Mine Water Environ (2010) 29:116–134
DOI 10.1007/s10230-009-0096-2

TECHNICAL ARTICLE

Tracking the Aquatic Impacts of a Historical Metal Mine Using Lacustrine Protists and Diatom Algae

Susanna Kihlman · Tommi Kauppila

Received: 20 May 2009 / Accepted: 11 December 2009 / Published online: 14 January 2010

Abstract Two lake sediment cores collected near a closed Cu–Au mine were analyzed for testate amoebas, diatoms, and geochemistry to compare their utility for assessment and monitoring of aquatic impacts of metal mines. Geochemical profiles displayed the mine history as increases in mineral matter-related elements during the mining period, and as post-mining metal peaks. Biotic assemblages co-varied with geochemical shifts, and the most notable ecological changes coincided with the peaks in metal concentrations. Additionally, nutrient enrichment caused a major shift in biotic assemblages. According to the results, the mine affected the lake environment over a relatively large area but the changes were transient. Major ecological effects occurred only after the actual mining period as the tailings weathered, which delayed the metal release. This suggests that mine impacts can be significantly reduced by careful design and after-care of the waste facilities.

Keywords Arcellaceans · Diatoms · Ecological impacts · Geochemistry · Lake sediment · Metal mining

S. Kihlman (✉)
Department of Geology, University of Turku, 20014 Turku, Finland
e-mail: susanna.kihlman@gtk.fi

S. Kihlman
Geological Survey of Finland, PO Box 96, 00251 Espoo, Finland

T. Kauppila
Geological Survey of Finland, PO Box 1237, 70211 Kuopio, Finland

Introduction

All metal mining operations affect their surrounding environment to some degree. One of the most common and widespread environmental problems related to sulphide metal mining is metal-rich acid mine drainage (AMD; e.g., Wolkersdorfer and Bowell 2004, 2005a, b), which is a potentially serious problem for the surrounding surface waters and their ecosystems. While the characteristics of the ore and overburden, and the physical environment at the site are the main factors that determine the nature of the mine water-related pressures that each mine may generate, the impacts of such factors may be different at the onset of mining, during various phases of operation of the mine, and after closure. This variability increases the importance of predicting and assessing processes in the mine waste dumps that are often a major source of contaminants from a mine site. As environmental issues are increasingly being taken into account during mine design, operation, and closure (e.g., BRGM 2001; Heikkinen et al. 2008; Ripley et al. 1996), better tools for monitoring the effectiveness and ecological relevance of these management and rehabilitation measures need to be developed.

However, the ecological effects of metals may be suppressed in mining environments due to the adaptation of local aquatic biota to naturally elevated metal levels. Furthermore, it can be challenging to distinguish the effects of the mobilized metals on biota from the impact of low pH. In the absence of pre-mining ecological data, sediment-based methods may be used to obtain data on local ecological and geochemical conditions pre-dating the expected disturbances. In addition, down core (stratigraphic) studies make it possible to follow the course of chemical and ecological changes during different phases of mine operation, helping establish the current status of the environment for informed management decisions. Such records of the temporal evolution of mine-derived pressures and the resulting impacts also serve as analogues for other mine sites with similar characteristics.

Two diverging ecological indicators were used, in combination with geochemical data, to provide a temporal record of the possible impacts of the Haveri Cu–Au mine in SW Finland on both the sediment and water compartments of the aquatic environment. The mine has been closed for decades and its tailings currently produce AMD that discharges to the nearby Lake Kirkkojärvi (Parviainen and Eklund 2007). This makes geochemical and palaeoecological sediment studies suitable for assessing the historical impact of the mine on aquatic conditions during the mine's different phases, up to the present day. The surface water bodies in the area are also susceptible to eutrophication due to human activities, providing an opportunity to compare the effects of different environmental stress factors.

Testate amoebas are simple sac or cap-like tests-forming unicellular organisms that are found in nearly all moist habitats, such as freshwater bodies, peatlands, moss, and soil. The tests can be proteinaceous, siliceous, calcareous, or agglutinated using foreign particles (e.g., diatoms, mineral grains) glued with mucopolysaccharides (Patterson and Kumar 2000). They have been used as proxies in lacustrine settings to study both natural and anthropogenic changes, including shifts in land use, pH, and eutrophication (e.g., Ellison 1995; Escobar et al. 2008; Patterson et al. 2002; Reinhardt et al. 2005) and in palaeoclimatic research (Boudreau et al. 2005; Dallimore et al. 2000; McCarthy et al. 1995). The group has further been used in studies of sea-level changes in salt-marshes (e.g., Charman et al. 2002; Gehrels et al. 2001; Roe et al. 2002), flood characterisation in fluvial environments (Medioli and Brooks 2003) and for palaeo-hydrological and -climatic studies in peatlands (Booth 2002; Tolonen 1986; Warner and Charman 1994).

Lacustrine forms of the group (mainly arcellaceans) have proven to be very promising indicators of industrial and mining-related pollution and remediation, recording lake-bottom acidity and high metal concentrations in aquatic environments (Asioli et al. 1996; Kauppila et al. 2006; Kihlman and Kauppila 2009; Kumar and Patterson 2000; Patterson and Kumar 2000; Patterson et al. 1996; Reinhardt et al. 1998). The ability of some of the forms (i.e., intraspecific strains) to live in harsh conditions (e.g., under high heavy metal concentrations or low oxygen concentrations) makes the group very good environmental indicators, together with their living habitat at the water–sediment interface, and their high abundance in sediment samples, which facilitate the use of very thin samples for high resolution studies. In addition, their high reproduction rate (Ogden and Hedley 1980) and sensitivity to environmental conditions enables rapid environmental responses, and tests are well preserved, even in the very low pH environments that are often associated with mining. Even though most such research has focused on temperate regions, these organisms are found all over the world, from polar regions (Beyens et al. 1995; Dallimore et al. 2000; Mathur et al. 2006; Mattheeussen et al. 2005) to tropical environments (Dalby et al. 2000). This cosmopolitanism supports the potential usefulness of arcellaceans as a tool in future mine impact studies throughout the world, although much research is still needed to establish the method.

In contrast to the emerging mine impact indicator group of testate amoebas, diatom algae are widely used palaeolimnological indicators of environmental change (e.g., Stoermer and Smol 1999). Diatoms live in several lacustrine habitat types (planktonic, attached to sand grains or rocks, motile on mud, attached to plants, and loosely associated with macrophyte stands); sedimentary diatom assemblages thus contain an ecological signal derived from all these sources. Diatoms have also been employed in studies of metal contamination and mining impacts (Cattaneo et al. 2004, 2008; Cunningham et al. 2005; Ek et al. 2001; Kauppila 2006; Laperrière et al. 2008; Loukola-Ruskeeniemi et al. 1998; Michelutti et al. 2001; Ruggiu et al. 1998; Salonen et al. 2006).

The aims of this research were: (1) to examine if mining-related effluents from the former Haveri Cu-Au mine have increased metal concentrations in the sediments of the nearby Lake Kirkkojärvi and whether contamination is also detectable in the more distant Viljakkalanselkä Basin; (2) to determine, based on sediment chemical profiles, the characteristics and timing of different mine water inputs to the lake during various phases of the mine's history; (3) to assess and compare the responses of arcellaceans and diatoms to changes in mine water contamination, using sediment geochemical properties as a proxy for mining-derived stress and numerical methods to separate the effects of different environmental variables such as metals, arsenic, pH and nutrients; and (4) to test and further develop the use of arcellaceans as mine impact indicators by comparing arcellacean responses to mine water loading with those of diatoms.

Materials and Methods

Study Site

The closed Haveri Cu–Au mine (61°43′N, 23°14′E) is situated in the township of Ylöjärvi within the Tampere Schist Belt in SW Finland. The mine site is located on a cape between two lake basins: Lake Kyrösjärvi to the west and Lake Kirkkojärvi to the east (Fig. 1). Another

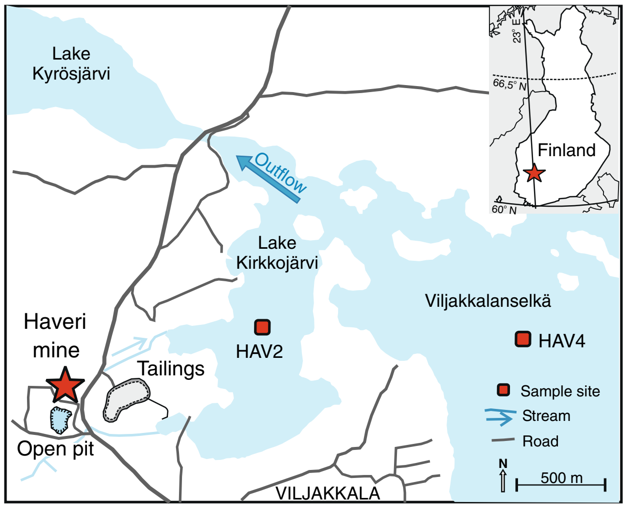

Fig. 1 A map of the study area and its location in Finland

lake basin, Viljakkalanselkä, is located still further west. The mine lies near the village of Viljakkala, but the region is rural with fields and forests. The lake system is currently meso-eutrophic with an epilimnetic total phosphorus (TP) concentration of 20–24 µg/L and a pH of 6.6–7.4, measured at the strait between Lake Kyrösjärvi and Lake Kirkkojärvi in 1996–2002. Soil in the area mainly consists of fine-grained material (clay, silt). The bedrock of the Haveri formation includes limestone and tholeiitic basic metalava, metalava breccia, metatuff, and metatuffite; the other main rock type consists of calc-alcalic intermediate metavolcanic rocks (Mäkelä 1980).

