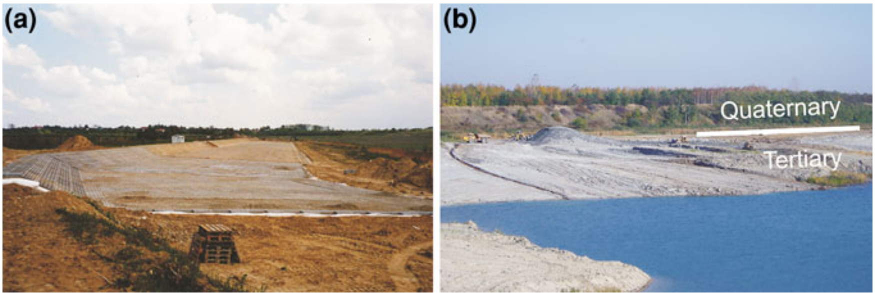


Fig. 5.22 **a** Machów, construction of embankment—on the geotextiles are arranged openwork concrete plates; **b** Piaseczno, trimming slopes and isolation of gypsum and sulfur limestone outcrops by 2–5 m layer of cinereous clay and loam, photo Z. Pantula

also more aesthetic. Simultaneously with the hydrotechnical system being put in place, road building starts on the dumping ground. The roads are used for transporting the hydrotechnical equipment and for approach roads for forestry.

Sometimes decisions about open-pit reclamation change, as occurred with the Bogdałów opencast (Adamów mine), where the final opencast had been largely backfilled with overburden material from the neighboring Koźmin strip mine. In 1994, a reservoir was made from a partially filled pit. Public demand encouraged engineers to continue filling reclaimed sites with water. In the future, seven artificial lakes will be connected by a hydrologic net equipped with hydrotechnical constructions. Some reservoirs will be used for recreational purposes, whereas others will act as nature reserves.

In contrast, at the Konin mine, pits are still being backfilled with overburden material from the excavation of new mines. For example, the waste rock from the Jóźwin strip pit were transported to the Pątnów pit, those from the Kazimierz Północ strip pit to the Kazimierz Południe, and those from Jóżwin IIB to Jóźwin IIA. In the case of these mine sites, the presence of boulder clay in the overburden is propitious to agricultural and forest reclamation. Apart from typical reclamation, some unusual projects are being undertaken, such as using the clay for trough isolation of a local stockyard and sealing the bottom of the pits with clay and using them for a landfill.

Open-pit mines can also be a good place for depositing fly ash from power stations. Aqueous leachate from ash has a pH ranging from 8.0 to 12.0, with a concentration of SO_4 anions above 500 mg L^{-1} and elevated concentrations of As (up to 0.62 mg L^{-1}). However, the aqueous leachate from a mixture of fly ash and overburden soils can have a relatively low concentration of trace elements and anions because of the sorption capacity of clay minerals, a major component of many overburden soils, as in the Turów open-pit (Rybicki and Helios-Rybicka 2005). Since 2006, this mine has filled their pits with a mixture of overburden soils and fly ash from the Turów power station.

Reclamation of the sulfur mines has been slow due to limited funding. In the past, most of the money for reclamation came from the state budget, which was supplemented with funds from the National and Voivod Funds for Environmental

Table 5.6 Basic sources of the hydrological balance for the Piaseczno reservoir; efficiencies of inflows/outflows [$m^3\ d^{-1}$] (Kirejczyk et al. 2007)

State	Ordinate	Constituent of balance							
	masl	Q_P	Q_E	Q_S	Q_1	Q_2	Q_3	$Q_4 + Q_5$	Q_6
Initial state	122.4	768	922	156	3,601	3,098	4,202	1,808	538
Prognosticated state	146.0	2,496	2,995	53	1,289	3,811	0	154	269

Q_P: direct precipitation on reservoir surface; Q_E: evaporation from reservoir surface; Q_S: surface run-off from reservoir basin; Q_1: quaternary underground inflow through dump; Q_2: inflow through remaining quaternary alluvia; Q_3: inflow through quaternary alluvia from Vistula River; Q_4: inflow of tertiary water through ‘hydrogeological window’ (on W and N–W from pit), flux through inner dump; Q_5: inflow of tertiary water from ‘hydrogeological window’ (on W and N–W from pit), flux bypassed inner dumping ground; Q_6: inflow of tertiary water from remaining area of infiltration, mainly on E from pit

Protection and Water Management (NFOŚiGW and WFOŚiGW). Since 2000, reclamation has been financed only by NFOŚiGW and WFOŚiGW. The full cost of reclaiming the Piaseczno mine amounts to 37.5 × 10^6 €, while the cost of reclaiming the Machów mine is estimated at 370 × 10^6 €.

5.2.6 Mine Water

Mine water has a lot of suspended impurities such as coal particles, sand, silt, and clay. Colloidal particles have an electric potential of 70 mV and cannot be removed by mechanical methods. Therefore, these particles are coagulated and flocculated in settling ponds. The sediment (which is 99% H_2O) is scraped into settling cones, pumped onto sedimentary lagoons, settled, and decanted. Clean water is then discharged into streams.

As noted above, all the acid and acidic lakes created after the mining of brown coal are situated in the Muzhakow Arc. Acid reservoirs are not useful to the economy. Therefore, local communities have an interest in managing them. There are two ways of doing this: do nothing and wait until the water becomes neutral through natural processes, or do something to accelerate the process. The natural process of neutralization of an acid reservoir can take a very long time. The reservoirs in the Muzhakov region reached pH 6–7 through natural processes within 50–70 years. About half of these reservoirs that are from 35 to over 110 years old are neutral (the youngest, No 54, has existed since 1973). These lakes were all simply abandoned and no reclamation has been carried out there.

In contrast, at the Piaseczno sulfur mine, the formation of the bottom and slopes of the reservoir commenced 36 years after exploitation ceased. A detailed water balance (Table 5.6) and modeling of the flooding process indicated that it would take five to six years to fully flood the mine.

For the purposes of the reclamation project, Kirejczyk et al. (2007) tried to calculate the mean concentrations of the trace ions chloride and sulfate in the Piaseczno reservoir at the final water level of 146.0 masl. For the actual water level (122.4 masl) model (MODFLOW), the anticipated chloride concentration was 153 mg dm^{-3}, i.e. similar to the concentration in the surface layer. For this reason, the authors consider that the model result is correct. Hydrobiologists are troubled that the model used by the engineers treated the meromictic lake as if it was perfectly polymictic. The inflow of tertiary water will diminish from the present 2,348 to 423 m^3d^{-1} in the future, and the reservoir will remain meromictic. Frankiewicz and Pucek (2006) agree. Despite all this, a new equilibrium state will be established.

In 2009, the pumps were turned off and the water level began to rise. Restoration of the historical aquifer will necessitate drainage of 3,000 ha of fields and orchards since the waterlogged Vistula valley has historically been drained by the opencast operation.

5.2.7 Conclusions and Lessons Learned

Professor Walery Goetel, the creator of sozology (the science of the systematic protection of the biosphere), authored the phrase ‘What man devastated, man must repair’. This idea has not always been followed. We know of thousands of abandoned, contaminated, and devastated opencasts. However, improving ecological education and awareness of their threat to our natural environment has caused changes in the legal systems of states. These legislative tools have had the desired effect. All European Union member states are now obliged to manage their water resources. Elsewhere, the situation can be much worse.

Understanding the chemical, hydrogeological and biological processes in post-mining sites and lakes enables the recovery of ecological status in a relatively short period. Nowadays, opencast mining creates and embellishes the landscape, which can make it more attractive for both people and wildlife.

5.3 Mine Pit Lakes of the Iberian Pyrite Belt: Some Basic Limnological, Hydrogeochemical, and Microbiological Considerations

Javier Sánchez-España, Marta Diez and Esther Santofimia

5.3.1 Introduction

The Iberian Pyrite Belt (IPB) can be considered an end-member or worse-case example of mine-related pollution, due to, among others: (1) abundant pyrite and very scarce carbonate, (2) no environmental protection during past mining activities (especially during the period, 1880–1980), (3) immense accumulation of mostly unremediated mine wastes in the surroundings, and (4) strong acidity and metal pollution of the water courses (as well as the associated sediments and adjacent soils), which have all been affected by acid mine drainage (AMD).

This chapter provides an overview of the acidic mining lakes formed in the IPB, and discusses their limnological, hydrogeochemical, and microbiological characteristics. The state-of-the-art is presented with respect to our current knowledge about the biotic and abiotic factors that seem to control the composition and stratification style of these lakes. Basic limnological and hydrogeochemical information is supplied for a number of pit lakes (from López-Pamo et al. 2009 and Sánchez-España et al. 2008, 2009). The chapter is especially focused on meromictic pit lakes, with special emphasis on the Cueva de la Mora pit lake, which represents a remarkable example of a vertical gradient of redox chemistry and water composition.

5.3.2 Environmental Context

5.3.2.1 Geology

The IPB is a world-class metallogenic province situated in the southwestern corner of the Iberian Peninsula, extending from north of Seville to south of Lisbon. The IPB has a long history of extensive mining, which dates from pre-Roman times (up to the Chalcolitic age, 3 ka B.C.; Pinedo Vara 1963) and comprised more than 80 mines, including historical ore deposits such as Ríotinto, Tharsis, La Zarza, Sotiel, and Aznalcóllar (Leistel et al. 1998; Tornos 2006).

The lithostratigraphic sequence of the IPB comprises Upper Devonian to Middle Carboniferous volcanic and sedimentary rocks, including the PQ group (composed of phyllites and quartzites), the volcanic-sedimentary complex (VSC; formed by shales, greywakes, and mostly acid volcanic rocks), and the culm group (a flysch-like sequence of shales and greywackes). The mineralization is dominated by pyrite, with lesser amounts of sphalerite, chalcopyrite, and galena, and minor quantities of tetrahedrite-tennantite, arsenopyrite, pyrrhotite, cassiterite, magnetite, and hematite. Pyrite is texturally variable from fine-grained (colloform, framboidal) to coarse-grained (Saez et al. 1999; Sánchez-España 2000; Velasco et al. 1998). Gangue minerals include abundant silicates (quartz, chlorite, muscovite, feldspar), and minor amounts of carbonate and barite. Thus, the pit lakes of the IPB share a common geological framework defined by the ubiquitous presence of pyrite, abundant aluminosilicates, and a marked scarcity of carbonate minerals. These mineralogical features have favoured the oxidative dissolution of pyrite, and the subsequent formation of AMD (Sánchez-España et al. 2005a).

5.3.2.2 Hydrology

The hydrological characteristics of the IPB are typical of a Mediterranean region. Rainfall discharge is highly variable and especially concentrated in autumn and winter (up to 10–70 mm/day from October to March). Evapotranspiration is also very variable (<1 mm/day in winter, and up to 10 mm/day during the summer). Despite the low permeability of most volcanic and sedimentary rocks hosting the mineralization, significant groundwater inflow exists (mainly channelized through former mine galleries and fractures). This groundwater input is mostly responsible for a relatively fast flooding stage (of only a few years) of the mine pits after they are abandoned and pumping wells are definitively stopped. As an example, rates of groundwater inflow on the order of 10–40 L/s ($\approx$1,000–3,000 m^3/day) have been calculated for some pits that are still being flooded, such as those of Los Frailes in Aznalcóllar or Corta Atalaya in Riotinto (López-Pamo et al. 2009; Sánchez-España et al. 2008).

5.3.2.3 Environmental Aspects

The IPB mining legacy has resulted in one of the world's largest accumulations of pyritic mine wastes, with tens of abandoned waste piles and tailings impoundments that totalize more than 200 Mm^3 in volume. These wastes are continuing sources of environmental contamination, mostly AMD, which has severely polluted the Odiel and Tinto rivers (Braungardt et al. 2003; Cossa et al. 2001; Davis et al. 2000; Elbaz-Poulichet et al. 1999; Olías et al. 2004; Sánchez-España et al. 2005a, 2006a; Van Geen et al. 1991).

In most cases, mining was accomplished by both underground and open pit mining simultaneously, so that a typical feature of the IPB mining record is the development of mine pits connected to dense networks of shafts and mine galleries. Many of these mine pits were abandoned and flooded during the 1960–1990s, although some pit lakes have existed for more than a century (e.g. Confesionarios mine, closed in 1888; Pinedo Vara 1963). The oxidative dissolution of pyrite and other sulfides, such as chalcopyrite, sphalerite, arsenopyrite, and galena, sulfosalts like tetrahedrite-tennantite, and gangue aluminosilicates like feldspars, chlorite, and sericite from the country rocks has caused most of these pit lakes to contain very acidic water, with high concentrations of dissolved sulfate and metal(oid)s (Fe, Al, Mn, Cu, Zn, Pb, Co, Ni, Cd, As; Sánchez-España et al. 2008, 2009).

Former mining towns were abandoned after the decline of the mining industry, and today the population density is very low in most mining districts of the IPB. Therefore, there is not a strong social demand for environmental remediation or restoration of these strongly degraded mine sites, and only very recently have these lakes been protected by security fences by Junta de Andalucía (the regional government). From a biotic perspective, it is not uncommon to observe birds like swallows and storks in these artificial lakes, which are also inhabited by benthic green algae and some specialized species of insects (e.g. *corixidae*) that have colonized their shores.

Table 5.7 Age, morphometric data, and stratification type for 17 acidic pit lakes of the Iberian Pyrite belt (modified from López-Pamo et al. 2009 and Sánchez-España et al. 2008)

Pit lake	Age (year)	Max diameter (m)	Min diameter (m)	Area (ha)	Max depth (m)	Rel. Depth (%)	Vol. Mm^3	Strat. type
Corta Atalaya	4	300	150	4.70	>70	>29	1.4	Meromictic ?
Filón Sur	?	65	50	0.20	5	10	0.01	Meromictic
Filón Centro	40	430	140	3.80	40	18	0.6	Meromictic
Confesionarios	120	200	160	2.48	80	45	1.0	Meromictic
N^a. S^a Carmen	?	110	80	0.70	32	34	0.1	Meromictic
Peña del Hierro	42	200	120	1.87	>50	–	–	Meromictic
La Zarza-E	12	220	100	0.70	>40	–	–	Meromictic ?
La Zarza-W	12	240	100	0.77	>40	–	–	Meromictic ?
Cueva de la Mora	>60	300	90	1.78	40	27	0.3	Meromictic
Herrerías I	42	110	90	0.81	65	64	0.2	Meromictic
San Telmo	16	510	380	14.36	120	28	7.0	Meromictic
Concepción	>30	280	60	1.20	15	12	0.4	Meromictic ?
Angostura	>70	110	90	0.84	>40	–	–	Meromictic ?
T° S^a Rosa	77	160	80	1.11	23	19	0.1	Meromictic
Aznalcóllar	13	850	400	28.40	38	6	6.0	Holomictic
Herrerías II	42	230	90	1.42	15	11	0.10	Holomictic
Los Frailes	7	460	280	13.30	105	26	6.30	Holomictic

5.3.2.4 Pit Lake Morphometry

The pit lakes of the IPB show very variable size, surface area, depth, and age. Some relevant morphometric data of these pit lakes are provided in Table 5.7.

The surface area of the lakes ranges from less than 1 ha in the smallest lakes (e.g. 0.2 ha in Filón Sur or 0.7 ha in NaSa del Carmen) to tens of ha in the greatest lakes (e.g. >28 ha in Aznalcóllar, or >14 ha in San Telmo). Water depths are also variable, and range from around 15 m in Concepción to more than 120 m in San Telmo and Los Frailes. These measurements have made it possible to calculate the relative depth of several lakes, defined as the depth to surface ratio by the equation $z_r = \frac{50 \cdot z_m \cdot \sqrt{\pi}}{\sqrt{A_0}}$, where z_r is the relative depth (in %), z_m is maximum depth (in m) and A_o is surface area in m^2 (Anderson et al. 1985; Doyle and Runnells 1997; Wetzel 2001; Table 5.7). This relative depth ranges from around 6% in Aznalcóllar to around 64% in Confesionarios and Herrerías I. The low relative depth of the Aznalcóllar pit lake is not realistic, but is due to backfilling carried out during recent years in this lake (Santofimia et al. 2007a; Schultze et al. 2006). The relative depth of the IPB pit lakes typically ranges from 10 to 50%, which agrees with the relative depths of 10–40% reported for pit lakes in USA and Canada (Doyle and Runnells 1997).

5.3.3 General Water Quality Aspects

5.3.3.1 Surface Water Composition

The pit lakes of the IPB also show a great variability of water compositions. The surface water chemistry of twenty-two pit lakes has been recently reported in Sánchez-España et al. (2008), including pH and concentration of SO_4^{2-} and some selected metal cations (Fe, Al, Cu, Mn, Zn) and trace metal(oid)s (As, Pb, Cd, Cr). These chemical data are illustrated in Fig. 5.23.

This data set reflects a wide range of water compositions, from waters with neutral pH and relatively low metal contents (e.g. Los Frailes pit lake: pH 7.2, 0.07 mg/L Fe, 1 mg/L Al, 0.01 mg/L Cu) to extremely acidic and metal-enriched waters (e.g. Corta Atalaya: pH 1.2, 36.7 g/L Fe, 1.9 g/L Al, 1.3 g/L Cu). However, the two end-members (Los Frailes and Corta Atalaya) represent anomalous cases that are not representative of the hydrogeochemistry of the pit lake province; for a deeper insight into the hydrogeological and hydrogeochemical conditions of these two lakes, see Sánchez-España et al. (2008) and Santofimia et al. (2007b). For somewhat different reasons (backfilling with mine wastes and materials of very different composition), the Aznalcóllar pit lake is not representative of pit lakes in the IPB (Sánchez-España et al. 2008; Santofimia et al. 2007b; Schultze et al. 2006).

With the cited exceptions of Corta Atalaya, Los Frailes, and Aznalcóllar (also Herrerías II-Santa Bárbara), the surface conditions of the IPB pit lakes typically include a pH of about 2.8 (mostly in the range of 2.2–3.5), a high redox potential characteristic of highly oxidizing conditions (550–850 mV; data not shown), total Fe chiefly composed of Fe(III), dissolved SO_4^{2-} ranging from 940 to 18,000 mg/L, and very variable metal contents, on the order of 0.38–4,620 mg/L Fe_T, 3.7–773 mg/L Al, 0.47–430 mg/L Cu, 3.3–254 mg/L Mn, and 5–834 mg/L Zn (Fig. 5.23), in addition to 6–22,000 μg/L As, 16–1,900 μg/L Cd, and 12–1,000 μg/L Pb (Sánchez-España et al. 2008).

The lithology of the rock substrate has undoubtedly determined the water chemistry of these pit lakes. The high contents of Fe and SO_4^{2-} dissolved in the waters result from the oxidative dissolution of pyrite, whereas the rest of metals are thought to be due to the subsequent dissolution of sphalerite (Zn ± Cd), chalcopyrite (Cu, Fe), galena (Pb), arsenopyrite (As, Fe), tetrahedrite-tenantite (Fe, Cu, Zn, As), and gangue aluminosilicates like feldspars (Al, K, Na, Ca), chlorite (Al, Fe, Mg ± Co ± Ni), and sericite-muscovite (Al, Na, K). In addition to these primary sources, the dissolution of secondary sulfate salts must have also influenced the pit lake water chemistry, especially during the initial flooding phases.

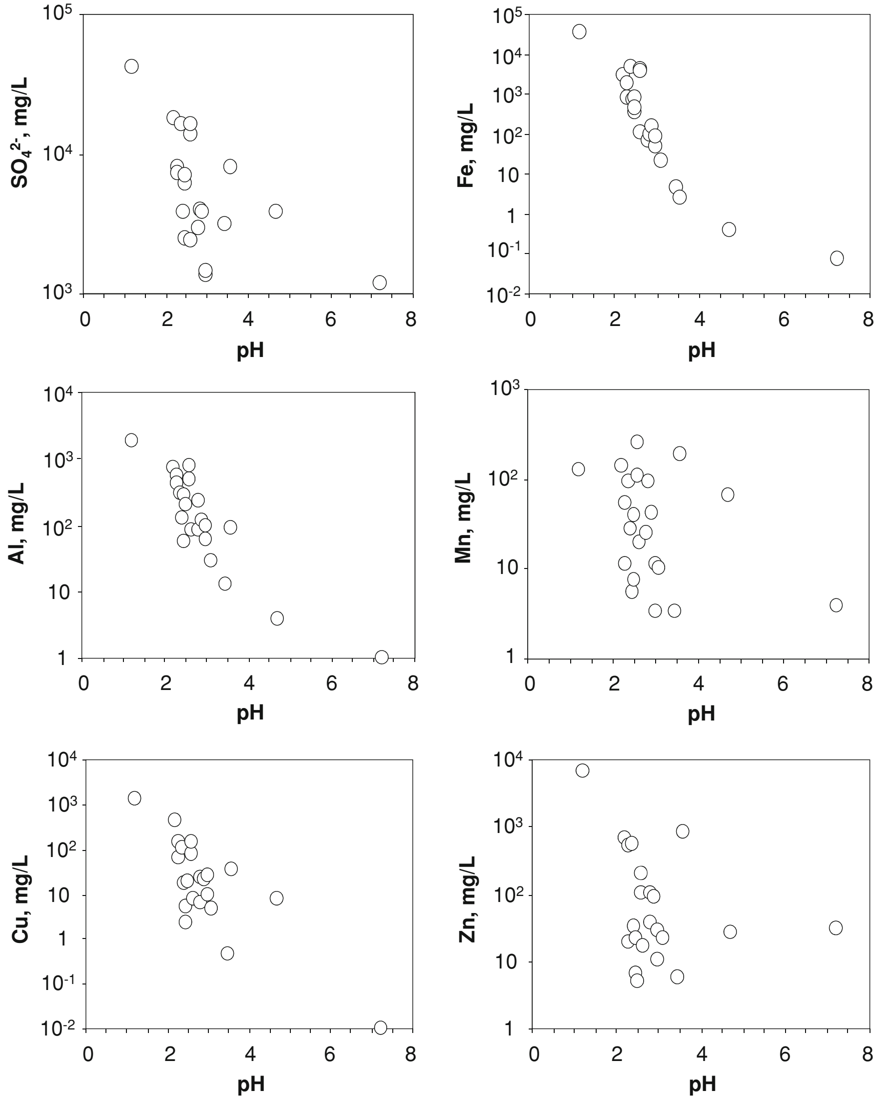


Fig. 5.23 Plots of pH versus major ion and trace metal concentration for twenty-two pit lakes of the IPB. The data correspond in all cases to surface conditions (data taken from Sánchez-España et al. 2008)

5.3.3.2 Mineral Controls of Aqueous Element Concentrations

Using the chemical compositions of the pit lake surface waters shown in Fig. 5.23, Sánchez-España et al. (2008) calculated the activities of dissolved Fe^{3+} and Al^{3+} with the PHREEQC geochemical software, and plotted these data as a function of pH. These ion-activity plots showed that the pH-dependent decrease of the activity of Fe^{3+} fitted reasonably well to a solid line defining the solubility of schwertmannite in the pH window of 2.2–3.5, which is the typical pH range for the occurrence of this mineral in AMD waters of the IPB (Sánchez-España et al. 2005a). Below pH 2.2 and above pH 3.5, there were not enough data to suggest a possible mineral control of the iron activity. Jarosite would be a likely candidate at the lower pH range, while ferrihydrite is stable at $pH > 4–5$ (Bigham et al. 1996; Bigham and Nordstrom 2000). The calculated aluminum activities below pH 4.0 plotted reasonably well along the solubility line for jurbanite, although the relevance of this mineral to solubility control of aqueous Al^{3+} was already questioned by Bigham and Nordstrom (2000), and has been recently discarded in these systems (Sánchez-España et al. 2011). Only one case (Herrerías II pit lake) plotted within the stability field of alunite, whereas another case (Los Frailes) plotted within the stability field of gibbsite. These minerals, however, have not been found as precipitates or neoformed phases within the sediments of the studied pit lakes.

The values of the saturation index (defined as $SI = [\text{Log } IAP/K_{sp}]$, where IAP is the ion activity product and K_{sp} is the solubility product constant) for selected Fe(III) and Al minerals were also computed with PHREEQC and plotted as a function of pH by Sánchez-España et al. (2008). These plots confirmed the observations made on the ion-activity plots that the pit lakes seem to be saturated with respect to schwertmannite in the pH window of 2.2–3.5, so that this mineral appears to control the iron activity in this pH range. Jarosite also shows saturation at all pH's, although the formation of this mineral is usually favoured at very low pH ($pH < 2.5$; Bigham and Nordstrom 2000; Bigham et al. 1996). This mineral has been observed to precipitate in different lakes during the summer, when pH approaches values around 2.2 near the lake surface (Sánchez-España et al. 2009, 2010, 2011). All waters were invariably undersaturated with respect to ferrihydrite below pH 5.0, and only the water from Los Frailes (with a near-neutral pH) was saturated with respect to this mineral. The SI-pH plots suggested undersaturation of the pit lakes with respect to basaluminite below a pH of about 4.5, and undersaturation with respect to alunite below a pH of 3.5–4.0.

5.3.3.3 Relevance of the Schwertmannite Buffer

As stated above, the concentration of Fe(III) in the pit lakes of the IPB seems to be essentially controlled by the solubility of schwertmannite. This oxyhydroxy sulfate mineral is usually formed in acid- sulfate waters by the reaction (Bigham et al. 1996):

$$8Fe^{3+} + SO_4^{2-} + 14H_2O \Leftrightarrow Fe_8O_8(SO_4)(OH)_6 + 22H^+ \tag{5.1}$$

This mineral has been also described to be the main buffering system in acidic mining lakes of Lusatia, Germany (Regenspurg et al. 2004; Totsche et al. 2003) and in the acidic mine pit lake of Berkeley, Montana (Gammons et al. 2006). The formation of schwertmannite through reaction 5.1 is thus probably buffering the great majority of pit lakes in the IPB. Only a few cases escape from this general pattern, including pit lakes with very low pH in which only dissolved chemical species of Fe(III) exist in solution (e.g. Corta Atalaya), or those with pH values above 3.5 (e.g. Herrerías II, Los Frailes) in which most of the iron has already precipitated.

Due to their physical properties (small particle size, very low crystallinity, and high specific surface area), schwertmannite and other hydrous ferric oxides act as efficient sorbents of dissolved metals (Bigham and Nordstrom 2000; Dzombak and Morel 1990; Kinniburgh et al. 1976; Sánchez-España et al. 2006b; Smith 1999; Webster et al. 1998). Hence, the presence of schwertmannite colloids in the pit lakes may affect water quality, as this mineral usually sorbs not only toxic elements like As or Pb (Sánchez-España et al. 2008), but also biologically important nutrients like PO_4^{3-}, NO_3^{-}, or dissolved organic acids.

5.3.4 Stratification Styles of the IPB Pit Lakes

As shown in Table 5.7, the great majority of pit lakes studied to date in the IPB are meromictic, and show a typical stratification with an anoxic monimolimnion underlying an upper, oxygenated mixolimnion. The monimolimnion is perennially isolated from the atmosphere by a permanent chemo(redox)cline. Only three pit lakes (Aznalcóllar, Los Frailes, and Herrerías II) are holomictic and mix entirely due to winter overturn, although they undergo seasonal thermal stratification during early spring to late summer-early autumn (López Pamo et al. 2009; Sánchez-España et al. 2008). The holomictic nature of these lakes seems to be related to hydrogeochemical and geological factors more than geometric considerations. For example, the small pit lake in Herrerías II mine (rel. depth = 11%, max depth = 15 m) is holomictic and vertically homogeneous while other pit lakes with very similar geometry and relative depth are sharply stratified (e.g. Concepción, rel. depth = 12%, max depth = 15 m), and may exhibit an anoxic monimolimnion at only 4 m below the surface (e.g. Filón Sur, rel. depth = 10%, max depth = 5 m; López-Pamo et al. 2009). The abnormally high calcium concentration of the Herrerías II lake (565 mg/L, the highest of those measured in surface waters of the IPB pit lakes; Sánchez-España et al. 2008) and its relatively high pH of 4.7 (much higher than the average) may be an indirect evidence of neutralization reactions between the acid released by pyrite oxidation and the carbonates of the wall rocks, which were locally abundant in this mine (Pinedo Vara 1963). This neutralization could have favoured the chemical homogenization of the lake, as well as its further hydrogeochemical evolution. The mixing status of Aznalcóllar and Los Frailes, is deeply influenced either by human activity (e.g. backfilling in Aznalcóllar, with more than 130 m of sediments filling the lake;

Santofimia et al. 2007a), or by the inflow of alkaline groundwater (estimated flow of 2,550 m^3/day; Santofimia et al. 2007b).

Meromictic pit lakes show a mixolimnion of variable depth (e.g. 2–3 m in Confesionarios, and 30 m in San Telmo). Recent research has revealed the existence of two stratification patterns that are differentiated by the vertical structure of the monimolimnion (Sánchez-España et al. 2008, 2009). A first type is represented by San Telmo, which has a chemically uniform monimolimnion with no vertical gradients. In contrast, the second type of meromictic pit lakes, as exemplified by Cueva de la Mora, Herrerías I, or Filón Centro (Tharsis), the monimolimnion shows marked vertical changes in physico-chemical parameters, with decreasing redox potential, and increasing temperature, pH, and dissolved solids content with depth. No significant difference of volume, age, or relative depth, has been recognized between both types of lakes, but the pit geometry could exert some influence on the stratification type (the first type of lakes usually show an oval surface area, whereas the second type normally display a more elongated, ellipsoidal surface area; Sánchez-España et al. 2009).

5.3.4.1 Meromictic Pit Lakes with Homogenous Monimolimnion: The Example of San Telmo

As an example of the first type of meromictic lakes with an homogenous monimolimnion, vertical profiles of T, pH, specific conductivity (SC), dissolved oxygen (DO), and Eh obtained in several periods from 2005 to 2008 are provided for San Telmo pit lake (López-Pamo et al. 2009; Sánchez-España et al. 2007a; Fig. 5.24). With a surface area of 143,600 m^2, a maximum depth of 120 m, and a volume of around 7 Mm^3, the pit lake of San Telmo is amongst the biggest of the IPB. This pit was finally abandoned in 1989, and the flooding stage lasted from then until 1995, so that the pit lake is only around 15 years old.

The profiles reported in Fig. 5.24 reveal the existence of a sharp layer boundary at around 30 m depth, which separates an oxygenated mixolimnion with dominantly oxidizing conditions, from a 70 m deep anoxic monimolimnion. The observed differences in T, SC, DO, and Eh indicate a marked physico-chemical (redox, thermal, densimetric) distinction between both layers, which is permanent during the entire year. The mixolimnetic concentration of total iron in San Telmo is dominated by ferric iron, with $\approx$ 140 mg/L Fe(III) and $\approx$ 0 mg/L Fe(II), whereas the monimolimnion is more balanced, with 79 mg/L Fe(II) and 76 mg/L Fe(III).

Although this vertical configuration is stable all year round, slight shifts in the absolute values of the different parameters (DO, Eh, pH, and SC) probably indicate the influence of groundwater input to the pit lake (this lake is connected to a number of old mine galleries and shafts, and is also intersected by local groundwater flow). The progressive heating of the topmost water layer during the summer results in a temporary stratification of the mixolimnion, with development of a warmer epilimnion, a transitional metalimnion, and a slightly cooler hypolimnion ($\Delta T = 1.5°C$; Fig. 5.24). The slight density difference (equivalent to a density

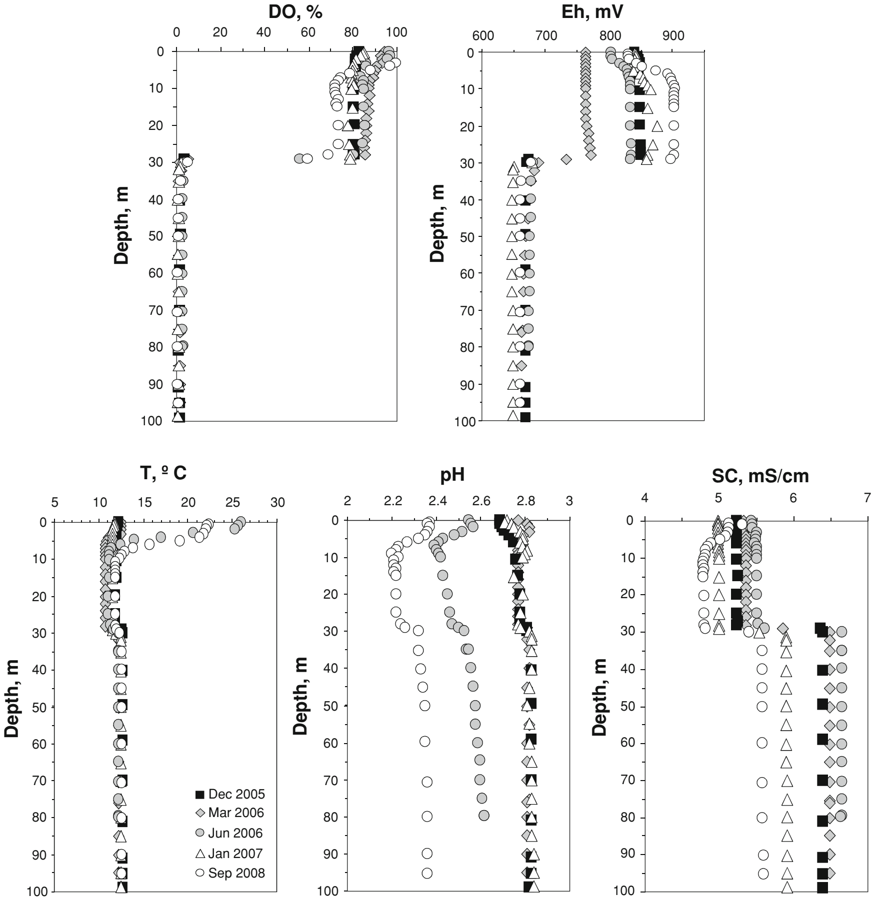


Fig. 5.24 Depth profiles of dissolved oxygen (*DO*), Eh, temperature (*T*), pH, and specific conductivity (*SC*) for the San Telmo pit lake (modified after López-Pamo et al. 2009 and Sánchez-España et al. 2007a)

difference of around 0.3 mg/cm^3) provoked by this thermic gradient is not sufficient to compensate for the density contrast caused by the salinity difference, as indicated by the electric conductivity (around 1 mS/cm, equivalent to a density difference of around 1 mg/cm^3). Consequently, the chemocline represents a permanent physicochemical barrier that isolates the layers.

5.3.4.2 Meromictic Pit Lakes with Gradient-like or "Staircase"-Type Monimolimnion: The Example of Cueva de la Mora

A second type of meromictic pit lake with gradient-like or "staircase"-type monimolimnion is well represented by the pit lake of Cueva de la Mora. This small

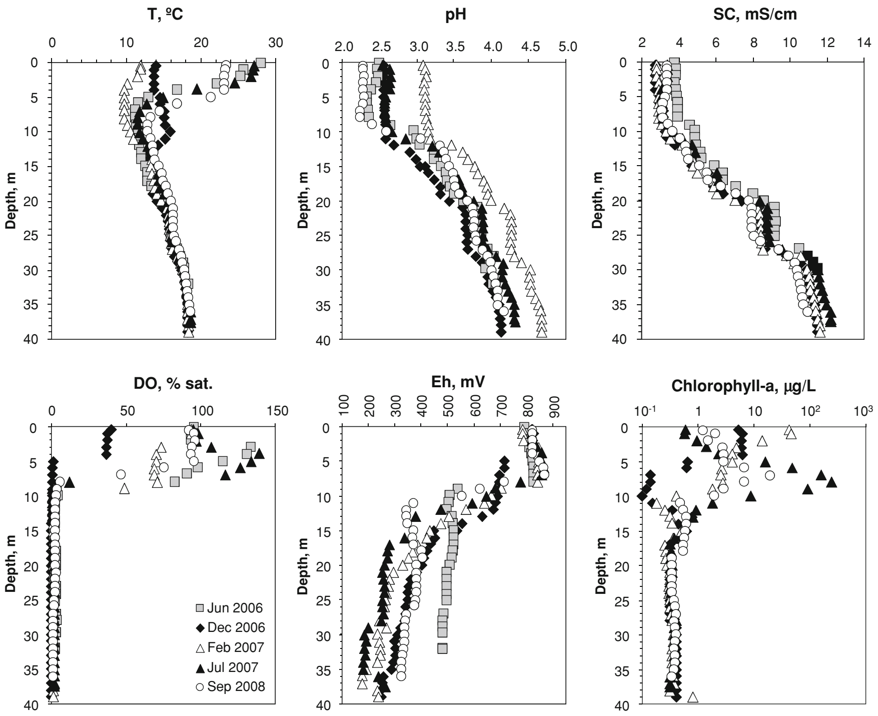


Fig. 5.25 Depth profiles of temperature (*T*), pH, specific conductivity (*SC*), dissolved oxygen (*DO*), redox potential (*Eh*) and chlorophyll-a concentration for the Cueva de la Mora pit lake (modified after Sánchez-España et al. 2009, and López-Pamo et al. 2009)

lake has a surface area of 17,800 m^2 and a maximum depth of 40 m. It was formed in the early 1970s, and represents a mature stage of pit lake development with more than 40 years of hydrogeochemical evolution. At present, the pit lake shows an upper mixolimnion of about 10 m depth, and a lower, 30 m deep monimolimnion that is sharply stratified and shows several sub-layers of increasing temperature, density, and metal- and sulfate concentrations towards the lake bottom (Figs. 5.25 and 5.26; Sánchez-España et al. 2009). The lake bottom is considerably warmer than the upper monimolimnion (18 and 12–14°C, respectively), and shows significantly higher pH (pH 4.1–4.7 vs. 2.7–3.1, respectively). Besides, the bottom waters show a much lower Eh (200–300 mV vs. 850 mV, respectively) and much higher concentrations of dissolved solids, as indicated by the SC (11–12 vs. 2–4 mS/cm, respectively). Although the vertical trends of these parameters show slight seasonal variations, the general features remain relatively constant throughout the year.

The redox values of the mixolimnion correspond to oxygen-saturated conditions where Fe is predominantly in its oxidized form (Fe(III) $\approx$ 100% Fe$_{\text{total}}$). Conversely, the reducing environment of the monimolimnion is characterized by

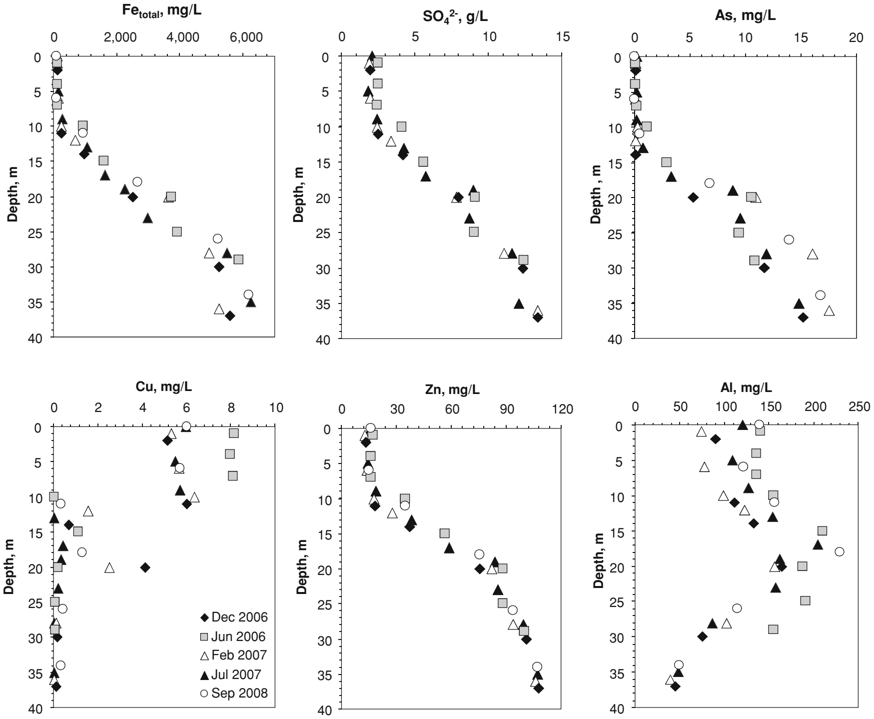


Fig. 5.26 Depth profiles of selected element concentration (Fe, SO_4^{2-}, As, Cu, Zn, Al) for the Cueva de la Mora pit lake (modified after López-Pamo et al. 2009, Sánchez-España et al. 2009)

anoxia and a very high Fe concentration, which is essentially all ferrous iron (Fe(II) ≈ 100% Fe_{total}). Marked metalimnic maxima of oxygen concentration (with values approaching 12.2 mg/L O_2 and 140% O_2 saturation) have also been observed in the summer months (e.g. June 2006, July 2007; Fig. 5.25). These O_2 concentration maxima occur not far above the location of the chlorophyll-a concentration peaks. This fact suggests a strong microbial control on the mixolimnetic O_2 concentration, probably as a result of enhanced photosynthetic activity during this period.

Element concentrations in the bottom waters of Cueva de la Mora are very high compared to the mixolimnetic concentrations (Fig. 5.26). The most clear examples are Fe (110–130 mg/L near the surface, and more than 6,000 mg/L in the deepest part of the monimolimnion), SO_4^{2-} (≈2 g/L in the mixolimnion and exceeding 13 g/L in the bottom layer), and As (70–120 μg/L in the uppermost layer and 15,000–17,500 μg/L in the bottom layer). Other trace metals also display a vertical trend of increasing concentration with marked differences between the surface and the deepest part of the lake, such as Mn and Zn (10–20 mg/L at the surface and 110–120 mg/L in the bottom in both cases), or Co and Ni (from 1,700 μg/L to 13,200 μg/L for Co, and from 440 μg/L to 850 μg/L for Ni in July 2007; data not

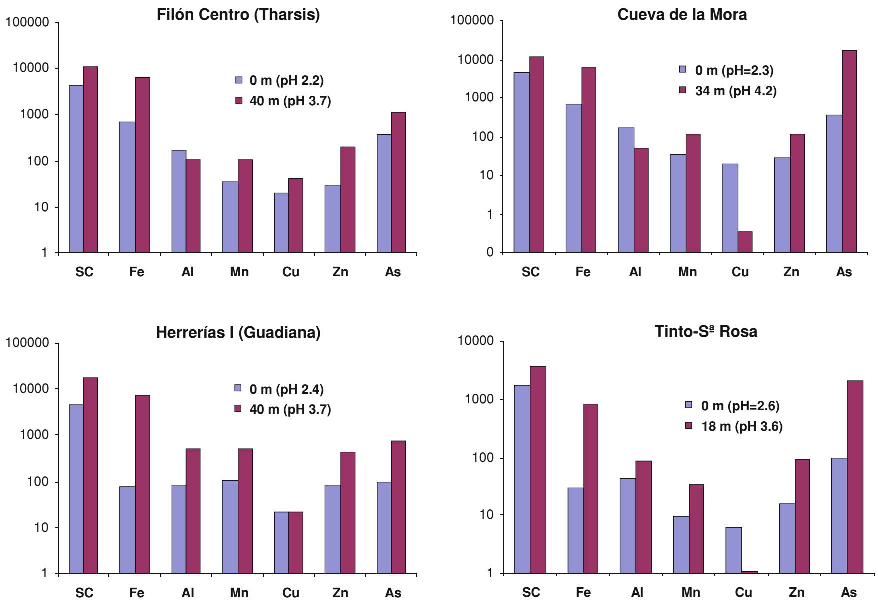
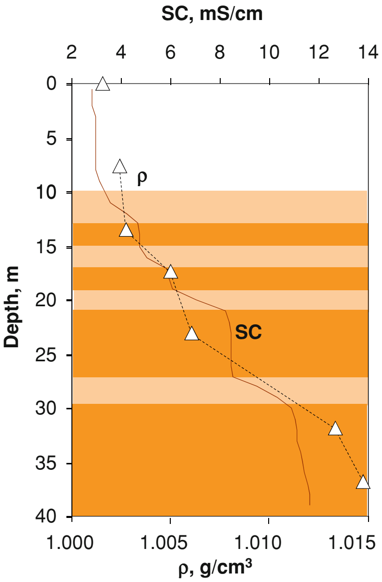


Fig. 5.27 Comparison between surface (0 m) and deep conditions for four selected pit lakes of the IPB. Specific conductivity (*SC*) is given in µS/cm; Fe, Al, Mn, Cu and Zn in mg/L, and As in µg/L (data taken from López-Pamo et al. 2009)

shown). Only Al and Cu show a reverse trend, which is probably due to precipitation of Al hydroxysulfates (basaluminite, alunite) at pH 4.0–4.5 and formation of CuS below the redoxcline (Sánchez-España et al. 2010, 2011). These vertical gradients of sulfate and metal concentration have been observed in other pit lakes of the IPB, including those of Filón Centro and Filón Sur (Tharsis), Herrerías I, Tinto-S^{a} Rosa, and Concepción. These contrasts in water composition between the surface and the deepest waters are illustrated in Fig. 5.27 for a number of pit lakes.

Another interesting feature of the Cueva de la Mora pit lake is the "staircase" pattern displayed by the SC and pH profiles (Fig. 5.25), with homogenous water layers separated by sharp compositional and thermal boundaries. This type of stratification is usually diagnostic of double-diffusive convection (DDC), and has been reported in very different environments such as oceanic trenches in polar regions, the Black Sea, volcanic crater lakes, and other natural lakes (Kelley et al. 2003; Schmid et al. 2004; and references therein). DDC occurs when both temperature and salinity increase downwards in such a manner that the thermally induced density decrease is compensated by a density increase caused by higher salinity (Kelley et al. 2003; Turner 1973, 1978). In contrast to other mixing processes, DDC results in an upwards flux of both salinity and heat, which results in discrete layers where thicknesses can be calculated by semi-empirical equations (e.g. Fedorov 1988; Kelley 1984). Cueva de la Mora may represent a singular

Fig. 5.28 Vertical profiles of specific conductance (*SC*, measured Feb 2007) and density (ρ, measured Feb 2009) for the Cueva de la Mora pit lake (modified after Sánchez-España et al. 2009). The sub-layers recognized in the monimolimnion (as deduced from the SC profile) are also delineated



example of DDC influencing the monimolimnion of a mining pit lake (Fig. 5.28). Based on the profiles of Fig. 5.25, four different conductive layers can be recognized with thickness varying from 2 m (upper layers) to 10 m (bottommost layer). The boundary zones between these layers, which are 2–2.5 m thick, are characterized by strong gradients in specific conductance (SC) and, hence, in salinity (Fig. 5.28). The staircase arrangement seems to be rather stable throughout the year, and could be related to the flooding history of the lake. The described vertical arrangement is further supported by in situ density measurements performed at different depths, which have confirmed that the vertical increase of specific conductance (which is only indicative of the dissolved solids content) is closely associated with a corresponding increase of water density with depth. The proportion by which the different elements (dissolved substances such as sulfate and metals), dissolved gases (mainly CO_2), and particulate matter (both mineral and organic) contribute to the lake density is currently under study.

5.3.5 *Vertical Cycling of Fe, Al, and Other Related Elements (As, Cu, Si, P, C)*

The solubility controls described in an earlier section referred to surface water quality data and are only valid for near-surface conditions. A more in-depth study of the whole pit lake water column depicts a more complex geochemical scenario. In fact, geochemical modelling carried out with PHREEQC strongly suggests vertical cycling of a number of metals across the water column of these

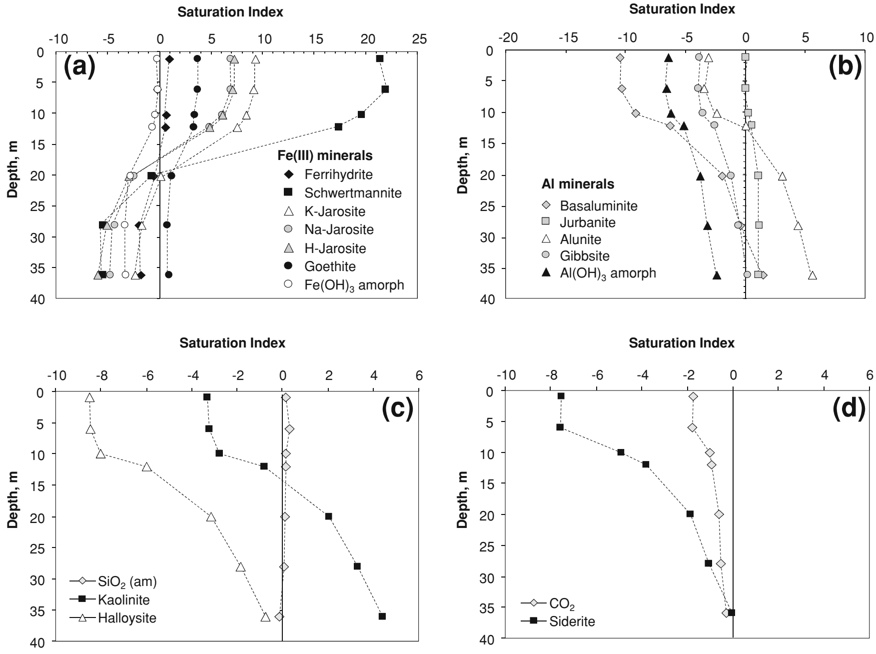


Fig. 5.29 Vertical evolution of the saturation index (*SI*) for selected Fe(III) minerals (**a**), Al minerals (**b**), selected silicates (**c**) and CO_2-siderite (**d**) in the pit lake of Cueva de la Mora. Data from February 2007 and February 2008 (modified after Sánchez-España et al. 2009)

meromictic lakes. Specifically, these calculations indicate oversaturation of the mixolimnion with respect to a number of Fe(III) minerals, including schwertmannite, K- and Na-jarosite, and (in a minor extent) goethite, while the anoxic and reducing monimolimnion seems to be undersaturated with respect to all these phases (Fig. 5.29a). Both schwertmannite and jarosite are metastable with respect to goethite (Bigham and Nordstrom 2000; Bigham et al. 1996), and conversion of schwertmannite to goethite during aging seems to be rather common (Sánchez-España et al. 2010, 2011).

These results are compatible with a vertical cycling model for iron, with precipitation in the mixolimnion and redissolution in the monimolimnion. Such precipitation-dissolution reactions can deeply influence both the trace metal and nutrient chemistry of the pit lakes. Thus, the reductive dissolution of ferric precipitates such as jarosite, schwertmannite, or goethite, could account for some of the observed increases in trace elements such as arsenic, which is usually adsorbed on these compounds (Sánchez-España et al. 2005a, b, 2007a, b). Arsenic could be mobilized into the aqueous phase by desorption and/or direct re-dissolution of the solid phases. A similar process could result in releases of phosphate and organic carbon, both of which adsorb onto freshly precipitated ferric oxides at low pH (e.g. Cameron et al. 2006; Spiteri et al. 2008, references cited therein). Moderate concentrations of phosphate and organic carbon have been detected in mine drainage minerals of the IPB (0.1–0.3%wt P_2O_5 and 0.4–1.4% C_{org}). In the particular case of phosphate, its dissolved concentration in the deep monimolimnion could be somehow counterbalanced by the release of adsorbed phosphate and the formation of diverse metal-bearing phosphates (e.g. strengite, plumbgumite, $MnHPO_4$), for which PHREEQC predicts fairly positive SI values at depth (data not shown). Some rare-earth phosphates have recently been found during SEM investigations of suspended sediments in the Cueva de la Mora pit lake (unpublished), although their occurrence and significance are not yet understood.

The geochemistry of Al shows a reverse trend, with a clear undersaturation of Al-minerals (and thus a strong tendency for dissolution) in the mixolimnion, and oversaturation in the monimolimnion, which results from the pH gradient (pH 2.2–3.1 near the surface and pH 4.1–4.7 near the bottom). As discussed above, the aluminum solids that appear to be closest to equilibrium saturation are basaluminite/hydrobasaluminite and alunite (Fig. 5.29b). The formation of these minerals can be described by the following reactions (Bigham and Nordstrom 2000; Nordstrom 1982):

$$4Al^{3+} + SO_4^{2-} + 14H_2O \leftrightarrow Al_4(SO_4)(OH)_{10} \cdot 4H_2O_{(s)} + 10H^+ \tag{5.2}$$

$$3Al^{3+} + K^+ + 2SO_4^{2-} + 6H_2O \leftrightarrow KAl_3(SO_4)_2(OH)_{6(s)} + 6H^+ \tag{5.3}$$

Between these two minerals, the SI trends for basaluminite more closely mimic the vertical trends in Al concentration in solution. Basaluminite is predicted to precipitate (Eq. 5.3) near the lake bottom, where the pH approaches 4.0–4.5 (Fig. 5.29b). Alunite shows oversaturation and could theoretically precipitate (Eq. 5.2) below depths of around 10–12 m, which does not fit with the field observations, which include Al precipitation below 20 m depth (Fig. 5.26). Other Al phases, such as gibbsite or amorphous $Al(OH)_3(s)$, are undersaturated at all depths and do not seem to play a significant role in the Al geochemistry of the Cueva de la Mora pit lake.

There exist some other possibilities that are much less probable, but still possible. For example, considering the high concentrations of silica dissolved in the water of this pit lake (see Fig. 5.31 in a later section), the aqueous concentration of Al in porewaters within sediments could be locally influenced by the solubility of clay minerals such as kaolinite, for which the water is saturated in the deep monimolimnion (Fig. 5.29c). Further, the formation of amorphous gels of SiO_2 in the water column also seems possible since the water is close to equilibrium ($SI \approx 0$) at all depths (Fig. 5.29c), although amorphous silica has not been found during SEM studies conducted to date (Sánchez-España et al. 2010, 2011).

The precipitation of Al hydroxysulfates in the monimolimnion could be responsible for some Cu removal at depth, as sorption of Cu onto Al hydroxysulfate precipitates has been demonstrated to occur by laboratory experiments with different acid mine waters of the IPB (see Sánchez-España et al. 2006b).

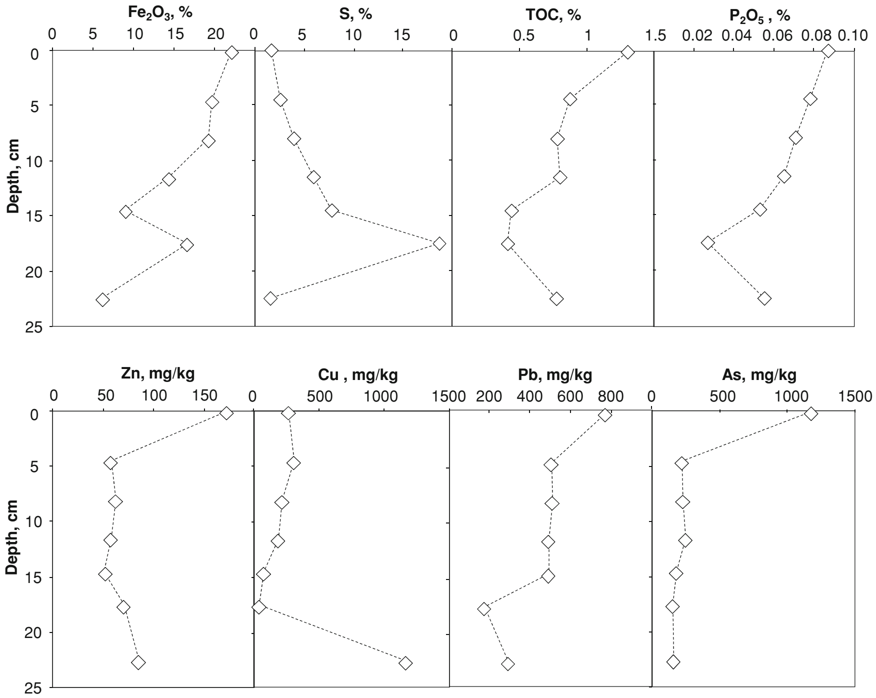


Fig. 5.30 Chemical profiles of selected major and trace elements (including Fe_2O_3, S, TOC, P_2O_5, Zn, Cu, Pb, and As) for a 25 cm-long sediment core taken from the anoxic bottom of the Confesionarios pit lake in 2007 (IGME-UFZ, unpublished)

Given the low pH conditions prevailing in the lakes, most carbonates (including calcite, dolomite, and ankerite; data not shown) are clearly undersaturated at all depths. However, the SI profile obtained for siderite (Fig. 5.29d) suggests that, although thermodynamically unfeasible in the water column, the formation of this mineral could be possible within the porewaters of the sediments, where less acidic conditions ($pH > 5.3$) and trace amounts of HCO_3^- could locally exist as a result of alkalinity-producing, anaerobic bacterial activity (Wendt-Potthoff et al. 2012).

5.3.6 Mineralogy and Chemistry of the Sediments

A number of studies are already available on the compositional, mineralogical, and microbiological characteristics of sediments of the IPB pit lakes (Sánchez-España et al. 2009, 2010, 2011; Wendt-Potthoff et al. 2012). Chemical and diffractometric analyses of suspended and bottom sediments and precipitates have confirmed the above described geochemical predictions, revealing a predominance of ferric compounds such as schwertmannite and jarosite, with lesser amounts of goethite and detrital minerals such as quartz, chlorite, muscovite, or feldspar. The examination of sediments collected from the anoxic, deep part of other pit lakes (e.g. San Telmo, Herrerías, Confesionarios) by XRD and SEM–EDS studies has given identical results, with ubiquitous presence of schwertmannite, jarosite and goethite, together with detrital minerals like quartz, chlorite, muscovite, kaolinite, and feldspar. The pH seems to be the master variable, and slight changes in this parameter leads to the formation of different Fe(III) minerals. For example, the pH in the epilimnion of Cueva de la Mora ranges from 2.2, which only allows formation of jarosite, up to 3.1, which is more typical of schwertmannite formation (Sánchez-España et al. 2010, 2011). Goethite is commonly considered as a product of transformation of jarosite and schwertmannite, which are both metastable with respect to the former (Bigham and Nordstrom 2000; Bigham et al. 1996). Thus, the presence of this mineral could be indicative of the degree of aging of the ochreous precipitates, as already observed by Regenspurg et al. (2004).

As an example to illustrate the chemistry of these sediments, a set of chemical profiles obtained for a 25 cm-long sediment core taken from the bottom of Confesionarios pit lake is shown in Fig. 5.30. These profiles depict a general trend of decreasing metal content with depth, including Fe (22–5% Fe_2O_3), Zn (170–50 ppm), Cu (300–45 ppm), Pb (780–120 ppm), and As (1,200–150 ppm). Total organic carbon and phosphate also depict a similar tendency (1.3 to <0.5% TOC and 0.08–0.02% P_2O_5); only sulfur showed a reverse trend, with local enrichment (6–19% wt S) between 15 and 20 cm depth, where both pyrite and native sulfur have been detected by XRD. These profiles are compatible with a model of Fe(III)-mineral particle deposition (schwertmannite, jarosite) on the pit lake bottom, with progressive desorption of trace elements as these minerals are either transformed by mineralogical maturation (*aging*) or re-dissolved by chemical and/or bacterially catalyzed reactions (see next section).

5.3.7 Microbiology and Trophic State of the Pit Lakes

5.3.7.1 Microbiology of the Water Column and Nutrient Availability

Some findings have recently been obtained that suggest that the hydrogeochemistry of these lakes may have a strong microbial control. For example, in the extremely acidic pit lake of Corta Atalaya (pH 1.2), an introductory microbiological survey of the pit lake water conducted in 2006 (D.B. Johnson, University of Bangor; written communication) identified abundant acidophilic iron-oxidising autotrophic and heterotrophic bacteria, including *Acidithiobacillus ferrooxidans* and *Ferrimicrobium acidophilum*, which were present in significant numbers (ca. 10^5 bacteria/mL). The presence of these bacteria would account for the presence of soluble ferric iron (at ≈ 4 g/L) in the pit lake. Microbial oxidation of iron would be limited by the extremely low concentrations of dissolved oxygen present in the

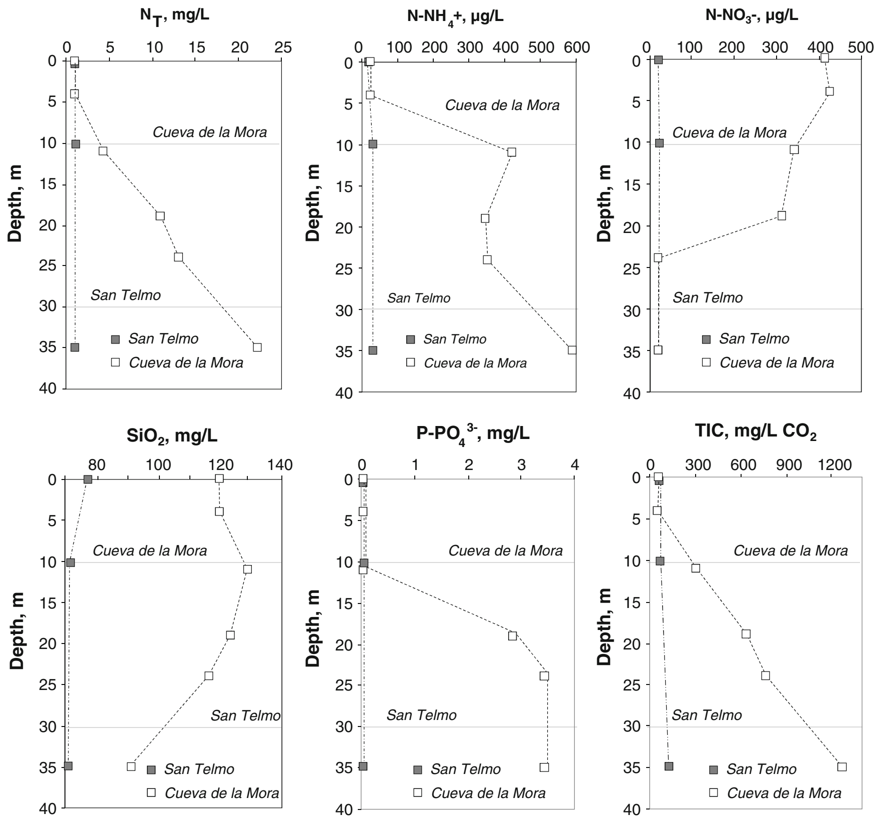


Fig. 5.31 Vertical evolution of nutrient concentration, including total nitrogen (N_T), ammonium nitrogen ($N\text{-}NH_4^+$), nitrate nitrogen ($N\text{-}NO_3^-$), silica (SiO_2), phosphate-phosphorus ($P\text{-}PO_4^{3-}$) and total inorganic carbon (*TIC*, given as mg/L CO_2) in the pit lakes of Cueva de la Mora (*white squares*) and San Telmo (upper 35 m of its water column; *grey squares*). The location of the chemocline (*horizontal grey bar*) is shown for both lakes. Data from February 2009

lake (which was practically anoxic at the time of sampling), though this would be higher at the air/water interface. The extremely low pH of the water would not preclude microbial oxidation of ferrous iron, as this may occur at pH values of <1 (Johnson and Hallberg 2003). Interestingly, both *At. ferrooxidans* and *Fm. acidophilum* are facultative anaerobes, and can grow in the absence of dissolved oxygen (Johnson and Hallberg 2003).

Another study conducted in the acidic pit lake of San Telmo reported three different microbial levels that match the different layers distinguished in the lake (Sánchez-España et al. 2007a; Table 5.8). Thus, the first five m of the water column, which corresponded to the epilimnion and metalimnion, were characterized by a high biomass ($\approx 10^8$ cells mL^{-1}), and a low biodiversity, which was mainly characterized by α-*Proteobacteria* ($\approx 78\%$). The second layer, between 5 and 26 m and corresponding to the rest of the mixolimnion, was characterized by a

Table 5.8 Total cell numbers and the percentages of different bacteria identified at several depths (m) in the acidic pit lake of San Telmo, Iberian Pyrite Belt (modified from Sánchez-España et al. 2007a) cell numbers/mL; % of bacterial groups refer to numbers of total bacteria; BDL-below detection limit

Depth	Total cells	*a-Prot.*	*b-Prot.*	*g-Prot.*	*Leptospir.*	Total bacteria
1	1.1×10^8	77	BDL	<1	<1	77
5	0.9×10^8	78	BDL	BDL	<1	78
10	0.2×10^7	47	0.8	9	18	74
26	8.0×10^5	47	BDL	15	22	84
30	3.7×10^6	6	7	2	2	17
50	3.5×10^6	5	2	1	2	10

considerably lower biomass ($\approx 10^6 \times$ cells mL^{-1}) but a higher biodiversity in which, in addition to α–*Proteobacteria* ($\approx$47%), both γ-*Proteobacteria* (8–15%) and *Leptospirillum* (17–22%) were also common, and small numbers of archaea ($\approx$3%) were detected. Finally, a third layer, representing the deeper and anoxic monimolimnion was recognized, in which both the biomass ($\approx 3.7 \times 10^6$ cells mL^{-1}) and the biodiversity increased again with respect to the lower mixolimnion. This vertical zonation is similar to that described in thermally stratified lakes (Wetzel 2001). Furthermore, the notably higher numbers of bacterial cells detected near the surface with respect to those observed at depth correspond to a pattern that has already been described in comparable acidic mine pit lakes, like that of the Berkeley pit, Montana, USA (University of Montana 1999). However, it is worth noting that the observed bacterial numbers near the surface are notably higher than those reported in other acidic pit lakes like Berkeley ($\approx 10^5$ cells mL^{-1}; University of Montana, unpublished report), the pit lakes of the Lusatian region (10^5–10^6 cells mL^{-1}; Nixdorf et al. 1998), natural lakes of Germany ($\approx 10^5$ cells mL^{-1}; Wetzel 2001), or in the adjacent and highly acidic Tinto river (10^5–10^7 cells mL^{-1}; González-Toril et al. 2003). Because growth of microorganisms is controlled by nutrient availability and environmental factors such as temperature, and is closely correlated with primary production (photosynthetic and chemolithotrophic; Wetzel 2001), it was hypothesized that a close correlation exists in San Telmo between solar radiation, primary productivity, and numbers/diversity of bacterial cells.

A first integral study of the microbial ecology of the water column and sediments of the Cueva de la Mora pit lake is currently under study, and the provisional results point to an intense biogeochemical cycling of Fe, S, and C in the lake (Wendt-Potthoff et al. 2012).

Phytoplanktonic species also appear to be abundant in the pit lakes of the IPB. A study conducted in July 2007 in Cueva de la Mora revealed a significant number of photosynthetic microorganisms, including green algae (e.g. *Zygnema*, *Chlamydomonas*) and diatoms, in the surface waters of this lake (Sánchez-España et al. 2009). Similar or related species of green filamentous algae and diatoms have previously been observed and studied in waters and sediments of acidic mining lakes and acidic volcanic crater lakes by a number of researchers (e.g. Baffico et al. 2004; Kleeberg et al. 2006; Koschorreck and Tittel 2002; Koschorreck et al. 2007; Nixdorf et al. 1998). Primary production taking place in the photic mixolimnion provides a continuous source of organic substances (dissolved organic acids, dead algal and bacterial biomass) for decomposers and heterotrophic bacteria living in the anoxic lake bottom (e.g. Fe and S-reducing bacteria; Ehrlich 2002; Kleeberg et al. 2006; Wetzel 2001). A detailed study of the distribution and dynamics of phytoplanktonic communities is currently under study (C. Falagán, *unpublished*).

The chlorophyll-a profiles illustrated in Fig. 5.25 suggest that the phytoplanktonic communities can migrate vertically as a response to environmental changes, being mostly located near the lake surface during the winter, and very close to the redoxcline (and thus to the anoxic monimolimnion) during the summer. This suggests that the distribution and growth of these eukaryotic microbes could be strongly influenced not only by physical parameters such as temperature or light intensity, but also by nutrient availability. In this sense, the phytoplanktonic communities observed in Cueva de la Mora could obtain substantial benefit from inhabiting at depths of around 7–8 m during the summer, where these microorganisms would still obtain significant light energy for their photosynthetic metabolisms. For example, in September 2008, the chlorophyll-a maximum was situated at around 7 m depth, where the photosynthetically active radiation intensity was only 24 μmol s^{-1} m^{-2}, about 1.5% of that measured at the surface. Subsequent field sampling has shown that this chlorophyll-a maxima may reach depths up to 9 m (*not shown*). These microbes were located only a few tens of centimeters above the anoxic monimolimnion, which usually has much higher nutrient availability (Table 5.9; Fig. 5.31). Nutrients accumulated in the anoxic monimolimnion include total nitrogen, phosphorus, and total inorganic carbon (TIC), which all show concentrations orders of magnitude higher than those measured in the mixolimnion (e.g. 4–22 mg/L N_T in the monimolimnion compared to <600 μg/L in the mixolimnion, 3–4 mg/L PO_4^{3-} in the monimolimnion compared to <50 μg/L in the mixolimnion, and 300–1,300 mg/L CO_2 in the monimolimnion compared to 55–60 mg/L in the mixolimnion; Table 5.9, Fig. 5.31). An important supply of carbon, phosphorus, and nitrogen would therefore be available for the photosynthetic microbes by ionic diffusion through the chemocline.

This strong contrast of nutrient concentration between water layers implies some complexity relative to the trophic classification of these lakes. According to its nutrient concentration (Table 5.9), the mixolimnion of Cueva de la Mora would be oligotrophic. However, the chlorophyll-a concentrations measured at around 7–8 m depth (up to 240 μg/L; Fig. 5.25) and the high concentration of nutrients in the monimolimnion of this lake (e.g. inorganic carbon, phosphorus and nitrogen; Table 5.9, Fig. 5.31) are typical of hypereutrophic conditions. In fact, nutrient concentrations are, in general, orders of magnitude higher than those normally reported in other acidic pit lakes, such as those of the Lusatian lignite mining region, and even those reported in natural eutrophic lakes (Table 5.9). The ultimate sources for some of these nutrients (e.g. N, P, C) have not been fully

Table 5.9 Concentration of biologically important substances in natural lakes of different productivity and acidic mine pit lakes of Lusatia and the Iberian Pyrite Belt (data for San Telmo and Cueva de la Mora correspond to September 2008 and February 2009) P_T, N_T, Chlor-a in μg/L; TIC, TOC, SiO_2 in mg/L

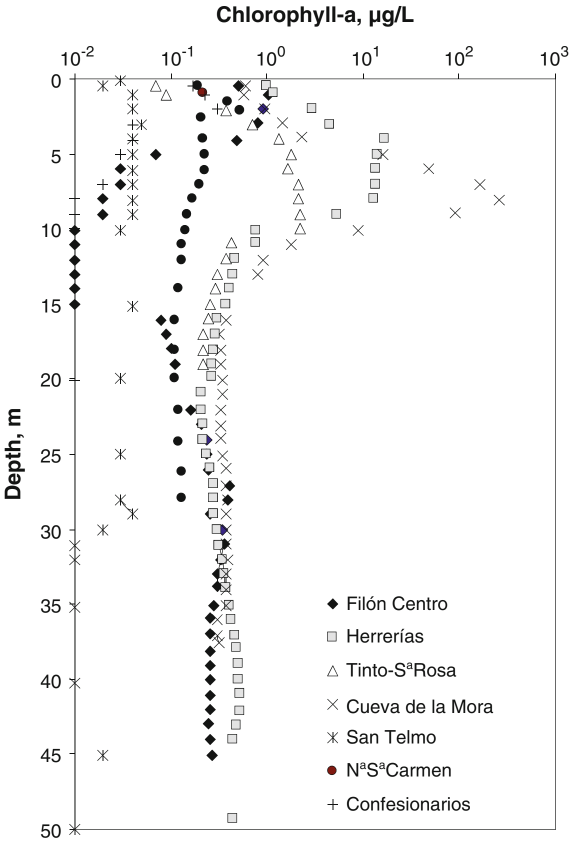
	P_T	N_T	TIC	TOC	SiO_2	Chlor–a
Natural lakes						
Oligotrophic lakes[a]	3–18	307–1,630	–	–	–	0.3–4.5
Mesotrophic lakes[a]	11–96	361–1,387	–	–	–	3–11
Eutrophic lakes[a]	16–386	393–6,100	–	–	–	3–78
Hypereutrophic lakes[a]	750–1,200	–	–	–	–	100–150
Pit lakes						
Lusatian mining lakes[b]	8–78	0.8–6.5	0.5–80	0.9–6.4	0.1–22	<30
San Telmo[c]	<50	<1,000	55–100	1–16	<75	<1–4
Cueva de la Mora (mixolim)[c]	<50	<600	55–60	1–3	120	0.6–240
Cueva de la Mora (monim)[c]	3,000–4,000	4,000–22,000	300–1,300	3–37	90–130	<1

[a] Wetzel (2001), [b] Nixdorf et al. (1998), [c] This work

identified yet, and the reasons for this degree of eutrophication are still unclear. A reasonable hypothesis suggested by recent bioreactor experiments is that these nutrients are basically released during the degradation of organic matter within the sediments (C. Falagán, unpublished).

Also, important differences of phytoplanktonic development appear to exist between the pit lakes of the IPB, as deduced from the different profiles of chlorophyll-a concentration obtained in different pit lakes (Fig. 5.32). As an example, the peak values of chlorophyll-a concentration in Cueva de la Mora are orders of magnitude higher than those measured in San Telmo or Confesionarios. Such variability is well correlated with the above cited differences in nutrient availability. For example, when compared with Cueva de la Mora, San Telmo presents invariably low concentrations of nitrogen (including total nitrogen, nitrate-nitrogen, and ammonium), phosphorus, silica, and TIC along its entire depth (e.g. <1 mg/L N_T, ≈30 μg/L NH_4^+, <50 μg/L P_T, ≈100 mg/L CO_2; Table 5.9, Fig. 5.31). However, the mixolimnetic concentrations of phosphorus and dissolved inorganic carbon (around 55–60 mg/L CO_2, which is equivalent to 15–16 mg C/L; Fig. 5.31) are not substantially different from those observed in Cueva de la Mora, nor are the rest of physico-chemical parameters (e.g. T, pH, SO_4^{2-}, Fe(III)), which are also very similar in the mixolimnia of both lakes. Therefore, nitrogen could be considered a likely candidate to control algal growth in the studied pit lakes. In particular, nitrate-nitrogen in San Telmo is particularly low (<30 μg/L N-NO_3^-) compared to Cueva de la Mora (≈400 μg/L N-NO_3^-; Fig. 5.31), so that the input of this substance to the lake could have favoured eutrophication and algal growth. This hypothesis contrasts with the results of Nixdorf et al. (1998) who found that algal growth and phytoplankton development in Lusatian pit lakes was most likely phosphorus- and carbon-limited, but not nitrogen-limited.

Fig. 5.32 Vertical profiles of chlorophyll-a concentration in selected pit lakes of the IPB (after López-Pamo et al. 2009)



5.3.7.2 Microbiology of the Sediments

Although there is not much information about the microbiology of the sediments formed in these lakes, recent findings in fresh sediments sampled from different points of Cueva de la Mora (Wendt-Potthoff et al. 2012) suggest an intense bacterial activity at the water/sediment interface. This bacterial activity could be substantially influencing the pit lake hydrogeochemistry. The CO_2 profile depicted in Fig. 5.31, which shows a clear concentration increase of dissolved CO_2 towards the pit lake bottom, is coherent with the observation of a high density of gas bubbles in these anoxic sediments, and also with the high concentrations of total organic carbon measured in pore waters of these sediments (80–90 mg/L TOC; data not shown). All together, these data suggest that the CO_2 present in the monimolimnion of Cueva de la Mora could be partially derived from decomposition of organic matter settling from the upper layers and accumulating in the sediments. The presence of ferrous iron (up to several tens of mg/L Fe(II)) in the pore waters of the Fe(III)-rich sediments, and the detection of sulfate reduction

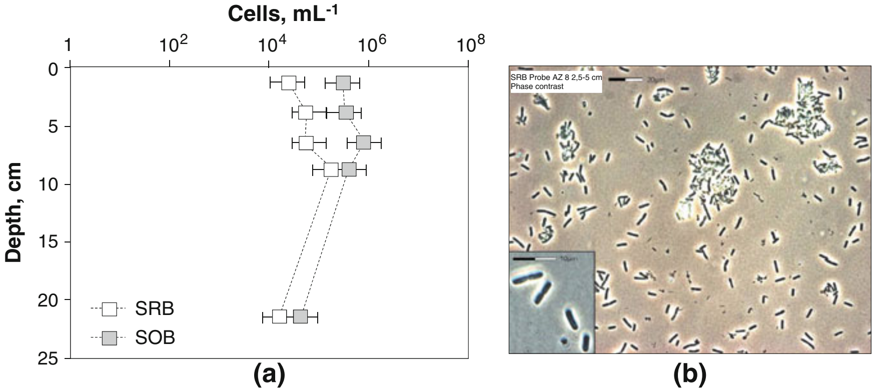


Fig. 5.33 Evidences of bacterial activity in sediments of the Aznalcóllar pit lake: **a** vertical profiles of bacterial cell concentration (obtained by the Most Probable Number method) for a 25 cm-long sediment core taken from the bottom of the pit lake (*SRB*, Sulfate-reducing bacteria; *SOB*, Sulfur-oxidising bacteria; after Vollrath 2006); **b** Phase-contrast photomicrograph showing scattered cells and colonies of sulfate-reducing bacteria (*SRB*) detected in a sample corresponding to a depth of 2.5–5 cm in the sediment core shown in (**a**) (from Vollrath 2006)

activity are indicative of the existence of different consortia of anaerobic bacteria coupling the oxidation of organic matter with Fe(III) and SO_4^{2-} reduction (see next section). In fact, microbial activity and microbial numbers in studied waters and sediments of Cueva de la Mora suggest a biogeochemical cycling of iron, sulfur, and carbon in this lake (Wendt-Potthoff et al. 2012).

Substantial evidence of bacterial activity was also obtained by researchers of the Helmholtz Centre for Environmental Research-UFZ (Magdeburg, Germany) in sediments sampled from the bottom of the Aznalcóllar pit lake (Vollrath 2006, unpublished; Fig. 5.33). The sediments taken from this lake were not naturally deposited but the result of backfilling carried out during recent years (Santofimia et al. 2007a; Schultze et al. 2006). However, the microbiological study of these sediments revealed the existence of significant numbers (ranging from 10^4 to 10^6 cells mL^{-1}) of iron- and sulfur-related acidophilic bacteria, including both Fe- and S-oxidisers, and Fe- and S-reducers. In general, most probable number (MPN) results in samples from sediment cores indicated a peak bacterial concentration at the 5–7.5 cm depth interval, and lower bacterial concentrations above and below this depth (Vollrath 2006, unpublished thesis; Fig. 5.33). Cell counts of sulfur-oxidizing bacteria were always higher than those of the sulfate-reducing bacteria in the first 7.5 cm, although both types of microorganisms displayed similar MPN of cells below this depth. The fact that these sediments were very recent (probably less than 2–3 years) may suggest that the colonization of the lake sediments by different consortia of acidophilic bacteria can be relatively fast.

5.3.8 Biotic and Abiotic Controls of Pit Lake Composition and Stratification

The strong pH-Eh trends observed in pit lakes like Cueva de la Mora, with lower Eh values and higher pH near the pit lake bottom, suggest that anaerobic reducing reactions are actually taking place. These reactions are commonly catalyzed by colonies of anaerobic bacteria that inhabit the water/sediment interface and couple the anaerobic oxidation of organic compounds (e.g. decomposing biomass settled from the mixolimnion) with the reduction of oxidized substances, such as Fe^{3+}-containing sediments, Mn^{4+} oxides, or dissolved sulfate (Boehrer and Schultze 2008; Koschorreck et al. 2007; Schlesinger 2005; Wetzel 2001; Eqs. 5.4–5.6):

$$CH_2O + 2MnO_2 + 4H^+ \rightarrow CO_2 + 2Mn^{2+} + 3H_2O \qquad (5.4)$$

$$CH_2O + 4Fe(OH)_3 + 8H^+ \rightarrow CO_2 + 4Fe^{2+} + 11H_2O \qquad (5.5)$$

$$2CH_2O + SO_4^{2-} + 2H^+ \rightarrow 2CO_2 + H_2S + 2H_2O \qquad (5.6)$$

A common feature of these reactions (Eq. 5.4–5.6) is that all of them consume protons and can provoke pH shifts (if no buffering mechanism such as reaction (Eq.5.1) exists), also generating CO_2. Given the high hydrostatic pressure prevailing in the deepest waters (4–13 bars, depending on depth), CO_2 remains dissolved and accumulates in the monimolimnion for decades. Elevated concentrations of dissolved CO_2 have been recently observed in the monimolimnion of Cueva de la Mora (Fig. 5.31) and Herrerías, and are envisaged in other pit lakes like Tinto-Santa Rosa, and Filón Centro (Tharsis), in which water samples taken from the deepest zones usually show an elevated gas pressure and a high density of gas bubbles. The detection of high concentrations of total organic carbon (up to 30–37 mg/L TOC) and biogenic products such as ammonium (400–500 μg/L NH_4^+; Table 5.9) in the monimolimnion of Cueva de la Mora, are also suggestive of anaerobic microbial activity in this lake. Furthermore, some H_2S (0.1–0.2 mg/L; data not shown) and trace amounts of CH_4 have also been detected at depth (Wendt-Potthoff et al. 2012).

In addition to the biological processes discussed above, several abiotic processes must also be considered to account for the stratification of the IPB pit lakes. Possible abiotic processes include: (1) subaqueous oxidation of pyrite by O_2 and/or Fe^{3+}; (2) acid dissolution of carbonate and aluminosilicate minerals on the pit walls; (3) changes in the history of progressive filling of the pit lakes; (4) influx of groundwater; and (5) influx of acidic water from flooded underground mine workings connected to the pit lakes. Dissolution of large amounts of secondary sulfates accumulated in the mine voids could have strongly affected the water quality of the lakes. Supporting this explanation are the high temperatures recorded at the bottom of some pit lakes (e.g. up to 27°C in Herrerías I), which are difficult to explain without the input of a warm, saline water migrating from the underground mines into the deep pit lake. A similar idea has been proposed to help explain the elevated temperature and poor water quality of the Berkeley pit lake in

Montana, USA (Davis and Ashenberg 1989; Gammons and Duaime 2006; Gammons et al. 2006). Pit filling by waters of very different chemistry, density, and/or temperature can be a key factor in developing meromictic conditions (Castendyk and Webster-Brown 2007).

Pit lakes with homogeneous monimolimnion (such as San Telmo or Confesionarios) typically show abundant ferric iron in their monimolimnia, despite the absence of detectable DO. For example, at Confesionarios, Fe(III) comprises 84–87% of the total iron in the upper monimolimnetic layer, and 12–25% in the lower layer. Therefore, it is possible that pyrite that still remains on the pit lake walls (or in the underground workings connected with the pit lake) could undergo some degree of subaqueous oxidation mediated by Fe^{3+} through the reaction:

$$FeS_2(s) + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (5.7)$$

Some of the aforementioned processes are schematically illustrated in Fig. 5.34, where a model for the biogeochemical cycling of Fe is represented for the particular case of Cueva de la Mora (the model should be valid for other pit lakes with a similar geometry and stratification pattern). The connection of the pit lake to an adjacent underground mine framework such as the one depicted in Fig. 5.34 (characterized by circulation of highly acidic and metal-polluted mine water) could have been a key factor in the initial stages of the pit lake flooding history, and could have thus determined the meromictic nature of most pit lakes in the IPB, as well as their subsequent hydrogeochemical evolution. Bacterially catalyzed oxidation of Fe(II) followed by hydrolysis and precipitation of Fe(III) (mostly in the form of jarosite and schwertmannite) are probably the most important geochemical processes taking place in the oxygenated mixolimnion, although photoreduction of Fe(III) (either dissolved or suspended; Diez et al. 2009) and oxidation of pyrite by O_2 and Fe(III) may also influence the redox chemistry of this metal. The anoxic monimolimnion is perennially isolated from the oxic mixolimnion and the atmosphere. This reducing environment would have been colonized by different consortia of Fe(III)-reducing bacteria (also SO_4-reducing bacteria, to a minor extent) and carbon-decomposers, which could further sustain the meromixis observed in these lakes. Chemoclines are not totally impermeable and some slight diffusion of iron could thus take place in both directions (Fe(II) into the oxic mixolimnion, Fe(III) into the anoxic monimolimnion). The trace amounts of Fe(III) existing in this reducing layer would be quickly removed from solution by bacterial reduction and/or precipitation (probably in the form of schwertmannite). The Fe(III)-rich mineral particles settling from the upper layer would be partly or totally re-dissolved and re-incorporated into the aqueous solution in the deepest waters of the lakes, where most ferric minerals (schwertmannite, jarosite, goethite) are unstable. This re-dissolution would also lead to desorption of different substances such as As, phosphate, or organic carbon, which are usually associated with these solids. This model is similar to those proposed for other meromictic lakes in other parts of the world (Boehrer and Schultze 2008, and references therein; Wetzel 2001).

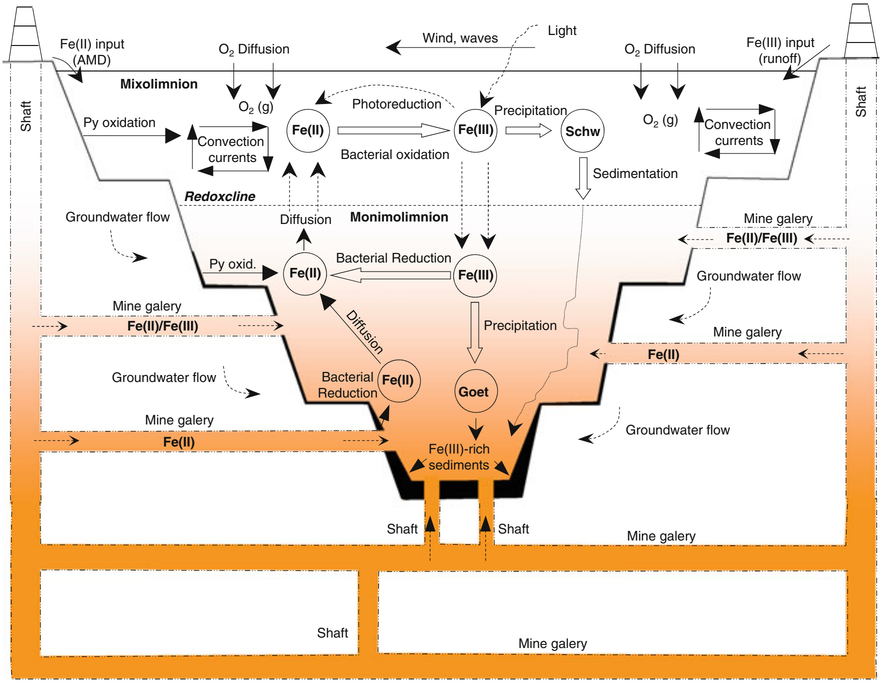


Fig. 5.34 Schematic model showing the main biological and physico-chemical processes involved in the biogeochemical cycling of Fe in the pit lake of Cueva de la Mora (model not to scale). Abbreviations: Schw, schwertmannite; Goet, goethite

5.3.9 Summary and Conclusions

This chapter has reported some basic limnological, hydrogeochemical, and microbiological features of the acidic mine pit lakes of the Iberian Pyrite Belt. A wide spectrum of aqueous chemical compositions is observed, from extremely acidic with very high metal concentrations to circumneutral and low-metal contents; most have highly acidic water (pH 2.2–3.5) and high sulfate and metal concentrations. Different stratification styles have been recognized, including holomictic lakes (e.g. Los Frailes, Herrerías II), meromictic lakes with homogenous monimolimnion (e.g., San Telmo), and meromictic lakes with gradient-like or staircase-like monimolimnion (e.g. Cueva de la Mora). Finally, distinct trophic situations have been observed, varying from oligotrophic to hypereutrophic conditions (sometimes even within the same lake, depending on the parameters and depths considered). Meromixis seems to predominate in most pit lakes, probably favoured by very high relative depths, but also by the connection of the open pit with underground mine tunnels and shafts. In many pit lakes (as in Cueva de la Mora, Herrerías I, Filón Centro, and Filón Sur in Tharsis, Concepción, and Tinto Sa Rosa), pronounced vertical gradients of pH, Eh, T, and sulfate and metal concentrations exist in the anoxic monimolimnion towards the bottom of the lakes. These chemical gradients seem to result from different biotic and abiotic factors, although these are not well understood yet. Especially interesting are the 'staircases' observed in lakes like Cueva de la Mora, which may be partially caused by double-diffusive convection with a coupled upwards flux of heat and dissolved substances.

Bacterial reduction of Fe(III)-rich minerals coupled with oxidation of organic matter in the water column and underlying sediment appears rather probable (based on geochemical evidence). In addition, bacterial reduction of SO_4^{2-} could be taking place in pore waters within the sediment cover. However, our knowledge of these biogeochemical processes in the sediments of the IPB pit lakes is still limited. Therefore, it is difficult to ascertain the degree to which the microbial activity (including primary photosynthetic productivity and Fe(II)-oxidation in the mixolimnion, and carbon decomposition coupled with Fe(III) reduction in the pit lake bottom) may have contributed to the observed chemical configuration. Abiotic factors that could influence stratification patterns would include, among others, (1) the pit lake morphometry, (2) the oxidation of pyrite by Fe(III) in the anoxic waters in contact with pyrite-rich wall-rocks, (3) dissolution of secondary salts from flooded galleries and shafts, (4) influx of groundwater or mine water from flooded underground galleries, and (5) changes in the composition of the mine water inputs during the flooding history of the lakes.

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5.4 Pit Lakes in Australia

R. Naresh Kumar, Clint D. McCullough and Mark A. Lund

5.4.1 Introduction

Australia is among the top producers for many of the world's most important minerals (Geoscience Australia 2008; Mudd 2007). Major mining resources include diamonds, uranium, black coal, iron, gold, copper, lead, zinc, bauxite, and mineral sands. Most historic and contemporary mining activity is centred on the states of Western Australia (WA), Queensland, and New South Wales (NSW; Fig. 5.35). Tasmania, Victoria, South Australia (SA), and Northern Territory (NT) are generally only important for certain minerals i.e. copper, gold, uranium (Mudd 2007). Mining is recognised as the most significant industry contributing to the Australian economy. However, environmental sustainability has become an increasingly

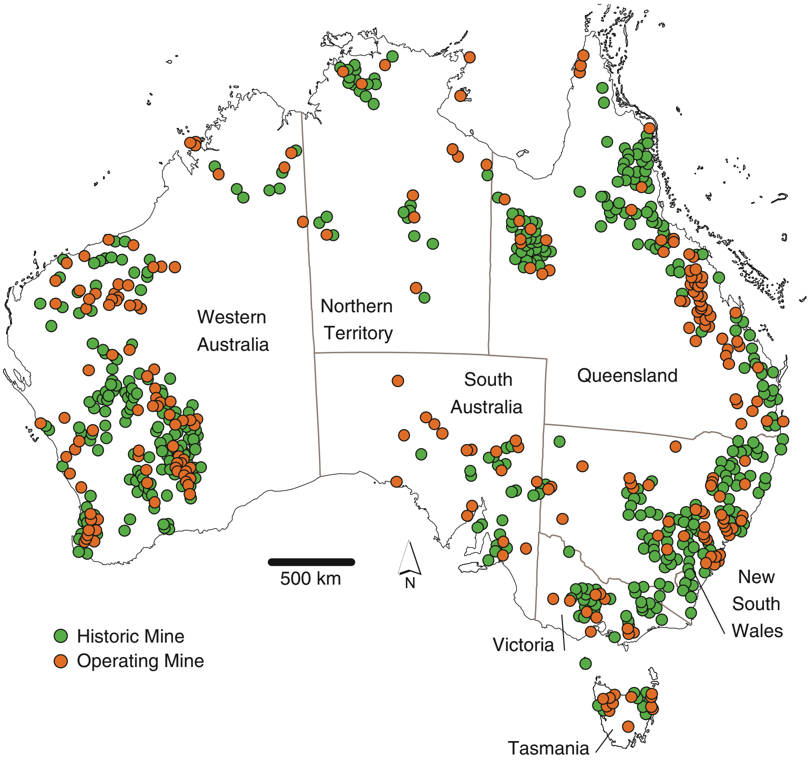


Fig. 5.35 Distribution of historic and operating mines in Australia; note: this list includes underground mines and pits that may or may not fill to form lakes (modified after http://www.australianminesatlas.gov.au/?site=atlas)

important consideration, requiring the industry to reflect a greater understanding and awareness of both positive and negative impacts of mining (DITR 2006; Nichol 2006).