Mining in the area had already started in the eighteenth century, and continued periodically until the end of the nineteenth century with small-scale open-pit Fe mines. However, the presence of sulphides made the exploitation of the iron ore unprofitable (Karvinen 1997). The discovery of the first Cu–Au deposit led to the onset of a mine in 1939 and developing processing methods enabled more efficient production in 1949, up to 100,000 t/year. The ore was extracted from an open pit as well as from underground workings. The most active mining period was from 1942 to 1962, and the official production of the mine was ≈1.6 Mt of ore, containing on average 2.85 g/t of Au and 0.39% Cu (Puustinen 2003). All the mine tailings (1.4 Mt) were piled at an average depth of 7 m onto a small cape protruding into Lake Kirkkojärvi (Fig. 1); none were dumped into the lake. The facility covers ≈18.5 ha (Parviainen and Eklund 2007). The main sulphide minerals in the ore and in the tailings are pyrrhotite, chalcopyrite, magnetite, and pyrite, of which pyrrhotite is the most oxidizable and chalcopyrite the most stable. The amount of waste rock stored at the site is 4,500 t.

The tailings area has been used for motor sports and is partly covered with dirt and asphalt to prevent dust (Parviainen et al. 2006). However, due to historical exposure to air, rainwater, and snowmelt, the uppermost vadose layer of the tailings is oxidized to a depth of 0.9–2.0 m and contains secondary Fe precipitates, primary iron oxides, and scarce remnant primary sulphides (Parviainen and Eklund 2007). This oxidized zone produces acidic and heavy metal rich AMD, but despite the low pH of the water emerging from the tailings pile (pH 3.4–3.9), the pH in the southern outflowing stream and Lake Kirkkojärvi has remained near neutral (≈6–7) (A. Parviainen, personal communication). Nevertheless, significantly elevated concentrations of some elements (e.g., Cu 2,430 µg/L, Co 2,180 µg/L, Mn 5,540 µg/L, Fe 299 mg/L) have been measured from the stream water originating from the tailings.

Coring

Two short sediment cores were retrieved from the lake basins surrounding the mine site in March 2006 using a Kajak-type corer (Fig. 1). The core HAV2 was taken from a depression located immediately outside the tailings pile in Lake Kirkkojärvi ('impacted core'), while HAV4 was taken from the Viljakkalanselkä Basin, ≈2.3 km from the mine. The Lake Kirkkojärvi coring site is a gently sloping 7 m depression ≈300 m in diameter while the Viljakkalanselkä site is a wide mid-lake basin 22 m in depth. HAV2 was sectioned into continuous 1 cm slices (0–28 cm), while HAV4 was sectioned into 1 cm slices down to 10 cm and into 2 cm slices between 10 and 26 cm. The Viljakkalanselkä Basin was selected as a potential reference site because of its fairly distant 'net upstream' position: the lake system drains from the Kyrösjärvi basin on the other side of the mine. However, currents may transport mining-related effluents in complex patterns in a lake. The HAV4 site is also deeper than HAV2 (24.2 vs. 6.9 m), and the profundal conditions are therefore likely to differ between these sites, resulting in different baseline faunas. Nevertheless, the more distant site allows the detection of possible nutrient enrichment in the area, an important stress in the aquatic environment that should be distinguished from mining-related impacts.

Estimation of Sediment Age

The ages of the sediment layers in the HAV2 and 4 cores were estimated based on the current depth of the fallout peak from the Chernobyl nuclear accident. This ^{137}Cs fallout peak dates to 1986 and is often distinguishable in lake sediments in Finland. Caesium activity was determined from wet sediment samples with an Ortec gamma spectrometer equipped with a 10 cm NaI(Tl) crystal, two amplifiers, and a 2048 channel pulse height analyzer (Äikäs et al. 1994). This method gives an estimated date for one sediment layer only, so ages for the rest of the sequence were approximated based on the dry matter content of each sediment slice, assuming a constant dry matter deposition rate. This average annual dry matter deposition rate was determined for both cores between the sediment surface (March 2006) and the 1986 level in the sediment. While this method ignores any changes that may have occurred in dry matter inputs, it should improve the age estimates over simple linear extrapolation by accounting for sediment compaction. Furthermore, no changes or events that may induce significant changes in dry matter deposition are known for the area during the period of interest.

Geochemical Analyses

Sediment chemistry was used both to record sediment metal concentrations that may have affected aquatic biota and as a proxy for mine-derived loading to surface waters (e.g., Couillard et al. 2004). Freeze-dried sediment samples were analyzed for element chemistry after microwave-assisted HNO_3 digestion (US EPA 1994). Both ICP-MS and ICP-AES were used for determinations, depending on the element. All analyses were performed in the accredited testing laboratory of Labtium Ltd (FINAS T025). The extraction provides a record of mine-derived elements because it breaks down sulphides, most salts (e.g., apatite), carbonates, trioctahedral micas, 2:1 and 1:1 clay minerals, and most of the talc. In contrast, it does not dissolve major silicates such as quartz, feldspars, amphiboles, or pyroxenes, though it may liberate some elements if these grains are weathered or by minor etching of fresh mineral surfaces. The method thus extracts certain fractions that are not bioavailable and the sediment concentrations are thus not directly comparable, for instance, to pore water concentrations or other more bioavailable fractions at the sediment surface at the time of deposition. However, the concentrations are more stable than those obtained with weaker extractions (less prone to post-depositional alteration) and therefore more suitable as proxies of the original mine water loading.

Determination of Arcellaceans and Diatoms

All sediment levels were analyzed for arcellaceans and diatoms. Samples used to determine arcellaceans were first weighed ($\approx$2 g fresh weight) and then wet sieved with distilled water. Sieves of 500 and 56 µm mesh were respectively used to remove coarse organics and to retain arcellaceans while removing clay and silt sized particles. Mechanical stress was avoided to protect fragile tests from breaking. The sieved samples were divided into eight aliquots using a wet splitter described by Scott and Hermelin (1993) to optimize the amount of tests for counting while retaining statistical significance. The portions were studied with an Olympus SZH (7.5×–64×) stereomicroscope and, in most cases, at least $\approx$200 specimens were identified. However, in some samples, the test amount was too low to reach that number. Medioli and Scott (1983) and the identification key of Kumar and Dalby (1998) were mainly followed and were used as the sources of authors for the species. Certain forms were identified based on additional references (e.g., Charman et al. 2000; Ogden and Hedley 1980).

Samples for diatom analysis were first treated with H_2O_2 for 3–4 days. The test tubes were then heated in a water bath and a few drops of H_2SO_4 and HNO_3 were added to further oxidize the organic matter. The suspension was washed four times and a drop of the resulting slurry was dried on a cover slip that was mounted with Naphrax®. A minimum of 300 diatom valves (300–403, average 339 for HAV2, 328 for HAV4) was identified from each sample, mainly using Krammer and Lange-Bertalot (1986, 1988, 1991a, b) as a reference.

Numerical Methods

Both the arcellacean and diatom species data were summarized using multivariate statistical methods. For cores HAV2 and HAV4, indirect and direct-gradient ordination analyses were used to define the relationships between microfossil assemblages and various geochemical elements used as environmental variables. These analyses were done and ordination plots were generated using the CANOCO 4.5 WIN software of ter Braak and Šmilauer (2002). Relative abundances of arcellaceans and diatoms were used for unconstrained principal components analysis (PCA). The PCA axis sample scores from these analyses (i.e., the amount of faunal and floristic change) were compared to concentrations of chemical variables based on linear correlations.

The linear redundancy analysis (RDA) method was selected for constrained ordination because of the shortness of species gradients (<1 SD unit) based on exploratory (detrended correspondence analysis DCA) ordinations. Marginal effects of element concentrations on both arcellaceans and diatom assemblages were tested individually with Monte Carlo testing and by using the time series option available in CANOCO. Sample depth was employed as a co-variable in the analyses to detect any short-term changes that diverged from the continuous long-term trends.

Arcellacean species assemblages were also defined by diversity indices. Stressed environmental situations may reduce the diversity of the species composition and lead to the domination of only a few resistant and opportunistic taxa. The Shannon index H ranges from 0 for samples with only a single taxon to high values for samples with many taxa, each represented by a few individuals. The Berger-Parker dominance index gives the proportion of the dominant taxon in the sample. Diversity indices were calculated using the PAST program version 1.68 (Hammer et al. 2001). This software was also used for exploratory unconstrained and constrained clustering of the HAV2 and HAV4 short core samples using different distance measures (Euclidean, chord) with the paired group method to detect species assemblage zones.

The responses of diatom assemblages to nutrients and pH were studied using inference models developed for total phosphorus (TP) concentrations and pH. TP was reconstructed with the inference model of Kauppila et al. (2002), based on weighted averaging and a calibration set collected from southern and central Finland (3–89 µg P l^{-1}, RMSEP: 0.16 log µg P l^{-1}, r^2 of 0.76). The goodness of fit of the HAV2 and HAV4 assemblages to the TP gradient was determined by entering these fossil assemblages as passive samples in an ordination of the original calibration set samples constrained to TP and examining the squared residual length of the samples from the TP axis. The trends in past pH values were estimated with simple abundance weighted averaging of the species optima from the PIRLA II project (Dixit et al. 1993) to detect whether the mine water inputs have caused notable acidification in the study lake. The PIRLA II dataset has an extensive species list and it represents a general geological and climatic setting similar to the present study area. An average of 57% of the diatoms identified from the HAV2 and HAV4 core samples were included in the pH reconstruction.

Results

Sediment Age Estimation

The ^{137}Cs depth profiles showed rapid increases in the radiocaesium levels in both HAV2 and HAV4 cores. In HAV2, cored from a near-shore site, activity concentrations increased rapidly between 12 and 9 cm in the sediment, with the highest concentrations in the 9–10 cm sample, and gradually declined towards the sediment surface. The ^{137}Cs profile for the deep water, mid-lake HAV4 core was even more distinctly peaked and the highest activity concentrations at 6–7 cm showed less tailing to deeper sediment layers and a rapid decline towards the sediment surface. The sharp ^{137}Cs peak in HAV4 thus suggests low sediment disturbance and minor post-depositional mobility of ^{137}Cs while the more gradual upward decline in HAV2 suggests continuing Cs inputs from the surroundings. Both the linearly extrapolated and adjusted age estimates are presented in Fig. 2. Based on the adjusted estimates, the sediments deposited during the most active Cu–Au mining period (1942–1962) are found at approximately 26–20 cm in HAV2 and 20–14 cm in HAV4. Geochemical results also support the age models (see below).

Chemical Results

Geochemical results demonstrated a succession of shifts in element concentrations in the near-mine core HAV2 (Fig. 3). In general, the geochemical profile can be divided into four sections: the lowermost pre-mining samples (28–26 cm), the mining period (25–20 cm), post-mining

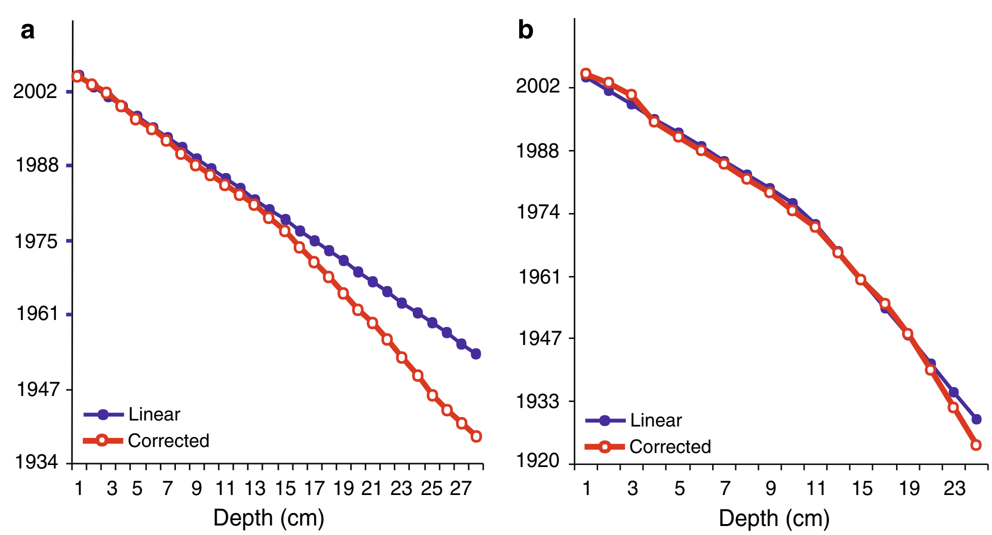

Fig. 2 Linear and corrected age-depth curves of sediment cores HAV2 (**a**) and HAV4 (**b**)

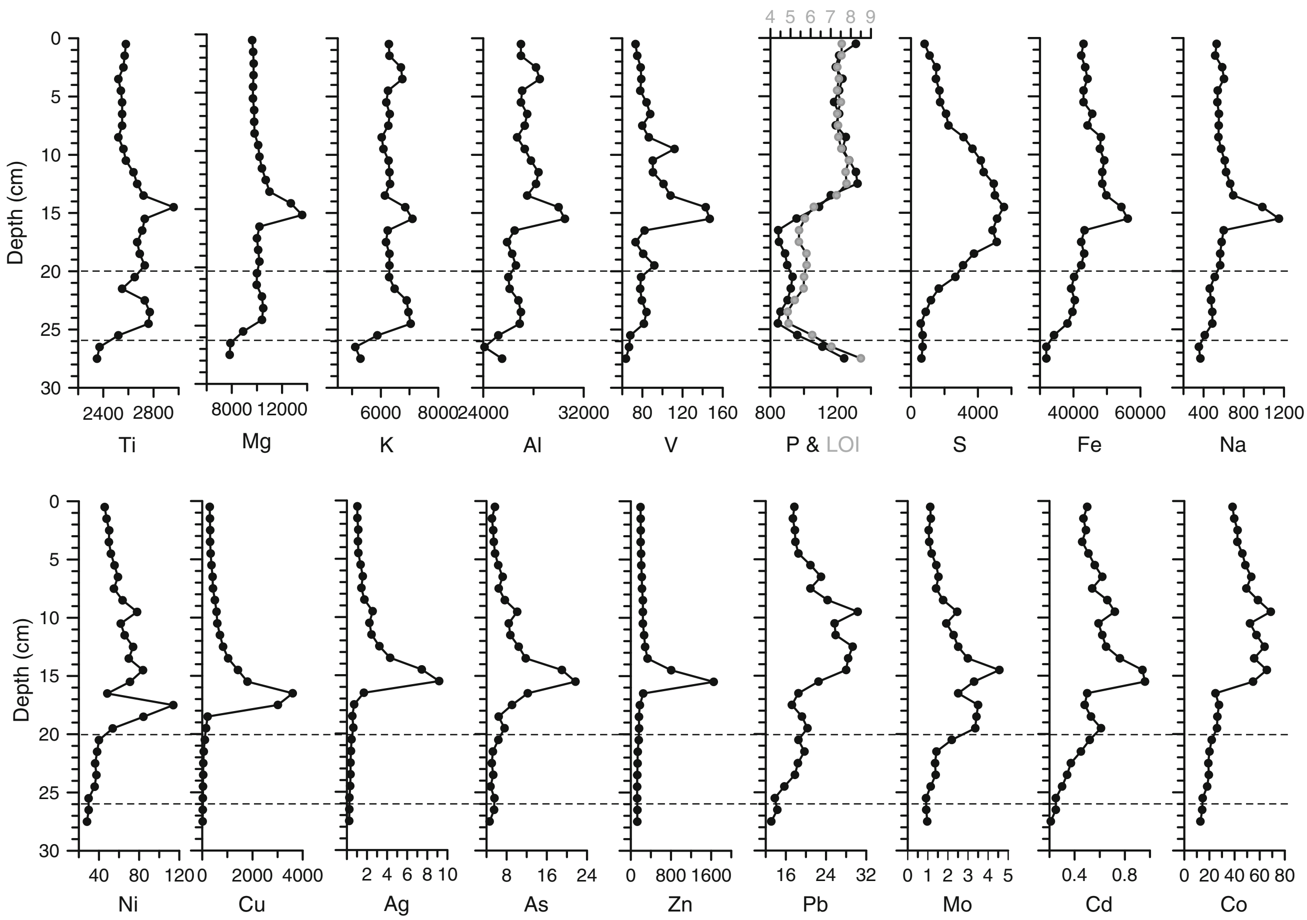

Fig. 3 Distribution of selected elements and loss-on-ignition (LOI) in the core HAV2 from Lake Kirkkojärvi. LOI is shown in *grey* and *dashed lines* show phases of pre-, active-, and post-mining

concentration peaks (18–14 cm), and the post-impact recovery section (13 cm). The first geochemical changes appeared at the depth of 25 cm, corresponding in time to the early Cu–Au mining period, when concentrations of the mineral matter-related elements Mg, Ti, V, Al, and K increased, sediment organic matter content declined, and concentrations of P decreased. This change in sediment chemistry was followed by a phase that continued until 18 cm, where concentrations of S and certain sulphide ore-associated metals (Pb, Co, Mo, Cd, Ni, and Ba) as well as Fe and Na gradually increased.