High labour costs in Australia have led to substantial technical innovation and a focus on large scale open-cut operations. As a result, the scale of most modern open cut operations ensures a legacy of mining pit(s) left after operations are completed, with the depth of most open cut operations leading to part of the pit positioned below local groundwater tables. Therefore, once dewatering operations that permit mining stop, these pits will form pit lakes, with pit lake water coming from surface sources and groundwater returning to pre-mining levels (Castro and Moore 2000; Doupé and Lymbery 2005). Quality of pit lake water can vary considerably and is dependent on surrounding geology and exposure of measures previously buried. Acid mine drainage (AMD) results when exposed measures are oxidised and release acidity, which in turn can cause the dissolution of metal contaminants from surrounding strata, resulting in pit lake waters with elevated concentrations of metals (Banks et al. 1997). Pit lake waters are therefore often

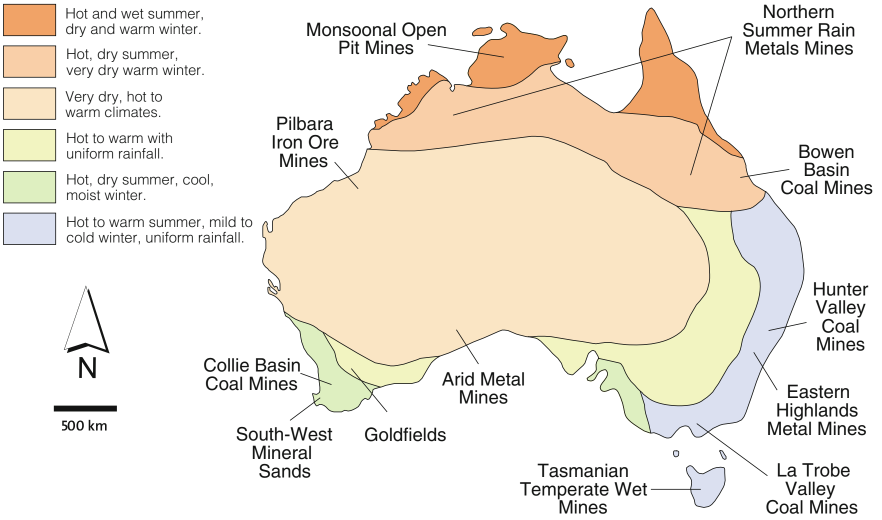


Fig. 5.36 Australian pit lake classification (modified after Mallet and Mark 1995; Johnson and Wright 2003)

toxic to biota and may pose a risk to groundwater. A survey of mining operations in Australia found that out of 517 mining operations, 317 contained potentially acid-generating wastes (Harries 1997). The same survey reported that of the 176 mines that answered the questionnaire, 60 mines had water-filled pits that contained pit lake water that was similar to pre-mining groundwater. However, seven sites had a total of 6×10^6 m^3 of acidic water at a pH of 2.5–3.5.

Pit lakes in Australia occur across a divergent set of climatic conditions (Fig. 5.36). Approximately one-third of Australia is arid with rainfall less than 250 mm per year and another third is semi-arid (250–500 mm per year). There are few areas where rainfall exceeds evaporation on an annual basis (Bell 2001). Low rainfall and high evaporation rates exist in most parts of the country, which may lead to net evaporation and the formation of hyper-saline pit lakes. Furthermore, the groundwater in many parts of inland Australia is also brackish to hypersaline. Low annual rainfall delays filling rates for new pit lakes, facilitating further oxidation of measures. A limited range of rivers and streams presents few opportunities to rapidly fill pit lakes in many areas. However, in many areas, surface discharge from pit lakes is unlikely, which reduces a major source of environmental impact often seen in wetter climes. Contamination of groundwater in many arid areas can also often be a minimal risk as high evaporation rates ensure that the pit lake remains a groundwater sink.

There is no central database of existing or future pit lakes currently available in Australia. There has also been very little research on pit lakes in general; a detailed literature review for this chapter produced little information. Published information that is available is typically *ad hoc* opportunistic studies across a diverse range of disciplines, including environmental engineering, geology, chemistry, and aquatic ecology. Many State and Federal primary industry and environmental agencies do collate mining data, including sometimes those of pit lakes and their characteristics. However, these data are generally limited to current or only recently decommissioned pit lakes. Many Australian pit lakes are on unrelinquished mining leases, which companies retain with an option to over-mine as technologies/economics alter their viability. This situation makes the long-term acquisition of data required to study the evolution of the quantity and quality of pit lake water a very challenging exercise. It is suspected that many pit lake related studies are not generally available because they are considered commercially sensitive.

The primary focus of mine rehabilitation and relinquishment across Australia is generally towards terrestrial communities; and predominantly landscape vegetation. Strangely, for a country with limited water resources, neither "pit lake" or even "lake" are even mentioned in the Federal government's recent 'Mine Rehabilitation Handbook" guidelines (DITR 2007). Doupé and Lymbery (2005) and McCullough and Lund (2006) have highlighted the potential for pit lakes in Australia to be used for a variety of environmental and social beneficial end uses. However, many may require remediation before they can provide a potentially valuable source of water (Gray 1997; Johnson and Wright 2003). This is particularly relevant in Australia with its history of extensive mining activity, a predominantly arid climate, and strong demand on very limited water resources. Increasingly, many Australian legacy mining pits are too large to backfill and would require extensive dewatering operations to keep them dry. As a result, many pits are destined to form large, deep pit lakes. These new lakes have few natural counterparts in the Australian landscape, especially in depth. Where remediation can achieve suitable water quality, then these pit lakes may become a potentially valuable asset to rural and remote Australian communities.

This chapter aims to review what is known about Australian pit lakes in terms of type, water quality, and current status. Examples of remediation and rehabilitation will be discussed as current legislative requirements.

5.4.2 Pit Lake Types

Mallet and Mark (1995) produced the first national classification of types of mining voids, creating eight broad climatic regions with associated mine types (see Fig. 5.36). This classification was further refined by Turner and Jones (1998), who focused more on ore type; they classified pit lakes as metalliferous (base metals, gold, iron ore), coal, and others (bauxite and mineral sand mining, quarrying). Metalliferous mines were further broadly divided into base metals, iron, and gold. The major base metals extracted in Australia by open cut operations are copper, lead, and zinc. In some cases, where economic ore extends to depth, underground mining operations are undertaken after initial open cut mining. As these metals primarily occur as sulfide ores, pit lakes formed have the possibility of low pH water with high metal load. Most of these mines are located in tropical northern Australia, where rainfall (primarily in summer) is significant and often intense, which poses particular challenges for these pit lakes. Iron is primarily extracted in the Pilbara region of Western Australia, which has an arid climate. Although some iron ore deposits are associated with some acidity-producing overburden, these are generally localised and can be managed. Groundwaters are generally fresh, but high evaporation rates can lead to problems of evapo-concentration in pit lakes, leading to hyper-salinity. The major gold producing region is in the Goldfields around Kalgoorlie in Western Australia. In much of the region, groundwaters are highly saline and pit lakes reflect this, with evapo-concentration enhancing the problem. The northern part of the region near Laverton has some fresh water pit lakes; however, it appears that this is primarily due to surface inputs creating a freshwater lens over saline groundwater. A unique feature of gold mining is the use of cyanide and, in the case of multi-pit mines, the option of disposal of contaminated tailings in pits.

The sedimentary geological sequences of coal mines are distinct from those of metalliferous mines. Substantial coal deposits are found in Australia, located in the wetter regions of the Collie basin (WA) and the Latrobe valley (Victoria), in the drier Hunter Valley (NSW), and in the Bowen basin (Queensland), which is subject to tropical and cyclonic rains. Coal and overburden often contains acidity-producing strata that can result in AMD. The sedimentary nature of many coal deposits can also cause issues with the stability of pit lake walls.

Australian bauxite and mineral sand mining operations involve relatively shallow excavations that are often quite rapidly backfilled with progressive rehabilitation of mined area. Pit lakes are therefore uncommon and are usually small and shallow (Johnson and Wright 2003; Turner and Jones 1998). However, these post-mining pit lakes are also often in close contact with disturbed spoil (Turner and Jones 1998), which can cause problems with AMD.

Johnson and Wright (2003) created nine regional categories for Western Australian pit lakes based on geology, climate, groundwater quality, type of ore, and regional setting. This classification overlaps for key mining areas with those of Mallet and Mark (1995). The very dry, hot to warm climatic region is divided into the Pilbara iron ore area, and to the south is split into the Murchison-Northern Goldfields and the Goldfields (this also overlaps the hot to warm with uniform rainfall climatic region). There are no publically available documents indicating that other states have undertaken a similar classification of their pit lakes.

Commander et al. (1994) provided a useful alternative classification scheme based on how groundwater moves through pit lakes. These classifications are more commonly associated with particular climatic regions but may vary at the individual pit lake scale. Pit lakes may act as a groundwater "sink" under low rainfall high evaporation climes, becoming increasingly saline whilst lowering surrounding groundwater levels. Alternatively, in higher rainfall environments, groundwater may "flow-thru" the pit lake; in this case, clean groundwater is potentially contaminated/concentrated as it passes through the lake. Lastly, in areas of high rainfall, low evaporation and/or artificial filling, situations can arise where the pit lake recharges surrounding groundwaters. This is typically temporary as pit lakes and groundwater levels will eventually equilibrate.

The authors reviewed available information on Australian pit lakes and contacted over 250 individuals in State, Commonwealth government departments, as well as peak industry bodies and large companies. This was combined with an extensive literature search. It is clear that no one knows how many pit lakes there are in Australia. However, a recent study estimated that there were 1,800 mine pits in the state of Western Australia that contain significant amounts of water (Johnson and Wright 2003). It is also clear that pit lakes generally have received little attention from researchers and little is known of water quality, limnological processes, biota and development over time.

5.4.3 Physical, Chemical, and Biological Characteristics of Pit Lakes

The size of mining pits in Australia ranges from that of urban fringe borrow pits of about 100 m in diameter to enormous pits such as the Mount Whaleback mine in the Central Pilbara, (WA), which will have final pit dimensions of 5.5 km by 2.2 km, with a depth of 500 m (Johnson and Wright 2003). However, not all of these pits will fill with water, especially pits located in arid regions, although most will contain at least some water. The majority of pit lake studies conducted in Australia have focussed on physical and chemical pit lake characteristics (Boland and Padovan 2002; Jones et al. 2008; McCullough et al. 2008a). These studies have demonstrated that water quality in a pit lake is influenced by many factors, including climate, groundwater quality, depth, pit filling method, and local mineralogy.

Despite the lack of water quality data for pit lakes across Australia (publically available data are shown in Table 5.10), there appears to be four major categories for Australian pit lake water qualities: AMD, saline (which can co-occur with AMD), neutral pH with metal/metalloid contamination, and good water quality (though not necessarily equivalent to natural wetlands). Water quality of pit lakes of Collie, north Bowen, and Mt Morgan are degraded by AMD. However, Collie pit lakes generally have low levels of contaminants despite low pH, while north Bowen and Mt Morgan show classic AMD conditions of extremely low pH and high concentrations of metals, along with ongoing salinisation.

Semi-arid and arid climates dominate the Australian landscape, and pit lake solute concentrations tend to increase significantly as a lake forms. In semi-arid regions such as the north Bowen, high rates of evapo-concentration result in significant increases in salinity each year (McCullough et al. 2008b). This phenomenon is

Table 5.10 Characteristics of pit lakes in Northern Territories (*NT*), Queensland (*Qld*), and Western Australia (*WA*); all values in mg L^{-1} unless otherwise stated, *N*: number of pit lakes in region considered, –: no data available, *DOC*: dissolved organic carbon

Parameter	Collie Basin, WA^{1} ($n = 4$)	Collinsville, N. Bowen Basin, Qld^{2} ($n = 4$)	Mount Morgan, Qld^{3} ($n = 1$)	Mary Kathleen, Qld^{4} ($n = 1$)	Ranger Mine, NT^{5} ($n = 1$)	Kemerton, WA^{6,7} ($n = 1$)	St. Barbara Mines, WA^{8} ($n = 2$)	Thalanga Mine, Qld^{9} ($n = 1$)
Coordinates	33°21′47S, 116°09′22E	20°33′51S, 147°49′52E	26°38′22S, 150°22′02E	20°45′1S 140°0′6E	12°41′S, 132°55′E	33°8′1S, 115°47′31E	28°53′50S, 121°19′23E	20°20′S, 145°46′E
Ore type	Coal	Coal	Au, Cu	U	U	Silica sand	Au	Cu–Pb–Zn
Depth (m)	8–70	4–14	–	–	–	6	–	70
Area (km^{2})	0.06–1.03	0.01–0.06	–	–	–	–	0.006–0.95	–
pH	3.8–5.0	1.5–4.9	2.8	6.1	7.6	8.5	8.0–8.6	7.7
Acidity (mmol$_{eq}$/L)	0.1–3.0	37–208	–	–	–	–	–	–
Total P	<0.005–0.009	<0.005	–	–	0.01	0.02	–	–
Total N	<0.05–1.5	0.51	–	–	1.96	0.573	7.3–22.8	–
DOC	3.1–7.3	1–59	–	–	–	22	–	–
Cond. (mS cm^{-1})	0.42–1.4	7.8–23.5	11	5.05	0.89	1.2	–	1.07
Sulfate	31–107	300–25,000	12,100	1,840	782	296	2,570–7,190	7,950
Aluminium	0.001–0.006	23–1,300	740	0.032	0.026	0.1	0.02–0.06	<1
Calcium	2.3–6.0	124–519	520	464	0.02	67	334–1,120	718
Cadmium	<0.002	<0.01–0.023	0.15	–	<0.0002	–	0.0002	0.16
Cobalt	<0.005	0.6–7.2	–	–	0.0005	–	–	–
Chromium	<0.10	<0.01–0.47	–	–	< 0.002	–	0.002	–
Copper	<0.002– < 0.05	<0.05–2.5	36	1.17	0.0024	–	0.03	< 1
Iron	0.0003–0.005	139–2,463	248	3.23	<20	0.14	< 0.05–0.06	0.575
Lead	–	<0.1–6.3	–	–	0.001	<0.1	–	<1
Magnesium	0.077–16.3	197–2,239	1,240	140	115	58	865–3,150	1,025
Manganese	0.0002–1.2	13–150	81	–	0.041	<0.01	–	–
Nickel	0.03–0.34	1.2–17	–	0.69	0.0053	–	0.09	–
Uranium		0.020–0.029	–	0.460	1.76	–	–	–

(continued)

Table 5.10 (continued)

Parameter	Collie Basin, WA[1] ($n = 4$)	Collinsville, N. Bowen Basin, Qld[2] ($n = 4$)	Mount Morgan, Qld[3] ($n = 1$)	Mary Kathleen, Qld[4] ($n = 1$)	Ranger Mine, NT[5] ($n = 1$)	Kemerton, WA[6,7] ($n = 1$)	St. Barbara Mines, WA[8] ($n = 2$)	Thalanga Mine, Qld[9] ($n = 1$)
Zinc	0.0005–6.9	1–46	25.3	0.088	0.0037	0.15	0.01	53.5
Chlorophyll *a* ($\mu g\ L^{-1}$)	0.1–64	0–64	–	–	–	6.5–8.5	–	–
Zooplankton studies?	Yes	Yes	–	–	–	No	–	–
Macroinvertebrate studies?	Yes	Yes	–	–	–	Yes	–	–
Periphyton studies?	Yes	No	No	No	No	No	No	No
Catchment rehabilitation?	Yes	Yes	Yes	Yes	Yes	Yes	Yes	–
Pit lake remediation?	1 lake	1 lake	1 lake	1 lake	Backfilling	No	–	Backfilling
Proposed end use(s)	Aquaculture, recreation	Industry use	–	–	–	–	None	–
Catchment lease	Bonded	Bonded	–	–	Bonded	Owned	Bonded	N/a
Potential closure criteria	Recreation	Bunded lake	–	–	Backfilled	Pond	Bunded lake	–

[1] (Derham 2004; Jones et al. 2008; Lund et al. 2006; Nguyen 2004; Salmon et al. 2008; Thomas and John 2006); [2] (McCullough et al. 2008b, 2008c); [3] (Tropical Water Solutions 2002); [4] (Lottermoser et al. 2005); [5] (Johnston and Milnes 2007); [6] (McCullough and Lund 2008); [7] (John 1993); [8] (personal comm.); [9] (Thienenkamp 2004)

particularly pronounced in lakes that are groundwater sinks (Commander et al. 1994). In arid Australian regions, such as the southern Goldfields of Western Australia, hyper-saline pit lakes may form, due to saline groundwater and evaporation (Johnson and Wright 2003). The generation of relatively dense, saline water at depth and periodic addition of fresh rainwater to pit lakes can result in a stratified lake (Johnson and Wright 2003). St Barbara, located in the northern Goldfields (WA), probably represents this latter type of lake. With sufficient inflow, such a lake can serve as a source of freshwater recharge (Gerrard 2002). Lack of empirical hydrochemical and post-mine closure data makes it difficult to assess the impact of salinity issues in Western Australia (Hall 1998). However, case studies support the long-term concern of WA pit lakes becoming point sources of hyper-saline water that could contaminate surrounding groundwater resources. For example, limited monitoring data from the Mount Goldsworthy pit, in Western Australia, demonstrated that the salinity of that pit lake increased from 1,400 to 5,500 mg L^{-1} TDS over a 14 year period (Johnson and Wright 2003).

Mary Kathleen and Thalanga (Queensland), and Ranger (Northern Territory) pit lakes have relatively good water quality but have been contaminated by a particular metal—in these cases, Cu, Zn, and U, respectively. These pit lakes, therefore, remain well suited to a variety of end-uses because individual contaminants are typically more readily dealt with than more complex chemistries.

Kemerton (Western Australia) is a silica sand mining operation with few geological considerations or mining processes that would cause contamination of pit lake waters; hence, water quality is very good. However, unpublished studies by the authors have found significant differences in the lake water quality compared to shallow natural wetlands nearby. In this landscape, which is dominated by shallow wetlands, the depth, permanence, hydrology and bathymetry of pit lakes does not have any natural counterparts that can be used as analogues or reference sites.

Very little is known about the aquatic ecology of Australian pit lakes. Proctor and Grigg (2006) have published one of the few studies to examine macroinvertebrate communities. The authors also have unpublished macroinvertebrate data from north Bowen (Queensland), and Kemerton (Western Australia) and have described the macroinvertebrate communities of pit lakes in Collie (Western Australia; Lund et al. 2000). Collectively, these studies have shown macroinvertebrate communities of limited diversity dominated by cosmopolitan and pollution-tolerant taxa. A list of macroinvertebrate families commonly occurring in Australian pit lakes is furnished in Table 5.11. These findings suggest that, regardless of water quality, pit lakes do not appear to have macroinvertebrate communities representative of natural waterbodies, possibly due to reduced habitat diversity of low quality.

Table 5.11 Macroinvertebrate families occurring in Australian pit lakes; *n*: number of pit lakes

Taxon	Collie Basin, WA ($n = 4$)	pH > 7 North Bowen Basin, Qld ($n = 1$)	pH < 3 North Bowen Basin, Qld[a] ($n = 6$)	Kemerton, WA ($n = 1$)
Acalyptrate	–	1	–	–
Aeshnidae	–	1	–	–
Amphipoda	2	–	–	1
Arrenuridae	–	1	–	–
Atyidae	–	2	–	–
Baetidae	–	3	–	–
Belostomatida	–	1	–	–
Caenidae	–	1	–	–
Calanoida	–	1	–	1
Ceratopogonidae	2	2	–	1
Chironomidae	2	4	2	1
Cladocera	–	3	–	1
Coenagrionidae	–	2	–	–
Corixidae	–	2	1	1
Corduliidae	1	–	–	–
Culicidae	1	2	1	–
Cyclopoida	–	4	–	1
Dytiscidae	2	1	1	1
Ecnomidae	–	1	–	–
Harpacticoida	–	2	–	–
Hemicorduliidae	–	2	–	–
Hydrachnidae	–	1	–	–
Hydraenidae	–	–	1	–
Hydridae	–	1	–	–
Hydrochidae	–	–	–	1
Hydrodromidae	–	2	–	–
Hydrophilidae	–	1	1	–
Hydroptilidae	–	1	–	–
Leptoceridae	1	1	–	1
Libellulidae	1	–	1	–
Limnesiidae	–	1	–	–
Lindeniidae	–	1	–	–
Lymnaeidae	–	1	–	–
Notonectidae	1	2	–	–
Oligochaeta	–	2	–	1
Ostracoda	–	3	–	1
Physidae	–	1	–	–
Planorbidae	–	1	–	–
Pleidae	–	1	–	–
Sphaeriidae	–	1	–	–
Tabanidae	–	1	–	–
Thiaridae	–	2	–	–
Unionicolidae	–	1	–	–

(Lund et al. 2000; McCullough and Lund 2008; Proctor and Grigg 2006); 1 = rare, 2 = occasional, 3 = common, 4 = abundant; [a] unpubl author's data

5.4.4 Examples of Australian pit lakes

5.4.4.1 Collie Basin

The Collie Basin is located approximately 160 km south-southeast of Perth, and is the centre of coal mining in Western Australia. Collie is situated in an area of Mediterranean climate, with hot, dry summers (range 12–29°C) and cool, wet winters (range 4–15°C). The 100 year mean annual rainfall for the Collie Basin is 939 mm, (Commonwealth of Australia Bureau of Meteorology 25/02/2009) although this has decreased to an average of 690–840 mm over the past 20 years (Craven 2003). Coal mining in Collie had resulted in the formation of pit lakes that range from <0.1–1.0 km^2 in surface area, <10–70 m in depth, 5–48 years in age, with pH ranging from 2.4–5.5. The sites also differ in the extent of rehabilitation (Lund and McCullough 2008). With the exception of Chicken Creek (pH 2.4–2.8), all other pit lakes are oligotrophic or ultra-oligotrophic, with very low concentrations of nutrients, particularly carbon and phosphorus (Salmon et al. 2008). Uncharacteristic of most AMD mine pit lakes, these lakes are only mildly acidic and the metal contaminant concentrations of these pit lakes are low (Lund et al. 2006). This is thought to be due to the low sulfur concentrations of Collie black coal (Sappal et al. 2000), combined with very low buffering from surrounding geologies. The few ecological studies that have been made on Collie pit lakes highlight nutrient-limited algal productivity and hence macroinvertebrate communities (Derham 2004; Jones et al. 2008; Lund et al. 2000; Lund et al. 2006; Nguyen 2004; Salmon et al. 2008; Thomas and John 2006).

5.4.4.2 Bowen Basin

North Queensland's Bowen Basin is a major Australian open cut coal mining area and Jones (1997) estimated that, potentially, 200 km^2 of final voids could be left after mining has ceased. The water table in the Bowen Basin Coalfields sits at 20–30 m below the surface and, since the depth of open cut mining greatly exceeds this depth, without backfilling, pit lakes are inevitable. There is, however, limited data on the hydrology of pit lakes in the Bowen Basin, as no pits that have yet been relinquished back to the State, since most pits are active components of both the mining operation and mine water management process. The development of more economic high wall mining methods in this region meant that many pits, which might otherwise have been classified as final and allowed to fill with water, are now being kept open as options for future over-mining. There are very few examples of pit rehabilitation efforts in the Bowen Basin Coalfields (McCullough et al. 2008b; Williams 2001). A study on the biological diversity of aquatic invertebrates in <1–22 year old pit lakes in an open-cut coal mine near Moura, central Queensland in the south Bowen Basin found cosmopolitan species of oligochaetes, cladocerans, ostracods, and copepods with a higher biodiversity of macroinvertebrates in older pit lakes with salinity <2,000 $\mu S\ cm^{-1}$ (Proctor and Grigg 2006).

5.4.4.3 Hunter Valley

The 22,000 km^2 Hunter Valley is located on the central coast and has historically been the largest and most productive coalfield in NSW, with over 60 Mt of coal extracted each year (Hancock et al. 2005). The Coal Industry Synoptic Plan (NSW-DMR 1999a, 1999b) indicated that planned final pit lakes will cover 12.7 km^2 across the Hunter Valley and that most pit lakes are likely to be groundwater sinks, eventually becoming saline. The long-term water quality implications of these pit lakes on the surrounding hydrological system are largely unknown.

5.4.5 Management, Remediation and Rehabilitation of Australian Pit Lakes

There are many environmental legacies of poor practices due to lack of well-planned mine decommissioning at many sites around Australia. Some of the most notorious examples include: Rum Jungle in the Northern Territory, Captains Flat in New South Wales, Mt. Lyell in Tasmania, and Mt Morgan in Queensland (Harries 1997). Impacts associated with these operations were mainly due to AMD. The extent of environmental problems due to mining-related issues varies between states, though only limited data is publicly available. In Western Australia, open cut mining disturbances account for 357 km^2, of which 88.15 km^2 has undergone preliminary rehabilitation and 61 km^2 has been revegetated (Mudd 2007). In Queensland, 736 km^2 has been disturbed, with 203 km^2 rehabilitated as of June 1997 (Anderson 2002). Although state totals may vary, these proportions are likely to be similar across Australia.

In addition to any corporate social responsibility, there may also be a legal responsibility for companies mining in Australia to leave behind a sustainable environment once production has finished. In some cases, bonds are not returned until adequate rehabilitation has been demonstrated (Bisevac and Majer 1999). Exploration and mining leases are issued to mining companies by governments on behalf of the community. Mining activities are therefore regulated by State and Territory governments with the Commonwealth Government only involved in matters of national significance or on Commonwealth land, e.g., national parks (Fox et al. 1976, 1977). Realisation that general decommissioning should be an integral part of mine planning and operations management developed in Australia during the 1990s, and is now the common practice of most current (and particularly the larger stock exchange-listed) mining operations.

Pit lake management strategies in Australia are required for officially closed leases, as well as mining operations under ‘care-and-maintenance’. Nevertheless, there are no specific water quality criteria or guidelines developed or applied in Australia for pit lakes. Instead, general environmental water quality guidelines are often used to determine acceptability of pit lake water quality, e.g., for surface water discharge (ANZECC/ARMCANZ 2000). Alternatively, pit lake water quality are sometimes regulated according to end use requirements or the safety of surrounding environments (Batley et al. 2003). Some states have proposed criteria; in Western Australia, water quality in pit lakes is planned to be regulated on a case-by-case basis depending on mine closure options (Johnson and Wright 2003). Nevertheless, while State Governments differ in the process and terminology they use, there are no significant differences in the levels of performance required to meet conservation, environment protection, and development.

Most states in Australia have an ongoing budget, albeit generally minor, for the rehabilitation of old and abandoned mine sites causing either environmental impacts or presenting public safety hazards (Mudd 2004). In Tasmania, the Rehabilitation of Mining Lands Trust Fund is subsidized by the portion of the royalties that is paid by the mining industry for the sole purpose of repairing abandoned mining lands. Commonwealth Government mine closure guidelines addressing best practices recommend decommissioning of pit lakes by either backfilling, e.g. where sulfidic material is maintained below the recovered water table level and the rest of the void is filled with benign material (Bell 2001), or treatment of contaminated water, e.g. AMD with lime, and reshaping of pit walls to a safe and stable slope angle (Environment Australia 2002). Pit lakes can be used to provide a permanent water cover over reactive wastes and geologies in the pit, but this is normally limited in Australia to the wetter regions of Tasmania and the wet tropics. Public and wildlife safety measures around pit lakes may include installation of a barrier to discourage human access, abandonment bunds (retaining walls) of competent rock, fencing, and appropriate signage. However, if properly managed, pit lakes can provide benefits to mining companies, local communities, and the environment (McCullough and Lund 2006; McCullough et al. 2009). Beneficial end uses of pit lakes demonstrated so far in Australia are summarised in Table 5.12. Development of post-mining beneficial end uses in Australian pit lakes can involve stakeholder engagement to decide between possible uses, such as aquaculture, recreational facilities, educational purposes, and water storage (McCullough and Lund 2006). Pit lakes can often simply have aesthetic values improved through revegetating lake riparian zones and surroundings, which may offer further opportunities for development of other aquatic habitat types such as wetlands that, may have been lost through mining. However, although many possible uses for pit lakes have been promoted, there are large numbers of pit lakes in regional Australia with no current or future use due to their remoteness, or due to not being relinquished by current or proposed mining operations (Farrell 1998).

Most environmental impacts associated with terrestrial mining activities are localised around the mine, whereas the effects on groundwater can extend over long distances. Environmental systems associated with surface expressions of groundwater, shallow groundwater aquifers, or subterranean groundwater ecosystems are often especially sensitive to change. For example, mining below the watertable may alter groundwater quality or levels. As many Australian mines occur in remote, low-rainfall regions, inappropriately managed pit lakes may present a significant risk to the local water resources (Brown 2003). Pit lakes with

Table 5.12 Demonstrated and suggested pit lake end uses in Australia, adapted from McCullough and Lund (2006)

Beneficial end use	Example of end use	Location, mining type	Reference
Aquaculture	Assorted fish, marron (crayfish)	Laverton, WA (gold), Collie (coal)	Otchere et al. (2004) and Syddell (2004)
Industry water use	Road dust suppression	Collinsville, Qld (coal)	McCullough et al. (2008b)
Irrigation	Mango horticulture	Pine Creek, NT (gold)	Pine Creek Comm. Govt Council (2003)
Livestock watering	Livestock production	Bowen, Qld (coal)	Harper et al. (1997)
Potable water source	Remote mining town	Laverton, WA (gold)	Australian Labor Party 5th Feb, (2004)
Recreation and tourism	Boating, water skiing, bathing	Collie, WA (coal)	Chapman (2002), Lund (2001) and WA Tourism Commission (2003)

waters degraded by salinisation and/or acidification may adversely affect the local and regional environment and groundwater resources with contaminated plumes from flow-thru pit lakes extending large distances down-gradient. The magnitude of an impact may vary from insignificant in low permeability rocks and groundwater systems already saline, to considerable in high-permeability rocks and low-salinity groundwater environments (Commander et al. 1994; Johnson and Wright 2003). A saline plume can extend for tens of kilometres from the pit lake, which is a consideration in evaluating potential impacts on nearby groundwater resources (Johnson and Wright 2003).

State and territory regulations require the identification and assessment of AMD risks in the environment and a social impact assessment in the determination of financial bonds for companies. The size of the bonds are based on adequate post-closure management of AMD issues, management of compliance with national water quality guidelines, and impact on local and regional water resources (LPSDPMI 2007). The selection of relevant (ANZMEC/MCA 2000) guidelines for pit lake water depends on the proposed final end use and any existing environmental requirements for the management of pit lakes specified by the state regulatory agencies. Generally, the States have addressed the issue of final voids by requiring that if a post-closure void is to be left, it should complement the surrounding rehabilitated landform and be part of a useful, stable, and non-polluting rehabilitated area. The Queensland Department of Mines and Energy specifies that mining and rehabilitation must create stable, non-polluting landforms with a defined beneficial post-mine land use (Roe 1997). Furthermore, Queensland specifies that the rehabilitated landscape must achieve the environmental objectives of an acceptable post-disturbance land capability, create a stable final landform, and ensure protection of downstream water quality. In NSW, the Department of Mineral Resources has developed several policy principles governing final voids (Summerhayes 1997). For instance, the principles relating to pit lake water quality include the provision that where practicable, the water body should be prepared for further land use such as a recreational waterway. Water-filled final voids should be made safe, with attention given to means of egress, and wherever possible, the pit lake should contain water of acceptable quality for the intended use. Water of poor quality should be stored within geotechnically stable storages. In Western Australia, mines are subjected to stringent environmental requirements and conditions as part of government legislation. The most important legislation with regard to mining and its possible impact on water resources is the Mining Act 1978, the Rights in Water and Irrigation Act 1914, and Environmental Protection Act 1986. The majority of mine sites in Australia are focusing on establishment of self-sustaining native ecosystems in their rehabilitation programs. Bell (2001) states that the bauxite and mineral sands industries have developed this technology to a high degree, while the coal industry is still trialling approaches to achieve satisfactory establishment and sustainability of such systems.

Current Australian closure strategies for pit lakes can be therefore be seen to be grouped into three main categories (Evans and Ashton 2000): (1) Enclose and forget approach, with the construction of a bund around the mining void to prevent access and protect mining companies from litigation arising from accidents; (2) Strategies addressing environmental issues, which are mainly concerned with development of environmental values such as biodiversity conservation (e.g. remediation of water quality in mine lakes and preservation of biodiversity through nature conservation projects); or (3) Initiatives intended to create employment and business enterprise opportunities (e.g., aquaculture, ecotourism, and various forms of horticulture), or result in the creation of a community resource, such as a recreational facility. The first strategy of enclosing pit lakes addresses most current legislative requirements and largely resolves the problem of liability but may not provide any benefits to local communities. End uses that fall into the other two strategies hold more promise for significant local community benefit (Evans and Ashton 2000; McCullough and Lund 2006). However, of equal importance to identification of social aspects of mine closure is the application of sound well-understood science to the end use development process, be it catchment rehabilitation or water quality remediation (Evans 2006; McCullough et al. 2009). Nevertheless, the absence of regulatory control or even direction given to mining companies ensures few examples of successful pit lake closure and lease relinquishment back to government.

The primary concern at mine closure in Australia has been ensuring that any pit lake is geologically stable and safe to the public under Department of Minerals and Energy (DME) guidelines (DME 1996). However, where communities reside nearby, pit lakes may present risks for recreational swimmers where there is a risk of drowning due to the limited shallow margin, e.g. Hatch (2007), Fig. 3. In agricultural areas, pit lakes may lead to poisoning or drowning of stock (Harper et al. 1997) and wildlife, the latter where there is a risk of falls from the pit high walls. In environmentally sensitive areas, mixing of local water resources with contaminated pit waters may lead to loss of biodiversity or ecosystem function

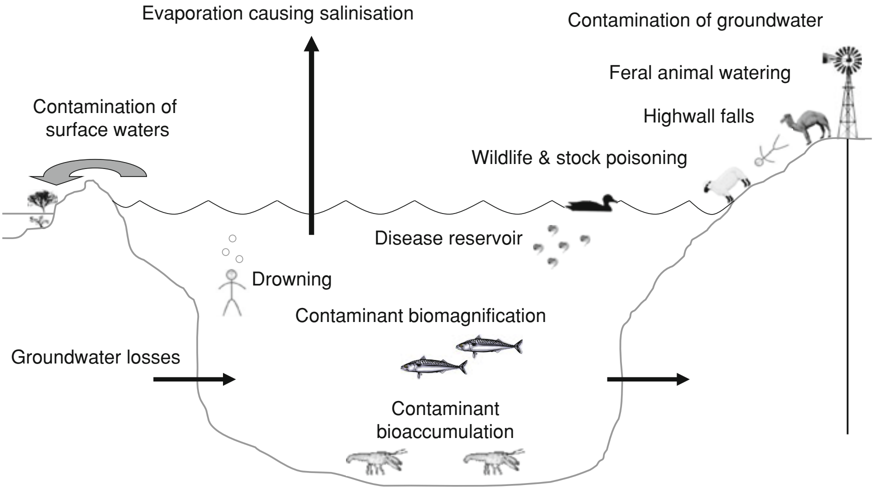


Fig. 5.37 Potential liabilities of pit lakes to communities and the environment (after McCullough and Lund 2006)

(McCullough and Lund 2006). Particularly in drier regions of Australia, pit lakes can become an ecological liability by supporting populations of feral animals (Nichol 2006). Water in Australian pit lakes can give rise to significant health and safety issues, beyond the risk of drowning, such as the potential for harbouring water-borne diseases, and risks to native fauna or human health if pit lake water becomes non-potable and is subsequently consumed (McCullough and Lund 2006). A crucial hazard with pit lake water in much of Australia is that pit lakes can provide a permanent breeding habitat for mosquitoes, some of which may transmit human disease. Tendency of native mammals to congregate around artificial or natural water bodies may facilitate the spread of these diseases to nearby communities. Risk of spreading these diseases increases because pit lakes may be visited by mine company or regulatory authority personnel for investigation and monitoring, and by local people for recreation. Some disease-causing mosquito species breed in saline water, so long-term salinisation may not decrease disease risk. Furthermore, the potential for pit lakes harbouring mosquito populations may also increase following acidification of water bodies (McCullough and Horwitz 2010; Fig. 5.37).

5.4.6 *Examples of Mine Closure and Rehabilitation of Pit Lakes*

Mount Morgan mine in central Queensland is one of the largest gold mines in Australia, and is significant in the context of Australian gold mining history. Gold was extracted for nearly hundred years until the mine closed in 1981 (Jones et al.

2003); tailings were then retreated until 1990. The Mount Morgan site contains about 3.7 km^2 of disturbed land, of which about 1.5 km^2 has been rehabilitated. The open cut was around 0.65 km^2 surface area with a depth of 210 m and a water capacity of 11×10^6 m^3 (Table 5.10). The open cut was formerly used as a dump for polluted industrial process water. Additional AMD problems were treated by pit water neutralisation and metal removal with calcium hydroxide. Pit lake water was then discharged to the adjacent river to initially attain and subsequently maintain the maximum operating level in the pit (Jones et al. 2003). The Queensland Government took over environmental responsibility for the mine in 1993 and has recently commenced a 10 year rehabilitation plan for the area.

The Garrick East pit lake is located at the northern end of the Bowen Basin (Collinsville, North Queensland) within the semi-arid tropics, and was mined during the 1990s. The lake has a pH of 2.4 and high concentrations of dissolved metals and sulfate. Following microcosm studies (McCullough et al. 2006, 2008b), the lake was split with an earthen barrier and one side was experimentally rehabilitated. Monitoring of water quality occurred both pre- and post-dosing in the treated section and in three control pit lakes over 34 months (McCullough et al. 2008b). This 7×10^4 m^3 section of the lake was filled with dried sewage sludge (60 t), liquid sewage sludge (3,190 t), and municipal green waste (980 t). Following organic additions, pit lake water chemistry displayed large pH increases through internal sulfate reduction processes. Nevertheless, pH declined again after 12 months of increase. This decline was thought due to ongoing surface water acidity inputs and mixing during heavy cyclonic rainfall events immediately before the decline, and/or to exhaustion of the organic carbon. Subsequently, pH has recovered again following stratification and this study suggests that addition of low-grade organic materials shows promise for remediation of acid mine waters, particularly in a tropical climate.

Open cut mining of oxidized and primary sulfide-bearing ores at the Mary Kathleen uranium mine took place in semi-arid Queensland from 1956 to 1982 (Lottermoser et al. 2005). Together, the pit lake, waste rocks dumps, tailings storage facility, former processing plant, and evaporation ponds cover an area of approximately 4 km^2. Rehabilitation of the mine site and waste disposal areas began in mid-1982 and was completed in 1985 at a cost of around AUS$19 million. However, the open cut pit has not been rehabilitated and is largely unchanged from when mining stopped. Largely self-contained, with internal drainage, the open pit is today partly filled by a pit lake and numerous waste rock dumps.

The Agricola gold mine (Kenilworth, Queensland) commenced open cut mining in 1987. However, in 1988, the pit wall collapsed leading to closure of the mine. The company went into liquidation leaving a 0.16 km^2 contaminated site with a pit lake containing 10^4 m^3 of AMD water with pH of 5.5–6.0 and copper concentrations of 8 mg L^{-1}. The Queensland Department of Mines and Energy undertook rehabilitation work from 1995 to 1996. Pit lake waters were treated with calcium hydroxide to remove copper and then backfilled with waste rock and finally capped with 1.5 m of compacted clay (Mine Decommissioning 2002).

The Enterprise Pit Lake is located in the monsoonal tropics southeast of Darwin (Northern Territory). The climate in this region is characterized by extremes of seasonal flood and drought (Taylor and Tulloch 1985). The original Enterprise operation was an open-cut gold mine that left a void of approximately 0.27 km^2 with maximum depth of 140 m (Fawcett and Sinclair 1996). To manage potential acid production in pit walls, Enterprise Pit was rapidly flooded by diverting nearby Pine Creek into it, beginning in the 1993–1994 wet season and finishing in the 1994–1995 wet season (Fawcett 1995). Final lake water levels were designed so that the majority of potentially acid-forming minerals would be located below the oxygenated epilimnion of the lake with an assumption that hypolimnion would be essentially anoxic for most of the year (Fawcett and Sinclair 1996; Varma 2002). However, later studies showed that a relatively small epilimnion volume and low productivity allows significant oxygen concentrations to remain in the hypolimnion of the lake. Low pH values in a layer of water at 35 m depth in the hypolimnion is thought to be due to pit wall oxidation and AMD production (Boland and Padovan 2002).

Woodcutters Mine near Darwin in Northern Territory involved underground and open cut mining of a large lead–zinc deposit between 1985 and 1999. In 2000, Newmont Australia Ltd commissioned a leading practice multi-disciplinary study to finalise the site closure plan, including a final rehabilitation plan for the backfilled open pit and cover design for the waste rock pile. The open pit was backfilled to near the surface with clean material following tailings relocation (LPSDPMI 2007).

The Ranger Uranium Mine is located approximately 250 km east of Darwin (Northern Territory) within the highly regulated boundary of the environmentally and culturally significant World Heritage listed Kakadu National Park (Humphrey et al. 1999). The mine started operations in 1981 and the first orebody was mined out in 1994; an adjacent orebody is now being mined. Rainwater that has only had contact with waste rock is released into nearby Magela Creek during the wet season (McCullough et al. 2008a), while process water is confined to the tailings pond and the first orebody pit and is disposed of by evaporation. A large store of degraded water has developed in mine storage facilities due to above-average rainfall at the site in recent years. An innovative treatment involving lime-softening and reverse osmosis was successfully tested late in 2001 (Johnston and Milnes 2007). The full-scale treatment plant has cost A$25 million and has a 7.5×10^5 m^3 throughput per annum. At closure, the intent is to backfill the pit lake with tailings (Jones et al. 2008).

Rum Jungle (Northern Territory) operated from 1954 to 1964, extracting uranium/copper ore by open cut. The site was abandoned in 1971 with three pit lakes, four waste rock dumps, a tailing disposal area, and a pile of low grade ore. Significant pollution of groundwater and surface waters by acid and heavy metals (mainly copper) occurred after mining ceased. The Rum Jungle mine site was rehabilitated between 1983 and 1986 by the Northern Territory Department of Mines and Energy with financial aid from the Commonwealth Government at a total cost of AUS $18.6 million. Contaminated pit lake water treatment of 2.1×10^6 m^3 required 6,670 t of calcium hydroxide at a cost of AUS $6.2 million (NTDME 1986; Richards et al. 1996). However, significant environmental problems, including ongoing acidity generation and discharge, remain.

Junction Reefs Gold Project, located in New South Wales, had pit lake issues of concern to the environment. The pit lake was treated by partial backfilling in the upper and lower sections, whereas the deepest section was allowed to fill with water to a level above the nearby river. Rehabilitation was completed by limiting public access to steep sections by fencing and bund walls (LPSDPMI 2007).

Lake Kepwari is a pit lake in the Collie basin, Western Australia. Prior to filling with water, reactive overburden dumps and exposed coal seams were covered with waste rock, lake edge inclines reduced and revegetated with endemic flora by direct seeding. In order to further reduce wall exposure and rates of consequent acid production, the lake was rapidly filled by a diversion from the South Branch of the Collie River over three winters until 2005 (Oldham et al. 2009). The volume of Lake Kepwari is now 25×10^6 m^3, with a maximum depth of 65 m and surface area of 1.03 km^2. The proposed end use for this pit lake was contact recreation, such as water skiing (Evans and Ashton 2000). Although the river water initially raised water pH, it has now returned to 4.8 with elevated metal concentrations (Salmon et al. 2008). Although the relatively good water quality of the pit lake potentially lends itself to a range of end uses, low pH and high Al concentrations still remain a challenge (Neil et al. 2009). Nevertheless, increasing state government pressure continues to encourage and support development of recreational activity infrastructure despite failure to meet Australian bathing guidelines (ANZECC/ARMCANZ 2000). This pit lake is good example of community-supported rehabilitation, but a lack of understanding of below water processes has resulted in water quality unsuited to the proposed end-use.

Silica and mineral sand mining in south-western areas of Western Australia is conducted by mechanical removal of topsoil and then extraction of the ore from below the water table by dredging. Sand mining dredge pits are usually rehabilitated as artificial wetlands for environmental values (John 1993; McCullough and Lund 2008). Small sand mining lakes in the Capel area have had low pH from acid sulfate soils (ASS) and a consequent depauperate biota. However, discharge of high pH effluent into the lakes from a nearby processing plant resulted in a transition towards more circum-neutral waters with a marked increase of periphyton, invertebrate, and waterbird biodiversity (John 1993). Circum-neutral silica sand mining lakes are still less diverse in macroinvertebrate species than natural wetlands surrounding the mine area, probably as a result of reduced food resources in these largely unrehabilitated dredge ponds (see Table 5.10; McCullough and Lund 2008). Pit lake riparian vegetation rehabilitation also appears to be more complex than originally expected, with special requirements for nutrient and water retention required for the return of representative regional wetland species (van Etten et al. 2009).