The most significant geochemical shifts in HAV2 were seen only after the estimated active mining period, between 18 and 14 cm in the sediment (mid-1960s to mid-1970s), as two successive concentration peaks of differing chemical compositions. Ni and Cu peaked first: the Ni concentration increased from 30 mg/kg to over 100 mg/kg at 17–18 cm while the Cu concentration rose from ≈200 mg/kg to over 3,000 mg/kg at 16–17 cm. These elevated levels notably exceed the natural concentrations typical of the stream sediments in the area (Lahermo et al. 1996) and correspond to what has been measured at other mine-impacted lakes (Couillard et al. 2004; Salonen et al. 2006). However, notably lower concentrations have been reported from mine sites as well, owing to local conditions (Kauppila et al. 2006; Kihlman and Kauppila 2009; Laperrière et al. 2008). In the next phase (peaking at 14–16 cm), concentrations of several other elements, including those related to silicates, increased (‘polymetallic peak’). However, concentrations of certain mine-related metals (e.g., Ag, As, Cd, and V) increased proportionally considerably more than those of Al or K. Furthermore, the shapes of the peaks for these elements were also different from the silicate metal peaks, declining gradually towards the sediment surface. In contrast, the peak for Zn was uniquely sharp and short-lived, showing little tailing towards the sediment surface.

After the post-mining section of peak concentrations, most of the elevated metal concentrations gradually declined towards the sediment surface. However, certain metals attained their highest concentrations only after the upper metal peak, most notably Pb and Co, which remained

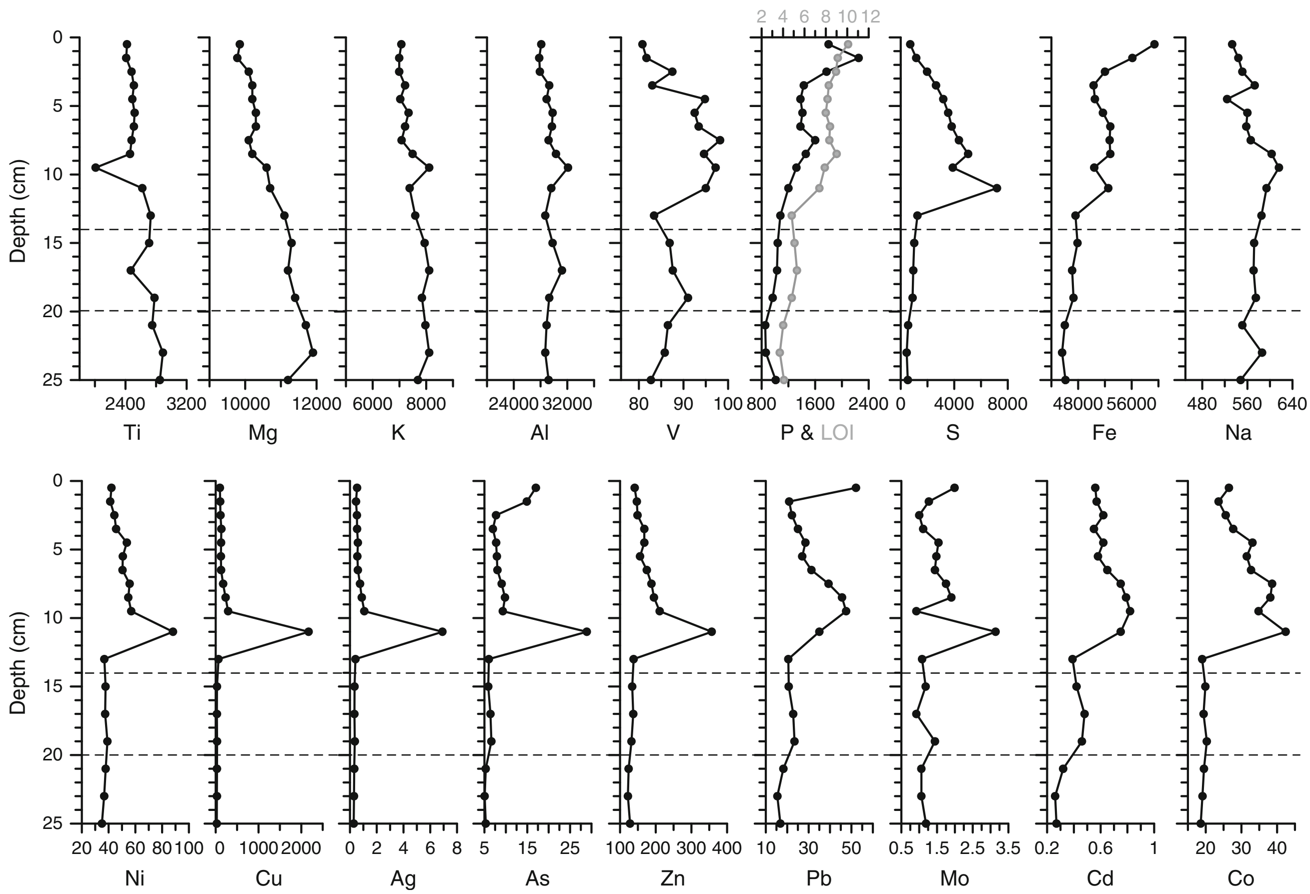

Fig. 4 Distribution of selected elements and LOI in the core HAV4 from the Viljakkalanselkä basin. LOI is shown in *grey* and *dashed lines* show phases of pre-, active-, and post-mining

elevated until 9–10 cm. In addition, several metals besides Co and Pb showed a minor peak at the depth of 9–10 cm, including Ag, As, Mo, Ni, Cd, and V.

The general geochemical trends of the core HAV2 can also be traced in the more distant core HAV4, with some modifications caused by the lower sedimentation rate and reduced sample resolution (Fig. 4). In contrast to HAV2, the mining period ($\approx$20–14 cm) was associated with only minor increases in the silicate-related elements in HAV4 and there was no decline in the sediment organic content. In general, the organic content gradually increased throughout the core while concentrations of Mg, Ti, K, and Al decreased. The two-peaked section of high metal concentrations in HAV2 was here seen as a single merged peak because of the lower sampling resolution and slower sediment accumulation. Even the peak in Ni, the metal that peaked first in HAV2, was merged with the rest of the metal peaks in HAV4. In addition to Ni and S, metals such as Ag, As, Zn, Cu, and Mo had high concentrations in the 10–12 cm sample. The slight increases in K and Al occurred immediately above this level instead of coinciding with the metal peaks.

Above the peak impact section, concentrations of metals such as Ag, As, and Cu rapidly declined in HAV4. The profile for Zn showed a slower decrease towards the sediment surface than in HAV2, as did S concentrations. The metals that declined slowly in HAV2 (Pb and Co) had the same trend in HAV4, but the Cd and V concentrations also remained elevated. Another feature that differed from the HAV2 core was the trend in redox sensitive elements. In this deep-water core, concentrations of Fe and P dropped at 6 cm and increased again at the sediment surface. A similar increase at the sediment surface was also evident in the profiles of As and Mo.

Arcellacean Results

Results of arcellacean analyses are illustrated in stratigraphic diagrams in Figs. 5 and 6 and the results are summarized as PCA plots in Fig. 7a and c. A total of 28 different arcellacean forms were identified and assemblage zones were delineated from both cores with clustering methods. The discussion below is organized according to these faunal zones. The largest changes occurred at the

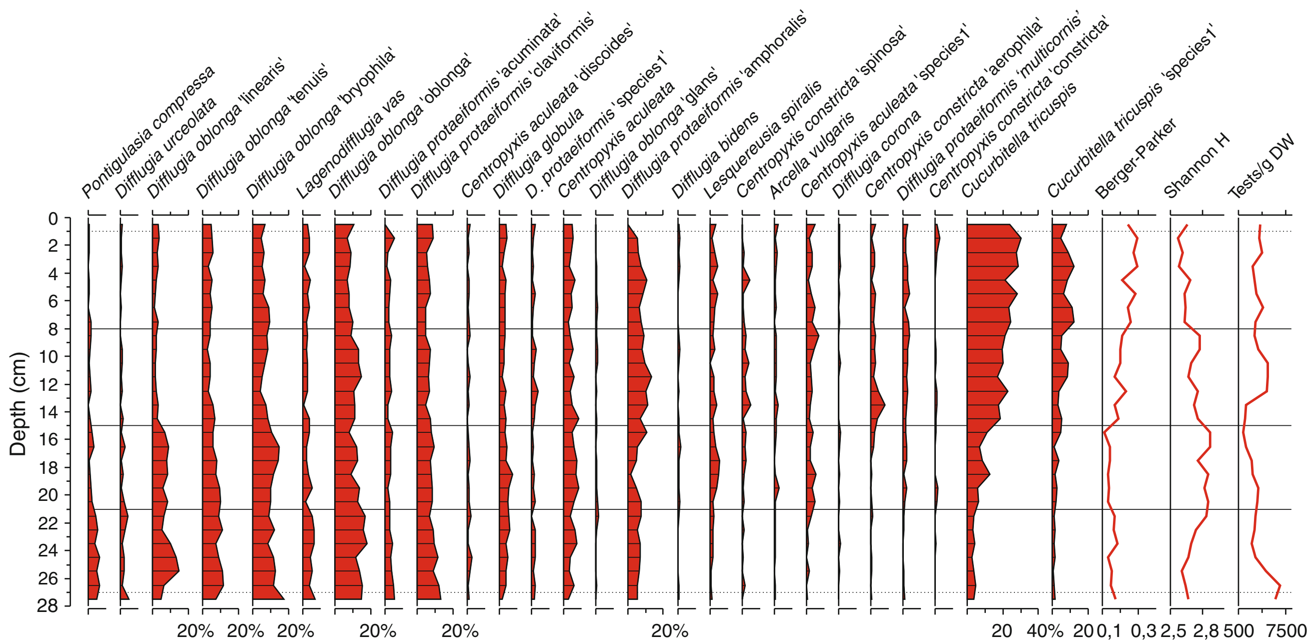

Fig. 5 Distribution of arcellacean forms in the near-site core HAV2 from Lake Kirkkojärvi. *Horizontal lines* show assemblage zones detected by clustering

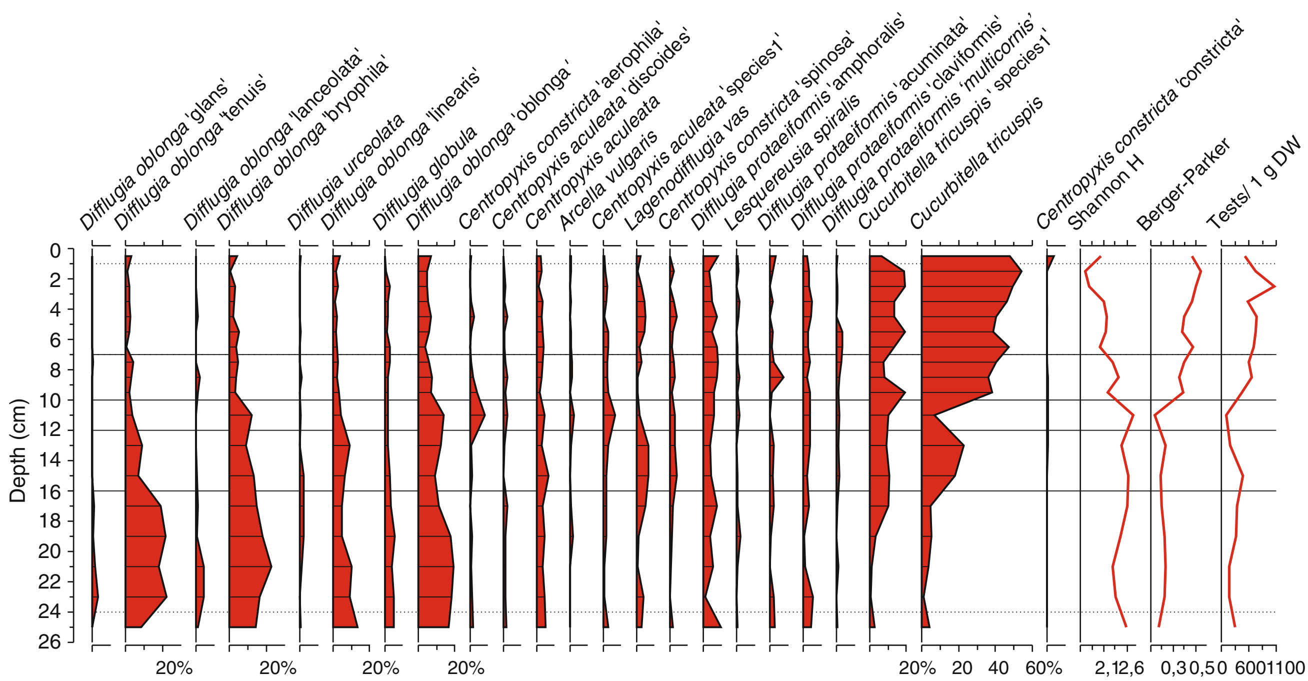

Fig. 6 Distribution of arcellacean forms in the core HAV4 from the Viljakkalanselkä basin. *Horizontal lines* show assemblage zones detected by clustering

depths of 15–16 cm (HAV2) and 10–12 cm (HAV4), mainly related to shifts in the abundances of strains of *Difflugia oblonga* and the well-known eutrophic indicator *Cucurbitella tricuspis*. PCA plots summarize the faunal successions of the cores: a major mid-core change divided the sediment sequences into two sections, whereas minor shifts reflected the observed geochemical phases of different periods in mining history. Environmental stress favours opportunistic species such as centropyxids, and *Centropyxis constricta* 'aerophila', in particular, occurred together with the highest metal concentrations. Besides the changes in faunal assemblages, the total concentrations of

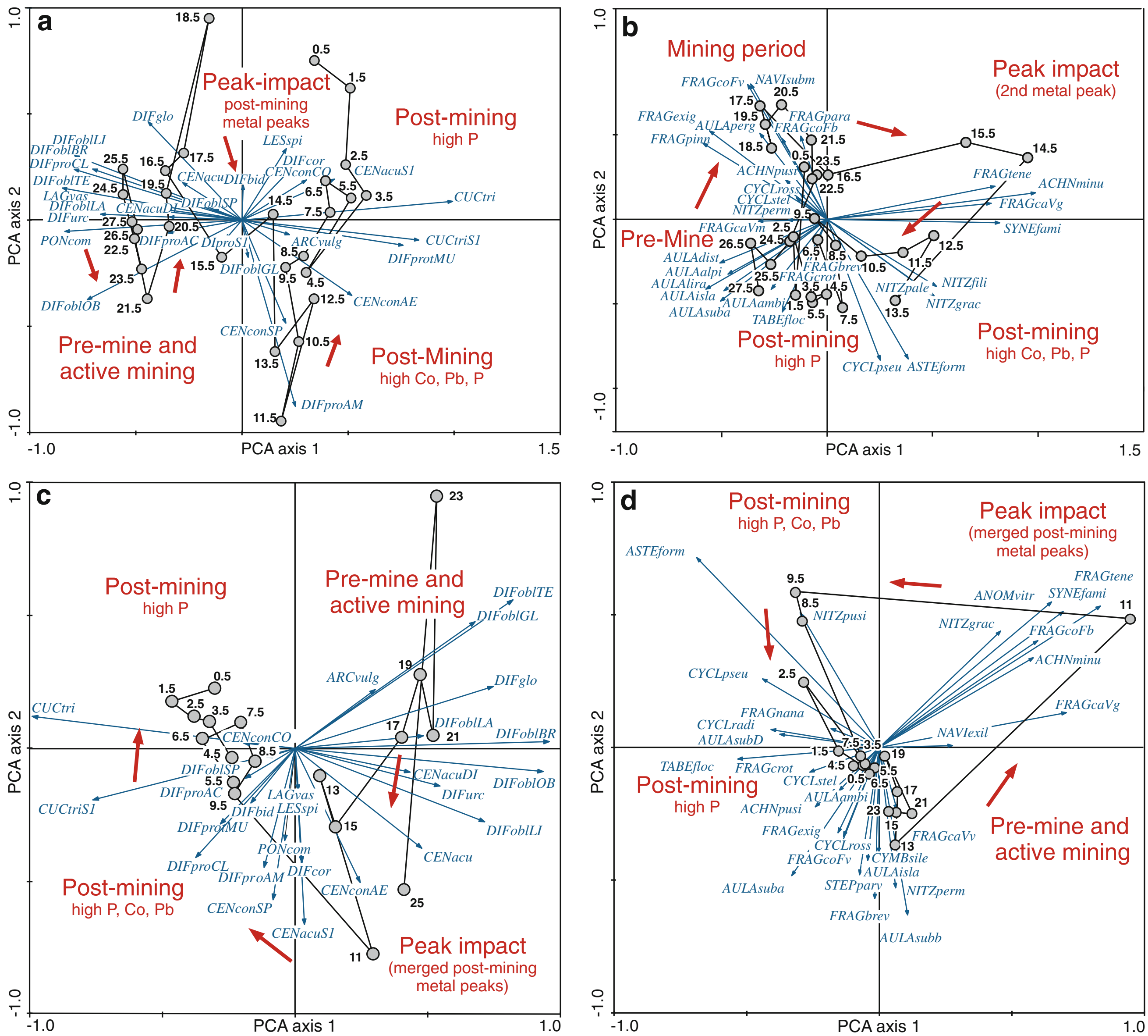

Fig. 7 Principal component analysis (PCA) plots show biotic assemblages and different mine phases in cores HAV2 (**a**, **b**) and HAV4 (**c**, **d**). Arcellacean plots are on the *left*, diatom plots on the *right*

tests (/g DW) also fluctuated, and were lowest when metal concentrations were highest; diversity diminished towards the sediment surface.