5.4.7 The Future of Pit Lakes in Australia

Mining has been an important activity for over 150 years for the Australian economy. Mining has come at a cost, with many examples of significant environmental damage. Much of this environmental damage is associated with pit lakes. Younger (2002) suggests that pit lakes are the most environmentally important legacy of mining.

Former Queensland Premier Peter Beattie compared the state's water resources to liquid gold, during the launch of the Queensland Water Plan 2005–2010 (August 2005). There are many giga litres of water in pit lakes across the country and located in typically inland, arid areas. While much of this water might be saline, there is a fraction that is potentially fresh enough to be used for some type of end-use (including industry processes or dust suppression). Doupé and Lymbery (2005), Evans et al. (2003) and McCullough and Lund (2006) have advocated and explored the potential for pit lakes to be useful additions to Australian water resources. In Western Australia, there is an ambitious plan to use the Collie pit lakes as part of an integrated plan to make more drinking water available for Perth as well as achieving enhanced environmental outcomes. The first part of this plan involves using a pit lake as a sacrificial storage for saline waters from the Collie River, which in turn reduces salt loads to the secondary salinised Wellington dam (see Bills 2006). A complex set of water transfers and desalination is then intended to provide potable water for Perth (Tingey and Sparks 2006).

It is surprising in a country that has been in drought for a number of years that so little is known of the significant water resources available in Australian pit lakes and how they might be remediated. The environmental and social impact of contaminated mine waters has not been fully quantified and the cost of remediation is unknown (Environment Australia 1997). Many pit lakes represent a substantial liability for industry, government, and communities. While the Australian community has become increasingly aware of the importance of environmental protection and conservation over the last decade, abandoned mine sites, and pit lakes in particular, continue to pose significant problems to the environment and society. Although there is extensive data available on the economics of mining across Australia, the extent of rehabilitation of former and current mine areas as well as the long-term success of such efforts remains largely unaddressed. At present, there is no standard approach for tracking this aspect, with some states collating data while others do not (Mudd 2004). There is limited monitoring of pit lakes and it is usually associated with legislative compliance rather than enhanced understanding of these systems.

Historically, little attention has been paid to mine pit lake issues at the time of mine approval, and existing Australian guideline publications for mine closure (ANZMEC/MCA 2000; CME 1999; DITR 2007) provide only limited discussion on environmental considerations related to pit lakes. Mine closure plans were initially not integrated into feasibility, approval, and run-of-mine planning, and companies did not consider closure issues until a few years before mine cessation (Johnson and Wright 2003). Rehabilitation of mine sites has become increasingly important in recent years as a part of sustainable mining practices. Government regulators have been increasingly demanding strategies for rehabilitation after mine closure prior to approving new mines, e.g. Risbey (2006). Major mining companies have already started to recognise the merit of early mine closure planning as part of demonstrating sustainable development principles (McCullough et al. 2009). In Western Australia, the pit lake issue is often addressed in approval documentation with statements such as the pit will be allowed to fill with hyper-saline groundwater to the natural hydrostatic level, until its final end use is determined.

This approach assumes that the pit lake will act as a groundwater. However, there are increasing requirements for the mining company to demonstrate the geochemical functioning of the pit lake, and extent of impacts, where there are adjacent fresh to brackish groundwater resources and/or potential impacts on the environment or cultural sites. At the same time, the number of pits that have been virtually abandoned, with no clear activity from either the company or regulator to develop an end use or even relinquishment criteria, is also increasing.

Mallet and Mark (1995) generated a useful decision pathway to identify the steps and technical data necessary to develop a suitable beneficial end use for Australian pit lakes using climate, site geology, and social setting as the primary factors of consideration. The final end use choice requires careful cost-benefit analysis, considering engineering costs, liability risks, public perception of mining company (positive or negative), economic and environmental benefits, and regulatory approval. At a number of mine sites throughout Western Australia, this process has been followed, although a major shortcoming is a lack of consideration of off-lease impact on remaining water resources (Johnson and Wright 2003). Further, there remain significant difficulties in long-term predictions of water quality. The prediction of water quality evolution in pit lakes requires an understanding of hydrogeological, limnological, and biogeochemical processes in general, as well as in the pit lake in question. Present deterministic models do not adequately account for all of these processes (Jones 1997; Oldham et al. 2009). Instead, these models generally only provide information for advancing current conceptual models and likely pit lake response to different management scenarios (McCullough et al. 2009).

Planned mine decommissioning with respect to pit lakes is still at an early stage of development in Australia, and actual realisation of these often significant water resources is even less frequently explored. Industry and regulators have now started to focus on the environmental, visual, and social impacts associated with relinquished mine leases, with consideration of pit lakes following, albeit at some distance, behind. After more than half a century of the first large flooded mining pits occurring, the question of pit lakes remain a challenge for the Australian mining industry, and for both State and Federal governments.

5.5 The Berkeley Pit Lake, Butte, Montana

Christopher H. Gammons and Nicholas J. Tucci

5.5.1 Introduction

In the spectrum of mining lakes, the Berkeley Pit lake in Butte, Montana, USA is often referred to as a worst case scenario. Although there are other lakes with lower pH or higher concentrations of one contaminant or another, the Berkeley Pit lake is singular in its combination of high acidity ($pH < 3$), high toxic metal concentrations (e.g. >500 mg/L Zn, >100 mg/L Cu), and enormous volume (1.5×10^{11} L as of Dec-2008). This pit lake has also been in existence for over 25 years, and is therefore familiar to almost everyone concerned with environmental problems related to mining. The site achieved widespread publicity in November 1995 when the carcasses of 342 migratory snow geese (*Chen caerulescens*) were recovered from the surface of the pit lake.

The limnology and geochemistry of the Berkeley Pit lake were first described by Sonderegger et al. (1987) and Davis and Ashenberg (1989), and more recently by Robins et al. (1997), Jonas (2000), Gammons et al. (2003), Pellicori et al. (2005), and Gammons and Duaime (2006). Annual updates on the water quality and rate of filling of the lake are published by the Montana Bureau of Mines and Geology (MBMG, e.g. Duaime and Metesh 2007; Duaime and Tucci 2008), and quite a bit of information of general interest is available on the internet (Pitwatch 2008). In contrast, much less has been published on the biology of the Berkeley Pit lake. Mitman (1999) gave an overview of the subject with an emphasis on protists and algae. This initial survey was followed by several theses and interagency reports dealing with bioremediation studies of the acidic and metal-rich waters (e.g. Tucci 2006). Some of these results are discussed below. There have also been recent efforts to discover new biometabolites in the acidic waters of the Berkeley Pit lake that may have unique medicinal applications (e.g. Stierle and Stierle 2005).

5.5.2 Geology and Mining History

The Butte mining district has produced over 1×10^{10} kg of Cu, as well as 2.2×10^{9}, 1.7×10^{9}, 3.9×10^{8}, 1.5×10^{8}, 2.3×10^{7} and 0.9×10^{4} kg of Zn, Mn, Pb, Mo, Ag, and Au, respectively (Duaime et al. 2004). Underground mining in Butte began in the 1870s with the discovery of Ag- and Cu-rich veins up to 10 m wide and over 1 km in length. In the next 100 years, over 75 km of vertical mine shafts and over 16,000 km of horizontal tunnels were excavated. As the high-grade veins were systematically mined out, the emphasis eventually shifted to bulk-tonnage underground and surface mining. The Berkeley open-pit mine broke ground in 1955 and was a major U.S. producer of copper until its closure in 1982. Mining in Butte continues to the present day at the Continental open pit, located 2 km to the east of the Berkeley deposit (Czehura 2006, Fig. 5.38).

The main host rock to mineralization in the Butte district is the Butte quartz monzonite (BQM), a Cretaceous-aged granitic pluton. A large but relatively low-grade porphyry Cu-Mo deposit was later overprinted by a younger, shallower set of large and exceptionally rich veins, referred to as the Main Stage (Meyer et al. 1968). The Main Stage veins were zoned, with a Cu-rich Central Zone centered more or less on the present-day Berkeley Pit, grading concentrically outward into a Cu–Zn-rich Intermediate Zone, and outward still to the Ag-Pb–Zn-Mn-rich Peripheral and Outer Zones (Fig. 5.38). Because of its intense hydrothermal alteration and high pyrite content ($\approx 5\%$), wallrock in the Central Zone has a high acid-generating potential

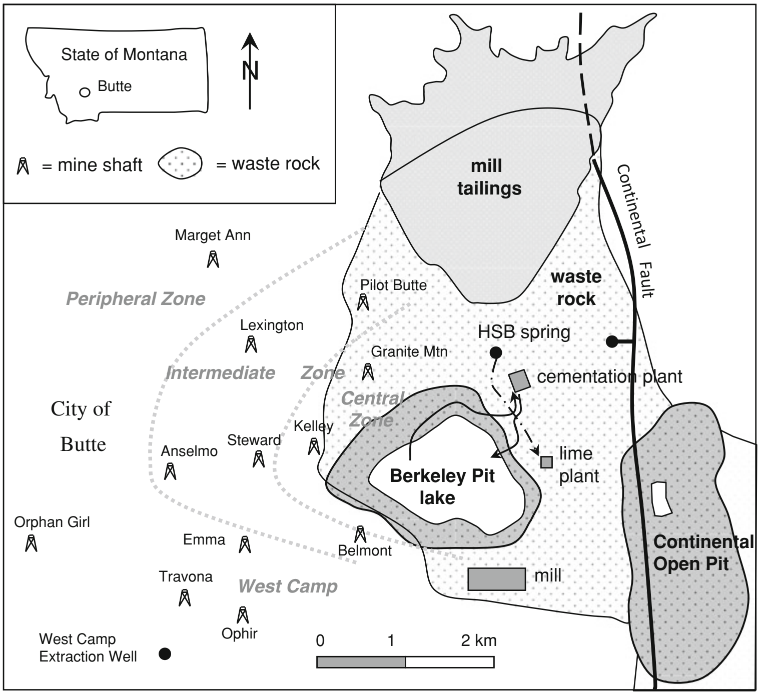


Fig. 5.38 Map showing major mining features in the vicinity of the Berkeley Pit, circa 2008. At the present time, the Horseshoe Bend (*HSB*) springs are treated with lime and the water is reused in the mill. The copper recovery circuit (*arrows*) pumps water from the monimolimnion of the Berkeley Pit lake to the cementation plant: the Cu-depleted water then returns to the pit lake. The gray dotted region approximates the extent of surface disturbance from past and present mining operations

($\approx$150 kg $CaCO_3$/ton) and essentially zero acid-neutralizing potential (Newbrough and Gammons 2002). Interestingly, the majority of the flooded underground mine shafts surrounding the Berkeley Pit currently contain water that is near neutral or only mildly acidic with relatively low metal concentrations (Metesh 2004; Gammons et al. 2006a). Some mine waters in the outer portions of the district contain elevated concentrations of H_2S, formed by bacterial sulfate reduction (Gammons et al. 2010; Roesler et al. 2007). Thus, zonation in primary ore and alteration mineralogy has resulted in district-wide trends in mine-water chemistry (Metesh 2004; Gammons et al. 2010). Long-term trends in the water quality of the flooded underground workings have been noted and are attributed to the complex history of mine flooding (Metesh 2004, 2006).

5.5.2.1 History of Mine Flooding

On April 23, 1982, mining in the Berkeley Pit ceased and the dewatering pumps in the nearby Kelley Mine shaft (Fig. 5.38) were turned off. Roughly 18 months later,

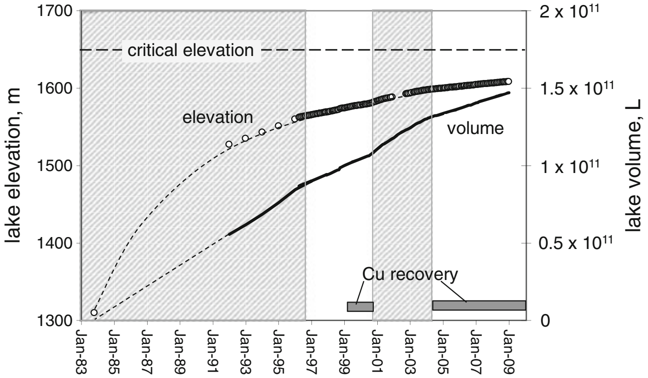


Fig. 5.39 Changes in the volume and surface elevation of the Berkeley Pit lake with time (MBMG data). Dashed lines are approximations due to a scarcity of data. The shaded bars show time periods when Horseshoe Bend (*HSB*) was diverted into the lake

the water level in the underground mine pool reached the elevation of the base of the open pit and a lake began to form (Metesh 2006). Fig. 5.39 summarizes changes in the pit-lake volume and surface elevation from 1983 to the present. Between 1982 and 1996, the lake filled at an average rate of roughly 20 million L d^{-1}, mainly from a combination of groundwater from the adjacent flooded underground mine complex and diverted surface water. The latter included several large volume seeps and springs discharging at the base of the tailings pond and adjacent waste rock piles, collectively referred to as Horseshoe Bend (HSB). Beginning in April 1996, the HSB flow was diverted away from the pit and pumped to the tailings impoundment for lime treatment and disposal. This decreased the rate of filling of the pit lake to roughly 12 million L d^{-1}. In June 2000, mining operations were temporarily suspended, and HSB was again allowed to dump into the pit lake. This continued until November 2003, at which time a modern lime-treatment plant was brought on line to treat HSB and recycle the water for the active mining operation. Since then, alkaline sludge from the HSB treatment plant has been discarded into the Berkeley Pit at a rate of approximately 1 million L d^{-1} (Duaime and Metesh 2007). The volume of this sludge is small compared to the total volume of the lake, and therefore has had little impact on water quality. If sludge disposal were to continue for a long period of time, one would expect a measurable increase in pH and a decrease in concentration of certain metals (such as dissolved ferric iron). However, to date, no such changes have been observed. A much more dramatic factor influencing the limnology and geochemistry of the pit lake has been the ongoing Cu-recovery project (discussed below; see also Duaime and Tucci 2008).

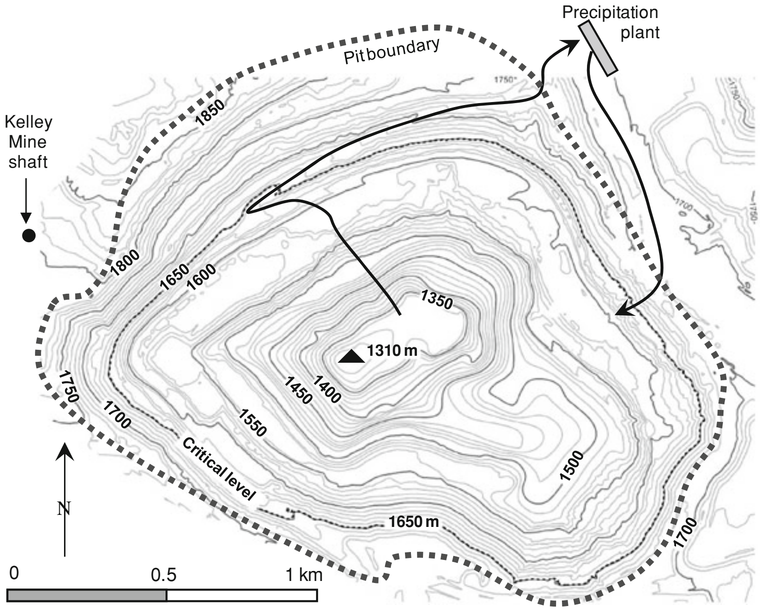


Fig. 5.40 Morphometry of the Berkeley Pit, based on mine records circa 1982. The critical level (1,650 m) is shown in bold, as is the outline of the open pit. As of December 2008, the elevation of the lake surface was approximately 1,608 m. Arrows denote the copper recovery circuit

5.5.3 *Limnology*

5.5.3.1 Morphometry and Climate

The Berkeley Pit lake is presently a terminal lake with no surface or subsurface water outputs. The lake is approximately 1.8 km (E–W) by 1.2 km (N–S) in size at its present surface elevation ($\approx$1,620 m above mean sea level), and partially fills a larger void left behind by open pit mining (Fig. 5.40). Based on the configuration of the mine when it closed in 1982, the maximum water depth should now be over 300 m. However, an unknown mass of sediment from slope failures and chemical precipitation has partially filled in the lake, so the elevation of the current lake bottom is not known with confidence. Access to the lake is provided by a haul road on the north highwall, which is also the location of the pipeline used in the copper recovery project (bold arrow in Fig. 5.40). A boat moored on the north shore is used to collect water samples, usually from the deepest portion of the lake.

Precipitation in Butte averages 30 cm year^{-1}, about half as snow. Annual evaporation exceeds precipitation by a factor of roughly 2. Based on trends in stable O and H isotopes, Gammons et al. (2006b) estimated that water in the epilimnion of the lake was 15–25% evaporated in October 2003, whereas the hypolimnion was about 10% evaporated. Thus, the lake has experienced a

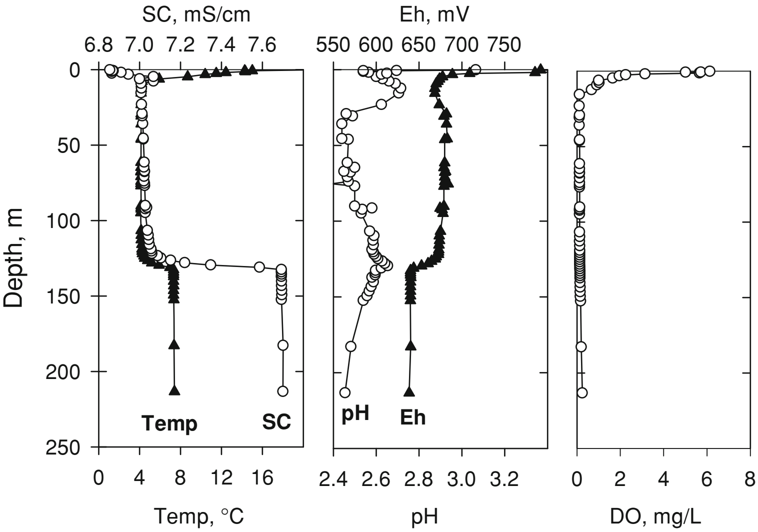


Fig. 5.41 Vertical pit-lake profiles in specific conductance (*SC*), temperature (*Temp*), redox potential (*Eh*), pH, and dissolved oxygen (*DO*) collected on June 20, 2008 (MBMG files)

moderate amount of evapoconcentration of solutes in its 25 year history. The surface of the lake froze in the winter of 2009–2010, but prior to this time had not frozen since 2001.

5.5.3.2 Vertical Stratification

Vertical profiles in water temperature and specific conductance (SC) taken on June 20, 2008 (Fig. 5.41) show a classic meromictic pattern with a near-surface, relatively warm epilimnion (0–5 m depth), a cold hypolimnion (10–130 m depth), and a more saline monimolimnion (130 m to the bottom of the lake). The epilimnion and hypolimnion mix seasonally. Although the temperature of the monimolimnion is slightly warmer (7–8°C) than the overlying water (4–5°C), the difference in salinity prevents vertical mixing. The somewhat elevated temperature of the deep water is explained by the influx of deep groundwater that has an average year-round temperature >10°C, and also to a higher-than-normal local geothermal gradient caused by elevated concentrations of radionuclides in the BQM (Gammons et al. 2010). Dissolved oxygen and Eh values decrease rapidly with depth in the epilimnion (Fig. 5.41), and the lake contains negligible concentrations of DO below a depth of 10 m. The redox potential (Eh) of the lake is controlled by dissolved Fe^{2+}/Fe^{3+} (see below). The pH of the lake is strongly buffered by reactions involving dissolved Fe and SO_4^{2-}/HSO_4^{-}, and shows no clear structure with depth, other than a slight increase towards the lake surface.

During its history, the Berkeley Pit lake has shifted several times between being holomictic (seasonally mixing) vs. meromictic (permanently stratified). Jonas

(2000) and Madison et al. (2003) presented evidence that the lake experienced complete seasonal turnover between 1997 and 2000. During this time there were no external diversions of surface water into the lake, which would have built up a low-density shallow layer. On Sept. 29, 1998, an estimated 1.0×10^6 m^3 of poorly indurated alluvium and weathered bedrock slid into the lake and raised the elevation of the water surface 0.76 m. A seiche wave caused by the slide threw the MBMG research boat onto its side on a mine bench $\approx$12 m above the lake surface. If it wasn't already holomictic, such a catastrophic event would probably have mixed the entire lake. Beginning in June 2000 and continuing until November 2003, surface water from the Horseshoe Bend area was discharged to the Berkeley Pit lake. Although HSB water is acidic with elevated concentrations of metals, it has a lower SC than the Berkeley Pit lake, and therefore pooled near the lake surface, causing the pit lake to become meromictic (Pellicori et al. 2005). The lower-density shallow layer gradually increased in thickness to a maximum of $\approx$15 m in the Fall of 2003, at which time a new lime-treatment plant became operational and Horseshoe Bend water was no longer discarded to the pit lake. Most recently, a large scale, multiple year pumping operation (discussed below) has resulted in the lake again returning to holomictic conditions.

5.5.3.3 Copper Recovery

Between August 1998 and June 2000, and again from January 2004 to the present day, a large-scale copper recovery project has taken place in the Berkeley Pit lake. Deep water from the monimolimnion is pumped to the surface and is passed over scrap iron to precipitate dissolved copper in its elemental form. The overall process is referred to as cementation, and can be written as follows:

$$\mathrm{Cu^{2+} + Fe(s) \rightarrow Fe^{2+} + Cu(s)} \tag{5.8}$$

The Cu-depleted and Fe-enriched water is then channeled back to the surface of the pit lake by gravity. Because the rate of pumping is very high (averaging roughly 50 million L d^{-1}), this project has had a profound impact on the vertical profile of the lake. The main effect has been to steadily lower the elevation of the chemocline at the mixolimnion/monimolimnion interface (Fig. 5.42). The chemocline completely disappeared at some time during 2009, and sampling by the MBMG in the spring of 2010 indicates that the lake is now vertically mixed.

5.5.4 Geochemistry

Table 5.13 gives representative chemical analyses of Berkeley Pit water collected in November 2007 from the surface, 10 m depth, and 210 m depth. The dominant solutes are $SO_4 > Fe \geq Zn > Mg > Ca > Al \geq Mn > Cu \geq SiO_2$. A number of

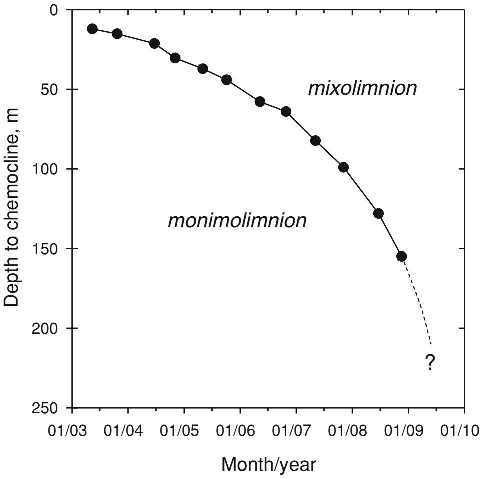


Fig. 5.42 Increase in depth of the chemocline with time during the period 2002–2008. Each data point corresponds to the depth of maximum change in SC as determined by vertical datasonde profiles

other metals are present at concentrations exceeding 1 mg/L, including Cd, Co, Ni, Sr, U, and the rare earth elements (Gammons et al. 2003). Total acidity values in Table 5.13 were calculated using two different equations:

$$\text{Acidity} - 1 = 3\{\text{Al}\} + 2\left\{\text{Fe}^{\text{II}}\right\} + 3\left\{\text{Fe}^{\text{III}}\right\} + \left\{\text{HSO}_4^-\right\} + \{\text{H}^+\} \qquad (5.9)$$

$$\text{Acidity} - 2 = \text{Acidity} - 1 + 2\{\text{Cu}\} + 2\{\text{Mn}\} + 2\{\text{Zn}\} \qquad (5.10)$$

where the brackets denote molal (*m*) concentrations. Acidity values range from 0.061 to 0.079 *m* using Eq. (5.9), and from 0.091 to 0.112 *m* using Eq. (5.10). In general, dissolved metals are a much greater source of acidity in the pit-lake waters than H^+ or HSO_4^-, and also pose a greater challenge in terms of treatment.

Jonas (2000) reported DIC concentrations of $\approx$2 to $\approx$25 mg/L in the shallow and deep pit-lake waters, respectively, in 1997–1998. Given the low pH values, essentially all of this DIC must have been present as dissolved CO_2. The upper range of DIC values measured by Jonas (2000) equates to a CO_2 partial pressure of $\approx$0.04 atm, which is more than 100 times higher than present atmospheric levels. The elevated P_{CO2} values in the deep lake may be a result of the influx of higher pH groundwater with elevated alkalinity entering the pit from the surrounding underground mine workings (Gammons et al. 2006a). It is also possible that some CO_2 was contributed by bacterial oxidation of organic carbon, although evidence presented below suggests that the activity of heterotrophic bacteria in the deep pit lake and underlying sediment pile is low.

Based on limited data, it appears that primary production by photoautotrophs in the Berkeley Pit lake is N-limited. Jonas (2000) reported dissolved P concentrations of 0.5–0.8 mg/L, with a slight decrease towards the surface of the lake. Recent samples collected by MBMG have yielded lower P concentrations, around 0.1 mg/L (see below). Concentrations of nitrate in the lake are below detection by conventional ion chromatography. In contrast, concentrations of nitrate in groundwater wells in Butte that are completed in granitic bedrock but are located away from the mining complex are elevated, averaging 2.6 mg/L as N (Lafave 2008; n = 89). The scarcity of nitrate in the pit lake suggests denitrification, possibly coupled to oxidation of pyrite (Postma et al. 1991), a mineral that is abundant on the submerged pit walls. Cameron et al. (2006) measured concentrations of dissolved organic carbon (DOC) on the order of 2–4 mg/L in the pit lake, concentrations that were similar to the influent surface and groundwaters.

5.5.4.1 Fe(II)/Fe(III) Chemistry

The Berkeley Pit lake has a redox chemistry that is dominated by iron. Field Eh measurements typically agree within ±50 mV with calculated Eh values based on the Fe(II)/Fe(III) couple (Table 5.13, see also Pellicori et al. 2005). Selected profiles showing changes in Fe(II)/Fe(III) speciation with depth are given in Fig. 5.43. All of the data sets show a predominance of Fe(II) over Fe(III) in the deep lake and a cross-over point at shallower depths where Fe(III) exceeds Fe(II). In 1999–2000, when the lake was presumably holomictic (Madison et al. 2003), the cross-over points occurred at relatively shallow depth (≈ 20 m). Between 2004 and 2007, when the lake was meromictic, the depth of the cross-over point increased with time as the chemocline was steadily drawn down from copper recovery (Fig. 5.43).

The persistence of high concentrations of dissolved Fe(III) throughout the entire water column led previous workers (Gammons and Duaime 2006; Madison et al. 2003; Pellicori et al. 2005) to speculate that subaqueous oxidation of pyrite could be an important process in the Berkeley Pit lake. As shown in the following reaction, each mole of pyrite oxidized by Fe(III) releases 16 mol of H^+:

$$FeS_2(s) + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (5.11)$$

However, to sustain this reaction, a large supply of Fe^{3+} is needed. Gammons and Duaime (2006) noted a long term trend of lower concentrations of dissolved Fe(III) in the monimolimnion between 2000 and 2005, and argued that this trend was evidence of subaqueous pyrite oxidation. More recent data are less supportive of this hypothesis, as dissolved Fe(III) concentrations in Nov-2007 were similar to those measured in March 2000 (Fig. 5.43). Thus, although subaqueous oxidation of pyrite by Fe^{3+} must occur, it probably is not a dominant process controlling pH in the deep pit lake.

Influence of Copper Recovery on Dissolved Metal and P Concentrations

The copper recovery project has resulted in a drastic decrease in the concentrations of Cu and Fe in the mixolimnion of the lake (Fig. 5.44). Loss of Cu occurs *ex situ*,

Table 5.13 Representative chemical analyses of Berkeley pit-lake water collected on 11/06/07

Depth (m)	pH[a]	Temp (°C)	SC (mS/cm)	Eh[a] (mV)	Eh[b] (mV)	Acidity[c] molal	Acidity[d] molal	Speciated charge balance[e] (%)
1	2.75	6.1	7.34	648	680	0.062	0.093	−4.4
30	2.78	5.8	7.35	646	679	0.061	0.091	−3.3
210	2.53	7.2	8.16	604	642	0.079	0.112	−5.7

	Ca	Mg	Na	K	Al	As	Be	B	Cd	Ce	Co	Cu
1	475	534	74	9.6	275	0.135	0.13	0.118	2.26	2.17	1.84	79.0
30	457	516	73	9.1	266	0.133	0.10	0.077	2.23	1.62	1.79	76.5
210	442	515	74	7.6	268	0.097	0.10	0.069	2.27	1.53	2.22	153

	Fe^{II}	Fe^{III}	Mn	Ni	Pb	SiO_2	Sr	U	Zn	SO_4	Cl	F
1	181	383	261	2.40	0.057	80.9	1.55	1.97	627	8,170	<50	30
30	193	386	255	1.76	0.266	81.5	1.49	1.31	610	7,880	<50	29
210	693	314	248	1.63	0.032	76.6	1.43	1.45	638	9,090	<50	30

[a] measured in situ with a datasonde; [b] calculated by Visual Minteq; [c] calculated using Eq. (5.9); [d] calculated using Eq. (5.10); [e] calculated by Visual Minteq, negative sign denotes an excess of anions

All concentrations are mg/L unless otherwise specified. All solute concentration data are from GWIC (2008) except Fe speciation (MBMG unpublished files)

by cementation. Because the cementation process adds Fe^{2+} to the water (reaction 5.8), removal of Fe must occur in the lake itself, i.e. by oxidation of Fe^{2+} and subsequent precipitation of Fe as amorphous ferric hydroxide or crystalline Fe(III) minerals. As shown by the following reactions, precipitation of Fe(III) minerals, such as ferrihydrite, schwertmannite, or jarosite, releases protons:

$$5Fe^{2+} + {}^{19}\!/_{2}H_2O + {}^{5}\!/_{4}O_2 = Fe_5O_3(OH)_9(s) + 10H^+ \tag{5.12}$$

$$8Fe^{2+} + 10H_2O + SO_4^{2-} + 2O_2 = Fe_8O_8(OH)_6SO_4(s) + 14H^+ \tag{5.13}$$

$$3Fe^{2+} + K^+ + {}^{9}\!/_{2}H_2O + 2SO_4^{2-} + {}^{3}\!/_{3}O_2 = KFe_3(OH)_6(SO_4)_2(s) + 3H^+ \tag{5.14}$$

In terms of acidity, the release of protons is offset by consumption of Fe^{2+} on the left so that the total acidity of the water is unchanged during precipitation of ferrihydrite, but decreases during precipitation of schwertmannite or K-jarosite. Previous field and laboratory studies have shown that schwertmannite rapidly forms during oxidation of Berkeley pit water (Gammons et al. 2003), whereas jarosite is more abundant in the pit-lake sediment (Newbrough and Gammons 2002; Twidwell et al. 2006).

Interestingly, the precipitation and gravitational settling of secondary Fe(III) minerals—an indirect result of the copper recovery project—has resulted in a drastic decrease in the concentration of dissolved As in the pit lake (Fig. 5.44). In 2002, prior to the onset of the Cu recovery project, concentrations of dissolved As in the lake were greater than 250 μg/L at all depths, with values exceeding

750 μg/L in the monimolimnion. After 5 years of cementation, As concentrations throughout the entire lake have dropped to less than 100 μg/L (Duaime and Tucci 2008). The major sink for As is assumed to be adsorption onto freshly-formed Fe(III) solids. Based on the measured Eh values of Berkeley pit water, all dissolved arsenic should be in the oxidized (+5) valence state, most likely as the species $H_2AsO_4^-$. Fig. 5.44 also shows a similar drop in dissolved P concentrations, although in this case there are fewer data owing to analytical difficulties. P most likely exists in the Berkeley Pit as the inorganic pentavalent species $H_2PO_4^-$, which has the same stoichiometry as $H_2AsO_4^-$. Numerous studies have documented the affinity for both dissolved arsenate and dissolved phosphate to adsorb strongly onto secondary ferric oxy-hydroxide minerals in acidic waters. It is not known whether the drop in P concentrations has had an impact on primary production in the pit lake.

5.5.5 *Biology*

5.5.5.1 Microbiology of the Pit Lake

Few data exist on the microbiology of the Berkeley Pit lake. Mitman (1999) isolated six species of algae from shallow water, including *Chlamydomonas acidophila, Chlorella ellipsoidea, Chlorella vulgaris, Chromulina freiburgensis, Euglena mutabilis, and Pinnularia obscura*. However, cell densities were extremely low, being near the lower limit of quantification. Bacterial concentrations in the epilimnion were approximately 200,000 cells mL^{-1} (80% live, 20% dead), values corroborated by the more recent study of Tucci (2006). To date, only the chemolithotrophic bacterium *Acidithiobacillus ferrooxidans* has been isolated from the Berkeley Pit. Mitman (1999) also found 16 species of heterotrophic protists, most of which were amoebae. In 2001, a graduate student photographed a water boatman (*Corixidae*) skimming across the surface, most likely grazing on plankton, which was highly publicized in local newspapers. Nonetheless, the biological productivity of the lake appears to be very low. There are several possible reasons for this, including: (1) low pH; (2) high concentration of toxic metals; (3) low levels of nutrients and bioavailable C; and (4) poor light penetration. The first two points are unlikely to be the main factors, considering that many forms of algae are well-adapted to acidic and metal-rich conditions (Das et al. 2009). On the other hand, low (i.e. oligotrophic) nutrient levels are probably a major impediment to primary production and subsequent heterotrophic production in the Berkeley Pit lake. As discussed above, the lake is impoverished in nitrate and DOC, and concentrations of dissolved P have dropped sharply in the past decade. During nutrient enrichment experiments, Dakel (2001) found the system to be N-limited; algal growth was greatly enhanced (from undetectable levels in surface water to 10^8 cells mL^{-1}) by addition of nitrate.

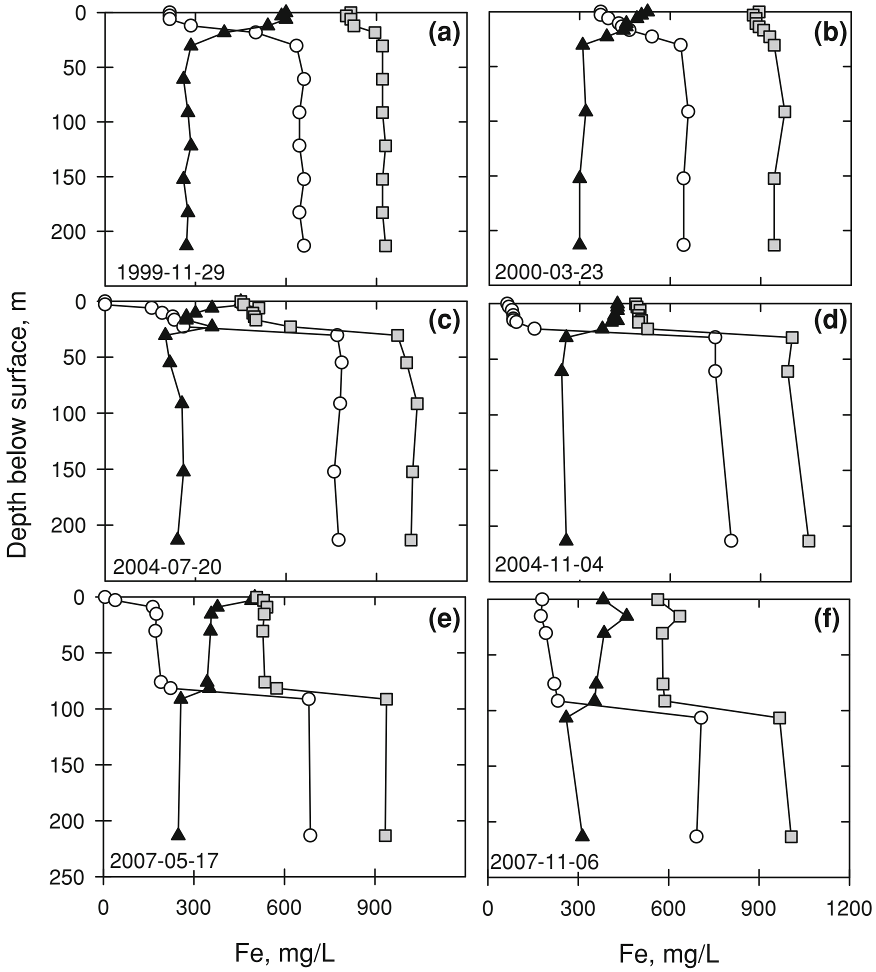


Fig. 5.43 Vertical profiles in redox speciation of dissolved Fe. Black triangles: Fe(II); open circles: Fe(III); gray squares: Fe(total). Data in **a** and **b** were taken from Jonas (2000). The rest of the data come from MBMG files (e.g. Duaime and Tucci 2008)

Another serious limitation on primary productivity in the Berkeley Pit is light penetration. Tucci (2006) found that visible light dropped rapidly in the top 1.5 m of the water column and calculated an average light extinction coefficient of 3.42 m^{-1}. Extinction coefficients in natural waters range from 0.05 m^{-1} for mountain lakes to 6.9 m^{-1} for highly turbid waters (Thomann and Mueller 1987). Although some of the light attenuation in the pit lake is due to suspended sediment (most of which is inorganic), the biggest factor is probably the very high dissolved Fe(III) concentrations in the water (>300 mg/L, Fig. 5.43). Dissolved Fe(III) absorbs light in both the UV and visible spectra, causing acidic, Fe-rich lakes to appear black when viewed

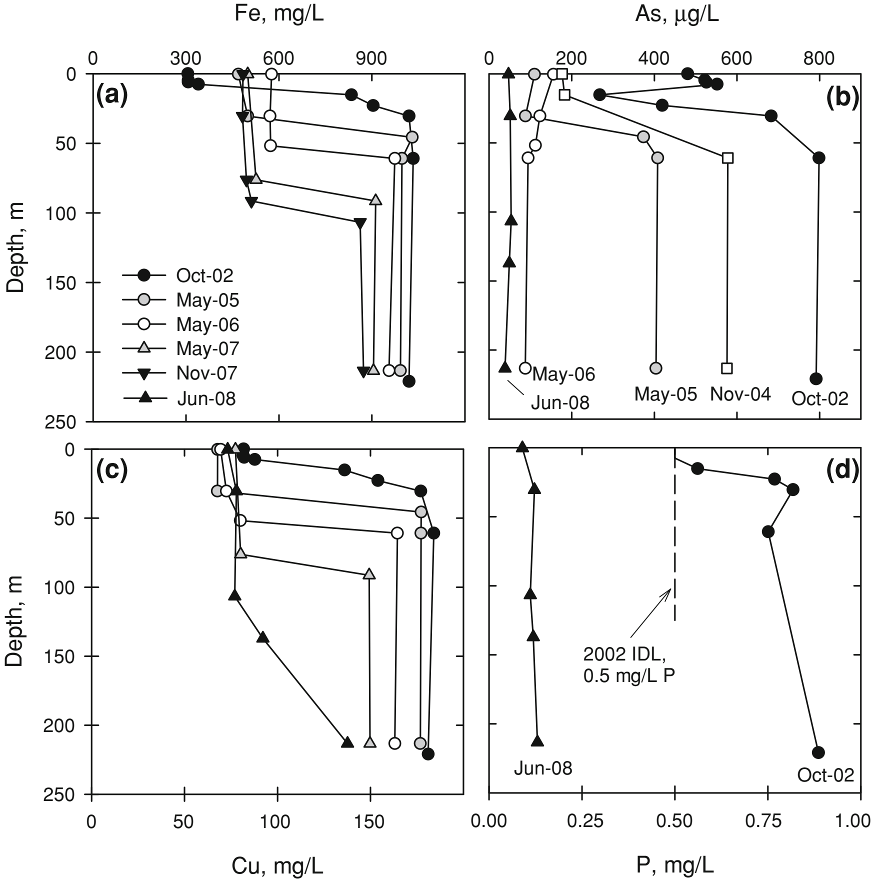


Fig. 5.44 Changes in dissolved Cu, Fe, As, and P concentrations as a function of depth between 2002 and 2008. All data come from MBMG and are summarized in GWIC (2008). *IDL*: Instrument Detection Limit

from above. For comparison, Kamjunke et al. (2004) showed a 90% decrease in light intensity in the top 3 m of Lake 111 (pH 2.6) in Germany, and attributed most of this light attenuation to the presence of aqueous Fe(III). Significantly, the concentration of Fe(III) in the shallow Berkeley Pit lake is about twice that of Lake 111, while the depth of light penetration is about half that of the German lake.

Ambient conditions in the Berkeley Pit lake do not seem to be conducive to host populations of iron-reducing (IRB) or sulfate-reducing bacteria (SRB). Phillip (1999) performed an extensive evaluation aimed at culturing IRBs and SRBs from Berkeley Pit sediment samples, and all attempts were unsuccessful. Furthermore, an examination of the mineralogy and aqueous geochemistry of the top meter of sediment at the bottom of the Berkeley Pit (Twidwell et al. 2006) showed no obvious zones of Fe- or sulfate-reduction based on color change or mineralogy.

The sediment was a mixture of detrital minerals from weathering of the pit walls and secondary chemical precipitates dominated by gypsum, schwertmannite, and K-jarosite. The geochemistry of the pore waters was similar to that of the overlying lake water, with slightly lower Eh values and higher dissolved Fe(II)/Fe(III) ratios. Significantly, Cameron et al. (2006) measured elevated concentrations of total organic carbon in the solid fraction of the sediment core (0.2–0.33 wt%), as well as extremely high DOC in the sediment-pore water (50–380 mg/L). The persistence of dissolved sulfate and Fe(III) minerals such as K-jarosite in the presence of an abundance of organic carbon implies that the activity of IRB and SRB must be low, a conclusion supported by the study of Phillip (1999). Recent work (Koschorreck et al. 2003) has documented microbial reduction of Fe and S in sediment at the bottom of a volcanically-acidified lake in Argentina with a similar pH to the Berkeley Pit lake. However, water in the Berkeley Pit has orders of magnitude higher concentrations of dissolved Cu and Zn (>100 mg/L) than the Patagonian lake (<1 mg/L). Unlike algae, which can survive at extreme levels of acidity and heavy metals, heterotrophic microorganisms such as S-reducing bacteria are more sensitive to toxic metals (e.g. Poulson et al. 1997).

5.5.5.2 Bioremediation Studies

The first serious effort to use bioremediation to treat Berkeley Pit water was conducted in 1998–1999 by the Biomet Mining Corporation (Vancouver, B.C.). Their patented concept—termed the Biosulfide process—involved using partially-combusted diesel fuel as a source of H_2 gas, which was fed to a bioreactor containing SRB. The H_2S produced could then be mixed with Berkeley Pit water with pH adjustment to produce separate CuS and ZnS concentrates. Additional chemical treatment would be afforded by the alkalinity produced by the SRB reaction. Bench-scale experiments (e.g. Eleeas 2000) were followed by an on-site, pilot-scale demonstration of the technology in 1999. However, the project was discontinued after $\approx$4 months of operation due to problems with the reliability of the H_2 source and the slow rate of SRB growth in the reactor. Details of the Biosulfide project are proprietary, and have not been published.

In the early 2000s, the research team of Dr. Grant Mitman at Montana Tech conducted a number of bench-top studies using nutrification to promote growth of algae and bacteria. The hypothesis was that alkalinity-generating reactions, as well as passive adsorption onto cell walls and/or active metabolic uptake, would remove metals and raise the pH of the Berkeley Pit water (Bartkowiak 2002; Bocioaga 2003; Dakel 2001). This research culminated with an experiment using limnocorrals to examine the effects of in situ artificial nutrification (Tucci 2006). Three sets of three replicate corrals (1 m diameter × 3 m depth) were set up to examine the effects of low nutrient addition (5 mg/L NO_3 + 2 mg/L PO_4), high nutrient addition (10 mg/L NO_3 + 4 mg/L PO_4), and a control. Although the field experiment demonstrated enhanced growth of algae and bacteria in the nutrified systems (e.g. algal cell densities increased from below detect to $\approx 10^6$ cells mL^{-1}; bacteria concentrations increased from $\approx 10^5$ cells mL^{-1} to $\approx 10^7$ cells mL^{-1}), the study failed to show much improvement in water quality. There were no significant changes in the pH, Eh, or concentrations of most dissolved metals of concern (e.g. Al, Cd, Cu, Mn, Ni, Zn). Concentrations of dissolved Fe and As were lower in the nutrified corrals, presumably due to algal production of dissolved oxygen, which enhanced the rate of precipitation of hydrous oxides rich in Fe and As (Tucci 2006).

5.5.6 Looking to the Future

The U.S. Environmental Protection Agency (EPA 1994) has mandated that the water level in the Berkeley Pit lake and surrounding flooded underground mine workings cannot be allowed to reach a surface elevation of 5,410 ft (1649 m) above sea level—the so-called "critical level" (Fig. 5.39). Before this occurs, a pump-and-treat operation will be initiated and continued in perpetuity to maintain the surface- and ground-water elevations in the mining complex below the critical level. The treatment plant is already built, and is currently being used at a reduced capacity to neutralize acidity from the Horseshoe Bend springs so that the mine can use this source of water in their milling operation. For Berkeley Pit lake treatment, the plant will use a two-stage high-density sludge process, the details of which are still being optimized. Treated water will be discharged to the local stream, Silver Bow Creek, a tributary to the upper Clark Fork River. At the current level of flooding, it appears likely that the critical level will not be reached until after 2020 (Fig. 5.39, see also Duaime and Tucci 2008), which means that it may still be 10 years or more before large-scale treatment of Berkeley Pit water begins.