Diatom Results

Results of the diatom analyses are presented in Figs. 8 and 9 and summarized as PCA plots in Fig. 7b and d. In HAV2, the diatom composition gradually shifted from the pre-1942 samples, rich in *Aulacoseira* species, towards higher abundances of various *Fragilaria* forms during the active mining period. This trend is best illustrated in the PCA plot (Fig. 7b), where pre-mining samples plot in the lower left quadrant; the mining-period samples then gradually shift to the *Fragilaria*-dominated upper left quadrant. Other taxa that increased in abundance during the mining phase include *Achnanthes minutissima*, *Nitzschia perminuta*, and *Navicula submuralis*. The next geochemical phase, with a marked increase in sediment Ni and Cu concentrations between 20 and 16 cm in the sediment, was associated with only slight changes in diatom species composition, except for the 16.5 cm sample. In contrast, the following poly-metallic peak coincided with a major change in diatoms, in which especially the relative proportions of *Fragilaria tenera*, *Achnanthes minutissima*, *Fragilaria capucina* var. *gracilis*, and *Synedra familiaris* increased (Fig. 7b). Species that declined in this phase include *Fragilaria exigua*, *F. pinnata*, *F. parasitica*, *F. construens* f. *venter, Navicula*

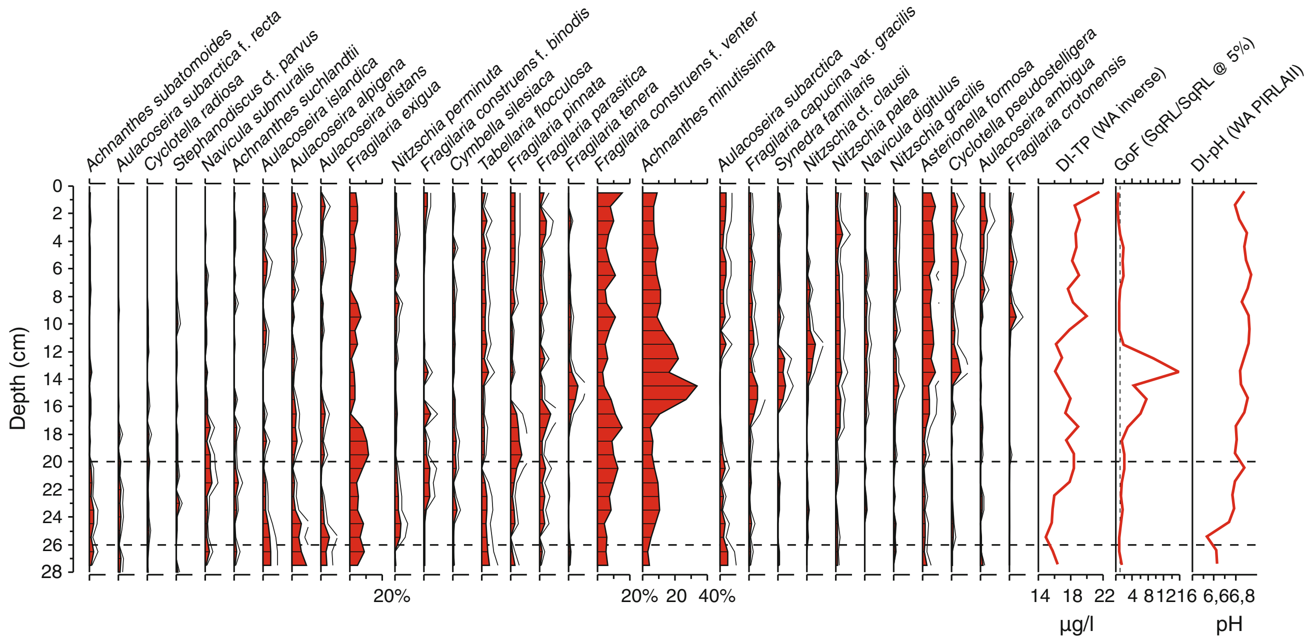

Fig. 8 Distribution of diatoms in the core HAV2 from Lake Kirkkojärvi. *Dashed lines* show phases of pre-, active-, and post-mining

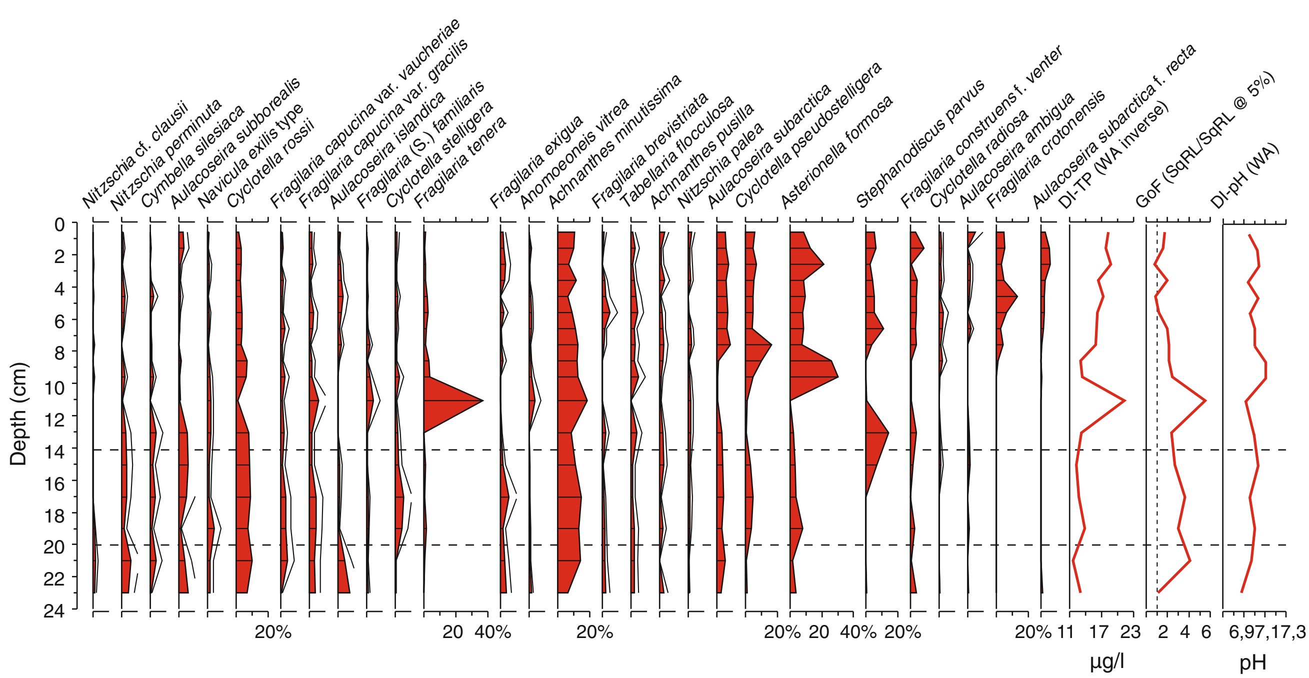

Fig. 9 Distribution of diatoms in the core HAV4 from the Viljakkalanselkä basin. *Dash lines* show phases of pre-, active-, and post-mining

submuralis, and *Aulacoseira subarctica*. Above this distinctive geochemical phase, diatom assemblages gradually moved towards the pre-mining species compositions via species compositions characterized by high abundances of certain *Nitzschia* species, *Cyclotella pseudostelligera*, and *Asterionella formosa* in the 14–10 cm samples. Further up the core, from 10 cm upwards, *Aulacoseira ambigua* and *Fragilaria crotonensis*, both typical for eutrophic conditions, increased in abundance.

Despite the coring site being located 2.3 km from the mine, the diatom assemblage changes in the HAV4 core resemble those of the HAV2 site, especially during the peak metal input phase. In contrast, the mining period sediments showed only minor changes in diatoms, with increases in *C. stelligera, C. pseudostelligera*, and *Asterionella formosa*. Close to the end of the mining phase, *Stephanodiscus parvus*, a small centric planktonic species common in highly eutrophic settings, increased in abundance. This increase was interrupted, however, during the peak metal input phase when species such as *F. tenera*, *S. familiaris*, *A. minutissima*, *Anomoeoneis vitrea*, and *Fragilaria construens* f. *binodis* became more common. With the exception of the latter two species, these are the same diatoms that peaked in HAV2 during the impact phase. After the metal peaks at 10–12 cm, diatom assemblages gradually approached the pre-impact species compositions. However, similar to HAV2, the samples immediately above the most metal-impacted section (8–10 cm) contained a distinctive species assemblage with high abundances of *A. formosa, C. pseudostelligera*, and *Nitzschia pusilla.* Above this section, proportions of *S. parvus* increased again and certain other eutrophic taxa also appeared (*A. ambigua, F. crotonensis*, and *A. subarctica* f. *recta*).

Relationships between Biotic Assemblages and Environmental Variables in Cores HAV2 and HAV4

Arcellacean and diatom species compositions changed with the shifts in sediment geochemistry in both cores (Table 1). In the near-site core HAV2, variables that remain elevated after the concentration peak at 15 cm showed the highest and statistically significant correlations with arcellacean PCA axis 1 sample scores (Co, P, LOI, Al, B, Fe, Mn, and Pb). None of the analyzed elements correlated with Axis 2 sample scores of arcellacean fauna, but elements of the first geochemical peaking phase (S, Mo, Ni, and Cu) had significant negative correlations with Axis 3 sample scores. In RDA, Co, Pb, and P were most closely and statistically significantly related to faunal changes in HAV2, followed by the sediment organic content, Cd, and U. These are again elements with clearly elevated concentrations in the upper part of the core, where the eutrophic species *C. tricuspis* dominates the arcellacean fauna.

Several chemical profiles correlated with diatom PCA Axis 1 sample scores in HAV2, with only phosphorus correlating with Axis 2 scores (Table 1). Variations in diatoms and chemical composition were complex, however, with differing ecological responses during different geochemical phases. Nevertheless, the early post-mining peak in Ni and Cu concentrations was not associated with notable changes in diatom assemblages, and the influence of these metals on diatoms was statistically non-significant, even with respect to residual variation, after accounting for the effects of any of the other metals in RDA (conditional effects, not shown). In contrast, more than half of the

Table 1 Summarized relationships between elements and biotic indicators in cores HAV2 and HAV4

Core		Signif. marg. effects*	Correlation PCA Ax 1**	Correlation PCA Ax 2**	Correlation PCA Ax 3**
HAV2, Lake Kirkkojärvi, close to mine site	*Arcellaceans*	Co, Pb, P, LOI, Cd, U	Co, P, Al, B, Fe, Mn, Pb, LOI	–	–S, Mo, –Ni, –Cu
	Diatoms	Ag, Ba, Fe, V, Bi, Ca, U, Al, Na, As, Mg, Cd, Co, Mn, Zn, Pb, S, B, Ti, Mo	Ag, V, Ba, Bi, U, Ca, Na, Al, Fe, As, Mg, Cd, Pb, Co, Zn, S, Mn	–P	B, Mn
HAV4, Viljakkalanselkä, 2.3 km from the mine	*Arcellaceans*	Ag, Cu, As, Mo, Zn	Mg, K, Ti, –LOI, –Ba, –P, –Cd, –Sr, –Sb, –Mn, –Co, –Pb	Zn, Ag, Cu, Mg, Ni, Bi, S, As, –Bi, –S	
	Diatoms	Ag, Cu, Zn, As, Ni, Mo, Bi, S, Cd, Na, U, Tl	Ag, Cu, Mo, As, Zn	Cd, Bi, Co, Ni, S, Zn, Pb, U, B, –Ti	K, Mg, Ca, Rb, Na, –Ba, –Fe, –P

* Redundancy analysis (RDA), sample depth as a co-variable; ** Axis sample scores of principal component analysis (PCA) of biotic assemblages

chemical variables, including most of the mining-related metals, had statistically significant marginal effects on diatom assemblages, but none of these effects was statistically independent of all other elements, making it impossible to attribute the floristic change to any single variable. When tested individually in RDA, Ag was the element most closely related to the major direction of variation in diatoms.

In the HAV4 core from the Viljakkalanselkä Basin, over half of the analyzed elements were statistically significantly correlated with arcellacean PCA Axis 1 and 2 sample scores (Table 1). The correlations divided the elements into three groups. The first of these groups includes the mineral matter related elements Mg, K, and Ti, which had a positive correlation with Axis 1. The second group, with negative correlations with Axis 1, consists of several heavy metals and P. In this group, organic content had the strongest association with faunal changes, followed by Ba, P, Fe, B, Cd, Sr, Sb, Mn, Co, and Pb. These environmental variables increased towards the surface of the core. The third group, which positively correlated with the second faunal axis, is formed by elements that peaked rather sharply at 10–12 cm: Zn, Ag, Cu, Mo, Ni, Bi, S, and As. Only elements from this last, sharply peaking group had significant marginal effects on arcellaceans in RDA. The strongest correlation was between arcellacean assemblages and Ag, Cu, As, Mo, and Zn. These were significantly correlated with both axes, positively with the first and negatively with the second one.

In the core HAV4, Ag was again the variable most closely associated with changes in diatom assemblages. However, in contrast to HAV2, not all variables were associated with the main direction of variation in diatoms. The metals that exhibited a narrow concentration peak at 10–12 cm in the sediment were best correlated with Axis 1 scores (Ag, As, Mo, Cu, Zn), while those that gradually declined from the peak level towards the sediment surface correlated with PCA Axis 2 scores (Bi, Cd, Co, Ni, Pb, Sb, U, B, S, Zn). Alkaline and alkaline-earth metals (K, Na, Ca, Mg) and redox-sensitive elements (Fe, P) were correlated with Axis 3. Similar to what was found for arcellaceans, the elements with statistically significant marginal effects on diatoms in RDA were mostly limited to the mining-associated elements (e.g., S, Cu, Zn, As, Ni, Mo, Bi, Cd, and V).

Diatom-based Environmental Inferences

The diatom-inferred TP profiles are illustrated in Figs. 8 and 9, together with the lack-of-fit statistics for each fossil assemblage to the TP gradient in the calibration set. The inferred TP concentration increased slightly during the mining period in HAV2, but decreased again in the section with high sediment metal concentrations. The most notable feature, however, is the poor fit of the assemblages to the TP gradient in the post-mining section of high metal concentrations, pointing to the influence of other environmental factors besides nutrients on diatoms. DI-TP increases again after the metal-rich phase, in accordance with the emergence of eutrophic species such as *Aulacoseira ambigua* and *Fragilaria crotonensis*, but only to levels typical for mesotrophic lakes ($\approx$20 μg/L). The inferred concentration for the recent sediments thus agrees with the measured concentrations. The recent nutrient enrichment is also seen in the DI-TP profile of HAV4, but here the highest nutrient levels are inferred for the metal-rich sediment section with a high relative abundance of *F. tenera*. Nevertheless, the diatom assemblages again show a poor fit to the nutrient gradient during this phase.

Figures 8 and 9 also present profiles of diatom-inferred lake water pH values based on pH optima from the PIRLA II project (Dixit et al. 1993). The inferred pH was fairly stable for both cores ($\approx$6.8 for HAV2 and $\approx$6.9 for HAV4) and agrees with the local measured concentrations. No significant declines in pH are suggested during either the mining phase or the post-mining peak metal section. In the HAV2 profile, the inferred pH increased at the start of the mining period and a slight increase was recorded for HAV4 after the peak metal input phase.

Discussion

Major Pattern in Biotic Assemblages

Geochemical shifts as well as arcellacean and diatom assemblages reflect the course of events in the operation of the Haveri Cu–Au mine in SW Finland, and the general land-use development in the area. In particular, cultural eutrophication appears to have resulted in a persistent major change in both biological groups and in both lake basins since the 1960s. The most notably defined faunal feature in both cores is the proliferation of *C. tricuspis* in the upper parts, because its abundance notably increases the number of tests (Scott and Medioli 1983). The species is known to co-occur with algae (Patterson et al. 1985), and in temperate regions it has mostly been associated with a high nutrient input, consequent high biological productivity, and eutrophication of water bodies (e.g. Asioli et al. 1996; Boudreau et al. 2005; Patterson et al. 1985, 2002; Reinhardt et al. 2005; Scott and Medioli 1983; Torigai et al. 2000). Nevertheless, mass occurrences of the species have also been related to drifting (Patterson et al. 1996) and high heavy metal concentrations, since specimens may escape hostile conditions by attaching to floating algae (Torigai et al. 2000). A similar connection between the species and metals to that found in the south basin of Lake Winnipeg by Torigai et al. (2000) was also observed in a lake by the Luikonlahti copper mine, but with contradictory indications of the lake's trophic level (Kihlman and Kauppila 2009). In Haveri, the reason for the proliferation is most probably a change in the lake's trophic level, because the area is susceptible to eutrophication and the faunal shift appears to be independent of the mine water signal in sediment. In addition, changes in diatom assemblages support this interpretation, with the appearance of and increase in eutrophic species in the upper part of the core (*A. ambigua, F. crotonensis*). In HAV2, the planktonic diatom *Asterionella formosa* increases in abundance concomitantly with *C. tricuspis* while in HAV4 the two-peaked trend in *C. tricuspis* matches with an increase first in *Stephanodiscus parvus*, then in *A. ambigua, F. crotonensis,* and *A. subarctica* f. *recta*. In a study on Swan Lake, Ontario, Patterson et al. (2002) related the proliferation of *C. tricuspis* to changing land use in the area, and especially to the increased use of chemical fertilizers. The present results thus suggest that the most distinctive ecological changes in arcellaceans and diatoms in Haveri are less related to the mine's impact, and are instead a consequence of other human activities. However, ecological changes related to mine water impacts also were clearly detectable.

Early Changes Close to the Mine (Core HAV2)

Arcellacean assemblages in faunal zone 1 in HAV2 (Fig. 5) were originally considered as natural, but according to the age estimation, only the deepest samples of the core pre-date the mine. Nonetheless, the zone has high diversity and high test concentrations with many strains of *D. oblonga*, features typical for stable climax communities (Patterson and Kumar 2002). *D. oblonga* is considered to be cosmopolitan and polyformic (e.g., Charman et al. 2000; Medioli and Scott 1983; Ogden and Hedley 1980; Reinhardt et al. 1998), tolerant (e.g., Arctic conditions), often ubiquitous and common in organic rich gyttja (Dallimore et al. 2000; McCarthy et al. 1995; Patterson et al. 1985). The overwhelming domination of only one or few forms, however, has been connected to harsh environmental conditions. For example, *D. oblonga* dominated the fauna on southern Baffin Island in the Arctic (Collins et al. 1990), *D. protaeiformis* dominated in the industrially polluted sediment of Lake Orta (Asioli et al. 1996), and domination of *D. oblonga* and *C. aculeata* alternated along with conductivity on Richards Island (Dallimore et al. 2000).

Mining activities (i.e., period of mine operation) did not seem to notably impact arcellaceans, regardless of changes in the test concentration and geochemistry. Physical and chemical features of the sediment suggest increased clastic input caused by land use changes and increasing erosion in the area. This may have caused the observed decrease in the test concentration. The simultaneous decline of P and *D. protaeiformis*, a species previously related to high organic content and chemical pollution (Asioli et al. 1996; Kihlman and Kauppila 2009), suggests the same.