Acknowledgements The authors thank Dick Berg, Mike Kerschen, James Jonas, James Madison, John Metesh, Damon Pellicori, and Larry Twidwell for past and present collaboration on Berkeley Pit research. We are also especially grateful to Pat Kennelly for creating the topographic base map in Fig. 5.40.

5.6 Mining Lake 111: A German Reference Lignite Pit Lake

Matthias Koschorreck

5.6.1 Introduction

Mining Lake 111 (ML 111) has been a model site for pit lake research in Germany for more than a decade. As a result, the lake is probably the most intensively studied pit lake in the world; more than 65 papers related to the lake have been published.

ML111 is located in the former Grube Agnes of the Koyne-Plessa lignite mining district of Lusatia in Germany (51°29′ north, 13°38′ east), where lignite was mined from 1929 until 1958 (see also case study 5.1). Subsequently, from then

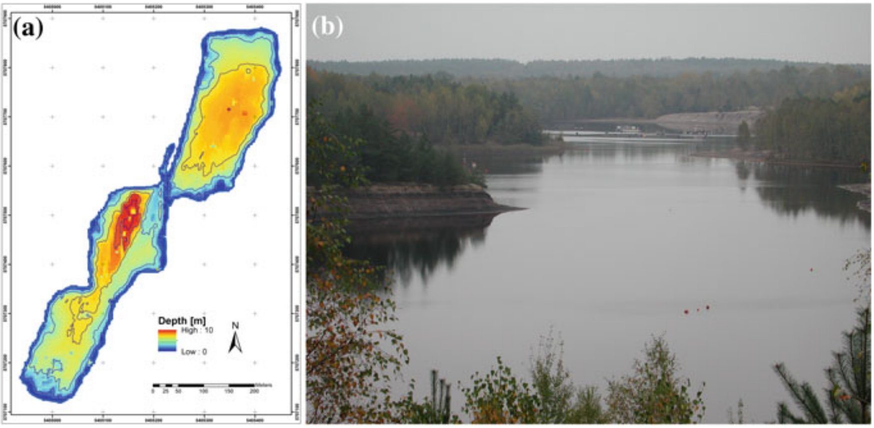


Fig. 5.45 Bathymetric map of ML111 (after Büttner et al. 1998) and photo looking north

until 1969, the open pit filled with groundwater (Nixdorf et al. 2001). The resulting lake has a surface area of 107,000 m^2 and a mean and maximum depth of 4.5 m and 10.5 m, respectively (Büttner et al. 1998). The lake is divided into 2 main basins, which are separated by a shallow connection (Fig. 5.45). The bottom is relatively flat, 6.5 m deep, with the exception of a “hole” of about 4,000 m^2 in the middle where the deepest point is located. The lake is surrounded by undisturbed sediments of Quaternary sand, clay, and Tertiary lignite on the western shore and mine dumps on the southern and eastern side (Bozau and Strauch 2002).

The lake is exclusively fed by groundwater (about 24,000 m^3 $year^{-1}$), of which much is strongly acidic, with a pH of 4 and up to about 1 g L^{-1} iron (Bozau and Strauch 2002). The annual acidity load of 3.6 eq m^{-2} $year^{-1}$ (Geller et al. 2009) is the reason why the lake has been strongly acidic since its formation. There is no surface outflow but there is groundwater outflow of about 16,000 m^3 yr^{-1}, mainly along the northern shore. The residence time of the water in the lake is about 5 years (Knöller and Strauch 2002). Since 1999, the water level has been at 95 ± 0.25 m above sea level, with the highest water levels in April and the lowest water levels observed during winter.

5.6.2 Water Quality

Stratification of the lake is governed by a temperature-dependent density gradient. Below 6.7 m, the chemical composition of the water contributes to the stratification (Karakas et al. 2003). With the exception of the deepest point, the lake is completely mixed in winter (Fig. 5.46a). The lake is usually ice-covered from January until March. In years with an ice cover, an anoxic monimolimnion of about 4,800 m^3 (1% of the lake volume) persists at the deepest point.

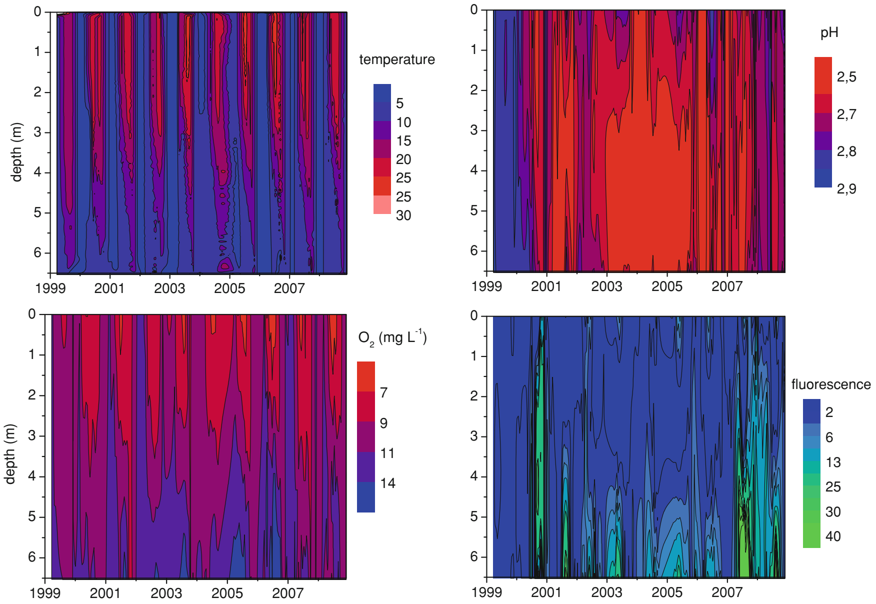


Fig. 5.46 Time-depth diagram of temperature, pH, O_2, and chlorophyll (measured as relative fluorescence signal) in the north basin in ML111, as measured by a multi-parameter probe during 9 years

As is typical for acidic mine pit lakes, the water has a low pH and high concentrations of Ca^{2+}, Mg^{2+}, SO_4^{2-}, Fe, and Al (Table 5.14). The pH is buffered at 2.6 by hydrogen sulfate (HSO_4^-), Fe, Al, and an ion exchange buffer including mineral formation (Totsche et al. 2003). The concentrations of Mn, Zn, and Ni are elevated but do not represent a serious problem for the lake's biogeochemistry.

The nitrate concentrations in the water are very low. Inorganic nitrogen is dominated by ammonium, most probably because nitrification is inhibited by the low pH. According to the phosphorus concentration, the lake can be classified as oligotrophic.

The water composition does not show pronounced seasonal fluctuations and there has been no long term change in water composition since our first investigations in 1999. The lake is obviously in chemical equilibrium with respect to acidity inflow and sedimentation. Occasionally, elevated concentrations of ferrous iron have been observed (Fig. 5.47), which can be explained by photo-reduction of dissolved ferric iron and diffusive supply from the sediment (Herzsprung et al. 1998). Concentrations of ferrous iron, sulfate, and other solutes are elevated in the small monimolimnion.

The high iron concentration also influences light penetration. Due to strong attenuation of short wavelengths, the light spectrum is red shifted and dominated by wavelengths from 600 to 700 nm (Gerloff-Elias et al. 2005). The mean depth of the euphotic zone is 5.8 m (K_d 0.8 m^{-1}; Beulker 2004).

Table 5.14 Mean chemical characteristic values of samples taken from ML111, 1999–2008; numbers in brackets show number of samples

Parameter	Value	Parameter	Value
pH	2.62 (335)	Cu	6.4^{a} μg L^{-1} (177)
$KB_{8.2}$	17 ± 2 mmol L^{-1} (233)	Ni	200^{a} (228) μg L^{-1}
EC (25°)	$2{,}500^{b}$ μS cm^{-1}	Total N	3.5^{b} mg L^{-1}
Ca^{2+}	219 ± 33 mg L^{-1}(166)	NH_4^+-N	2.8 ± 0.5 mg L^{-1} (271)
Mg^{2+}	30^{a} mg L^{-1} (183)	NO_3^--N	0.3 ± 0.1 mg L^{-1} (261)
Na^+	7 ± 1 mg L^{-1} (245)	Total P	0.009^{a} mg L^{-1} (186)
Fe	171 ± 70 mg L^{-1} (263)	SRP (PO_4^{3-} -P)	0.008 ± 0.005 mg L^{-1} (326)
Al	38 ± 5 mg L^{-1} (238)	Si	17.9 mg L^{-1} (287)
Mn	3.1 ± 0.4 mg L^{-1} (257)	TIC	6.1 ± 9.2 mg L^{-1} (143)
Zn	1.08^{a} mg L^{-1} (228)	TOC	2.1 ± 1.8 mg L^{-1} (189)

[a] data from Friese (2005); [b] data from Geller et al. (2009), EC: conductivity corrected after Karakas et al. (2003)

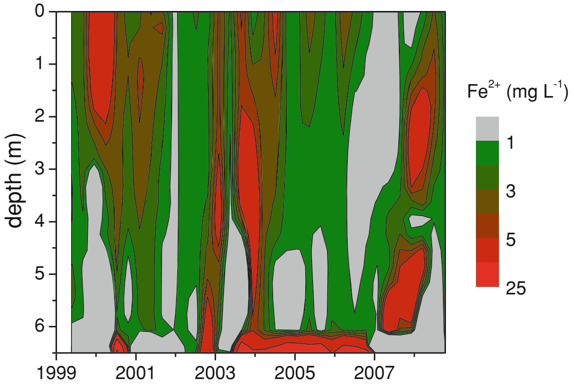


Fig. 5.47 Time-depth diagram of Fe^{2+} concentrations in ML111 during 9 years (modified after Büttner et al. 1998)

5.6.3 Biogeochemistry: Sediment, Element Cycles, Microbiology

As in most other acidic pit lakes, the biogeochemistry of ML111 is dominated by iron (Fig. 5.48). The sediment contains 18 ± 8.3 wt% iron, with the highest iron content (maximum 33 wt%) in the silt and fine sand fraction (Bachmann et al. 2001).

Ferrous iron entering the lake with the groundwater is oxidized as it flows through the oxic component of the sediment (Koschorreck et al. 2003) and so, iron in the water column is dominated by ferric iron. In contrast to many other mine lakes, where ferric iron precipitates as schwertmannite, in ML 111, the iron-hydroxosulfate jarosite ($KFe_3(SO_4)_2(OH)_6$) is the predominant primary precipitate. Jarosite is then further converted to more crystalline goethite (FeOOH). High numbers of iron-oxidizing bacteria in the surface sediment show that oxidation of iron is biologically enhanced. Iron-oxidizing bacteria of the genus *Acidithiobacillus*, *Leptospirillum, and Sulfobacillus* were found (Meier 2001, 2006; Porsch

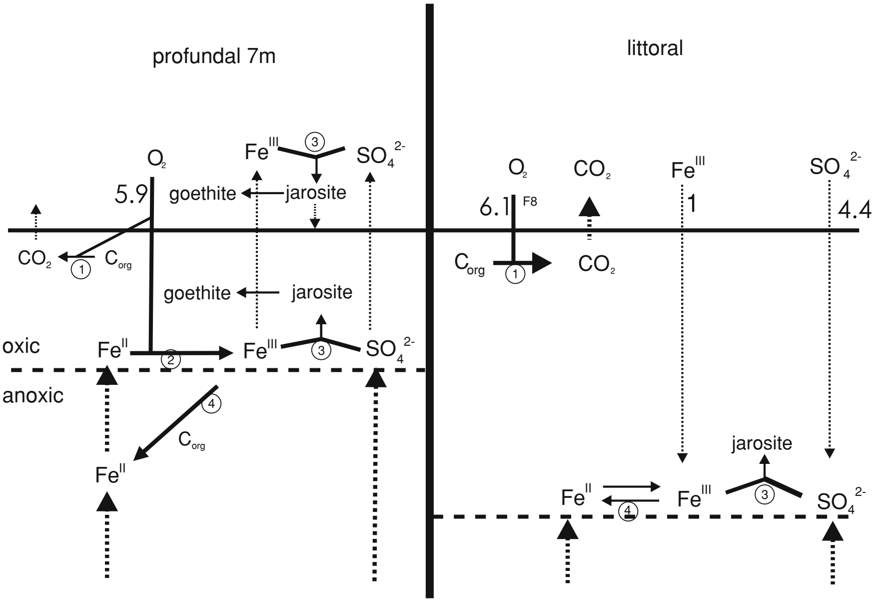


Fig. 5.48 Iron cycle at the sediment water interface. ① aerobic respiration, ② iron oxidation, ③ Precipitation of jarosite, ④ microbial iron reduction

et al. 2009). Heterotrophic Gammaproteobacteria of the genus *Fulvimonas*, which might also oxidize iron, were detected by molecular methods (Meier 2001, 2006; Porsch et al. 2009). Biofilms on submerged birch leaves contained *Acidophilium organovorum* and the presence of schwertmannite was shown by EDX-analysis (Lünsdorf et al. 2002).

Since denitrification is nitrate limited and sulfate reduction and methanogenesis were never detected, microbial iron reduction appears to be the dominant process of organic matter mineralization in the anoxic sediment. Most probable number (MPN) counts of iron-reducing bacteria in the sediment are in the range of 10^3–10^6 cells mL^{-1}. The presence of potentially iron-reducing bacteria, *Acidiphilium* and *Acidobacteria*, was shown by cultivation and molecular methods (Kleinsteuber et al. 2008; Meier 2006).

Conditions are more oxidizing in the littoral sediment, where oxygen penetrates about 10 mm into the sediment, compared to the profundal, where oxygen penetration is only about 3 mm (Koschorreck et al. 2003). Optically, the littoral sediment appears more ‘geogenic’ compared to the more ‘biogenic’ profundal sediment, and the Fe, S, K, and Na content is higher (Büttner et al. 1998). In the shallow water, organic matter degradation is mainly by aerobic respiration, and microbial iron reduction is probably carbon limited. Precipitation of jarosite is probably the dominant geochemical process in the littoral sediments (Fig. 5.48). The biogeochemistry of the littoral sediments is further influenced by groundwater inflow. At the southern end, where acidic groundwater is entering the lake, the

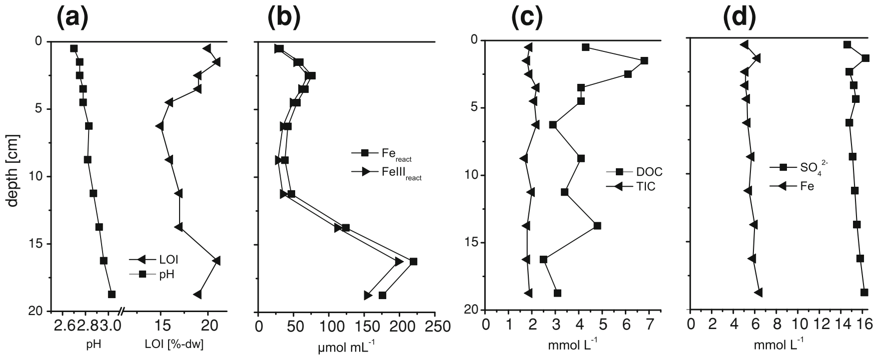


Fig. 5.49 Selected sediment properties (mean data of several samples from the north basin): pH and loss on ignition (**a**), reactive iron content per mL sediment (**b**), pore water concentration of DOC and TIC (**c**), SO_4^{2-} and dissolved Fe (**d**)

littoral sediment is characterized by elevated concentrations of ferrous iron and TIC (Stellmacher, unpublished).

The profundal sediment is a clay silt (3% sand/76% silt/21% clay) while the littoral is more sandy (26/69/5). Below 20 cm, the sediment mainly consists of mono-mineralic quartz sand, which probably represents the former open pit bottom (Bachmann et al. 2001). From this information, an annual mean sedimentation rate of 0.5 cm was estimated.

The pore water gradients of pH, dissolved TIC, SO_4^{2-}, and Fe are not very steep (Fig. 5.49a, c, d) which means that diffusive exchange processes between sediment and water are not very pronounced. There is a diffusive loss of SO_4^{2-}, Fe, and TIC from the sediment. The DOC concentrations are highest at a depth of about 2 cm (Fig. 5.49c), indicating organic matter mineralization in the surface sediment, which is in accordance with the decrease of organic matter content (measured as loss on ignition) with depth (Fig. 5.49a).

The biogeochemistry in the small anoxic hypolimnion is completely different from the rest of the lake. Here, microbial sulfate reduction was detected, with rates up to 7.2 nmol SO_4^{2-} cm^{-3} d^{-1} (Meier et al. 2004). A comparison with the long term sulfide accumulation in the sediment revealed a re-oxidation rate of 61%, which is a rather low value, demonstrating the limited access of oxidants to the monimolimnion. Probably as a consequence, the pH in the sediment increased with depth, reaching pH 6 at a sediment depth of about 6 cm (Friese et al. 1998).

5.6.4 Higher Organisms, Primary Production, Food Web

Compared to normal lakes, the food web in ML111 (see also Sect. 3.3.1.4) is species poor and higher trophic levels are missing (Fig. 5.50). Pelagic primary production is between 50 and 100 mg C m^{-2} d^{-1} with little seasonal variation

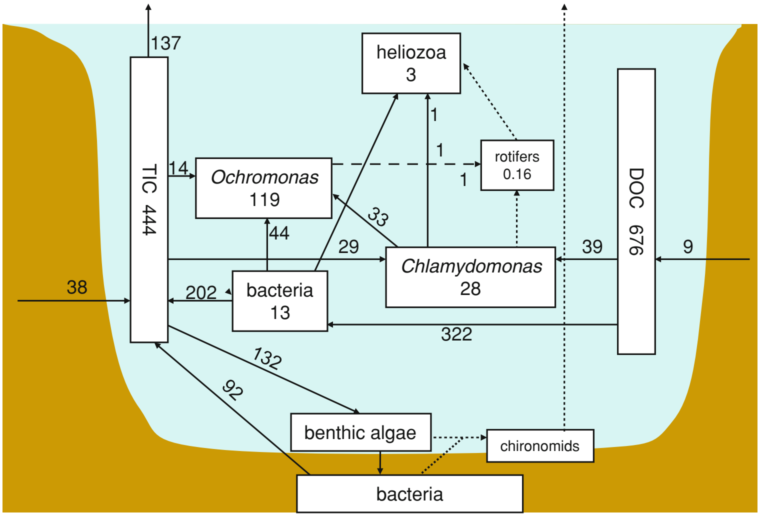


Fig. 5.50 Carbon flow scheme of ML111. Numbers in the boxes indicate pool size in μg C L^{-1}. Numbers at the arrows indicate rates in mg C m^{-2} d^{-1}. Rates were calculated from (Büttcher 2004; Kamjunke et al. 2004; Koschorreck and Tittel 2002). Numbers for the pelagic food web are from (Kamjunke et al. 2004), and assume that the epilimnion represents 85% of the lake volume

(Beulker 2004). Heterotrophic production of bacteria is 26–111 mg C m^{-2} d^{-1} and thus, in the same range as phototrophic primary production. Laboratory experiments showed that light induced degradation of DOC was a major energy source for bacteria (Kamjunke et al. 2005). The plankton consists mainly of bacteria, the two flagellates, *Chlamydomonas* sp. and *Ochromonas* sp., the rotifers *Elosa worallii* and *Cephalodella hoodi*, and Heliozoa (Wollmann et al. 2000). The bacterioplankton contained *Acidobacteria*, which constituted up to 8% of total counts (Kleinsteuber et al. 2008). Other predominant phyla detected by molecular methods were Alphaproteobacteria, Betaproteobacteria, and Gammaproteobacteria. Other phyla comprising *Nitrospira* (genus *Leptospirillum*), Planctomycetes, Actinobacteria (genus *Acidimicrobium*), candidate division TM6, plastid sequences of diatoms, and unclassified bacteria were present in minor proportions.

The epilimnion, which occupies about 85% of the water volume, is dominated by *Ochromonas*, and filamentous bacteria, *Elosa* and Heliozoa, while the hypolimnion is dominated by *Chlamydomonas*, single-celled bacteria, and *Cephalodella* (Kamjunke et al. 2004). *Chlamydomonas* is able to growth mixotrophically by using DOC as an additional energy source. Its abundance is controlled by grazing by the mixotrophic *Ochromonas* in the epilimnion, and thus, restricted to deeper layers, where *Chlamydomonas* forms a characteristic deep chlorophyll maximum (Tittel et al. 2003). At this depth, primary production by *Chlamydomonas* is light-limited, while above a light intensity of 60 μmol photons m^{-2} s^{-1}, growth is limited by CO_2 (Tittel et al. 2005). The nutrition mode of *Chlamydomonas* determines its food quality for the rotifers. *Elosa* is generally the superior competitor for the phytoflagellates (Weithoff 2005) but *Cephalodella* is superior with mixotrophic food (Weithoff and Wacker 2007; Sect. 3.3.1.4).

In the pelagial zone, the top predator is the small (30 μm) Heliozoan *Actinophrys sol* (Bell et al. 2006; Packroff 2000; Wollmann et al. 2000), with 7×10^3 individuals L^{-1}. *Actinophrys* feeds on filamentous bacteria and the flagellate *Chlamydomonas*, but not on *Ochromonas* (Bell et al. 2006).

The biggest animals living in ML111 are the up to 1 cm long larvae of *Chironomus crassimanus*, a collector-gatherer feeding detrivorous chironomid (Rodrigues 2001). It colonizes the littoral sediment down to a water depth of 3 m, with abundances between 100 and 5,000 individuals per m^2 (Lagauzère et al. 2011). It feeds on sedimentary bacteria and benthic algae. Benthic algae biomass in the littoral zone ranges between 1.9 and 18.5 mg chlorophyll-a m^{-2}. The diatom *Eunotia exigua* is the dominant species, and *Nitzschia paleaeformis* and *Euglena mutabilis* (occurring in patches) are present in low numbers (Kapfer 1998). Benthic primary production, as determined by ^{14}C incorporation, is as low as 12 mg C m^{-2} d^{-1}. The comparison of mean benthic (5 mg Chl-a m^{-2}) versus pelagic (10 mg Chl-a m^{-2}) chlorophyll concentration suggests that benthic primary production is probably an important part of the lake's carbon cycle (Nixdorf and Kapfer 1998). Benthic net primary production of littoral sediment, as measured with O_2-microsensors, was up to 422 mg C m^{-2} d^{-1} (Koschorreck and Tittel 2002). The benthic algae were adapted to the low light intensities (compensating irradiance 6.8 μE m^{-2} s^{-1}) and special light climate. An estimated 13% of the lake's surface area could support an oxygen-producing benthic community.

There are no submerged macrophytes growing in the lake but about 10% of the shoreline is colonized by *Phragmites australis* and *Juncus bulbosus*. Allochthonous organic matter input is mainly by birch leaves from the surrounding vegetation. These leaves are found in patches in the shallow water near the shore, and are colonized by *Chironomus* (Rodrigues 2001), but are degraded very slowly (Schlief, unpublished).

5.6.5 Remediation

In situ stimulation of microbial sulfate reduction by addition of organic matter can contribute to the neutralization of acidic pit lakes (Wendt-Potthoff and Neu 1998). Laboratory mesocosm experiments with water and sediment from ML111 had revealed a possible neutralization rate of 15 eq m^{-2} $year^{-1}$ (Frömmichen et al. 2004). Thus, ML111 was chosen as a model site to test different neutralization strategies in large field experiments (Fig. 5.51).

A passive method was tested by adding different combinations of straw, organic substrates, and lime in enclosures of different sizes (Geller et al. 2009). Experiments in small (2 × 2 m) enclosures showed that the addition of Carbokalk, a by-

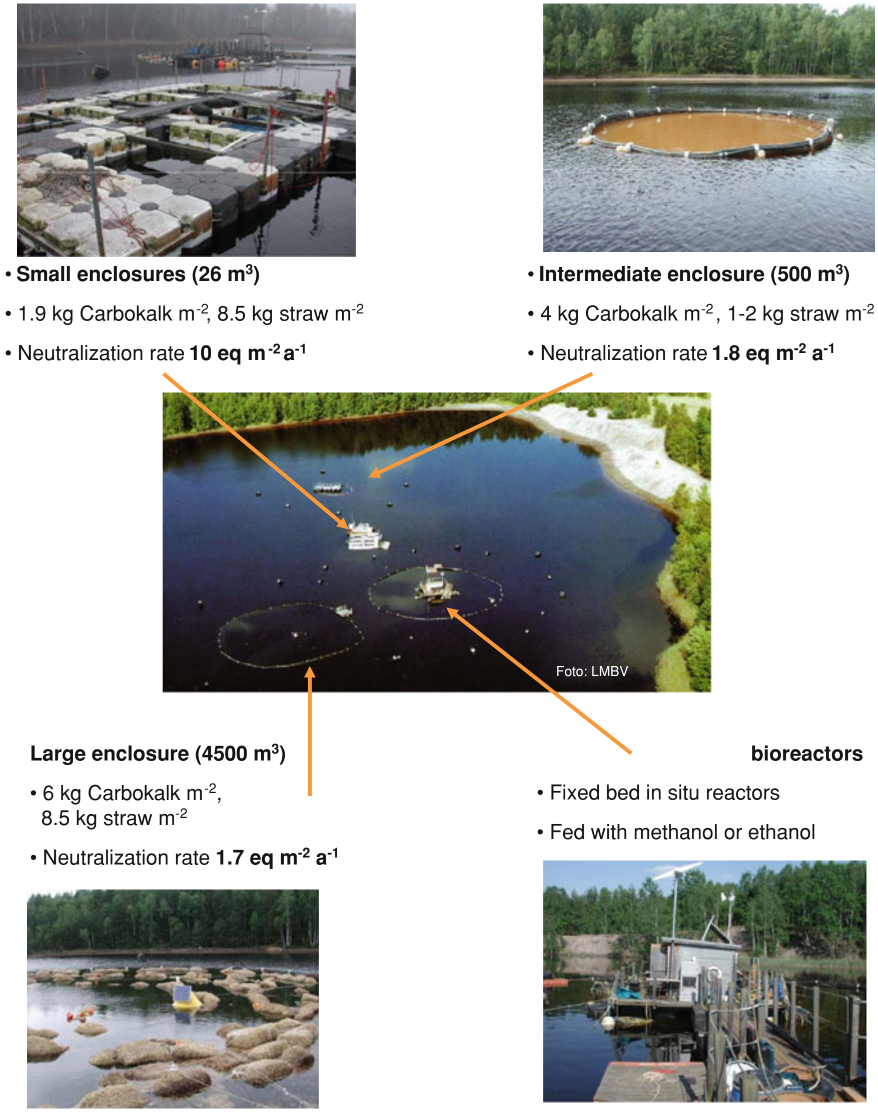
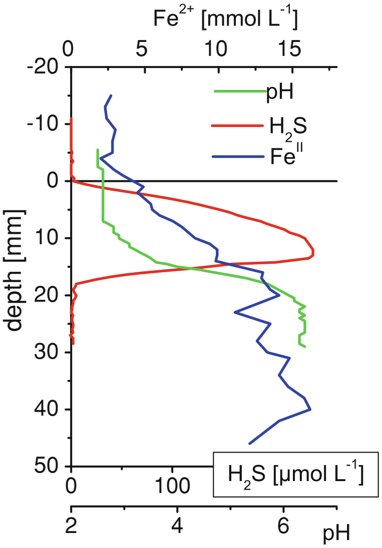


Fig. 5.51 Field experiments in ML111

product of sugar production, and straw was most effective (Frömmichen 2001). The experiments proved the development of a reactive zone at the sediment surface with pH 6 and active sulfate- and iron-reduction (Koschorreck et al. 2007). Microbial iron reduction started prior to sulfate reduction (Wendt-Potthoff et al. 2002) and was carried out by a well adapted microbial community (Porsch et al. 2009). Potential iron- and sulfate-reduction rates increased exponentially with

Fig. 5.52 Micro-profiles of pH, H_2S, and Fe^{2+} at the sediment–water interface in a field mesocosm after substrate addition



temperature, and high growth rates of sulfate-reducing bacteria at low temperature indicate a moderate psychrophilic community (Meier et al. 2005). In an experiment with only Carbokalk addition, the activity ceased after some months and iron sulfides were rapidly re-oxidized (Wendt-Potthoff et al. 2002). Thus, the addition of straw was necessary to maintain sustainable neutralization (Koschorreck et al. 2002a). Straw probably functions as a long term carbon source and protects against oxidative stress at the sediment surface by inhibiting turbulent transport. Substrate addition led to an algae bloom in the enclosure, but primary production was a negligible source of organic material during the experiment (Tittel and Kamjunke 2004).

Precipitation of fresh iron minerals led to a new sediment layer on top of the sulfate-reducing zone. In this acidic layer, iron sulfate could not precipitate but free sulfide diffused into the oxidized zone where it was oxidized by oxygen and/or ferric iron (Fig. 5.52). Due to this re-oxidation, the net rate of sulfate reduction was low despite a high gross rate. The reactions taking place at the sediment water interface during passive remediation are summarized in Fig. 5.53. A long term neutralization rate of 1.7 eq m^{-2} $year^{-1}$ was achieved, which is too low to compensate for the continuous inflow of acidity into the lake. In order to increase the net neutralization by inhibiting re-oxidation, an anoxic enclosure field experiment was started. An enclosure was covered by floating foil and, during a 15 month study, repeated addition of whey led to complete consumption of oxygen in the water column (Wendt-Potthoff et al. 2008). Although the addition of whey strongly stimulated aerobic respiration, microbial reduction of iron and sulfate was not significantly enhanced. First results show that reoxidation of the sediment was not prevented by anoxic conditions. The experiment showed that it is technically possible to manage an anoxic enclosure by addition of whey but that this does not necessarily increase neutralization rates.

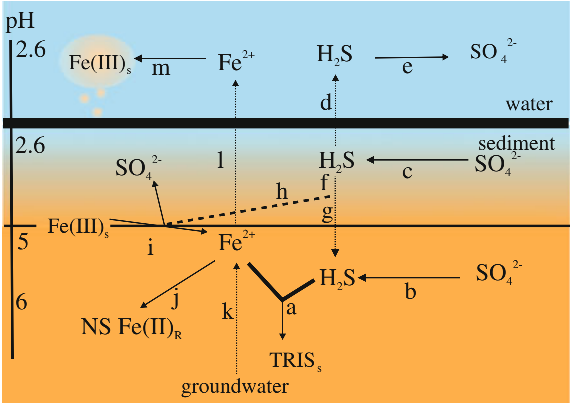


Fig. 5.53 Scheme of the reactions at the sediment–water interface during passive remediation (from Koschorreck et al. 2007): a net sulfate reduction, b + c gross sulfate reduction, d + f flux of H_2S, k + l flux of ferrous iron, j non-sulfidic-reactive Fe(II) accumulation, e H_2S oxidation, m Fe(II) oxidation and hydrolysis, g H_2S diffusing downward and precipitated, h H_2S diffusing downward and oxidized by ferric iron, i gross iron reduction

Because neutralization rates of the passive approach were low and the process was difficult to control, an active, bioreactor-based approach was developed. To make the technology applicable in remote locations, the reactors were constructed as floating in-lake reactors with an autonomous wind- and solar-driven power supply. First, a straw-filled vertical tube reactor (7 m long, 0.3 m diameter) was installed in a small enclosure (Koschorreck et al. 2002b). Bottom water was pumped through the fixed bed and ethanol was supplied as electron donor for microbial reactions. Sulfate reduction proceeded inside of the reactor although the pH remained below 3.8. This prevented the precipitation of FeS and thus, free H_2S was released to the enclosure, where it was re-oxidized to S^0. High concentrations of acetate accumulated due to incomplete oxidation of ethanol. Laboratory investigations showed, however, that acetate concentrations up to 15 mmol L^{-1} did not inhibit sulfate reduction (Koschorreck et al. 2004).

The second version of the reactor comprised 8 large straw-filled reaction vessels (3.5 m long, 1.5 m diameter) floating in a large enclosure (Luther et al. 2003). The pH inside the reactor was initially increased by the addition of Carbokalk. This resulted in the desired iron sulfide precipitation but also led to clogging and buoyancy problems. So, the fixed bed was changed from straw to artificial carriers. This successfully prevented the clogging. To prevent acetate accumulation, the reactor was run with methanol instead of ethanol. This prevented acetate formation but led to methanogenesis. Methanogenesis consumed 22% of the methanol (Koschorreck et al. 2010). Reactors were successfully run for a period of 8 months, and maximum treatment rates of 0.12 mmol L^{-1} h^{-1} were achieved (Preuß et al. 2007).

The combined results of the different experiments suggest that passive remediation by microbial reactions is possible in principal, but that achievable neutralization rates are low. Thus, microbial measures for acid pit lake treatment are not an option for strongly acidic lakes like ML 111. However, in lakes with lower acidity loading, the use of biological remediation should not be ruled out. Bioreactors offer a promising, though at the moment, uneconomical, option for biological mine pit lake remediation.

5.7 Biological Polishing of Arsenic, Nickel, and Zinc in an Acidic Lake and Two Alkaline Pit Lakes

Margarete Kalin and William N. Wheeler

5.7.1 Introduction

The physical and geochemical characteristics of open pits, and the pit lakes that develop at decommissioning, differ depending on the type of ore mined, the geomorphological setting, and the local geology, hydrology, and mineralogy. In most cases, pit lakes lack tributaries, surface drainage, or semi-aquatic and benthic vegetation zones, and are devoid of bottom sediment, since the soils and most of the low mineral-bearing waste rock that would support vegetation have been removed to extract the ore. These are all important components that fulfill essential limnological and geochemical aspects of water-cleansing processes in natural lakes.

Pit lake water usually contains elevated concentrations of metals specific to the mineralogy of the ore extracted from the pit. One mechanism by which these contaminants are removed from the lake water to the sediment is by adsorption: (1) to free-floating biomass or phytoplankton and (2) suspended, inorganic solids. Natural, biological water-cleansing processes have been termed ‘biological polishing’; ‘polishing’ is the general term for the removal (by flocculation) of particulates from waste water. With biological polishing, phytoplankton, picoplankton, periphyton, and microbial populations perform the flocculating/aggregating function.

Inorganic particles originate from erosion of the pit walls above the water level of the pit lake, along with windblown particles from the surrounding terrestrial mine waste management area. Phytoplankton and inorganic solids aggregate to form particulate suspended matter. As the particles increase in size, they sink to the lake bottom, providing nutrients for microbial consortia that maintain redox conditions favorable to the transformation of metals in the newly-forming sediments (Fyson et al. 1998a). In this way, metals are captured in the water column and transported to the sediment, where they are transformed back into bio-minerals, possibly into ore (Kaczorek and Sommer 2003; Kalin et al. 2004).

Initially, the pit lake restoration process has to focus on establishing a biogeochemically-active sediment. This can be accomplished by importing recalcitrant organic material such as alfalfa, hay, woody peat muskeg, and/or sugar cane wastes. Biofilms colonize these structural, slowly-degrading organic surfaces, using the degraded carbon fraction for growth. An on-going supply of easily degradable carbon is then provided by phytoplankton and periphyton growth. The sinking organic and inorganic particulates consolidate the newly-formed sediments, establishing reducing conditions and supporting the biogeochemical activities described above. These natural water cleansing processes are derived from basic limnological principles (Stumm and Morgan 1996; Wetzel 1983).

The three Canadian case studies discussed in this section highlight how ecological engineering concepts can be used to establish biological polishing in pit lakes, and the processes that are needed to provide a permanent sink for contaminant metals. These case studies describe the establishment or support of water-cleansing processes in large water bodies that differ in their hydrology, geochemistry, and sediment development. The three lake systems (Saskatchewan, Ontario, and Newfoundland) range from alkaline to very acidic. Each lake contained elevated concentrations of metals that had to be removed from the water column and relegated to the sediment within the waste management area. The approach was to: (1) utilize natural, indigenous flora and suspended solids (both organic and inorganic) to sequester the metals; (2) use natural processes of particle aggregation to increase density and promote settling; and (3) create organic sediment or enhance existing contaminated sediment on the lake bottoms, providing or supporting low redox conditions that would facilitate bio-mineralization through microbial transformations (Kalin et al. 2004).

5.7.2 Methods

5.7.2.1 Physical Parameters

Pit lake water data were collected using common limnological methodologies (Wetzel and Likens 2000). In the Saskatchewan pit lake, electrical conductivity, pH, oxygen, and redox potential (E_h) were determined with a hydro-lab at each meter depth at two locations in the pit lake. Only the data from the surface and 40 m are displayed. At the Ontario and Newfoundland sites, redox potential was measured using a Corning 103 m with Fisher electrodes. The pH was measured using a WTW 196 meter, and conductivity was measured with an Orion (WTW) Model 140 m.

5.7.2.2 Water Quality

All water samples from the Saskatchewan and Ontario sites were filtered through 0.45 μm filters and acidified, and then analyzed at the Saskatchewan Research Council (SRC) using inductively coupled plasma spectroscopy (ICP). At the Newfoundland site, zinc concentrations were sometimes analyzed by ASARCO on site, without filtration, by atomic absorption. Zinc concentrations were randomly verified by the SRC. Pond effluent data between 1995 and 2008 have been provided by the Pollution Prevention Division of the government of Newfoundland.

5.7.2.3 Biological Polishing

Phytoplankton and periphyton were sampled in each of the pit lakes for several years. Identification was generally carried out to the species level when possible. Phytoplankton and periphyton growth rates were determined in the field and in the laboratory (Cao and Kalin 1999). After testing different materials to increase surface area for periphyton, road-side brush cuttings (mostly spruce (*Picea mariana*) in Ontario, and other undergrowth consisting of cuttings of 2–3 m length) were found to be suitable, long-lasting, and economical. At the Ontario site, about 600 spruce brush cuttings were added in 1987, 3,400 were added in 1988–1991, and 14,000 were added in 1994/1995. Several brush cuttings (tree branches) were measured to determine the surface area available for periphyton growth. The estimates were derived by measuring length and diameter of branches, and counting the number of similar brush or tree branches. The derived surface area estimate was approximately 356 m^2 per spruce brush cutting. Periphyton growth rates were determined in the Newfoundland and Ontario sites by harvesting brush immersed for varying time periods. Brush segments were cleaned and the periphyton dried and weighed. Surface area and mass of the brush segments were then determined (Kalin and Wheeler 1992a). In Newfoundland, alder brush cuttings (*Alnus sp.*) were used in constructed biological polishing ponds (Kalin and Wheeler 1992b).

5.7.2.4 Underwater Meadow

In 1989, acid-tolerant moss (*Drepanocladus fluitans*) was introduced from other acidic mine site tailings ponds to the Ontario lake. Approximately 100 g of wet biomass was placed in each of 200 plastic netting bags, weighted and sunk onto the lake sediment. Growth rates were measured in 1987 and 1988 by removing the bags, rinsing, and removing excess water. The bags were then weighed and returned to the sediments. In 1998 and 2000, growth was again measured, this time as harvested biomass from square meter quadrats. Moss was harvested, rinsed, dried, and weighed. Samples were also taken for elemental content (ICP) after acid digestion.

5.7.2.5 Sedimentation Rates

Particulate matter, containing both contaminants and phytoplankton, was collected in sedimentation traps in all water bodies at different depths for differing time periods, using methods described by Kozerski (1994). Each sedimentation trap consisted of five Plexiglas^{TM} tubes, 50 cm long × 10 cm in diameter, held upright on a plastic plate. Traps were placed at: 2, 12, 22, and 32 m in the Saskatchewan pit lake, 0.5 m in the Ontario lake, and at 4, 11, and 20 m in the east, and 2 and 7 m in the west Newfoundland lakes, respectively.

The particulate material samples were analyzed after being oven dried and pulverized. A portion was ashed in a muffle furnace at 500°C for 30 min. The difference between the oven-dried mass and ashed-mass gave the loss on ignition (LOI). The LOI was used to estimate the inorganic and organic fraction of the collected material. Another portion of the ashed material was digested with hydrochloric/nitric acid, and analyzed by ICP at the SRC. At the Saskatchewan site, the collected particulates were additionally analyzed for total nitrogen and total organic carbon (TOC); secondary ion mass spectroscopy (SIMS) was used to identify the locations and associations of nickel and arsenic.

5.7.2.6 Sediment

Sediment samples were collected in the Saskatchewan pit lake with an Eckman dredge. These samples showed clear stratification, which allowed separation of particulate matter originating cumulatively from the water column. Layers were separated, dried, and analyzed using ICP and SIMS.

Core samples and Eckman grab sediments were also collected from the Ontario site. In these sediments, iron and other metal accumulations were extremely variable depending on location within the lake. This variability was due to localized pipe-like discharge channels of contaminated groundwater upwelling through the sediment from depth. These discharge locations were encrusted with iron and co-precipitated metals, and occurred in close proximity to sediments with low concentrations of iron and metal. This made an elemental mass balance between settled particulates and sediment layers unrealistic.

5.7.3 Case Study: B-Zone Pit Lake (CAMECO)

A five million cubic meter circum-neutral pit lake was created in northern Saskatchewan at the former CAMECO B-Zone uranium pit operation (Fig. 5.54). The ore body was located directly on the shores of Wollaston Lake (58° 15′ 42″ N, 103° 39′ 54″ W), a pristine oligotrophic lake. The geology was described by Fayek and Kyser (1997). A retaining steel pillar wall separated the pit from the clean lake. If allowed to fill naturally, the pit walls would have weathered and released contaminants over many years, since the lake would have filled with only contributions from rain and snow. Force-flooding from the adjacent, clean lake was recommended and implemented (Fig. 5.55a, b) to reduce continued contaminant generation from the pit walls. It was initiated during the winter months while the pit walls were frozen, which generated a large amount of inorganic particulate

Fig. 5.54 Map showing the relationship of the pit lake to Wollaston Lake. The pit lake to the north of the B-Zone Pit Lake is the D-Zone Lake. The waste rock pile is in the southeast corner of the map. © Google and Digital Globe (2011)

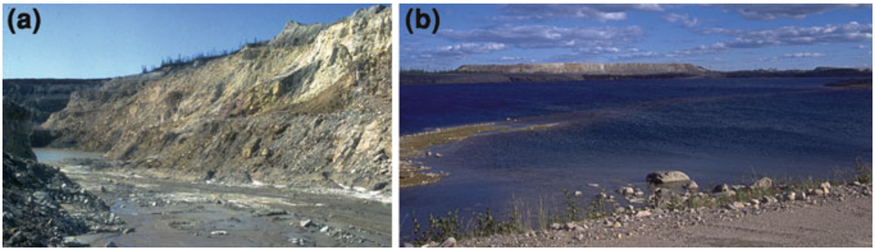


Fig. 5.55 B-Zone pit (**a**) before and (**b**) after force-flooding in 1991

matter. Peat, soil, and muskeg vegetation eroded in the first year, and provided recalcitrant organic matter for the newly-forming sediment. Groundwater input was low to absent, but annual atmospheric precipitation exceeded evaporation, raising the lake elevation annually. To prevent overflow back into Wollaston Lake, the excess water had to be pumped to a chemical treatment plant. With the support of the mining company, the biological polishing processes for arsenic and nickel were documented in detail. Reports can be found at 'www.boojumresearch.com/about/' or at the website described in Kelly et al. (2007).

Between 1992 and 2004, the lake's limnology was intensively documented. After filling, arsenic and nickel concentrations were present at 0.2 mg L^{-1}. The concentrations rose for the first two years, as further material dissolved from the pit walls (Fig. 5.56a, b). Nickel, however, while declining during the summer months (1993–1995), continued to rise after the strong thermocline developed, then decayed with the Fall turnover and the formation of an ice cover (Fig. 5.56b).

Initially, this seasonal rebounding was simply attributed to the decay of biomass at the thermocline, releasing nickel, but not arsenic. Later, we concluded that the rebounding of nickel concentrations in the Spring and Fall had three possible explanations: (1) with the changes in sedimentation rate it was possible that a

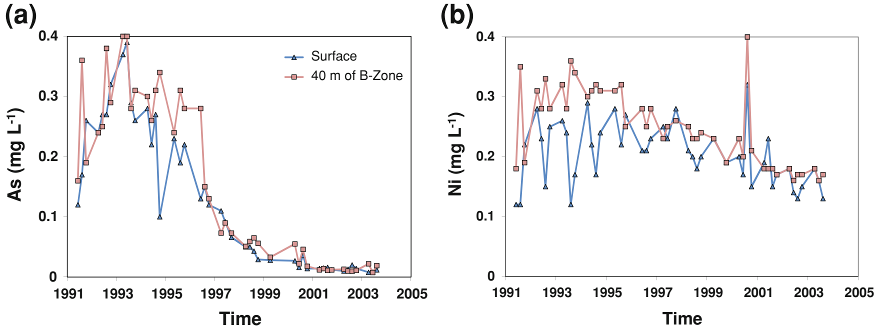


Fig. 5.56 **a** arsenic (As) and **b** Nickel (Ni) concentrations at the surface (*triangles*) and 40 m (*rectangles*) of the B-Zone pit lake from 1992 through 2004

change occurred in particulate surface charges, and hence adsorption characteristics, leading to the release of nickel. (2) It was also argued that if the composition of the biota and the suspended solids were changing with time, the biological polishing process would be compromised and short-lived. (3) As nickel was the only element rebounding, it was possible that an external source of nickel existed, which was washed into the lake in the Spring and Fall.

One aspect that had to be considered was that the phytoplankton standing crop and diversity changed over the duration of the project. In 1992, the sedimentation traps collected mostly inorganic material, while in the second and third year, the traps (see Fig. 5.57a) collected mostly biological material, dominated by a mucilage-forming alga, *Dictyosphaerium pulchellum* (Fig. 5.57b). Based on the quantity of material collected in sedimentation traps, it was estimated that 31 t of dry weight biomass were produced by *Dictyosphaerium* (with its associated inorganic precipitates and mucilage) over the first two growing seasons. In 1995, *D. pulchellum* still dominated the pit with an average density of 359 × 10^8 cells L^{-1}. In 1996, *D. pulchellum* retained its dominance, although diversity increased. By 1998, *D. pulchellum* was mostly replaced by a new green algal species, *Chlamydomonas*, which comprised 50% of the total density, 32 × 10^5 cells L^{-1} (Kalin et al. 2001).

The suspended solids composition also changed over time. In 1992, the sedimentation traps collected mostly inorganic material, while in the second and third year, the traps collected mostly biological material (Fig. 5.57b). But, the polishing abilities of the suspended solids did not change and were not short-lived. The arsenic was associated with iron hydroxide particles and nickel was present as a carbonate (SIMS data). These associations were aggregated to inorganic silica and clay particles, which were bound to organic particles. It was concluded that settling particles represented the dominant contaminant sequestration mechanism.

The change in surface charge was also eliminated as a cause of the returning nickel. Particulate surface charges were tested through the addition of negatively- or positively-charged bentonite to B-Zone bottom and top pit lake water.

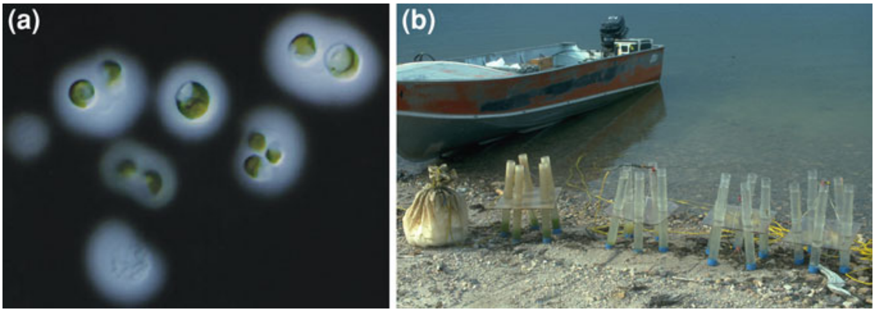


Fig. 5.57 *Dictyosphaerium pulchellum*, as seen **a** under the microscope and **b** in the sedimentation traps

Table 5.15 Comparison of sedimentation rates in traps and bottom sediment loads

Year	Sediment rate g m^2 d^{-1}	Per year g m^{-2}	As g m^{-2}	Ni g m^{-2}	Fe g m^{-2}	Al g m^{-2}	PO_4 g m^{-2}
1992	28.7	10,472	1.5	1.7	184	161	24
1993	28.7	10,472	3.8	4.7	99	77	22
1994	11.6	4,227	7.9	4.5	60	38	8
1995	13.0	4,758	12.8	3.4	62	30	9
1996	3.5	1,285	2.7	0.9	26	18	2
1997	2.4	876	6.7	1.1	41	14	3
1998	2.6	931	4.0	0.9	44	17	2
1999	2.0	737	2.7	0.4	38	10	2
Total		33,757	42	18	555	366	73
Mass in sediment, depth 0–7 cm, 1999			30	17	566	619	57

No changes in surface charges were noted between deep and surface water. To eliminate any further arguments that an internal process caused the nickel concentration to seasonally rebound, the bottom sediments were sampled. Eckman grab samples in 1999 displayed well-differentiated strata, up to a thickness of about 7 cm, below which a consistently gray, clay-like material was found. The sum of elemental masses collected in the sedimentation traps between 1992 and 1999 per m^2 and the elemental mass in the top 7 cm layers of the sediment were compared (Table 5.15). The amount of nickel in the trapped particles matched rather closely the nickel found in the sediments. This was also the case for arsenic, iron, and phosphate. Only aluminum did not match. The discrepancy could have been due to inadvertently sampling the gray, clay layer, which was installed at the pit bottom to bury special wastes prior to flooding.

Since there was no difference in surface charges, the polishing capacity of the suspended particulates was not diminished, and elemental masses in sediments and particulates were closely matched, it followed that there had to be an external source of nickel. The external source was identified as evaporates (Fig. 5.58), which had formed on the sandy pit perimeter road. The evaporites were water

Fig. 5.58 ‘Evaporate blooms’ of nickel precipitates found on the perimeter road

soluble and were washed into the lake during Spring and Fall rainstorms. After the evaporites on the perimeter road were removed in October 2001, nickel concentrations no longer increased seasonally, and started to decline slightly (Fig. 5.56b).

Based on the decrease in phosphate concentrations in the particulates (Table 5.15) and the dwindling phytoplankton biomass, it was suggested that a small amount (less than 1 t) of phosphate and calcium nitrate fertilizer would enhance the biological polishing. However, the company did not pursue this recommendation with the regulatory authorities and the project was completed by 2004.

5.7.4 Case Study: Boomerang Lake (South Bay Mine)

The South Bay Mine produced copper and zinc from 1972 to 1986, 85 km northeast of Ear Falls Ontario, on a peninsula surrounded by Confederation Lake in northern Ontario, Canada (51° 08′ N, 92° 40′ W). The geology is described by Seccombe and Clark (1981). After the mine’s closure in 1981, the owner was required to treat the effluent, and was considering a chemical treatment plant. However, geochemical calculations based on the inventory of sulfides in the tailings (45% pyrite and 5% pyrrhotite) suggested that such a treatment plant would need to be operated (at the present oxidation rate) for 1,000–35,000 years (Kalin et al. 1992). Instead, with the approval of the regulators, the area became an R&D test site, studying the decommissioning of mine wastes using the concepts of ecological engineering. The only requirement was that no effluent from the waste management area leave the already contaminated peninsula to the pristine lake surrounding it. The 75 ha mine waste management area on the peninsula contains the mine site (50 ha), tailings (23 ha), and two lakes, Mud Lake and Boomerang Lake (Fig. 5.59).

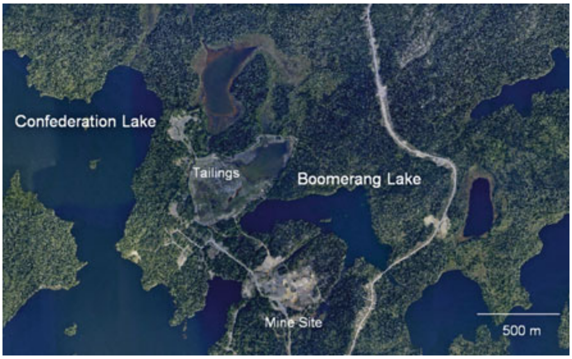


Fig. 5.59 South Bay Mine site and Boomerang Lake (air photo provided courtesy of the Ontario Ministry of Northern Development and Forestry)

The volume of Boomerang Lake, as calculated from bathymetry, is about 1 million m^3. It is 1.2 km long, 400 m wide, and covers 24 ha of open water. Because the lake is shallow (2–5 m deep), the water is well mixed throughout the ice-free season (May to November). Mill- and mine-contaminated surface run-off water enters the lake from the southwest and clean run-off enters from the northeast side of the basin. Contaminated and clean run-off together are estimated at 344,000 m^3 $year^{-1}$, which results in a theoretical lake retention time of approximately 3 years.

The pH in Boomerang Lake dropped gradually from about 6.3 in 1979, to 4.5 in 1986, when the project began. In 1986, zinc concentrations were in the range of 5–8 mg L^{-1} (Fig. 5.60). Zinc loading increased over the next 10 years from an original estimate of 5–20 t $year^{-1}$. Iron loadings also more than doubled, from about 28–80 t $year^{-1}$. The increased loadings were due to construction of a tailings diversion ditch in 1989, release of highly contaminated water from the mill pond in 1994, and, in 1995, the construction of another diversion ditch to accommodate the effluents that emerged from the underground workings, which had been allowed to flood since 1981. The diversions prevented the effluents from entering Confederation Lake (Kalin 2001). Previous metal loadings to Boomerang Lake were estimated from surface drainages and upwelling groundwater from the tailings.

The lake sediments were covered with a thick layer of iron hydroxide and were void of any emergent aquatic vegetation. The iron hydroxides covered not only the sediment, but also every submerged surface (e.g. shore rocks, deadfall brush) in the lake. Iron particulates are generally below 1 μm in size and can remain suspended in the water column for a long time (Buffle and van Leeuwen 1993). They adhere easily to any surface, producing the characteristic staining of areas affected by mine water.

Sedimentation traps in the lake collected orders of magnitude more iron than was estimated to enter the lake from the identified contaminant sources (Kalin et al. 2000), as iron was recycled from the sediment during spring and fall lake

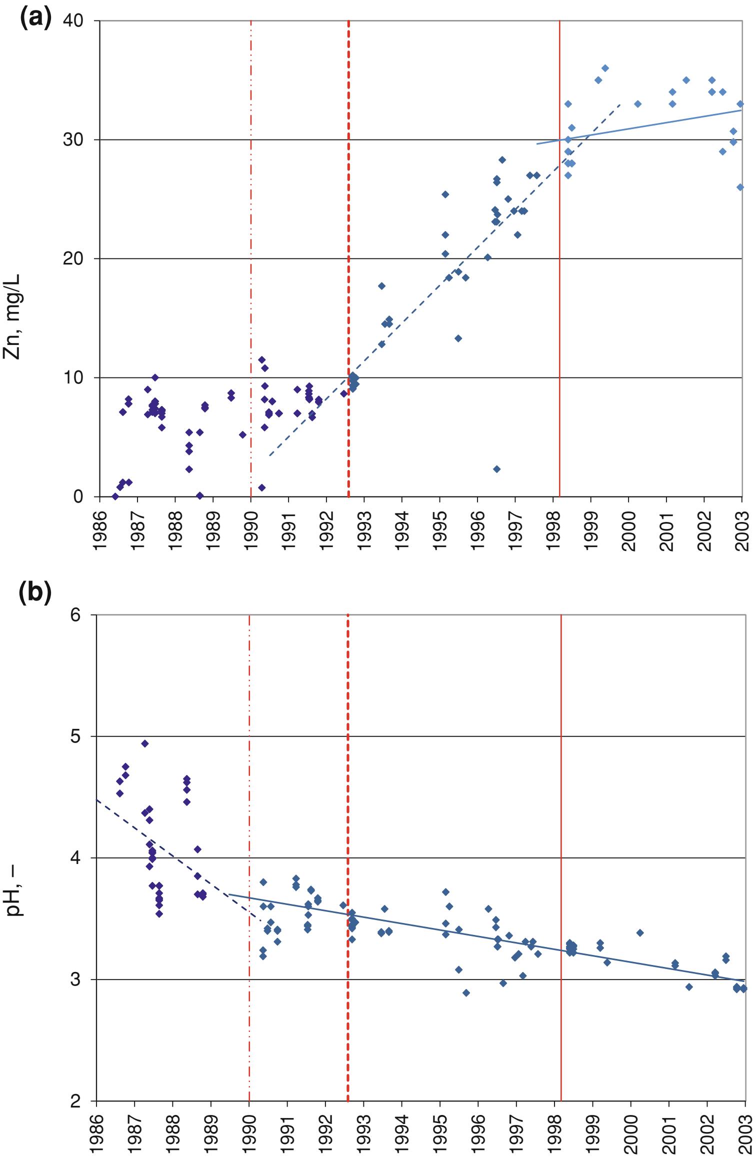


Fig. 5.60 Zinc and pH in Boomerang Lake; (*dash, dot, dot, dash*) indicates the first brush additions; (*dotted heavy line*) indicates the first phosphate additions; (*solid line*) indicates magnesium additions. The trend lines are linear regressions of data points between the vertical lines

turnover. Iron precipitates form solid particles of iron hydroxide, a transformation associated with hydrogen ion formation, which leads to further acidification (Barry et al. 1994; Chapelle 2001).

Boomerang Lake was developed as a biological polishing treatment system, where the project objectives were to: (1) enhance the existing periphyton and phytoplankton growth to provide a growing surface area for the adsorption of contaminants; (2) establish an oxygen-consuming cover over the iron-rich sediments to prevent physical iron particle cycling and encourage reducing conditions at the sediment surface; and (3) counteract the decreasing pH trend of the lake without affecting the indigenous acid-tolerant biota in the water. The three objectives were achieved gradually, each measure implemented after one or two years of smaller-scale testing in the lake. All R&D tests and the results for the entire site can be found at the Boojum web site or at the 'Mining and the Environment database' in the Laurentian University library (Kelly et al. 2007).

5.7.4.1 Periphyton and Phytoplankton Enhancement: Biological Polishing

The most prominent phytoplankton taxa in Boomerang Lake (>50% frequency) were *Ochromonas* sp., *Lepocinclis sp.*, *Klebshormidium sp.*, and *Staurastrum sp.* (Kalin et al. 2006). *Ulothrix sp.*, *Microspora sp.*, and *Zygogonium sp.* were the most prominent components of the periphyton mats. Many of these taxa were also frequently present in the pristine oligotrophic Confederation Lake, such as *Ochromonas* and *Chlamydomonas*, *Staurastrum, Pinnularia, Ulothrix, Eunotia*, and an unidentified chlorophyte (Kalin et al. 2006).

Periphyton populations in the lake occurred on deadfall trees and rocks in the shallower areas of the lake. These periphyton mats were composed of diatoms, moss, filamentous algae, and inorganic precipitates. The mats only contained about 35% organic matter, based on LOI (Kalin and Wheeler 1992a). The inorganic fraction was composed of 20% iron, 1.8% sulfur, and 0.4% zinc on a dry weight (dw) basis (Kalin and Wheeler 1992a). These concentrations suggested that if the periphyton and phytoplankton populations could be increased, so would the removal (sequestration) of contaminants. By providing the necessary nutrients and growth substrates, the biological polishing capacity of the lake could be expanded.

Enough spruce brush (branches, leaves, and needles) was added between 1989 and 1995 to provide an estimated 640 ha to the surface area available for periphyton colonization. Experimentation between 1991 and 1992 with slow-release fertilizer suspended in net bags in the lake suggested that the periphytic mats grew well on added brush, and faster when external nutrients were applied in the form of slow-release fertilizer (Kalin and Wheeler 1992b). At a nutrient-enhanced growth rate of 450 g (dw) m^{-2} $year^{-1}$ (from Table 5.16: 3.0 × 150 day growing season × 640 ha), about 2,880 dry tonnes of periphyton with precipitates could grow in the lake each year.

Acid lakes in Lusatia, Germany (pH 2.5–3.5) contain similar periphyton populations (Kleeberg et al. 2006). Their *Zygogonium* also contain high concentrations of iron. Primary production by *Zygogonium* was about 35 g (dw) m^{-2} $year^{-1}$. These numbers compare favorably with those in Table 5.16. Their fresh biomass, not on brush, contributed up to 820 g m^{-2}, with an average density of 236 g m^{-2}.

Table 5.16 Growth rate estimates from various experimental data

Rate, g m^{-2} d^{-1}	Description	Density, g m^{-2}
Periphyton growth rates		
3.0/0.12	Periphton on submerged brush	0.19–1.22
3.6	Suspended netting with slow release fertilizer additions	N/A
1.1/1.7	Laboratory experiments	2.25/33.7
Moss growth rates		
0.4/0.8	1987: first year of transplant	
1.5	1988: 2nd year of transplant	
0.75	1999: 2000 (295 days)	222

Table 5.17 Sedimentation rates of suspended solids in lake (t $year^{-1}$)

	Fe	Zn	SO_4
1991–1992	27	0.91	13
1993–1994	18	0.37	3.0
1995 pre P	35	0.61	13
1995 post P	51	0.66	6.0
1996	30	0.23	3.0
1997	97	0.78	23

5.7.4.2 Sedimentation Processes

The particles in the sedimentation traps were both organic and inorganic, reinforcing the concept that phytoplankton and periphyton can serve as nucleation sites for inorganic precipitates (Buffle and Leeuwen 1993; Lowson 1998). Sedimentation rates measured between 1991 and 1997 varied seasonally along with rainfall, light, and temperature which brought about spring and fall blooms of phytoplankton. The organic and elemental content of the collected particulates were extrapolated for the entire lake. A total 258 t of iron and 3.6 t of zinc, were estimated to have been transported out of the water column by particulates over the 6 year period (sum of columns in Table 5.17).

In an acidic (pH 2–3) Lusatian pit lake in Germany, Kleeberg et al. (2006) estimated iron sedimentation rates at 55 mg m^{-2} d^{-1} during the winter and 481 mg m^{-2} d^{-1} for the period from May to September. These data are remarkably similar to the data obtained in Boomerang Lake.

In an effort to stabilize the lake sediments, in 1987, *Drepanocladus fluvitans,* a metal- and acid-tolerant aquatic moss, was introduced to the sediment surface in moss bags made of netting. Over the next 7 years, the moss survived and slowly spread. Gradually, *Leptodictum* sp. and *Fontanalis sp.* invaded the underwater meadow and rooted macrophytes *Nuphar sp.* and *Potamogeton sp.* colonized along the shores. By 1997, 10 years after the introduction of the moss bags, almost the entire sediment surface of the lake was covered by the underwater meadow. Based on long-term growth rates determined by harvesting quadrats in the underwater meadow in 1999 and 2000, the average growth rate was 135 g (dw) m^{-2} $year^{-1}$

Table 5.18 Retained contaminants in polishing components in lake (t year^{-1})

	Meadow 2000 data	Brush growth 1995 data	Particulates 1997 data	Total
Zinc	0.018	0.59	0.78	1.39
Iron	23.9	146	97	267
Sulfur	0.185	10.1	23	25.5

(multiplying the avg. growth rate from Table 5.16 by the 150 day growing season). Biomass production was estimated to be about 32 dry t yr^{-1}. The biomass contained lower concentrations of iron and zinc than the periphyton, 15.5 and 0.2% of dry mass, respectively.

5.7.4.3 The pH Buffering Processes

Phosphate mining wastes (natural phosphate rock, NPR), which contained carbonates, were tested as a fertilizer, and as a means to precipitate iron (as iron phosphate) in the surface sediments, and buffer the lake water. Phosphate has been studied extensively as a limiting nutrient in freshwater environments (Wetzel 1983), and the use of NPR was tested on coal wastes by Renton et al. (1988). Phosphate is not known to react with reduced iron (Evangelou 1995), but forms stable precipitates with oxidized iron (Emerson and Widmer 1978). Lab-scale and mesocosm studies in the lake suggested that NPR additions to Boomerang Lake would provide the nutrients, buffering, and precipitation effects that were needed.

It was expected that the phosphorus would react with the iron being oxidized in the spring after ice break up. So, between 1993 and 1995, 162 t of NPR were added to the lake from barges. The NPR particles remained suspended in the water column for less than 8 h before all of the particles had sunk to the bottom. Hence, there was no measurable effect on the whole lake pH. These additions, however, contributed significantly to the inorganic carbon (from the carbonates) and alkalinity at the sediment surface, and precipitated much of the oxidized iron, resulting in an almost tripling of the iron-bound particulates by 1997 (Table 5.18). The high iron content of the sediments, along with the reducing conditions under the moss, provided a stable sink for iron phosphates, as shown by Hupfer et al. (1998). The underwater meadow expanded rapidly after fertilization. This suggested that the spread of the introduced moss was phosphate limited, as documented by Simmons et al. (2004).

Due to the large input of iron from underground workings effluent, a gradual but continuous consumption of hydrogen ions was needed to counter the decreasing pH trend. Raising the pH would prevent further iron cycling and increase inorganic carbon, which would increase phytoplankton growth in the water column. However, to abruptly raise the pH of the whole lake with lime was out of the question, since the emerging ecosystem would have been exposed to a sudden pH shock, which would likely have been detrimental. Furthermore, the resulting hydroxide sludge would have covered the underwater meadow, reducing light penetration and growth. Also, liming of the lake was practiced occasionally during mining operations to counteract severe spills, and the effects were very short-lived. Adding milk of lime (calcium hydroxide) to the snow, to produce an alkaline input to the lake during snow melt was considered. When tested, however, lime granules formed, but remained on land. Metallic aluminum chips from boat construction yards would also consume hydrogen when exposed to the acidic lake water. Tests showed that the metallic chips became encrusted with an iron/aluminum hydroxide slime coat within months, becoming ineffective. Finally, metallic magnesium scrap from the manufacturing of car wheels, or cell phone casings was tested. The corrosion of metallic magnesium splits water, evolves hydrogen, and produces hydroxyl ions, which increases the pH.

After a year of small scale tests in the laboratory and the field, 4.6 t of scrap metal were suspended on barges in Boomerang Lake over the winter 1998/1999. A slight increase in the pH was gradually noticed, although once, in the barge under the ice cover, a pH value of 8 was recorded. Although the scrap took 6 years to dissolve, zinc concentrations in the lake started to decline almost immediately (Fig. 5.60).

The metallic scrap suspended on the floating barges was sampled yearly. Precipitates were quantified and investigated with x-ray diffraction at the University of Toronto's Civil Engineering Department. The precipitates (corrosion products) contained copper, zinc, and extensive carbonates and sulfates, explaining the zinc concentration decline. Secondary minerals that could be associated with the analytical results were, for example, hydromagnesite $MgCO_3.Mg(OH)_2{\cdot}9H_2O$, and nesquehonite [$MgCO_3{\cdot}3H_2O$]. No applications of metallic magnesium scrap in acid mine drainage are reported in the literature, although in 2005, Kumar and Chakraborty advocated the use of magnesium metal to remove nitrate from waste water.

It was initially assumed that a simple corrosion reaction took place, but analyses of the encrusted material around the corrosion pit indicated that the reaction mechanisms in the mixed medium of acid mine drainage were more complex. The stability of the metal carbonates in the encrustation was most striking, as they were expected to dissolve in the acid water. Tests with 0.1 N sulfuric acid released no carbon dioxide.

5.7.4.4 Estimating Total Polishing Effects

The biological polishing capacity of the emerging ecosystem in the acid lake was estimated by: (1) adsorption and precipitation on periphyton growing on submerged brush, (2) the living portion of the underwater meadow on the sediment, and (3) metal capture by particulates forming with phytoplankton in the open water column. An approximation of the removal capacity of each of these components is presented in Table 5.18.

From measurements of the contaminant inputs, an estimated 283 t of zinc and 770 t of iron entered the lake between 1986 and 1999 from the mine/mill complex and the groundwater from the tailings. Multiplying the annual removal rates of the three quantified components of the ecosystem (Table 5.18) by 14 years gives an

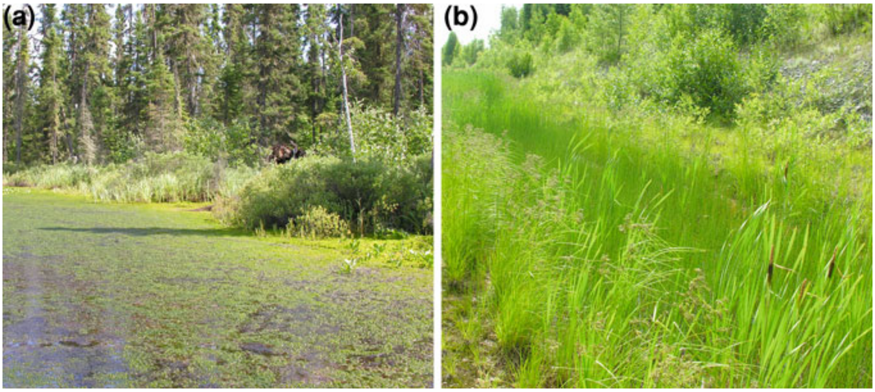


Fig. 5.61 **a** Boomerang Lake outflow. **b** diversion ditch in 2006 after addition of natural phosphate rock (NPR) and Mg scrap metal

estimate of the total amounts removed (8.3 t of zinc by periphyton, 0.25 t by the moss, and 10.9 t by particulates). Together, these sinks accounted for 6.9% of the zinc, but 485% of the iron that entered the lake during this period, a consequence of iron cycling within the lake. The contribution of the meadow biomass to contaminant removal was low, only 1.3% of the total, but stability of the sediments was its primary function.

Although whole lake input and output estimates are naturally associated with a large error, the excess iron found in the polishing components supports the concept of iron resuspension and oxidation. To quantify the reduction of iron particulate resuspension would have required the determination of sedimentation rates after 1997, when they increased three-fold (Table 5.17), but this was not done.

Periphyton accounted for 42%, but phytoplankton and inorganic particulates accounted for 56% of the total removal, indicating that phytoplankton and inorganic particulates are the major component of the biological polishing process. This is reasonable since the sequestration is primarily through adsorption onto particulate surfaces, and phytoplankton-particulates have a high surface-to-volume ratio, providing a large number of nucleation sites (Lowson 1998).

In 2000, water samples were collected at the sediment surface under the moss, and in the open water column. The combined effect of magnesium, phosphate rock waste, periphyton, and moss produced a small but consistently measurable pH difference of about 0.2 units (bottom higher). However, the iron, sulfur, and acidity concentrations were all lower at the sediment surface by 3.4, 70, and 9.2 mmol L^{-1}, respectively.

In 2006, the extensive biomass in Boomerang Lake likely added significant particulates to the water column for metal sequestration (Fig. 5.61a). Also, the extensive vegetation growth in a diversion ditch (Fig. 5.61b) is reducing the probability of iron-hydroxide particles entering the lake. Although no measurements could be carried out, these pictures suggest that the biological polishing (biota) capacity is maturing.

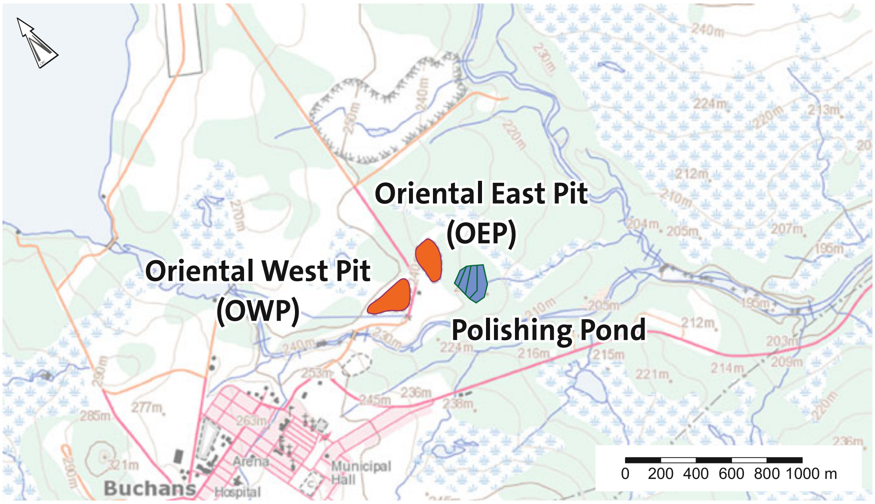


Fig. 5.62 Waste management area of Buchans, Newfoundland; the Oriental East and West Pit Lakes are in the *center*. Polygon to the right of the Oriental East Pit represents the polishing ponds

5.7.5 Case Study: Buchans, Newfoundland (ASARCO)

Buchans is a mining town located in central Newfoundland (48° 49′ 74″ N, 56° 50′ 15″ W). Mining for zinc, copper, gold, silver, and barite commenced in 1928 and ceased in 1984 (Thurlow et al. 1975). All water bodies discharged to the Buchans River, a trout fishery resource (Fig. 5.62). The owner was required to decommission a mine waste management area that included several underground mines, two tailings ponds, seeps from waste rock piles, drainage from mine workings, and three filled or filling glory holes (Fig. 5.62). Glory holes are open pits with adits dug into the pit wall and haulage or drainage tunnels located at the pit bottom. These adits and tunnels present hydrological conduits for groundwater and thus create very unusual flow and circulation conditions in the pit lakes. In 1986, work was initiated to treat two of the glory holes using the principles of ecological engineering.

5.7.5.1 Oriental West Pit

The Oriental West Pit (OWP) had filled to groundwater level by 1984, forming an acidic lake (pH 3.7–6.3) with a surface area of 0.46 ha, a maximum depth of 7 m, and a volume of 66,200 m^3, with no measurable groundwater recharge or discharge. During the first two summer seasons of the project, the limnological, geochemical, and hydrological characteristics of the pit lakes were determined.

Zinc and iron were the main contaminants released from the extensive underground workings of the various mines. Indigenous phytoplankton and periphyton were identified. Periphyton growth rates and the iron and zinc content of the periphytic mats were determined (Kalin and Wheeler 1992b) and the phytoplankton populations were identified. A report on the phytoplankton community structure, control factors, and biological monitoring can be found at: www.boojumresearch.com/about/. Particulate matter was also quantified with sedimentation traps. Geochemical simulations identified the zinc species and precipitation conditions.

In the OWP, the pit lake walls above the water line contained sulfidic zones, which generated acid, resulting in the low pH found during the summer months. Since the lake is stagnant and relatively shallow, an organic sediment layer needed to be established on the pit floor to generate alkalinity and reducing conditions. In 1992, one section of the lake was curtained off, and hay and peat were added to the lake (Fig. 5.63a). These materials were previously tested in the laboratory with several other available recalcitrant organic materials.

To supply easily degradable carbon to the sediment, phytoplankton growth was encouraged, and floating vegetation islands were established (Fig. 5.63b). The vegetation islands, composed mostly of cattails, formed an artificial littoral zone to protect the lake from the eroding sulfates in the exposed pit lake walls (Fig. 5.63b). The rafts also: (1) collected particulates in the root zone, (2) reduced wind circulation, and (3) promoted the formation of a chemocline in the shallow pit lake. Although the installation of the rafts and amendments had progressed well, the mine operator in 1993 decided to combine a nearby drainage tunnel effluent with the OWP lake water and channel it into the Oriental East Pit (OEP) lake. This changed both the hydrology and the geochemistry of the OWP. Since the remediation measures were designed for a stagnant water body, work on the OWP was terminated.

5.7.5.2 Oriental East Pit

The adjacent OEP lake has a surface area of 1.95 ha, a maximum depth of 20 m, and a volume of 208,200 m^3. This pit lake has a continuous recharge of alkaline pH composed of clean and contaminated groundwater ([Zn] 10–45 mg L^{-1}) with an average discharge of 20 L s^{-1}.

Zinc concentrations in the OEP effluent decreased naturally, but significantly, throughout the project (Pearson's $r = -0.78$, $P < 0.01$), but in the last five of those years (1993–1998), they decreased more slowly (Fig. 5.64). By the time the drainage tunnel effluents were added to the OEP, the combined effluent zinc concentration was mostly between 10 and 30 mg L^{-1}, with most of the fluctuations coming from the drainage tunnel effluent. This new source of variability may have been due to the rising water level in the Lucky Strike pit lake, which was flooding very slowly. The gradual water level rise in the exposed underground sulfide rock would exit through the drainage tunnel.

Fig. 5.63 **a** The acidic Oriental West Pit lake when peat and straw were added to form microbial active sediments. **b** Vegetation rafts to reduce wind circulation to the bottom of the pit

Chemical treatment of this water would form a very unstable sludge and require a high pH for removal. However, in the OEP, iron(II) groundwater oxidized and precipitated as iron(III) hydroxide in the alkaline pH surface layers of the pit lake, co-precipitating the zinc. This was most striking during the summer, when the pit lake would turn reddish brown (Fig. 5.65). A detailed study of the collected material in the sedimentation traps found that zinc was also precipitated on phytoplankton cell walls and enclosed in extracellular polymers (EP). Microbial cells were often found at the center of iron hydroxide particles, where they appeared to serve as nuclei for the formation and growth of precipitates (Lowson 1998). At higher than circumneutral pHs, some of the zinc precipitated as zinc-carbonate,

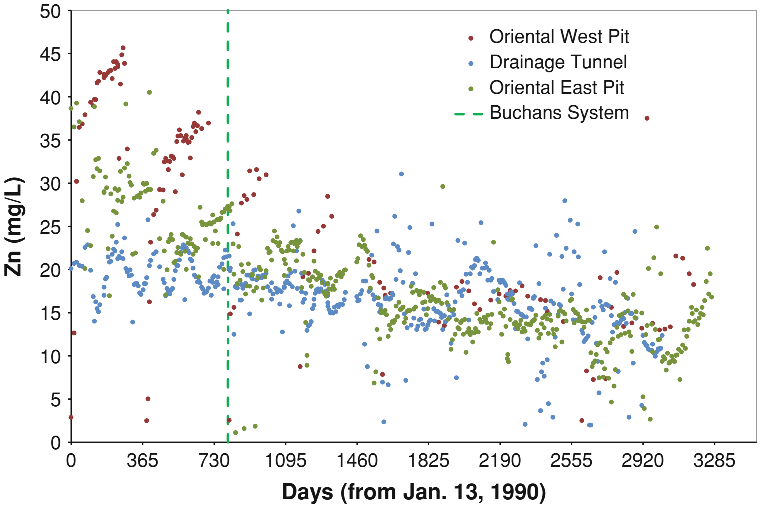


Fig. 5.64 Zinc trends in the Oriental system: red dots represent OWP, blue dots the underground workings and green dots the OEP 1989–1998

as geochemical simulations predicted. This precipitate was commonly found on the cell walls of the periphytic algae, which were found growing in the discharge area of the pit lake (Fig. 5.65).

Even though there were significant quantities of periphyton (*Zygogonium*) at the outflow, a curtain of floating vegetation islands was installed inside the pit lake to assist in removal of particulate matter, and a polishing pond was constructed downstream. Pilot-scale pond design criteria for full scale up were described by Kalin (1998). Two full-scale ponds, each covering 1.3 ha, performed well above design criteria, which were based on the original OEP outflow of 20 L s^{-1}, not the combined drainage tunnel flow. Alder brush cuttings were added for surface area in the ponds. No sediment was needed as the floor of the ponds was a living muskeg meadow, which, when decomposed, would provide an initial source of carbon for microbial transformations. Fertilization with a commercial slow–release fertilizer significantly enhanced periphyton growth in laboratory and pilot-scale tests with effluent from the OEP. However, growth was not enhanced in the mixed OWP and drainage tunnel effluent.

Generally, the summer performance between 1995 and 1998 was better than predicted (Fig. 5.66). Only three winters showed a negative retention, i.e. the system released zinc, in part due to a thick ice cover and the absence of oxygen in the water, which inhibits iron oxidation and the formation of precipitates. The most prominent release was recorded in 2001 (winter retention was −21%), after on-site personnel cleaned the pond of brush. Similar negative retentions occurred in 2007 and 2008, when the ponds were again cleaned out. The ponds were cleaned

Fig. 5.65 Brown strands of periphytic mats covered in iron hydroxide (mostly *Zygogonium* sp.) at the outflow of the Oriental East Pit lake.

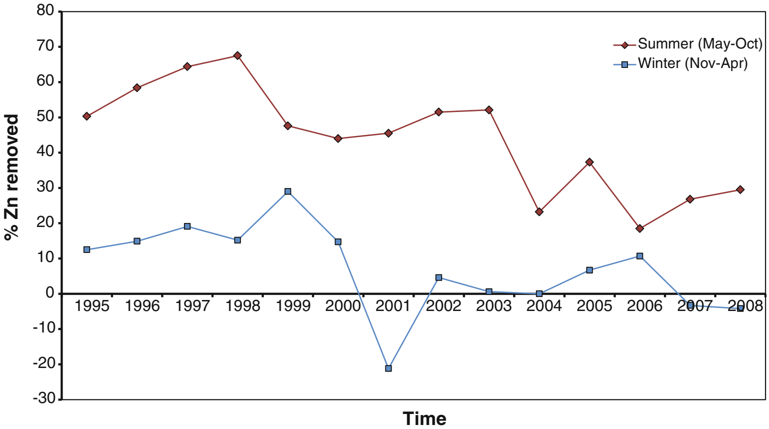


Fig. 5.66 Removal of zinc by the polishing ponds; diamonds represent summer removal rates (May-Sep) and rectangles represent winter removal rates (Oct–Apr), 1995–2008

out to increase removal efficiency. However, it had the opposite effect, since the surface area was reduced and the sediments were destabilized.

When the original ponds were constructed, it was suggested that measures be taken to reduce ice cover and thereby enhance oxidation during winter, but this option was not pursued. The project was cancelled in 1998, after the death of the mine manager. A site visit in 2009 revealed that the previously extensive periphytic growth was limited to the second pond system.

5.7.6 Conclusions

Three lake systems, ranging from alkaline to very acidic, have been described. Each site required general ecological measures (e.g. biological polishing, sediment conditioning), that varied based on the specific geochemistry of the site. Our approach was to: (1) utilize natural, indigenous flora and suspended solids (both organic and inorganic) to sequester the metals; (2) use natural particle aggregation processes to increase density and promote settling, and (3) create organic sediments or enhance existing contaminated sediments on the lake bottoms, providing or supporting low redox conditions where the particulate matter with mainly oxidized metals would facilitate bio-mineralization through microbial transformations.

Algae can grow in acidic lakes, albeit slowly. Their productivity appears to be principally related, not to the acidity or metal content of the water, but to the lack of nutrients, such as inorganic carbon and phosphorus (Kalin et al. 2006; Simmons et al. 2004; Spijkerman 2005). Recent literature on the use of periphyton and phytoplankton to remove metals supports what has been documented in these case studies (Boshoff et al. 2004; Crusius et al. 2003; Das et al. 2009). Algae have also been considered as a potential carbon source for microbial metal transformations (Boshoff et al. 2004) that can increase the alkalinity of acidic lakes (Kleeberg et al. 2006). Phytoplankton have also been used to remove metals in uranium pit lakes (Dessouki et al. 2005).

Moss covers on the sediment provide a natural means to stabilize lake sediments. Moss is unique in that the rhizoids (root-like structures) that hold the plants to the sediment do not transmit oxygen into the sediment, allowing them to stabilize the sediments, photosynthesize and grow, yet not disturb the redox conditions below (Jaynes and Carpenter 1986). At the same time, moss can sequester metals and provide oxygen to the water over the sediments (Gstoettner and Fisher 1997).

A significant component of the restoration process, as exemplified by the above case studies, involves the promotion of biogeochemical polishing by suspended solids. Suspended solids are composed of biomass, sediments, organic detritus, and inorganic precipitates. Increasing primary productivity contributes to the biological component. Biological activity in waste water contributes not only suspended solids, but macromolecules such as extracellular polymerics, humic, and fumic substances, and other organic acids produced by degrading biomass. These macromolecules contribute to the chelation of metals and aggregation of metal complexes into colloidal matter (Buffle and van Leeuwen 1993). As the particles aggregate, due to the attractive forces of surface coatings and dissolved organics, they become more dense, eventually settling to the lake bottom. The goal is to produce reducing conditions in the sediments where microbial consortia can reduce oxidized iron and zinc, and in the presence of sulfate, produce metal sulfides.

All three case studies were carried out and largely financed by mining companies. All effluents were monitored by the respective environmental regulatory bodies. Each project was intended as an R&D project to showcase ecological engineering concepts, and to demonstrate the feasibility of providing a long-term, sustainable solution to mine waste water management at the end of a mining operation. Each project lasted longer than a decade, and was brought to a conclusion by the mining companies. Each project also received concurrent university and/or government-supported research support, which enabled laboratory and scale-up experimentation. All three case study sites still exist and provide fertile ground for further research. Most importantly, though, they are proof in principle, directly or indirectly, of the feasibility of ecological engineering measures.

5.8 Acid Inventories and their Impact on Groundwater in the Rhineland Lignite Mining District (Germany)

Frank Wisotzky, Stephan Lenk and Vera Eisenberg

5.8.1 Introduction

The Rhineland Lignite Mining District, which is located in the triangle between the cities of Düsseldorf, Cologne, and Aachen, is the largest lignite mining area in Western Europe, with a reserve of 55×10^9 t of lignite. There are currently no large pit lakes in the Rhineland lignite mining area but three huge pit lakes are projected when mining ends in 2045. The determination of acid inventories and the resulting groundwater quality in overburden dumps are discussed below.

When overburden containing sulfide minerals (pyrite) are exposed to atmospheric oxygen, partial oxidation of geogenic pyrite occurs (Evangelou and Zhang 1995; Ludwig 2001; Van Berk and Wisotzky 1995; Wisotzky 1998; Zimmer et al. 2005). The total amount of acidity that is formed and released by this weathering depends on the degree of pyrite oxidation (Moses et al. 1987; Sánchez et al. 2005). Consequently, the amount of oxidized pyrite is the major control on all of the hydrogeochemical reactions in a mine dump (Wisotzky and Obermann 2001). However, accurate determination of this parameter is challenging.

In the case of projected mines, no pyrite oxidation has yet occurred, so the amount and rate of pyrite oxidation in the associated dumps needs to be predicted. In the case of operational mines, the degree of pyrite oxidation can be measured based on a representative number of overburden samples. Finally, if a mine is closed and vegetated and a groundwater body has developed, the oxidized pyritic sulfur content of mine dump material may be inversely calculated based on groundwater analyses. The oxidized pyritic sulfur content cannot be measured directly based on solid matter analysis because after oxidation, sulfur is present as sulfate and stored as soluble alteration minerals and dissolved in the pore water (mostly under unsaturated conditions) or in the dump water (saturated conditions).

Neutralization of acidic water with carbonate minerals like calcite and dolomite increases the concentrations of dissolved calcium and/or magnesium. This reaction is enhanced by the relatively high carbon dioxide concentrations commonly present in seepage water and mine dump groundwater (Lenk and Wisotzky 2011). The ability of carbonate minerals such as calcite and dolomite to neutralize acidity is called neutralization potential (NP). However a precise commonly accepted definition of this capacitive measure does not exist (Morin and Hutt 1997, 2009).

Acid mine drainage (AMD) production, i.e. pH and mineralization of the mine water, depends on the ratio of acid-producing and acid-consuming reactions. The ratio of those components is influenced by several site specific factors (e.g. pyrite and inorganic carbon content of the overburden, exposure time, rate of oxygen diffusion, pH, temperature, as well as the configuration and type of the dump). Thus, it is necessary to estimate the oxidized pyrite content of the dumped rock and its effective acid-neutralizing capacity to predict the future water chemistry of groundwater and pit lake water.

5.8.2 Leaching of Sulfate from Overburden Materials

The overburden of the Rhineland Lignite Mining Area in Germany contains, on average, about 0.1–0.3 wt % pyritic sulfur, which is partially oxidized to sulfate during mining. Lenk and Wisotzky (2008a) developed a method to determine the actual degree of pyrite oxidation as well as the effective acid–base-balance (ABB) of an entire, operational coal mine. The method is based on sulfate analysis from a number of overburden samples in combination with geometric and exposure time factors to determine the average oxidized pyritic sulfur content of dump material and its effective ABB.

Acid–base-balance is a capacitive measure equal to the difference between the acid-neutralizing capacity (ANC) and the base-neutralizing capacity (BNC; Morin and Hutt 1997; Wisotzky 2003):

$$\mathrm{ABB_{pH7}[mmol\,H^+/kg] = ANC_{pH2}[mmol\,H^+/kg] - BNC_{pH7}[mmol\,H^+/kg]} \quad (5.15)$$

A positive ABB value indicates the ability of a (partially oxidized) sample to neutralize acidity. A negative value indicates that the sample will release acidity within the dump. If pure, degassed water were to be titrated, the resulting ABB value would be zero.

Within the Rhineland Mining Area, overburden is extracted via bucket wheel excavators. Afterwards, it is transported through belt conveyors to the dump site and is disposed via spreaders (after addition of crushed limestone). Therefore, the newly-dumped material contains all of the pyrite oxidation products formed on the extraction site. Hence, sulfate analyses from a representative number of spreader samples allow an exact determination of the oxidized pyritic sulfur content. The average value reflects the effects of reaction kinetics and gas transport processes,

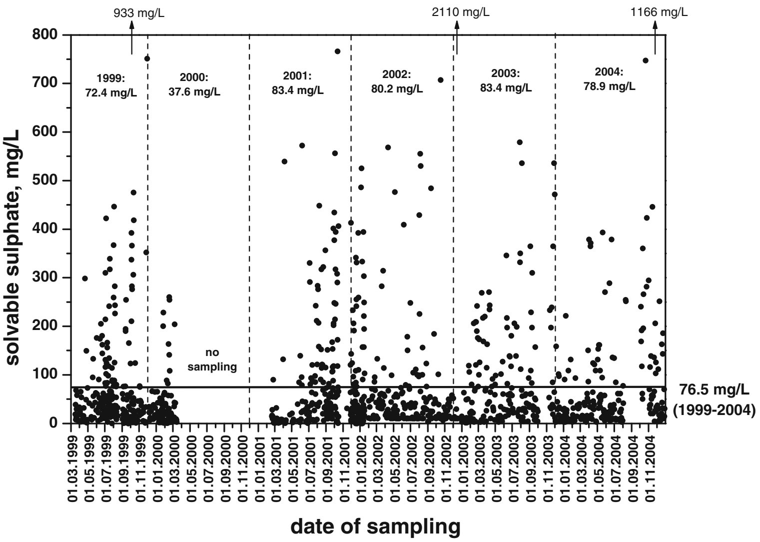


Fig. 5.67 Change of the soluble sulfate concentrations over time leached from limed spreader samples (*n* = 1212; modified after Lenk and Wisotzky 2008a)

so that utilization of extensive kinetic laboratory tests, as suggested by Sobek et al. (1978), is not necessary at operational mines similar to the Rhineland type.

Lenk and Wisotzky (2008a) examined about 1,200 limed spreader samples of the Garzweiler open pit mine over a period of six years to determine the soluble sulfate concentration and the oxidized pyritic sulfur content, respectively. For this purpose, the authors suspended 42.5 g of moist overburden in 280 mL of distilled water and shook it for 2 h under an argon atmosphere. The analyzed sulfate concentrations were used to calculate the amount of oxidized pyrite sulfur on a dry matter basis. Afterwards, the ABB of the formerly shaken samples was determined.

Within the Garzweiler lignite mine, soluble sulfate compounds are transported to the dump with a high spatial and temporal variability (Fig. 5.67). This means that acidic sediments are located close to near-neutral sediments within the dump. After the groundwater rebounds, natural titration of acid-forming and acid-consuming subzones by the moving groundwater will occur.

The annual mean sulfate concentrations have been relatively constant at about 80 mg/L since 2001. This value is nearly equal to the six-years-mean of 76.5 mg/L (Fig. 5.67). Calculated on a dry matter basis, a sulfate concentration of 76.5 mg/L is equal to an oxidized pyritic sulfur content of 0.0183 wt %. This value comprises the effects of dewatering and exposition of the overburden material at the extraction site. Since the overburden contained 0.225 wt % pyrite sulfur prior to being exposed to the atmosphere, the oxidation degree of the analyzed material is equivalent to 8.1% directly after dumping. Additional oxidation takes place after dumping, especially on freshly exposed or formed surfaces.

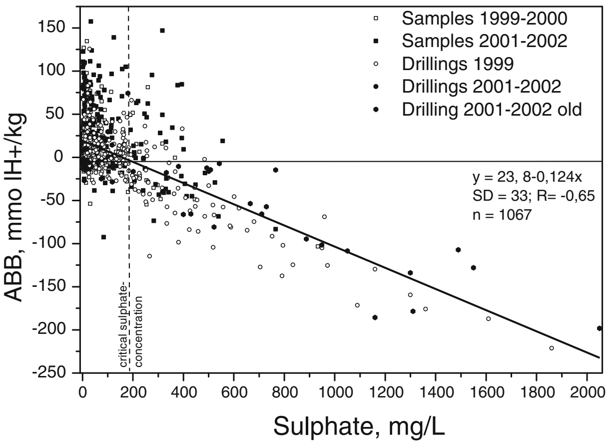


Fig. 5.68 Correlation between ABB and soluble sulfate concentrations for 1067 limed soil samples of the Garzweiler overburden dump (critical sulfate concentration = 190 mg/L; modified after Lenk and Wisotzky 2008a)

Since representative sampling of a dumping site is complex, determining its average oxidized pyrite sulfur content is much more difficult than for an extraction site. Therefore, Lenk and Wisotzky (2008a) determined the extent of pyrite oxidation on the dump site with the aid of an empirical conversion factor. On this basis, it was possible to assess the total oxidized pyritic sulfur content of the entire overburden dump. The conversion factor of 2.12 accounts for geometric features of the dump and exposure times. This factor reveals that pyrite oxidation is slightly more intensive on the dumping site than on the Garzweiler extraction site. The use of this conversation factor leads to an average oxidized pyritic sulfur content of the entire dump of 0.039 wt %, while the content of the extraction site is about 0.0183 wt %. This is consistent with a total oxidation degree of 17%.

In the procedure provided by Lenk and Wisotzky (2008a) the soluble sulfate concentrations and the corresponding values for ABB of limed samples have to be compared to evaluate whether a dump will become acidic or not after closure (Fig. 5.68).

Under the given geochemical conditions at Garzweiler, acidification of the limed dump would occur when soluble sulfate concentrations exceed 190 mg/L (Fig. 5.68). Above this point, the linear regression equation results in negative values for ABB. Additional soluble sulfate increases the intensity of acidification of the dump water, which will evolve in the future.

However, acidification of the limed dump water is not expected at Garzweiler. An average soluble sulfate concentration of 76.5 mg/L was determined by the analysis of 1,212 spreader samples. Because further oxidation of the overburden takes place on the mine dump site, this value has to be multiplied by the empirical conversion factor of 2.12 (see above). This leads to an average sulfate concentration of 162 mg/L, which is less than the critical value. Lenk and Wisotzky

(2008a) concluded from these calculations that the limed dump and pit lake water in Garzweiler will be near-neutral and not lime aggressive.

5.8.3 Container Tests

Since 1998, crushed limestone has been added to the overburden at the Garzweiler lignite mine prior to tipping (Boehm and Von Schwarzenberg 2000; Kwasny 2011). The added limestone neutralizes the sulfide and metal acidity and induces the precipitation of gypsum, which in turn reduces the dissolved sulfate concentration of the future dump and pit lake water. Additionally, the precipitation of iron carbonates removes dissolved ferrous iron and other metals from solution. Direct addition of alkaline solids to overburden, as practiced in the Rhineland Mining District, is not widespread, because the total amount of acidity stored in a dump is often unknown and this parameter needs to be determined in order to add the optimal amount of limestone.

To investigate the future groundwater composition of the limed Garzweiler dump under controlled conditions, Wisotzky (2001, 2003) conducted pilot-scale container tests. On the basis of hydrochemical measurements, it was possible to calculate the oxidized pyritic sulfur content of sediments by thermodynamic modeling. Additionally, the transformed amounts of other relevant mineral phases (e.g. carbonates and silicates) as well as the dominant geochemical processes was modeled and determined.

Each container test was conducted with 13 t of moist overburden. The pyrite content as well as the oxidation degree of the test material had to be similar to the average geochemistry of the overburden dump. Crushed limestone was added to one of the containers, using a quantity based on earlier laboratory studies (Kringel 1998). The material in a second container was kept untreated (reference container). Subsequently, both containers were filled with 2.7 m^3 of native groundwater and sealed under an atmosphere of nitrogen to prevent further pyrite oxidation. All principal constituents, pH, E_H, and trace elements had been analyzed. Therefore, forward modeling with PHREEQC-2 (Parkhurst and Appelo 1999) was feasible.

High sulfate concentrations of up to 4,500 mg/L in the pore water of the reference container indicated intense dissolution of pyrite oxidation products (Fig. 5.69a). The consequence of sulfide mineral oxidation and acidic weathering was low pH (between 3 and 4) due to the low content of naturally occurring carbonates (Fig. 5.69b). Furthermore, the considerable negative saturation indices computed for calcite showed that the pore water is lime aggressive under these acidic conditions (Fig. 5.69c). As calcium concentrations were low, precipitation of gypsum was not possible, although sulfate concentrations were very high. This is indicated by negative saturation indices with respect to gypsum (Fig. 5.69d).

In contrast to the reference container, the addition of limestone caused near-neutral pH values (as high as 6.7) after a reaction time of half a year (Fig. 5.69b). This is consistent with the system being in equilibrium with calcite (Fig. 5.69c).

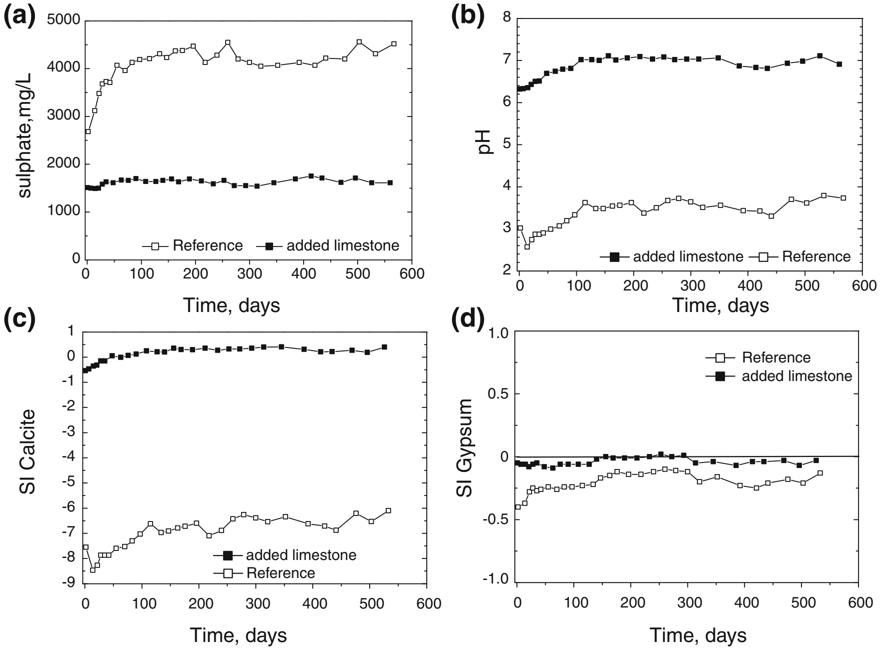


Fig. 5.69 **a** Evolution of sulfate concentrations during container tests (modified after Wisotzy 2003). **b** Evolution of pH during container tests (modified after Wisotzy 2003). **c** Saturation state of water samples with respect to calcite during container tests (modified after Wisotzy 2003). **d** Saturation state of water samples with respect to gypsum during container tests (modified after Wisotzy 2003)

The alkaline material was a source of calcium ions and led to decreased sulfate concentrations due to precipitation of gypsum (Fig. 5.69a, d). The container experiments also showed that the addition of crushed limestone caused a decrease in dissolved ferrous iron concentrations by the precipitation of iron carbonates and ion exchange processes. The final iron concentration in the container with the alkaline additive was less than 100 mg/L, which was only 8% of the iron concentration in the reference container (data not shown).

Using forward computer modeling, it was possible to reconstruct the main chemical reaction paths that caused the measured evolution of the pore water chemistry within the two containers. The strategy was to solve mass balance equations using initial and final water compositions, a specified set of mineral assemblages identified in the field and cation exchangers. In Table 5.19, the initial conditions of the simulations and the required set of primary and secondary minerals are displayed.

The simulations show that the initial amount of soluble sulfate, i.e. the amount of oxidized pyritic sulfur, was nearly the same in both containers. About 22.4–22.7 mmol/L of the pyrite was already oxidized in the mine prior to their emplacement (Table 5.20). On a dry matter basis, this is equal to an oxidized

Table 5.19 Mineral assemblage, gas phases and cation exchange capacity of the forward model to reconstruct the evolution of the pore water chemistry in container experiments

Mineral phases				Gases
Carbonates	Sulfides	Silicates	Hydroxides	CO_2
Calcite	Pyrite	Albite	$Fe(OH)_{3amorphous}$	O_2
Dolomite		Orthoclase	$Al(OH)_{3amorphous}$	
Siderite	Sulfates	Kaolinite		
Rhodochrosite	Gypsum	$SiO_{2amorphous}$		

Cation exchange capacity: 0.34 mmol(eq)/L (Wisotzky 2003)
Mass ratio of water to solids: 3.387 : 1 (Wisotzky 2003)

Table 5.20 Calculated amounts of mineral and gas phases as well as changes of the cation exchange configuration during container experiments

		Reference container			Container with added limestone		
		1st day	602nd day	Amount	1st day	602nd day	Amount
Cation Exchange, mmol(eq)/L	$Ca\text{-}X_2$	9.487	3.400	−6.087	9.487	8.441	−1.046
	$Mg\text{-}X_2$	1.928	0.640	−1.288	1.928	1.051	−0.877
	K-X	0.054	0.222	+0.168	0.054	0.141	+0.087
	$Fe\text{-}X_2$	2.1×10^{-4}	6.618	+6.618	2.1×10^{-4}	1.789	+1.789
	$Al\text{-}X_3$	1.2×10^{-7}	0.444	+0.444	1.2×10^{-7}	0.000	±0.00
Mineral phases, mmol/L	FeS_2			−22.44			−22.71
	$CaCO_3$			−1.52			−35.00
	$CaMg(CO_3)_2$			−1.00			−1.50
	$FeCO_3$			−9.20			+5.61
	$MnCO_3$			−0.50			−0.08
	$Fe(OH)_{3amorphous}$			0.00			+10.06
	$Al(OH)_{3amorphous}$			0.00			0.00
	$CaSO_4 \times 2H_2O$			0.00			+26.07
	Albite			−1.00			−1.00
	Orthoclase			−1.20			−0.60
	Kaolinite			−0.71			+0.80
	$SiO_{2amorphous}$			+6.47			+1.64
Degassing, mmol/L	CO_2			−16.08			−28.64

pyritic sulfur content of 0.042–0.043 wt %. Since the average pyritic sulfur content of the overburden in Garzweiler amounts to 0.258 wt %, the degree of oxidation was about 16.5%.

The amounts of modeled dissolved calcite and dolomite were low in the reference container because of its low original calcite and dolomite content. Siderite is unstable under these strongly acidic conditions. Hence, 9.2 mmol/L were dissolved after 600 days (Table 5.20). Given the acidic conditions and the associated high mobility of iron and aluminum, nearly all of the exchange sites were saturated with these metals. Adsorbed calcium and magnesium were exchanged with the mobilized ferrous iron and aluminum. The water of the reference container was undersaturated with respect to gypsum. Precipitation of gypsum did not occur because calcium concentrations were insufficient.

In the container with the added crushed limestone, 5.6 mmol/L of siderite and about 10 mmol/L of amorphous $Fe(OH)_3$ precipitated. These precipitation reactions reduced the dissolved iron concentration and the amounts of exchangeable iron, respectively. Since the calcium concentration increased strongly due to calcite dissolution, saturation was reached with respect to gypsum. Thus, 26.1 mmol/L of gypsum were precipitated in 600 days (Table 5.20).

Even though primary silicates are much more abundant than carbonates, the bulk of the released alkalinity was the result of carbonate dissolution rather than the hydrolysis of silicates. Slight formation of the clay mineral kaolinite was only modeled at the near-neutral pH conditions occurring in the container with the added limestone (Table 5.20).

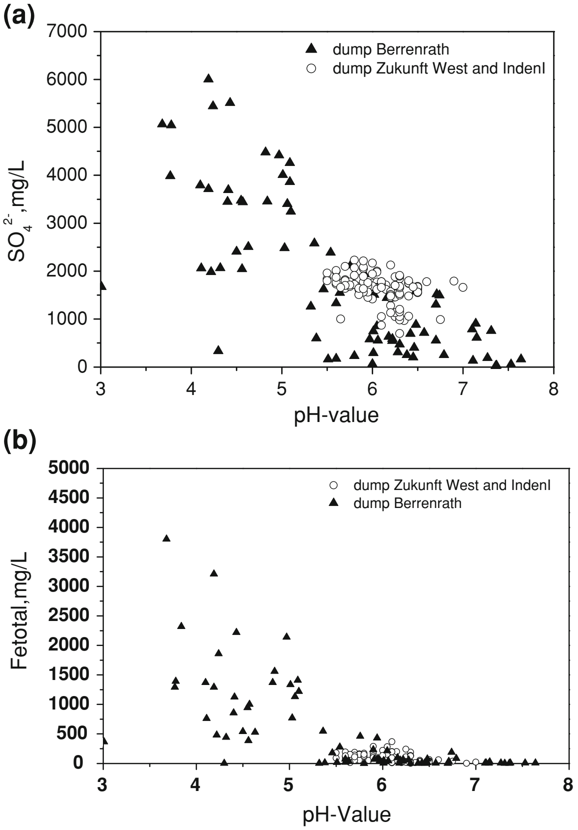
5.8.4 Groundwater Analysis and Inverse Modeling

Sulfate concentrations up to a several thousand mg/L are quite common in lignite mine dumps. The groundwater of the Berrenrath, Zukunft/West, and Inden mine dumps of the Rhineland lignite mining area have sulfate concentrations between 20 and 7,000 mg/L (Fig. 5.70a). Lower concentrations, up to 2,000 mg/L, are observed in groundwater samples with a pH above ca 6. The sulfate concentrations are mainly limited by the precipitation of gypsum (see below). Sulfate concentrations are generally higher in groundwater samples with lower pH values. Below pH 5, the sulfate concentrations are mainly between 2,000 and 7,000 mg/L (Fig. 5.70a). The sulfate concentrations in the groundwater are normally lower than in the seepage water of pyrite oxidation zones (Wisotzky 1998). This is because overburden dumps contain both pyrite oxidation zones and zones with unoxidized material (Wisotzky 2003). The groundwater is a mixture of waters from both.

Depending on the degree of pyrite oxidation and pH buffering, the pH values are between neutral values and acidic values in lignite overburden dumps (Fig. 5.70a). In the groundwater of the Berrenrath and Zukunft/West dumps, the pH values range between 3.5 and 8.

In the seepage water of the Garzweiler mine experimental dumps, iron concentrations up to 15 g/L (Wisotzky 1998) were observed, while in a column test, up to 97 g/L were measured (Zimmer et al. 2005). The iron concentrations were lower in lignite overburden dump groundwater than in pyrite oxidation zones. The measured iron concentrations in the groundwater of overburden dumps are strongly influenced by secondary fixation reactions if the pH is above 6, as in the Berrenrath and Zukunft/West mine dumps, where the measured iron concentrations were mostly lower than 200 mg/L, due to cation exchange or precipitation of

Fig. 5.70 **a** pH versus sulfate concentration in groundwater samples from the Berrenrath and Zukunft/West mine dumps. **b** pH versus iron concentration in groundwater samples from the Berrenrath and Zunkuft/West mine dumps

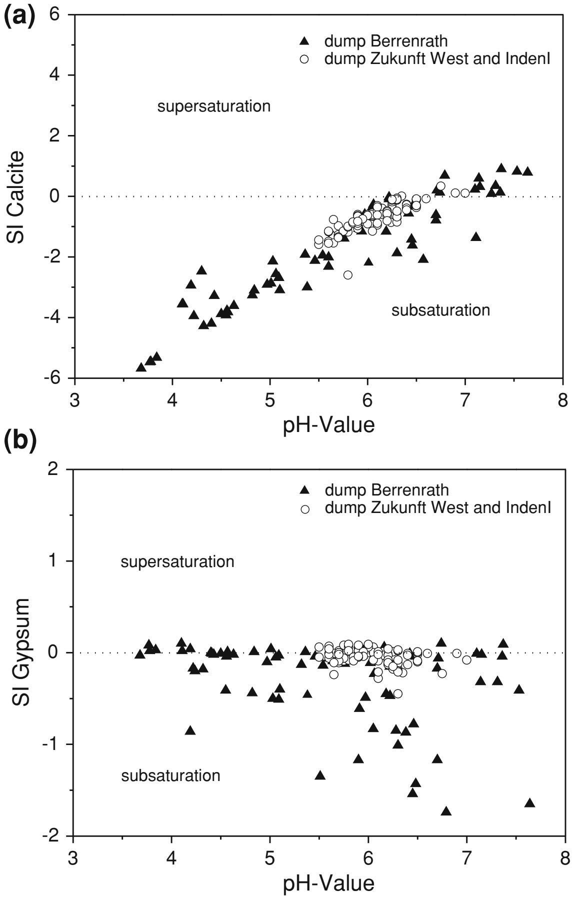


ferrous iron as iron carbonate (siderite) or iron-containing solid solutions in carbonate mineral phases. Groundwater samples with lower pH values can have higher dissolved iron concentrations. For example, iron concentrations of up to 4,000 mg/L have been observed (Fig. 5.70b) in the Berrenrath dump.

The pH in the groundwater of overburden dumps is of course also influenced by dissolution of carbonate minerals. Groundwater samples of the Berrenrath and Zukunft/West overburden dumps show calcite saturation indices around 0 (SI calcite) when the pH is above 6.3 (Fig. 5.71a), meaning that the pH values are determined by calcite dissolution reactions. Below pH 6.3, the SI calcite decreases with decreasing pH values. This explains the complete dissolution of calcite in many lignite overburden dumps.

Calcite dissolution leads to increased dissolved calcium in the groundwater of the lignite overburden dumps. High dissolved calcium concentrations are quite common and can lead to precipitation of gypsum, if the solubility product is exceeded. Many groundwater samples from the Berrenrath and Zukunft/West overburden dumps display gypsum SI values of 0 (Fig. 5.71b). In these samples, precipitation of gypsum likely controls the calcium and sulfate concentration of

Fig. 5.71 The pH dependence of calculated saturation indices of groundwater samples from the Berrenrath and Zukunft/West mine dumps with respect to calcite (**a**) and gypsum (**b**)



the groundwater. No substantial supersaturation was observed in the lignite overburden dumps groundwater.

Iron carbonate (siderite) can form in the dumps when the groundwater contains sulfate concentrations less than 20 mmol/L (Fig. 5.72). Groundwater samples with higher sulfate concentration (>20 mmol/L) display a sulfate:iron ratio around 2:1, like the ratio in the pyrite mineral phase, indicating that little or no secondary iron precipitates are forming (Fig. 5.72).

At locations where lignite dumps are connected to aquifers or lakes, there is a potential for highly mineralized dump water to migrate from the disposal area and degrade adjacent groundwater bodies and surface waters. The Inden and Zukunft/West lignite surface mines in the western part of the Lower Rhineland are connected to a complex aquifer system, which is used intensively for groundwater extraction. After mine dewatering ends, the local groundwater will generally return to its earlier flow direction. Thus, contamination of the aquifer system by infiltrating dump waters is expected. For this reason, the chemical groundwater

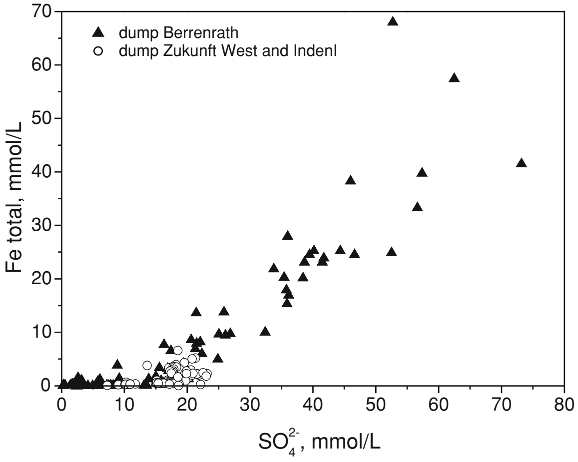


Fig. 5.72 Iron vs. sulfate in groundwater samples from the Berrenrath and Zukunft/West overburden dumps

Table 5.21 Hydrochemical composition of 91 groundwater samples from 16 observation wells in the Inden and Zukunft/West lignite mine dumps (1999–2004; data from Lenk 2008)

Parameter	Unit	Average value (minimum–maximum)
pH		6.2 (5.1–8.3)
Specific conductivity	μS/cm	2,720 (1,633–4,840)
Ca^{2+}	mg/L	538.3 (312.3–888.2)
Mg^{2+}	mg/L	87.5 (1.9–159.2)
Na^{+}	mg/L	16.8 (3.5–66.9)
K^{+}	mg/L	8.1 (3.3–17.6)
Fe-total	mg/L	106.6 (0.1–487.0)
SO_4^{2-}	mg/L	1,535.0 (680–2,810)
Cl^{-}	mg/L	59.3 (27.0–199.0)
HCO_3^{-}	mg/L	325.2 (20.7–675.3)
CO_2-total	mg/L	596.6 (92.8–979.9)
SI calcite		−0.55 (–2.53–0.57)
SI siderite		0.96 (–0.40–1.37)
SI gypsum		−0.07 (–0.20–0.20)

composition was simulated by Lenk (2008) and Lenk and Wisotzky (2011) for the next three centuries, using inverse hydrogeochemical modeling.

The observed groundwater chemistry in parts of the Inden and Zukunft/West surface mines where a dump water body (30–40 m in thickness) has already developed is displayed in Table 5.21.

Pyrite oxidation typically results in enhanced sulfate concentrations (from 680 to 2,810 mg/L) and high iron concentrations (107 mg/L, on average; Table 5.21). At near-neutral pH under reducing redox conditions, precipitation of siderite ($FeCO_3$) and cation exchange processes remove about 75% of the released ferrous iron, so iron concentrations in the dump water are relatively low compared to the

Table 5.22 Hydrochemical composition of the dump water in the Inden lignite mine and in the adjacent aquifers (data from Lenk and Wisotzky 2008b)

Parameter	Unit	Water and soil analyses	
		Dump water	Native groundwater
pH		6.3	7.1
Specific conductivity	μS/cm	2,788	535.8
Ca^{2+}	mg/L	504.4	72.2
Mg^{2+}	mg/L	72.7	13.3
Na^+	mg/L	15.1	9.4
K^+	mg/L	7.9	2.3
Fe-total	mg/L	121.5	6.3
Mn-total	mg/L	4.4	0.2
SiO_2-total	mg/L	19.8	10.7
Al^{3+}	mg/L	0.6	< 0.05
$SO_4{}^{2-}$	mg/L	1,484.2	39.3
Cl^-	mg/L	72.3	21.8
$HCO_3{}^-$	mg/L	398.8	267.0
CO_2-total	mg/L	627	235.9
SI calcite		−0.34	−0.26
SI siderite		1.24	0.80
SI gypsum		−0.11	−1.95
Pyritic sulfur	mg/kg	840	n.d.
Inorganic carbon	mg/kg	80	n.d.

concentrations of sulfate. Dissolution of calcite prevents intensive acidification of the dump water. A mean pH below 6.3 as well as a negative SI with respect to calcite indicates near-complete consumption of calcite during dump water evolution. The overall result is a near-neutral groundwater of high ionic strength, with sulfate, calcium, and ferrous iron being the dominant dissolved ions (Table 5.21).

Lenk and Wisotzky (2008b) carried out inverse modeling calculations to determine the oxidized pyritic content of the vegetated Inden mine dump and to account for the hydrogeochemical changes that occurred during the evolution of the dump water. Inverse modeling calculates the mole transfers of minerals and gases, i.e. the precipitated or dissolved amounts, by solving a set of linear equalities using the PHREEQC-2 computer code (Parkhurst and Appelo 1999). The analytical data for the dump water of the Inden lignite mine and the native groundwater in the adjacent aquifers are given in Table 5.22. The native groundwater was assumed to be the initial water composition that has filled the dump in the past and the dump water chemistry was defined as the final water composition.

The predominant reactions determined by inverse modeling are pyrite oxidation, calcite (and dolomite) dissolution, siderite precipitation, and ion exchange. The simulations indicate decomposition of geogenic pyrites as the initial reaction step, which is caused by a change in redox conditions. Next, the products of pyrite oxidation are leached from the acidic overburden into the dump water, causing

Table 5.23 Mass transfers during dump water evolution in the Inden lignite mine, given by Lenk and Wisotzky (2008b); 1 L of groundwater reacted with 4.145 kg of solid

Sulfide oxidation		
Oxidized pyritic sulfur	15.01 mmol/L	120 mg/kg
Carbonate dissolution		
Calcite	9.28 mmol/L	26.9 mg C_{inorg}/kg
Dolomite	2.45 mmol/L	14.2 mg C_{inorg}/kg
Rhodochrosite	0.08 mmol/L	0.2 mg C_{inorg}/kg
Precipitation of siderite	5.33 mmol/L	15.4 mg C_{inorg}/kg
Ion exchange ($2NaX + Fe^{2+} \Leftrightarrow 2Na^+ + FeX_2$)	0.25 mmol (eq)/L	0.06 mmol (eq)/kg
Precipitation of gypsum	0 mmol/L	0 mg/kg

sulfate concentrations to rise from 39 mg/L in the native groundwater to 1,484 mg/L in the dump water (Table 5.22). The modeled increase of sulfate is equivalent to an oxidized pyritic sulfur content of 120 mg/kg. Given the initial pyrite sulfur content, it appears that about 14.3% of the iron sulfides have been oxidized at Inden.

Pyrite oxidation and the associated release of sulfuric acid are the driving forces for all of the reactions that follow, especially dissolution of calcite (about 9.3 mmol/L, Table 5.23). The dissolution of calcite and dolomite prevents acidification of the groundwater, as illustrated by the 6.3 pH and high calcium and magnesium concentrations in the dump water (Table 5.22). Due to carbonate dissolution and impeded degasification of CO_2 (closed system conditions) a distinct increase of dissolved CO_2 was observed and modeled for the dump water. Bicarbonate (HCO_3^-) concentrations also rose during dump water genesis (Table 5.22).

The increased concentrations of sulfate and calcium are not high enough to reach equilibrium with respect to gypsum. Hence, no precipitation of gypsum was modeled (Table 5.23).

The oxidation of iron sulfides is a source of ferrous iron. Therefore, the iron concentrations rise from 6 mg/L in the native groundwater to 122 mg/L in the dump water (Table 5.22). Some of the iron from pyrite oxidation is taken up by ion-exchange sites, which release calcium to solution (Table 5.23). However, the bulk fraction of the released ferrous iron is removed from solution by siderite precipitation (5.3 mmol/L, Table 5.23). On the basis of inverse modeling, precipitation of siderite and ion exchange processes retained about 72% of the liberated ferrous iron.

5.8.5 *Conclusions*

Determining the average amount of oxidized pyrite at a mine or overburden dump is essential for predicting subsequent groundwater and pit lake water quality. The amount of oxidized sulfide together with the carbonate content is responsible for the acid inventory of overburden dumps, which dominates their groundwater quality and their discharge into adjacent aquifers (Lenk and Wisotzky 2011) and pit lakes. The overburden material of the Garzweiler Mine is limed before dumping to avoid acidic groundwater. The resulting groundwater quality was investigated with container experiments, which demonstrated that without liming, the overburden would produce acidic groundwater.

5.9 The Economics of Mine Pit Restoration: The Case of Pit Lakes in Lusatia, Germany

Nele Lienhoop and Frank Messner

5.9.1 *Introduction*

Lusatia, one of Germany's driest regions with merely 550–600 mm of annual precipitation, faces one of the most serious water scarcity problems in German history. Since the early 20th century, large-scale open pit lignite mining has been the dominant economic activity in Lusatia, which became the centre for energy production during the former socialist German Democratic Republic (Schultze et al. case study 5.1; Fig. 5.73). Until the closure of the pits in 1990, lignite mining seriously impacted the water balance in the catchments of the River Spree and Schwarze Elster. Mining required dewatering of the near-surface groundwater; on average, about six tons of groundwater were removed for each ton of lignite extracted. This lowered the groundwater table over an area of about 2,100 km^2, creating a cumulative groundwater deficit of 13 billion m^3 (BUND 2001; Grünewald 2005). However, the pumped groundwater was discharged into the rivers and, as a consequence, economic activities depending on water flourished. The 'Spreewald' wetland area, a UNESCO world heritage site, became larger and attracted increased numbers of visitors, and the capital city of Berlin with its three million inhabitants never experienced water supply problems (Messner et al. 2006).

With the termination of lignite mining after German re-unification in 1990, the pumping of groundwater ceased. At the same time, a whole economic sector collapsed, which triggered a regional socio-economic crisis, with high unemployment rates, a labile economic structure, and growing emigration (Koch et al. 2005; Wechsung 2005). While traditional water users (e.g. energy production, pond fisheries, and recreation at reservoirs and in wetland areas) suffered from the termination of groundwater pumping, a new surface water user entered the scene.

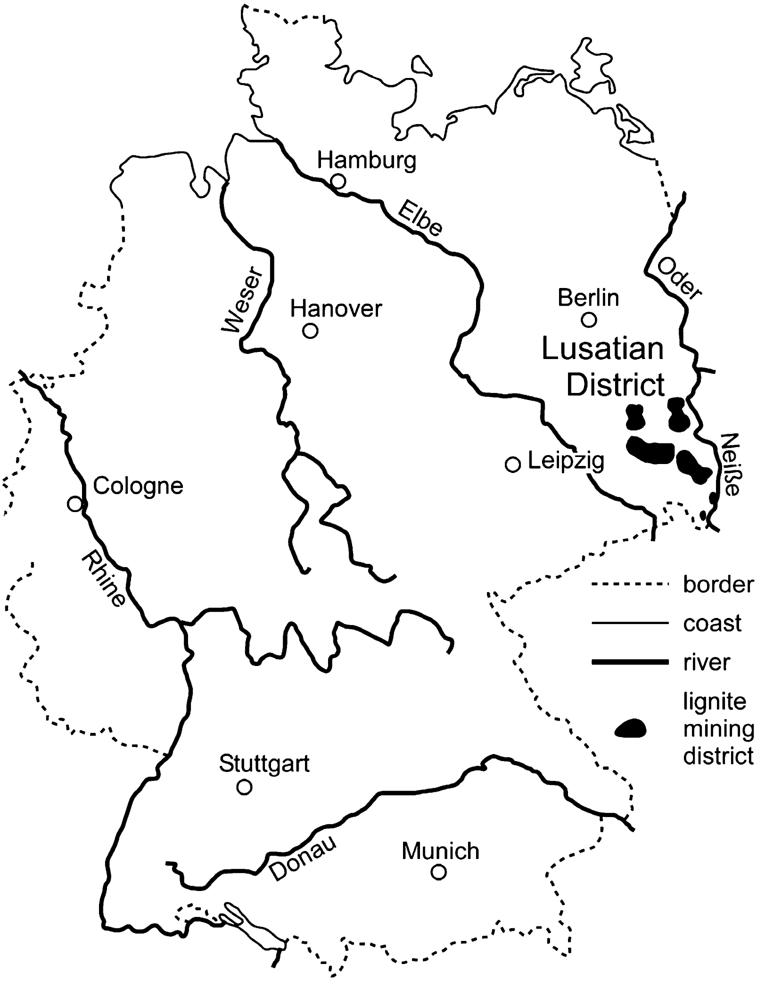


Fig. 5.73 Location of the mining district in Lusatia

The state-owned ‘Lusatian and Central-German Mining Administration Company’ (LMBV) is responsible for the rehabilitation of the decommissioned lignite mining area, comprising about 1,000 km^2, in accordance with the German Federal Mining Act. To remediate the groundwater deficit, the LMBV plans to fill the pits with surface water, creating a lake-district for recreational use by 2018 (Websources 1 and 2). While the entire lake-district will consist of 18 lakes, the nine core lakes will be unique in a sense that they will be connected by canals and offer a portfolio of recreational facilities. Details of the nine core lakes are listed in Table 5.24. Overall, they comprise an area of about 5,400 ha. This part of the lake district is expected to create the most economic benefits to recreational users and residents,

Table 5.24 Core lakes of the lake district and when they are anticipated to be filled

Lake	Surface area, ha	Volume (million m^3)	Estimated completion date, as of 31 Dec. 2009
Ilse See	771	153	2015
Sedlitzer See	1,330	206	2015
Partwitzer See	1,120	130	2012
Geierswalder See	620	92	2012
Neuwieser See	632	56	2015
Blunoer Südsee	350	64	2015
Sabrodter See	136	27	2015
Bergener See	133	3	2015
Spreetaler See	314	97	2015

Websource 1, modified

as it will offer a vast range of recreational uses, including bathing, sailing, kayaking, diving, angling, cycling, and walking.

After the phase-out of mining, a debate arose among traditional water users located in the Spree/Schwarze Elster river basins. Water users in the three riparian federal states of Saxony, Brandenburg, and Berlin were particularly concerned that their state would lose in the dispute over water allocation. Two major conflicts emerged: (1) Traditional water users were keen to defend their traditional water rights against the upcoming claims of the new water users (mine restoration and recreation in the new lake district). (2) Since water allocation is decided legally within the federal states in Germany, water users within each state, as well as the respective state authorities, wanted to retain 'their' water rights to secure undisturbed economic development. Consequently, a classic upstream–downstream conflict evolved, involving authorities and water users from three federal states (Messner and Kaltofen 2004; Messner et al. 2006).

An inter-state working group was established in 1998 to develop a compromise solution to the water allocation problem. The working group consisted of a range of stakeholders, including representatives of water, mining, and environmental authorities, as well as large water-using sectors (energy and mining). Furthermore, all other water users were represented by the 'Lusatia Initiative'. A water management strategy was eventually agreed upon in the year 2000. The strategy involved: (1) securing the water rights of traditional water users by giving them a higher priority in water allocation than pit mine restoration and recreational development, (2) reducing the discharge thresholds in the River Spree at specific user points (e.g. from 12 to 8 m^3/s for inflow to Berlin), (3) developing a computer-based water control system to optimise water use in the watershed, and (4) laying a pipeline for water transfer from the river Neiße to the river Spree (LIWAG 2000).

While filling mining pits with river water is the only option for restoration of the mining landscape, the water management strategy gave this surface water demand the lowest priority among water users. As a result, problems arise, since a constant and fast-filling process with river water is essential to avoid acidic drainage in the pits. If groundwater is allowed to rise naturally without adding external water, pyrite that remains in the pits will continue to oxidize. Hence, the failure to provide river water during the filling process jeopardises water quality and direct recreational uses of the lakes, in particular, bathing (Wisotzky, Sect. 4.6). The strategy has, in fact, led to cessations in the filling process during dry periods due to the lack of river water, thereby increasing the risk of acidification of the lakes (Friese et al. 2001, Koch et al. 2005; Wechsung 2005).

Furthermore, the water management strategy did not consider future climate change or socio-economic development in Eastern Germany. For example, water supply to some water users, especially pond fisheries, and water supply to different water users in Berlin (e.g. industry, power stations), has not met their demand in the past, and supply is unlikely to be satisfied in the future when climate and demographic changes may require more water resources in some areas.

The Germany Ministry of Education and Research has commissioned research to improve water allocation in the Elbe River basin (the GLOWA 'global change impacts on the water cycle'—Elbe project). The first phase of the project focused on the Spree and Schwarze Elster sub-basins within the Elbe River basin, due to the enormous potential for conflict. Water balance and climate models applied in the GLOWA-Elbe project predict that ecological viable discharge thresholds in the rivers are unlikely to be met after 2040, in particular during the summer months when flow is low. The reason for this is that, in addition to the fact that pumped groundwater is no longer being diverted into the rivers, precipitation is predicted to decrease. Overall, the water balance will deteriorate significantly in the two sub-basins (Kaltofen et al. 2005; Wechsung 2005). In order to tackle water scarcity induced by climate change and the phase-out of lignite mining, four management options were identified, in collaboration with stakeholders: The first option suggests reducing the allocation of water to smaller artificial water bodies feeding, among others, the Spreewald wetland, and instead increasing water supply for mine pit restoration. The second option gives the pit restoration preferential consideration compared to traditional water users. The third and fourth management options suggest the diversion of water from other river basins into the Spree and Schwarze Elster sub-basins.

To evaluate the potential effects of these management options on availability and economic impacts, valuation functions will be integrated using a water balance model (for detailed information, see Websource 3; Koch et al. 2005; Messner et al. 2007). This way, the most suitable management option can be determined using cost-benefit comparisons. Such economic assessments are relatively straightforward when effects can be measured in terms of changes in revenue, e.g. a reduced fish harvest leads to reduced profits or insufficient cooling water lead to reduced power production. However, it is more difficult to assess the benefits (e.g. recreational values) and costs associated with good or bad water quality in the lake district due to the absence of direct revenues. This chapter describes a study to evaluate the economic benefits of the future lake district in Lusatia in terms of people's willingness-to-pay. A specific aim of the study is to investigate which types of values people hold for the lake district, i.e. whether they merely obtain recreational benefits or whether non-use benefits also play a role.

5.9.2 The Economics of Pit Lakes

From an economic point of view, inefficient allocation of river water to mine pits can occur when malfunctioning markets fail to reflect the true benefits of this water use in terms of price. Such market failure often occurs when benefits are of public nature, such as recreational benefits (OECD 1995). Thus, benefits that would be provided by pit lakes with good water quality (e.g. bathing, cycling around the lakes) are not properly valued because they are public services. Public services are *non-rival* and *non-excludable*; that is, an individual using the lake district does not diminish someone else's use of the lakes and no visitor can be precluded from using the lake district. Public services often cause undervaluation by potential users, since others provide the service and they can use it without having to pay for it. The consequence of such behaviour is that public services are underprovided, as it is impossible to ask users to pay for the costs of their provision. In the context of water allocation, this means that traditional water users have no interest in relinquishing water for the creation of the lake district, as lake users do not compensate them for the financial loss caused by reduced water availability.

Even though markets fail to adequately reflect the value of public services in terms of price, the lake district would provide a range of economic benefits. The method that we used to assign a monetary value to the benefits of the lake district is based on the concept of total economic value (TEV). The TEV of public services has a number of different components; people may value the lake-district because they use it directly (e.g. swimming) or indirectly (e.g. appreciating the scenic landscape). Many people also derive value even if they do not use the lake district. For example, they value the uniqueness of the new lake district, are interested in habitat provision for wildlife, or they want future generations to have the opportunity to enjoy the lakes (Loomis 2000; Mitchell and Carson 1989). The different components of economic value are depicted in Fig. 5.74.

For the lake district in Lusatia, these non-market values are potentially more important than revenue gained from commercial activities, since it is very difficult to find suitable investors for an artificial lake district in a remote and sparsely populated area of Germany. A study by WILL (2004) compared the revenue generated by commercial activities (restaurants, boat hires) at existing artificial lakes in Germany with the costs of maintaining the recreational infrastructure (e.g. keeping beaches clean). The authors found that the benefits of the lakes are close to zero when costs are subtracted. Certainly, their calculations would have resulted in a different outcome if non-market benefits had been considered. By quantifying these benefits, the lake district can be fairly compared with other water users that generate revenue and thus be integrated in future decisions regarding water allocation in the river basin.

The contingent valuation (CV) method is particularly useful for the quantification of future benefits associated with the lake district for two reasons. First, it is the only currently available method capable of estimating both use and non-use values, and second, it allows *ex ante* valuation of future benefits (Mitchell and Carson 1989). The method quantifies benefits gained from public goods and services by asking

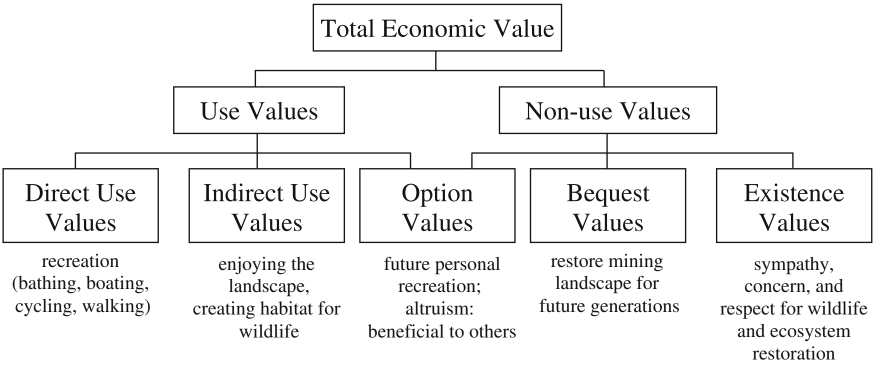


Fig. 5.74 Categories of total economic value for pit lakes (modified after OECD 1995)

households in a survey what they are willing to pay (WTP) to obtain a proposed provision of a certain good or service. Individuals are provided with a hypothetical market that explains the reasons and a way of paying for the service. According to economic theory, WTP bids reflect people's preferences or benefits that they obtain by a change in provision of a public good or service. From the obtained bids, CV researchers estimate mean WTP and total economic value estimates (Garrod and Willis 1999). The method is frequently used in the UK and the U.S. to aid government decisions regarding environmental policies and environmental liability payments (Lienhoop and Healy 2005; Loomis 2000). In the water resource context, CV has been used to assess the benefits of maintaining hydropower reservoir levels during the summer season for recreation, regulating in-stream flows below dams for rafting and fishing, and the costs of re-licensing dam decisions (Cordell and Bergstrom 1993; Loomis 2000; Loomis et al. 2005). With respect to mining, CV has been used to compare the benefits from pumping and discharging water from a gold mine into a river with the benefits from closing the mine and allow a lake to form, as well as supporting natural resource damage assessment either in terms of *ex ante* assessments or re-licensing decisions (Huszar et al. 2001; Smith 1994; Whitehead 1990).

5.9.3 Survey

The CVM questionnaire used to estimate the benefits of the lake-district was composed of four sections

- a definition of the goods and services provided by the lake-district,
- a description of the hypothetical market, in which non-market goods and services are made available to respondents,
- a description of the payment method used to elicit WTP bids, and
- validation questions about respondents' attitudes regarding the environment and their socio-economic characteristics.

Focus groups and a pilot survey were implemented to aid survey design. Considerable effort was spent to design the hypothetical market in a way that would allow participants to engage in a hypothetical monetary transaction that would be comprehensible and credible. The focus groups revealed that donations into a fund to finance the development of the lake district would be a feasible way to elicit WTP. Respondents' maximum WTP was obtained with an open-ended question format (i.e. what is the most that your household would be willing to pay into the fund each year for the next 10 years?). Since donations might be incentive incompatible, the WTP question was: (1) preceded by reminders to reduce strategic behaviour, such as free-riding, and (2) followed up by a query to explain the WTP decision. This is essential for the identification of invalid responses influenced by strategic bidding or protesting.

Since there is considerable uncertainty regarding the filling process of the lake district, two possible scenarios were considered in the valuation exercise. Two lakes had been successfully filled by the time of the interviews, so Scenario 1 anticipated the creation of 9 additional clean lakes (see Table 5.24) and complete recreational infrastructure by 2018, whereas Scenario 2 described a water scarcity situation causing low water quality in three lakes and less potential for recreation (see information box for exact wording).

Wording of the two hypothetical scenarios used in the questionnaire

Until now, two lakes have been successfully filled. There is still considerable uncertainty as to how fast the remaining nine lakes will be filled and how good their water quality will be. This also means that there is uncertainty about the recreational use of the lakes. In order to assure good water quality, it is important that the pits are to a large extent filled with river water. If river water is not diverted into the pits quickly enough, rising groundwater will accumulate at the bottom of the pits. In this case, minerals from the pit surface will be washed into the lake and consequently the water will become acid. Depending on water availability over the next 15 years, the lakes could have good water quality suitable for all recreational activities or they could become acid and not be directly used for recreation.

Scenario 1

Please imagine the following scenario:

Sufficient water will be available and the filling of the lakes will be completed within the next 15 years (see the picture below). All 9 new lakes will have good water quality. The lakes will be connected with canals, so boats can sail between the lakes. The lake district will offer several opportunities for recreationalists, such as swimming and sunbathing on beaches, sailing, kayaking, surfing, recreational walking, inline-skating and cycling on loop roads surrounding the lakes, camping, and trips on passenger ships.

While the mining company is merely responsible for the stabilisation of slopes and the filling process, recreational facilities (e.g. beaches, walking paths) will be provided by the federal states of Saxony and Brandenburg. However, creating the recreational infrastructure costs a lot of money. Since most of the facilities will be paid for by the federal states, the general public will have to contribute. Imagine that the recreational facilities will be financed by a specially created fund into which each household in Saxony and Brandenburg would need to pay each year over the next 10 years.

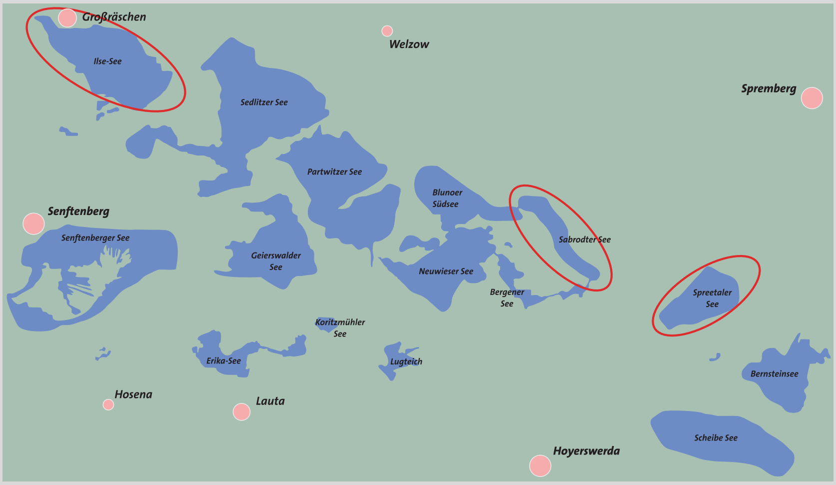
We would like you to think about whether your household would be prepared to pay anything (even a small amount) into the fund. What is the most that your household would be willing to pay into the fund each year for the next 10 years?

Scenario 2

Please remember that it is very uncertain how the filling process will proceed depending on the amount of river water available. Please imagine another possible scenario:

Remember, that if not enough river water is diverted into the lakes quickly enough, the lakes will become acid due to rising groundwater. This means that fish could not live in the water and swimming in such lakes would be harmful. Imagine that there is not enough river water available to ensure good water quality in all of the lakes and that the three pits that are filled last (see map) would not reach good water quality. Hence, swimming, surfing, and boating would not be possible in these lakes.

Imagine that the three lakes marked on the map will be acid.



Please think again about whether your household would be prepared to pay anything (even a small amount) into the fund to ensure that recreational facilities can be developed at all lakes that have good water quality.

Data were obtained between May and October 2005 using a personalised mail approach. Four trained students distributed approximately 1,500 questionnaires to visitors and households and explained the purpose of the survey face to face. Respondents were asked to fill in the questionnaire and send it back in a pre-paid envelope within five days. Respondents who had not returned the questionnaire after a week were sent a reminder postcard. This data collection mode was selected because it avoids the impersonal characteristics of mail or telephone surveys, but maintains the qualities of mail surveys, such as sufficient time to think about preferences and the possibility of discussing the issue with friends or family members.

In order to consider the whole range of non-market benefits, both users and non-users of the lake district were approached. Since we were not sure about the size of the household population from which to draw the sample, we initially conducted a visitor survey ($n = 690$) on-site at the two existing mining lakes. This gave us an idea about the travel distances to the lakes. Furthermore, sampling both visitors and, later on, households allowed us to compare WTP estimates stated by ‘users on site’, ‘users at home,’ and ‘non-users’. Fig. 5.75 shows that visitor numbers fell above a distance of 100 km. It was therefore decided to define the population as all households within a 100 km radius from the lake district. Following the visitor survey, four towns within this radius were selected for the household survey ($n = 843$, population: 850,000 households): Kamenz, Görlitz, Hoyerswerda, and Bischofswerda. The overall budget for the project precluded complex forms of probability sampling. Hence, households were selected by picking several starting

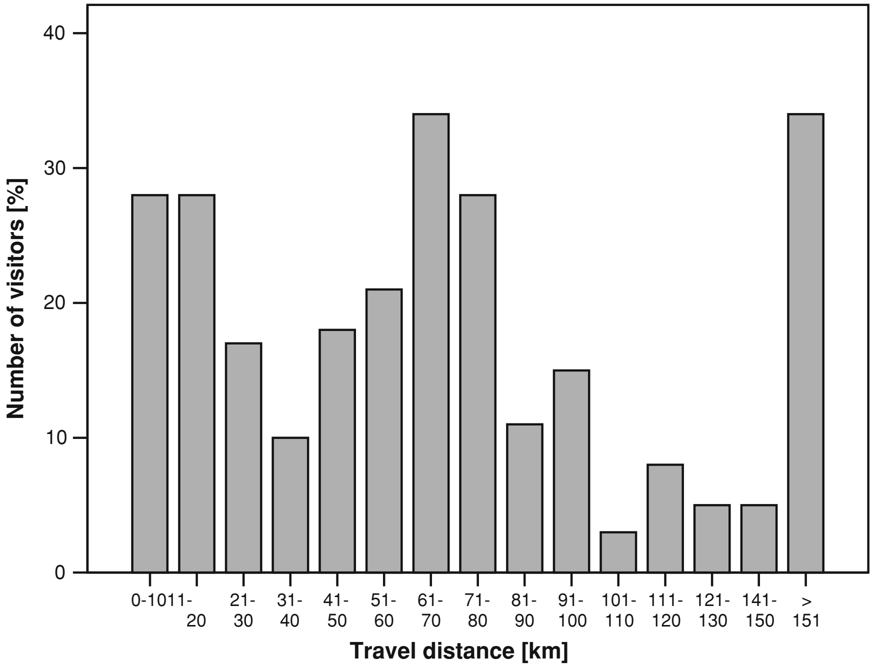


Fig. 5.75 Distribution of travel distance from home to the lake district

point addresses and moving on from there using a random-route approach (Diekmann 2003).

5.9.4 Results and Discussion

In total, 672 respondents returned the questionnaire, giving a response rate of 48%. The data shows that about 93% of the respondents are in favour of creating the lake-district, 1% does not support it, and 6% are unsure. Prior to statistical analysis, respondents' explanations regarding their WTP were examined to identify invalid responses (e.g. protest behaviour and strategic thinking). WTP estimates based on such non-utilitarian motives are usually eliminated from the data set to ensure that only genuine valuations are included in the analysis (Mitchell and Carson 1989). Overall, 74 zero responses were characterised by protest motives (e.g. 'the state should pay' or 'I don't like paying into a fund'), giving a protest rate of 11.3% and only one strategic bid was identified ('if everybody pays € 1, enough money can be raised for the rehabilitation project'). It was also decided to remove observations from visitors who travelled more than 100 km in order to get an undistorted picture of WTP in the 100 km core zone of the lake-district. The data set used for statistical

Table 5.25 Descriptive statistics for WTP in Euro per year

	Scenario 1	Scenario 2
n	522	522
Mean	18.96	15.94
Minimum	0	0
Maximum	700	300
Standard error	1.74	1.10
Standard deviation	39.58	25.03

analysis comprised 522 questionnaires. Data were analysed using SPSS 12.0. Table 5.25 reports descriptive statistics of mean WTP values for Scenario 1 and 2 as well as regression results.

The descriptive statistics show that mean WTP is higher for Scenario 1, assuming good water quality in all nine lakes, than for Scenario 2, which assumes poor water quality in three of the nine lakes. While this result was expected, we did not anticipate that WTP for Scenario 2 would drop significantly (paired samples t-test: $t\ (519) = 4.8$, $p < 0.05$). We anticipated that people might be saturated by the number of 'good quality' lakes and therefore not worry about three acid lakes, but answers to a closed-ended question explain this result:

- 32% stated that three acid lakes would mean a reduction of recreation for everyone,
- only 28% agree that there will be a sufficient number of remaining lakes for recreation,
- 44% of respondents want good water quality in all lakes,
- only 1% said that they do not care about acid lakes.

These findings also suggest that people were loss averse towards Scenario 2, and the order in which Scenario 1 and 2 were presented in the questionnaire might have amplified this. Future research that uses two or more scenarios should therefore use split-samples in which scenarios are presented in different orders to test for potential biases resulting from scenario ordering.

Regression results were generated using multiple OLS regression on a merged data set (users and non-users). The aim was to investigate whether the expected relationships between independent variables and WTP hold. In CV, variables on socio-economic characteristics, outdoor activities, familiarity, frequency of visits, as well as environmental attitudes have the potential power to explain WTP. Age and income did not seem to be important descriptors for WTP in our study; hence, the set of variables used in our regression model includes variables on recreational activities (e.g. the number of outdoor activities and fishing), personal views toward expenditure on environmental policies, and expected future use. A detailed description of the independent variables used in the analysis is displayed in Table 5.26.

The regression results in Table 5.27 show that the independent variables explain WTP values in both scenarios. While the direction of influence of the

Table 5.26 Description of independent variables

Variable	Description	Variable type	Coding	Mean
Activities	No. of lake-related recreational activities undertaken during last three years	Numerical	–	3.19
Fishing	Angling at lakes	Dummy	0—no 1—yes	0.07
INC_FUT_USE	Lake use frequency after completion of lake district compared to now.	Dummy	0—same frequency 1—increased frequency	0.57
Environm	Perceived importance of environmental protection as a policy task	String	1—lowest priority 2—low priority 3—moderately low priority 4—moderately high priority 5—high priority 6—highest priority	3.59
Econpercent	Percentage of WTP assigned to the improvement of regional economy	Numerical	–	14.75

Table 5.27 Regression estimates for scenarios 1 and 2

Variables	Coefficient *B*	*t*	*p*
Scenario 1			
Constant	9.01	2.19	0.03
Activities	1.93	3.03	0.00
Fishing	9.70	1.99	0.05
INC_FUT_USE	7.91	3.21	0.00
Environm	−2.04	−2.16	0.03
Econpercent	0.33	5.93	0.00
n: 522, df: 5	Adjusted r^2: 0.17	F: 18.52	p: 0.001
Scenario 2			
Constant	8.03	2.00	0.05
Activities	1.40	2.23	0.03
Fishing	10.45	2.21	0.03
INC_FUT_USE	8.68	3.62	0.00
Environm	-1.82	-1.97	0.05
Econpercent	0.29	5.50	0.00
n: 522, df: 5	Adjusted r^2: 0.15	F: 16.62	p: 0.001

variables related to recreational activities (ACTIVITIES, FISHING, INC_FUT_USE) is as expected, the negative correlation of ENVIRONM seems to be counterintuitive at first sight. Our explanation for this is that respondents who are interested in environmental protection might be worried about the environmental impacts of recreational infrastructure. Respondents who assigned a high priority to

Table 5.28 Descriptive statistics for WTP (€/year) in Scenario 1 for user and non-user groups

	Users on site $n = 187$	Users at home $n = 191$	Non-users $n = 144$
Mean WTP	30.49	17.50	6.17
Minimum	0.00	0.00	0.00
Maximum	700.00	100.00	120.00
Standard error	4.43	1.44	1.15
Standard deviation	60.07	19.90	13.83

environmental protection have a significantly lower WTP than people who gave it low priority. Interestingly, ECONPERCENT also strongly influences WTP. That is, respondents who assign a higher percentage of their WTP to an improved regional economy tend to state higher WTP bids than those who assign a smaller percentage.

One of our aims was to investigate whether people hold non-use values for the lake district and the recreational infrastructure. Non-users were identified by looking at respondents' motivation for valuing the lake district; accordingly, the household sample consists of 57% users and 43% non-users. Table 5.28 shows the descriptive WTP results for Scenario 1 for the three groups: 'users on site' (visitors interviewed at lakes), 'users at home' (people that sometimes visit the lakes, interviewed at home), and 'non-users' (people that have not visited/and do not plan to visit the lakes, interviewed at home).

According to a one-way ANOVA test, mean WTP varied significantly among the three groups ($F^{7,512} = 2.8$; $p < 0.01$). While the difference in WTP between users and non-users is in line with other studies (e.g. Barrick and Beazley 1990), we did not expect such a large divergence between the two user groups ('users on site' and 'users at home'). A comparison of age and income in these two groups shows that 'users at home' are older and wealthier, but when comparing WTP within each age and income group, the difference still remains. A possible explanation for this difference might be information and time effects: 'users on site' are experiencing the benefits of the existing lakes when asked to participate in the survey, and 'users at home' have to draw on memories of past visits to the lakes. The immediate experience of on-site users may generate a pronounced perception and more tangible information about the lake district. Our interpretation is that preferences can be labile to context factors or changes in bundles of goods. That is, when interviewed at home, the lake district might not have been such a high priority compared to when interviewed on site. Even though we did not find any studies that have looked at these particular effects, we believe that this hypothesis might be relevant for CVM research in terms of survey timing. Future researchers should therefore investigate whether use values for certain public good decrease with time passed since the last visit. A possible alternative explanation for the difference between 'users on site' and 'users at home' is associated with sampling effects. Bernath et al. (2007) found that forest users interviewed in the forest were WTP more than forest users interviewed at home. Their interpretation

Table 5.29 Mean and aggregated household WTP for different user and non-user groups in Euros

		Users on site	Users at home	Non-users
Scenario 1	Mean	30.49	17.50	6.17
	Aggregate	13.7 million	7.9 million	2.5 million
Scenario 2	Mean	25.75	15.11	4.76
	Aggregate	11.6 million	6.8 million	1.9 million

of higher WTP among on-site users is that this group uses the amenity more frequently due to the high value they place upon it and hence are more likely to enter the sample.

The overall non-market benefits of the lake district were calculated by multiplying mean WTP with the total population, that is 850 000 households within the 100 km radius surrounding the lake district (BBR 2004). According to the household survey, 450,000 households (57%) are users and 400,000 (47%) are non-users. A comparison of socio-economic characteristics between the overall sample and the population suggests that the sample was representative in terms of gender, age, and income. Table 5.29 reports aggregated WTP per year for each group and for both scenarios.

Due to the disparity between ‘users on site’ and ‘users at home,’ an uncertainty range was calculated for the total non-market benefits, where the lower value presents a more conservative estimate including ‘users at home’ and ‘non-users’ $(17.50 + 6.17 = 23.67)$ and the upper value includes ‘users on site’ and ‘non-users’ $(30.49 + 6.17 = 36.66)$. The overall range of non-market benefits amount to € 10.4–16.2 million per annum for Scenario 1 and € 8.7–13.5 million per annum for Scenario 2. This means that the loss in recreational benefit resulting from three acid lakes comprises about €1.7–2.7 million per annum. This finding is of high relevance when measures for remediation of acid lakes are discussed, as the monetary recreational value of lakes provides a justification for costly remediation action. Since we did not assess the recreational value per hectare due to the high cognitive demands this would impose on survey respondents, we are unable to compare ‘per hectare’ benefits and costs of remediating acid lakes. However, a rough comparison of loss in recreational benefits at the three lakes (€ 1.7–2.7 million for a lake area of about 1,221 ha) and ‘per hectare’ costs of liming in Swedish lakes (€ 80/ha) would give total costs of about € 98,000 for the same lake area, and shows that expensive remediation of acid lakes may be worthwhile (Bostedt et al. 2010).

5.9.5 Conclusion

Our findings have some implications on policy making in the context of water allocation in the Elbe river basin, given that the rehabilitation of large-scale open pit mining in the region of Lusatia is a major water user. According to our survey, there is strong support for the creation of the lake district, and non-market benefits associated with a scenario assuming nine clean lakes are substantial, lying between 10.4 and 16.2 million Euros per year. By quantifying the economic benefits of recreation in the lake district, it is possible to put this new water user on par with traditional water users, and thus enable decision makers to better assess current and alternative water allocation policies for the Elbe River basin. Furthermore, the estimates of non-market benefits presented in this study clearly show that a simple focus on market benefits (e.g. revenue) seriously underestimates the benefits of pit lakes. Thus, we strongly recommend the inclusion of all benefits in decisions regarding costly restoration of mine pits or remediation of acidic lakes.

Chapter 6
Lessons Learned, Open Questions, and Concluding Remarks

6.1 Physical Limnology

Pit lakes have some peculiarities that are insufficiently addressed in the limnological literature. Some of these are site-specific while others are more general in nature, e.g. temperature compensation of electrical conductivity, and implementation of density functions based on partial molal volumes in numerical models (Sect. 3.1). The important physical parameters needed for lake modeling are comprehensively presented in Sects. 3.1 and 3.4.

In many pit lakes, pronounced vertical gradients of pH, Eh, temperature, and sulfate and metal concentrations exist in the anoxic monimolimnion, near the lake bottom (Sect. 5.3). These chemical gradients are not well understood, but appear to result from different biotic and abiotic factors. Staircases of stratified layers observed in lakes like Cueva de la Mora (Spain) may be caused by double-diffusive convection with coupled down-/upward fluxes of heat and of dissolved substances. The effect of (biogeo-)chemical transformations on stratification has not been quantified yet. Numerical models might improve prognostication of the evolution of water quality in pit lakes. Such prognosticative tools may also be useful for predicting changes in natural lakes due to human use or climate change.

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6.2 Geo-Environmental and Hydrochemistry

6.2.1 Geo-Hydrochemistry of Coal Pit Lakes

Remarkable progress has been made in understanding lignite pit lake chemistry and pit lake processes during the past 15 years (Sect. 3.2.1). Lakes in former hard coal mines have not been as well investigated. Although many results from German and Australian pit lakes can be generalized, a more extensive data base is needed to better understand the causal relationships between deposit geology and hydrochemistry that control the final chemical conditions in such pit lakes. This includes the interactions between pit lakes and groundwater and the differences between unconsolidated versus solid rock. How residues of coal and lignite in overburden dumps contribute to the quantity, structure, and degradability of organic matter, and thus affect reductive alkalinity production in pit lakes, is not well understood.

6.2.1.1 Role of Schwertmannite at the Sediment–Water Interface

Changing the quantity or flow direction of groundwater can dramatically affect the water quality and the geo-environmental characteristics of acidic pit lakes. In extremely acidic pit lakes, there are conditions under which schwertmannite deposits form. An altered groundwater inflow following the cessation of dewatering in pit mines can dissolve sedimentary schwertmannite (Sect. 3.2.1.2), which can lead to increased lake acidity, especially if sulfate loading is low. In addition, substances previously adsorbed on schwertmannite are mobilized and can be transported into the lake. On the other hand, exfiltrating lake water will export acidity into the groundwater regime. Sediments underlying the schwertmannite-containing layer will thus receive acidity and other substances that might inhibit sulfate reduction and long-term neutralization.

6.2.1.2 Phosphorus Retention by Iron Prevents Eutrophication

Acidic pit lakes contain a high level of P-binding elements and compounds (Sect. 3.2.1.3), as indicated by high sediment Fe:P ratios (up to 370). Even in neutral pit lakes (without unusual high P loading), sediment Fe:P ratios are 2–20-fold higher than in natural lakes. As a consequence of the elevated sediment-based P-binding capacity, whole lake P-retention can be about 15% higher than predicted by the empirical OECD-Vollenweider (1982) model, as documented in eight Lusatian pit lakes in Germany. Significantly increased P-retention is even reported in lakes that are only slightly impacted (e.g. Fe surplus) by mining.

6.2.2 Geo-Hydrochemistry of Ore Pits

The concentrations of solutes in metal-mine pit lakes (Sect. 3.2.2, case study 5.3) show distinct trends that are primarily related to pH. The pH, in turn, is a complex function of the geo-environmental characteristics, sulfide mineral content and oxidation rates, water balance, solubility of secondary mineral phases, interactions between dissolved substances and colloids and settling particles in the water body, water column dynamics, sediment biogeochemical processes, and remediation efforts. Thus, geo-environmental characteristics are useful for interpreting the hydrochemistry of pit lakes, making predictions of water quality for future pit lakes, and designing remedial strategies. More detailed studies are needed on metal and nutrient cycling in the water column and sediments of pit lakes to better understand the role of biogeochemical processes on water quality and to allow validation of complex models that couple hydrology, hydrodynamics, and biogeochemistry.

6.3 Predictive Modeling of Lakes

Pit lakes exhibit a variety of physical and geochemical properties over a broad spectrum of spatial and temporal scales. Accurately assessing future environmental and economic impacts of pit lakes requires predicting the spatial distribution and evolution of pit lake properties using computer models (Sect. 3.4). DYRESM and PitMod are examples of models that determine pit lake properties by solving systems of mathematical equations, including mass and energy balances. PitMod also incorporates the geochemical predictive capabilities of the PHREEQC equilibrium chemistry model.

It appears essential to model not only the major physical and chemical processes of the lake, but also the groundwater flow field and the geochemical inventory of the lake environment. Müller's integrated process-oriented modeling scheme, MODGLUE, accomplishes this (Müller et al. 2001, 2008).

As is the case with all predictive models, the reliability and accuracy of predictions about lake water quality development depends strongly on the quality and completeness of the input data (Sects. 3.2.1 and 3.2.2). Large data gaps and missing parameters necessitate the use of proxy or interpolated data, resulting in high uncertainties or even predictive failures. A regularly updated, international database on water quality from existing pit lakes in different types of mining regions, deposit types, metal resource, climate, and hydrologic environments could be extremely valuable for testing numerical models, identifying important factors affecting water quality, and tracking remediation effectiveness.

6.4 Biology and Ecology of Acidic Pit Lakes

6.4.1 Special Adaptations in Acidophiles

Organisms living in strongly acidic lakes are exposed to extreme physiological conditions by the acidity and the potentially toxic levels of dissolved metals. Those organisms have evolved physiological mechanisms that make them 'acidotolerant' (able to live in neutral and acidic water), 'acidophilic' (preferring acidic water), or 'acidobiontic' (unable to live in non-acidic water). Many species perform as well at pH 2.6 as their relatives do at pH 7 (Sects. 3.3.1.4 and 3.3.1.2) and also appear to be less sensitive to metals. Heat shock proteins found in *Chlamydomonas acidophila* apparently allow photosynthesis in metal-rich water. Benthic Zygnematalean filamentous green algae, such as *Mougeotia spp.*, also have mechanisms that protect them from the toxicity of Al and other metals (Sect. 3.3.2.2). It is still not clear whether some of the species that thrive under these extreme conditions are exclusive found in acidic pit lakes. Considering an evolutionary time scale, these species may have evolved in the only natural counter parts—acidic crater lakes.

Cyanobacteria are found in thermo-acidic environments living in biofilms in association with algae in endolithic layers, acidic soils, and stromatolithes. Usually, planktonic cyanobacteria do not grow in acidic water <pH 4–5 (Brock 1973). Tolerance and sensitivity of cyanobacteria to acidic conditions might be different in rain-acidified soft water than in highly mineralized acidic mine water; therefore, acidity and other chemical characteristics of water should always be measured, in addition to pH.

Carbon-concentrating mechanisms (CCM) were found in planktonic and benthic algae (Diaz and Maberly 2009, Sects. 3.3.1.4 and 3.3.2.2). The evolution of CCMs, however, is generally considered in the context of decreased CO_2 availability (Sect. 3.3.2.1). This is also true in acidic pit lakes, and cannot be assessed as a special adaptation to the acidic pit lake habitat since all cyanobacteria, most algae and aquatic plants, and C4 and crassulacean acid-metabolism vascular plants use various mechanisms to accumulate CO_2 (Raven et al. 2008).

Another characteristic of acidic mining lakes are high ammonium (NH_4^+) concentrations, resulting from inhibited nitrification (Sect. 3.3.2.1). The problem of high ammonium concentrations persists in already neutralized lakes—at least for some time—because of groundwater inflows. This is critical because NH_4^+ is toxic to fish.

6.4.2 Species Richness and Diversity

The first and simplest biological question refers to the taxonomic inventory of species: what is living in this stressful habitat? There is a large body of knowledge that shows that the number of species in rain-acidified soft-water lakes diminish with decreasing pH. However, little is known about how specific ion composition and strength affects the community composition of biota in acidic pit lakes.

6.4.2.1 Phytoplankton

About 65–85 genera of phytoplankton, corresponding to about 75–100 species, can be expected in neutral natural lakes in certain regions of Europe (Muylaert et al. 2010). Rain acidification reduced the number of taxa from ca. 70 by about 50%, with pH changing from ca. 7 to 4.8 in the lakes of Newfoundland (Scruton et al. 1987). At 17 lignite pit lakes in Lusatia, the number of phytoplankton taxa decreased from ca. 30 at pH 4.3 to four species at pH 2.3 (Sect. 3.3.1.1). At pH 3 and below, typical taxa, often *Ochromonas* and *Chlamydomonas*, dominate the phytoplankton. In other extremely acidic pit lakes, *Chlamydomonas acidophila* is by far the dominant species (Sect. 3.3.1.1). The conspicuous littoral species in extremely acidic water, *Euglena mutabilis*, is not eu-planktonic. It is not clear whether (and if so, how) the observed gradient of lower diversity in more acidic water can be related to a functional classification of phytoplankton taxa, discriminating 31 associations in circum-neutral freshwater (Reynolds et al. 2002).

6.4.2.2 Benthic Filamentous Algae (Zygnematalean Green Algae)

Acidification increases the benthic Zygnematalean green algae (ZGA) biomass in both the littoral zones of lakes and in lotic systems (Sect. 3.3.2.2). Peri- and metaphyton in lakes at pH 5.5–4.8 is composed mainly of acidophilic ZGA, such as *Spirogyra* and *Mougeotia* spp. At pH < 4.8, they are displaced by *Zygogonium* spp. These acidophilic ZGA can be important for benthic carbon accumulation and for the mediation of the internal alkalinity generation of acidic mining lakes.

6.4.2.3 Macrophytes

The morphology of lake basins can promote intensive macrophyte growth by offering wide areas of shallow water to a depth of approximately 5 m. The extreme habitat conditions of strongly acidified mining lakes restrict the occurrence of macrophytes to a small group of adapted species, e.g. *Myriophyllum heterophyllum*. The predominant indigenous species in these lakes is *Juncus bulbosus*. Additionally, some invasive neophytic macrophytes can colonize acidified lakes (e.g. *Cabomba caroliniana, Crassula helmsii*). Although no neophytic macrophyte occurrence has been reported in the most acidic mining lakes, as pH increases, a great variety of neophytic as well as indigenous macrophyte species can immigrate and grow (Sect. 3.3.2.2).

6.4.2.4 Prokaryotes and Fungi

Microbial diversity in acidic pit lakes appears to be higher than at extremely acidic mine sites, but lower than in natural lakes. However, it is hard to definitely judge the microbial diversity in acidic pit lakes (Sect. 3.3.1.3) because species clone libraries are small and information on seasonal patterns is missing, often making identification impossible. Prokaryotic diversity is higher in the sediments than in the water column of acidic pit lakes (see Sect. 3.3.2). Organisms involved in iron cycling, such as *Acidithiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*, or *Acidiphilium* spp. are common to all these acidic water systems, but their share in the community varies considerably, from dominant to hardly detectable. Archaea are less numerous in acidic pit lakes than in extremely acidic ($\text{pH} < 2$) mine waters. Among the fungi, acid-tolerant yeasts are regularly detected and can reach high numbers. Their ecological role is not fully elucidated yet, but they may have mutualistic relations with microalgae. Further research is needed to understand the relationship between microbial community composition and environmental factors other than pH in acidic pit lakes.

6.4.2.5 Zooplankton

Species richness and diversity of metazoan zooplankton are low in acidic pit lakes due to multiple abiotic stressors. Zooplankton community composition in a particular lake is highly predictable from pH and has been suggested as a biological indicator of water quality (Nixdorf et al. 2005 Sect. 3.3.1.2). For example, zooplankton metazoan species numbers decreased from 10 to 2 across a pH range of 3.9–2.3 in Lusatian lignite pit lakes (Germany). The dominant acid-resistant planktonic metazoans were the rotifers *Cephalodella hoodi, Elosa worallii,* and *Brachionus sericus*, and the cladoceran *Chydorus sphaericus*. Some groups, which are common in acidic soft-water lakes, such as calanoid copepods, are absent in acidic pit lakes. Overall, zooplankton species composition in acidic pit lakes is considerably different from that found in rain-acidified soft-water lakes of the same pH. Most of the meta-zooplankton species that are typically found in acidic pit lakes appear to be cosmopolitan, although detailed taxonomic studies are often lacking.

6.4.3 Growth Rates and Limiting Factors

6.4.3.1 Primary Production of Phytoplankton

Zippel (2005) investigated plankton growth rates with daily sampling and found doubling times of 1 day for the phytoplankton, *Chlamydomonas* and *Ochromonas*, 2–3 days for the ciliate *Oxytricha*, and 3–5 days for the heliozoon *Actinophrys*. There was no clear relationship between pelagic primary production (PP) of algae and pH in Lusatian mine lakes (Germany). The highest PP was measured in the least acidic lake (Lake 117, pH 3.0), but moderate values were found in the most acidic lake (Lake 107, pH 2.3), and the lowest PP was found in the lake with a pH of 2.6 (Lake 111). Acidic conditions alone do not prevent the development of a high phytoplankton biomass if the P-concentration is high (Woelfl et al. 2000); they reported a maximum algal biomass of 22 g C m^{-2}, which is comparable to hyper-eutrophic lakes (Sect. 3.3.1.1). Corresponding values were observed in Australia where no relationship between pH and phytoplankton biomass was observed. The lakes with highest phytoplankton biomass also had the highest total phosphorus concentrations (Derham 2004).

Below pH 4.3, CO_2 is the only available inorganic carbon source for photosynthesis, and inorganic carbon was found to be PP-limiting, due to photosynthesis and loss of CO_2 to the atmosphere (Sects. 3.3.1.1 and 3.3.2.2). The Berkeley Pit Lake is impoverished in nitrate and DOC; during nutrient enrichment experiments, the system was found to be N-limited, and algal growth was greatly enhanced by adding nitrate (Sect. 5.5). Overall, mean PP in the above-mentioned three Lusatian mine lakes was far below the means observed in many other lake systems (Cole et al. 1988). PP was in the span observed in polyhumic brownwater lakes, where PP was mainly limited by light (Ahtiainen et al. 1985; Arvola 1984). PP in the acidic mine lakes could therefore be light limited, due to the high concentrations of dissolved ferric iron. Alternatively, the high molar C:P ratio of seston, ranging between 500 and 650 (Spijkerman 2008), suggests that phosphorus limits PP. Overall, primary production might be limited by interacting factors, and varies with water depth (light availability), season, and among different lakes (Sect. 3.3.1.1).

6.4.3.2 Bacterial Production and Heterotrophy of Pit Lakes

Bacteria apparently play a more important role in the cycling of matter in acidic mine lakes, where they often serve as the basis for the whole food web, than in other lake ecosystems. Bacterial production (BP) was the same order of magnitude as primary production (PP) in these lakes, and exceeded it in two-thirds of all cases (Sect. 3.3.1.4). Most values were far above the mean proportion of 20% BP compared to PP reported in many other lakes. The importance of bacteria and the degree of system heterotrophy increases in more acidic and iron-rich lakes.

Bacterial biomass was probably promoted by iron photoreduction. In iron-rich mine lakes, the photolysis of Fe(III) aqua-complexes generates hydroxyl radicals that react with refractory DOC (Brinkmann et al. 2003; Friese et al. 2002; Herzsprung et al. 1998). The light-stimulated formation of ferrous iron changed the DOC composition, rendering DOC more accessible to use by fungi and heterotrophic bacteria, and increasing the BP (Kamjunke et al. 2005). This may explain why measurements of BP were highest in the most acidic and most iron-rich lake and lowest in the least acidic lake (Sect. 3.3.1.4). It is an open question how much DOC comes from lignite (Sect. 3.2.1.1).

6.4.4 Food Web and Interactions

Mixotrophy is a common feature of most unicellular phytoplankton and some protist zooplankton species. *Chlamydomonas* and *Ochromonas* live autotrophically using osmotrophy and phagotrophy, respectively. The osmo-mixotrophic

Chlamydomonas acidophila can use natural DOC for its growth. The phagomixotrophic *Ochromonas* is able to feed on bacteria, thereby incorporating the growth-limiting elements, phosphorus and carbon (Sect. 3.3.1.4).

In contrast to the rather stable high-diversity plankton community of neutral lakes, the predator–prey relationship fluctuates in the extremely low-diversity plankton of acidic lakes. Population developments of planktonic predatory vs. prey species alternate between rising and declining phases. The guild of predators increases as long as prey densities are above a (predator-)specific threshold concentration; below this threshold, the predator–prey ratio decreases (Zippel 2005).

Depending on the given range of pH and acidity, the simplified food web has some new dominant components (e.g. Dinophyceae, water bugs; Sect. 3.3.1.1) and features. Whereas small rotifer species appear not to control phytoplankton biomass in the most acidic pit lakes, the appearance of larger zooplankton species, *Brachionus sericus* and *Chydorus sphaericus*, at $\mathrm{pH} > 2.8$ leads to top-down effects due to grazing on phytoplankton (Sect. 3.3.1.2). Heliozoa disappear from lakes at a pH above 3, and Corixidae play the role of top predators in these lakes.

Shallow acidic pit lakes show peculiar benthic mats of filamentous Zygnematalean green algae (Sect. 3.3.2.2). The observed increase in ZGA biomass in shallow acidic pit lakes and its community structure cannot be explained by decreased top-down regulation (Sect. 3.3.2.2). The importance of ZGA as a food base for invertebrate benthic organisms is not adequately known. The relation among acidification, algae development, and the grazer abundance is not clear.

Benthic primary production can become more important than pelagic PP (Sect. 3.3.2.3). The pelagic food web then appears as a coupled system depending on both PP on the ground and in the water column. Unexpectedly high rates of heterotrophic bacterial production (BP), which can surpass the pelagic PP of phytoplankton, indicate that the bacteria in the water mainly live on organic substances produced by benthic algae and allochthonous sources (Sect. 3.3.1.4).

Chironomid larvae, due to their bioturbation and feeding activity, play an important role in matter transport and biogeochemistry of the sediments (Sect. 3.3.2.4). Therefore, macrofauna studies on the effects of their bioturbating activity in sediments should be rewarding in acidic pit lakes.

Despite restricted colonization by benthic invertebrates and the practical absence of some microbial processes typical in freshwater lakes, the sediments of acidic pit lakes show considerable microbial diversity. Microbial biomass and total microbial activities are comparable to natural lakes. Further research is necessary to unravel the true microbial diversity of pit lake sediments and its relation to environmental factors. It will be of both scientific and practical interest to better quantify rates of Fe(III) reduction and to identify and isolate the organisms responsible for Fe(III) reduction at acid and intermediate pH values. This should include the more systematic study of different habitats in acidic pit lakes, such as littoral and profundal zones, vegetated and unvegetated sediments, and chemoclines in meromictic lakes.

6.5 Treatment Methods to Remediate Acidic Pit Lakes

Mining companies responsible for reclamation and water remediation during and after mine closure are seeking effective low-cost approaches to improve water quality. Technologies used to reclaim acidic pit lakes (and their scientific basis) are described in detail in Chap. 4 and demonstrated in case studies (Chap. 5). The case studies range from severely acidified lakes—often with high metal concentrations—to some with only slightly elevated metal levels. In all cases, the aims of treatments are circum-neutral water and metal concentrations low enough to facilitate the development of a lake ecosystem that will allow the pit lake water to be used as a resource. Approaches to reach this objective include avoiding continued contamination (e.g. diverting the water away from contaminated wastes) and treating the contaminated pit water in situ. Treatments can focus on the source of the contamination (the mining wastes), or on the pit lake, and finally at the lake outflow. The treatment processes are based on chemical reactions and on microbiologically mediated biogeochemical transformations. The suitability of chemical and/or biological processes in passive or active treatment depends on the magnitude of the flows, the residence time, and the degree and type of contamination to be addressed (Sect. 4.3). Often, small flows of low-concentrated AMD can be handled by passive treatment, whereas large flow volumes with high loads of acidity require active treatment plants.

6.5.1 *Avoidance and Source Treatment*

Prevention of pyrite oxidation was enhanced by adding alkaline substances to the overburden before dumping (Sect. 4.6; practiced at the Garzweiler mine since 1999). Decreased pyrite oxidation can be realized by changing dump construction and by using dry or wet covers to decrease the time that pyritic minerals are exposed to atmospheric oxygen. Pyrite can also be encapsulated and, thereby, protected against oxygen contact by enhancing the precipitation of ferric hydroxides with added alkaline substances (crushed limestone or $Ca(OH)_2$). The amount of acid drainage generated can also be reduced by sealing waste dumps to reduce infiltration of atmospheric precipitation and by increasing evapotranspiration through establishment of a suitable vegetative cover.

6.5.2 *Natural Attenuation of Acidity Load*

The AMD load is limited by the lifetime of the primary contaminant sources. For example, AMD concentrations at the Central German lignite mine dumps were significantly decreased after about 50 years (Hoth et al. 2005). Elution may take more time in other geologic and climatic regions.

Natural sulfate reduction in pit lake sediment was estimated to generate net neutralization rates of 4–107 mmol m^{-2} $year^{-1}$ (Peine and Peiffer 1996). This rate is insufficient, compared to the acidity load of the lake. For comparison, the neutralization potential of internal lake processes in productive natural lakes was estimated to average 1,800 mmol m^{-2} $year^{-1}$ (Koschorreck and Tittel 2007).

6.5.3 Treatment in Constructed Wetlands and Underground

Passive treatment systems with microbiological processes are not as readily controlled as chemically driven processes. Reactive barriers combine processes of chemical neutralization, biological production of alkalinity, and retention of metals by precipitation of sulfides or (oxi)-hydroxides. In constructed wetlands, the redox potential (Eh) is usually above the values needed for effective reduction of sulfate. Thus, for metals other than Mn, Fe, and Al (which can be removed as oxides or hydroxides), the dominant metal removal process is adsorption (Whitehead et al. 2005).

A semi-passive treatment approach involves initiating microbial sulfate reduction by injecting liquid organics underground and using the aquifer as reactor space. In field-scale tests to treat the AMD groundwater, a sulfate-reducing reactor developed after one year. FeS precipitated and acidity decreased (Schöpke 2008; Schöpke et al. 2011).

6.5.3.1 In-Lake Treatments to Neutralize Acidic Pit Lakes

Chemical Lake Treatments

High volumes of AMD are conventionally treated with chemicals in engineered structures or by treating the entire lake (Sect. 4.2). Whole lake treatment has been used successfully in several lignite pit lakes in Central Germany, in some metal and gold pit lakes, such as Rävlidmyran, Sweden (Lu 2004), and at the Gilt Edge Mine Superfund Site (Anchor Hill, USA; Lewis et al. 2003; Park et al. 2006). The neutralization agents were crushed limestone ($CaCO_3$) or dolomite ($Ca/MgCO_3$), soda (Na_2CO_3) or (hydrated) burnt lime (CaO, $Ca(OH)_2$), or caustic soda ($NaOH$). Alternatively, alkaline by-products, such as fly ash from power plants (with a caveat on contaminants) and low-density iron hydroxide sludge (that contains excess carbonate neutralization capacity) from lime treatment plants can be used. In situ treatments of acidic pit lakes using alkaline agents were tested in small-scale field experiments and then successfully scaled up to large volume lakes. Scaling up was difficult; initially, too simple techniques were used to disperse the neutralizing agents. Pumping and dispersal systems with floating pipelines, and circular large-area sprinklers improved treatment effectiveness. Distribution from ships, as done at rain-acidified lakes in Sweden, appears to be a technology that can be adapted to the conditions of acidic pit lakes.

An ex-situ process of copper recovery from the Berkeley Pit Lake water (cementation; Sect. 5.5) demonstrated the removal of the toxic metal copper by exchange treatment (copper vs. iron), although the pit remained acid.

Biological Lake Treatments

Pilot-scale experiments with sulfate reduction and metal sulfide precipitation (in situ redox manipulation) were promising but failed to perform when used in whole lakes and high volume experimental enclosures (Sect. 4.3). Seasonal turnover of the water column in holomictic lakes annually disturbs the anaerobic processes needed for sulfate reduction and metal sulfide formation. Lake experiments involving the additions of high amounts of organic substances (1–10 kg m^{-3}) were promising but lower doses did not show a lasting effect.

Seasonal re-oxidation of precipitated sulfide metals can be avoided when the pit lake is meromictic. Meromictic lakes do not turn over completely and, thus, no oxygen is carried to the deep strata in the water column. In other, initially holomictic pit lakes, meromixis was artificially induced and established. The permanent, oxygen-free monimolimnion can be used for passive subhydric deposition of oxygen-sensible end-products (final stage of the Anchor Hill pit lake) or as an actively managed in-lake reactor (Island Copper Mine pit lake). Metal(oid) elements (U, Se) were successfully removed in Sweetwater pit lake after full-scale treatment with ca. 0.5 kg m^{-3} of organic substances created low redox conditions (Paulson 2004).

Sustainability of Pit Lake Treatment

Lakes that are extremely highly contaminated with acidity and metals can be remediated effectively by removing the sources of contamination. The wastes can be placed back into the pit and the bottom sealed with a clay cover, if hydrological conditions are favorable. This treatment approach can lead to complete recovery of a pit lake, representing a truly sustainable long-term result. The critical acidity load that can probably be compensated by natural lake-internal processes was estimated at 5.1 mmol m^{-2} d^{-1} in productive lakes and 0.5 mmol m^{-2} d^{-1} in less productive lakes (Koschorreck and Tittel 2007). In pit lakes where the rate of acidification is higher than this, chemical neutralization is required regularly, and lake treatments do not result in self-sustaining systems.

6.5.3.2 Treatment of Acidic Outflows

Where an acceptable water quality cannot be achieved in through-flow lakes, treatment of the out flowing water is required (Sect. 4.4). Treatment of Berkeley Pit Lake outflow is planned using a chemical treatment plant with a two-stage high-density sludge process. The estimated volume of water to be treated is 5,000–10,000 m^3 per day. The water management system of the lignite mining district in Lusatia/Germany includes eight plants treating water from both operating mines and acid pit lakes. One plant is designed to neutralize 170,000 $m^3\ d^{-1}$ of acidic water, using 64 t of $Ca(OH)_2$ per day (0.37 kg m^{-3}). The resulting iron-hydroxide sludge contains unreacted $Ca(OH)_2$, which might be used for further in-lake treatment. Outflows of small volumes with low levels of contamination can be treated with passive technologies, using permeable reactive barriers, or in constructed or natural wetlands, where the water is neutralized and toxic metals are precipitated.

Ecological Treatment Measures in AMD Affected Lakes

In neutral pit lakes and AMD-affected lakes, natural processes can be used to produce alkalinity and to sequester metals. Supporting such processes by suitable means is considered “ecological engineering” and presents an alternative to chemical in-lake treatments or running ex-situ treatment plants. Use of natural processes by ecological engineering is still an emerging field, but as case studies describe, the potential to facilitate sustainable options to mine waste management exist (Sect. 5.7). An analysis of publications within the field by Barot et al. (2012) suggests that using ecosystem services as a treatment option is frequently practiced in China, where the approach originated, and to some degree in North America, but is less practiced in European countries.

It is essential to judge the success of remediation approaches using an appropriate temporal perspective. Chemical treatment processes show immediate results in contrast to usually slower improvements with biological processes. When measures of reducing sulfide mineral oxidation are integrated properly into the waste management area, the waste site will recover.

6.6 Economical Assessments: The Value of Pit Lakes

Current Australian closure strategies for pit lakes can be grouped into three main categories (Evans and Ashton 2000; Sect. 5.4): (1) The enclose-and-forget approach, with the construction of a bund around the mining void to prevent access and protect mining companies from litigation arising from accidents; (2) Strategies that address environmental issues, which are mainly concerned with development of environmental values such as biodiversity conservation (e.g. remediation of water quality in mine lakes and preservation of biodiversity through nature conservation projects); or (3) Initiatives intended to create employment and business enterprise opportunities (e.g. aquaculture, ecotourism, and various forms of horticulture), or result in the creation of a community resource, such as a recreational facility. The first strategy of enclosing pit lakes addresses most current legislative requirements and largely resolves the problem of liability but may not provide any benefits to local communities. End uses that fall into the other two strategies hold more promise for significant local community benefit (Evans and Ashton 2000; McCullough and Lund 2006). However, of equal importance to identification of social aspects of mine closure is the application of sound well-understood science to the end use development process, be it catchment rehabilitation or water quality remediation (Evans 2006; McCullough et al. 2009). Nevertheless, the absence of regulatory control or even directions given to mining companies ensures few examples of successful pit lake closure and lease relinquishment back to the government.

According to a survey (Sect. 5.8) in Lusatia, Germany, there is strong support for the creation of a lake district using the mine pits in the area. By quantifying the economic benefits of recreation in the district, decision makers can better assess current and alternative water allocation policies. The costs for chemical remediation of the lakes considered in the survey (with a total water volume of about 0.8 km^3) were estimated, assuming initial neutralization and secondary treatments to keep the lakes neutral against continuous re-acidification from the environment; it will require more than 100,000 t of ground limestone, dolomite, and hydrated lime initially, and about twice this amount during the following 10 years. The costs for chemicals, technical equipment and needed manpower would be less than the estimated benefits of neutral, usable lakes, especially when the non-market benefits (estimated between 10 and 16 million Euros per year) are included. These findings have implications on policy making in the Elbe River basin, making the rehabilitation of large-scale open pit mining in the Lusatia region a major water user. Furthermore, the estimates of non-market benefits clearly show that a narrow focus on market benefits seriously underestimates the benefits of pit lakes. The investigators strongly recommend the inclusion of all benefits in decisions regarding the costly restoration of mine pits and remediation of acidic lakes (see also McCullough and van Etten 2011).

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General Terms

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Mines, Lakes and Streams

Organisms and Taxa