While the first faunal changes may be derived from agriculture or forest clearances, the following rise in Ni and Cu concentrations in arcellacean zone 2 refers to major changes at the mine site, probably the beginning of AMD. This was also observed for Lake Retunen (Kihlman and Kauppila 2009), where the major environmental change occurred only after the active mining phase had already ended. Age estimation supports this model by dating the chemical peaks in Haveri to the 1970s, when the mine had already been closed for a decade. The increasing abundance of centropyxids suggests increasing environmental stress. Centropyxids are known to be opportunistic and thrive in high concentrations of pollutants such as As, Hg, Ni, and Co (Patterson et al. 1996; Reinhardt et al. 1998), as well as in brackish (Patterson et al. 1985), oligotrophic, turbid, and low-production conditions (Burbidge and Schröder-Adams 1998), and in environments with low oxygen concentrations (Reinhardt et al. 1998). However, despite their ability to withstand various hostile environments, they seem to be more sensitive to low pH than other species such as *A. vulgaris*, as was shown in James Lake (Kumar and Patterson 2000) and in Lake Retunen (Kihlman and Kauppila 2009). The proliferation of centropyxids thus suggests that the profundal environment in Lake Kirkkojärvi was not acidified at this stage. In addition, strains of *D. oblonga* were still well represented (Fig. 5), providing further evidence of a relatively minor mine impact.

Before the polymetallic second peak, *L. spiralis*, *D. protaeiformis* strain 'multicornis', and *A. vulgaris* increased, which is a feature that has also been found earlier in mine impacted faunal assemblages (Kauppila et al. 2006; Kihlman and Kauppila 2009, there identified as *D. fragosa*). On the other hand, *L. spiralis* already increased slightly in the active mining period with a higher clastic input but almost unaltered faunal assemblages. The species may thus indicate substrate characteristics rather than metal pollution. In James Lake, Ontario, greater numbers of *L. spiralis* were related to coarser sediments (Patterson and Kumar 2000).

Similar to what was found for the sediment-dwelling arcellaceans, diatom results for HAV2 suggest that the effects of mining on this group of algae were minor during the active mining period. Nonetheless, a gradual shift towards higher proportions of *A. minutissima* and certain *Fragilaria* and *Navicula* species was observed. Some taxa also declined, most notably *Aulacoseira* species, towards the end of the mining period. The impact on diatom algae in Lake Kirkkojärvi was thus limited during the mining phase from 1942 to 1962, but the effect was gradually increasing. Paleoecological accounts of incipient mine impacts are rare in the literature, but declines in *Aulacoseira* and *Cyclotella* taxa and increases in *A. minutissima* have been reported at the onset of metal pollution in other lakes (Cattaneo et al. 2004, 2008; Ruggiu et al. 1998; Salonen et al. 2006). In addition, Cattaneo et al. (2008) recorded increases in several *Fragilaria* species and *C. silesiaca* in Lac Caron under intermediate metal enrichment conditions. The diatom-based pH reconstruction shows an initial short-lived decline but suggests that an increase rather than a decline in pH occurred. This is in accordance with the commonly observed delay in AMD generation that results from the relatively slow process of sulphide mineral weathering.

The diatom results indicate that no drastic effects on algae resulted during the rapid and short-lived increase in Ni and Cu after the mining period. Diatom assemblages of this phase deviated only slightly from those observed at the end of the mining period, despite the documented effects of Cu and Ni on diatoms (Kauppila 2006; Ruggiu et al. 1998). Although it is likely that releases of these metals occurred in a soluble form after the cessation of mining activities (AMD effects), abiotic conditions along the exposure pathway at the time may have been such that the bioavailability of Cu and Ni was limited, at least in the lake water. Nevertheless, the detail species changes differed from those of the mining period, suggesting that different types of mine water inputs may have differing ecological effects (e.g., Cattaneo et al. 2004). Again, the stable DI-pH suggests that pH effects in the lake water were unlikely in this phase, similar to what was indicated for the profundal conditions based on arcellaceans.

Major Post-mining Disturbances Close to the Mine (HAV2)

The major chemical disturbance detected in the HAV2 core caused a significant faunal change in zone 3, which includes both the polymetallic peak at 14–16 cm and the samples that followed that had high Mo, Pb, and Co concentrations. Strains of *D. oblonga* gave way to *C. tricuspis*, a well known indicator of eutrophication. However, different forms of *C. constricta*, especially the strain ‘aerophila’, gave the strongest response; ‘aerophila’ was almost absent in the natural assemblage, but appeared soon after the peak in Ni and Cu, quickly increasing despite the metal enrichment. The same pattern is found in HAV4, which suggests that special attention should be paid to this species in future studies, as it appears to be an accurate indicator of metal pollution.

The pH sensitive species *L. spiralis* (Ellison 1995) and *L. vas*, preferring rather alkaline conditions (Boudreau 1999), were less abundant in the metal-rich sediment sections, suggesting that a decrease in profundal pH may have occurred along with the high metal concentrations. In addition, *D. protaeiformis* strain ‘multicornis’ and *A. vulgaris* were abundant, and both species thrived in a low pH environment near the Luikonlahti copper mine (Kihlman and Kauppila 2009). *A. vulgaris* has already been proven to withstand very low pH conditions in mining environments (Kumar and Patterson 2000; Patterson and Kumar 2000). In Haveri, the proportion of *D. protaeiformis* ‘amphoralis’ increased in the indicated low pH conditions, whereas in Luikonlahti, this species was slightly less abundant at a low pH, reacting almost instantly to the following rise in pH. Hence, this species seems to be more tolerant of low pH than many other opportunistic taxa, as Asioli et al. (1996) also found in Lake Orta, Italy. The persistence of *A. protaeiformis* ‘amphoralis’ in Haveri may be a consequence of a higher resilience of the system to acidification, so that mine waters have not affected the profundal environment as severely as in Luikonlahti.

In addition to affecting arcellaceans, the major geochemical shifts at 14–16 cm caused significant ecological effects on diatoms. Concentrations of several metals increased in this section, making it impossible to discriminate among the effects of different elements. Nevertheless, Ag showed the most significant effects on diatoms in numerical treatments, with only V having a significant co-variable effect. While Ag concentrations probably never exceeded toxic levels in Lake Kirkkojärvi, the metal can be regarded as a non-redox sensitive tracer for As in sediment cores, in which post-depositional mobility often distorts As profiles. However, no single element can be shown to be responsible for the effects observed in diatoms.

The most likely explanation for the metal inputs after the mining operations is the release of metals from the tailings and waste rock areas as a result of the acid-producing process that typically results in AMD. There were also signs in the arcellaceans that at least the profundal areas acidified to some degree. However, similar to the present day conditions in the area, diatom-based pH reconstruction implies that the low-pH waters from the facility did not cause marked acidification in the surrounding lake basins. A nutrient-related cause for the shifts in diatoms is also improbable because diatom assemblages showed a poor fit to the TP gradient during the peak metal input phases. The observed effects on diatom algae are, therefore, more likely attributed to other chemical effects, such as metal toxicity.

Changes in Biota after the Metal Input Phase (HAV2)

In the post-metal peak arcellacean zone 4, chemical and faunal results indicated ongoing eutrophication and continuing stress. However, the effects of the metal loading may have diminished and pH levels may have improved, since populations of many arcellacean forms of the natural assemblage (*L. vas*, *D. oblonga* 'linearis' and 'tenuis') in Lake Kirkkojärvi recovered, and indicator forms such as *C. constricta* 'aerophila' became scarcer.

While the polymetallic peak and the immediately following sediment section were merged in the same arcellacean zone, diatom assemblages already changed markedly after the 14–16 cm metal peak in HAV2. This sudden shift resulted in a unique species composition with high abundances of *C. pseudostelligera*, *A. formosa*, *Nitzschia palea*, *Nitzschia gracillima*, and *Nitzschia filiformis*. It is unknown whether this short-lived assemblage represents an intermediate stage between the impacted and natural species composition (recovery), or if it resulted from a unique set of environmental conditions at that time. In Lac Dufault in Canada, *A. formosa* and *N. palea* s.l. were important species in the recovery assemblages, together with *F. crotonensis*, *F. parasitica*, and *Diploneis marginestriata* (Cattaneo et al. 2004). Nevertheless, similar to what was found for arcellaceans, the reason that the diatom assemblages did not return to the pre-mining state was due to nutrient enrichment rather than continued metal inputs from the mine site, as evidenced by the increases in several eutrophic species (*Aulacoseira ambigua, Fragilaria crotonensis*, and *Aulacoseira subarctica* f. *recta*) and the recovery of *S. parvus*.

The major signals described above were largely detected in both planktonic and non-planktonic diatoms, as indicated by PCA plots where these two groups were used individually (not shown). However, when non-planktonic diatoms were removed, the difference between pre-mining and mining periods appeared more prominent, the 16–14 cm peak was less pronounced, and the recovery phase was not separated from the more recent samples. Certain differences were thus observed between the habitat-specific groups of diatoms.

Changes in the Viljakkalanselkä Basin (Core HAV4)

According to the arcellacean results, core HAV4, taken from the Viljakkalanselkä Basin some 2.3 km from the mine, was also affected by the mine. The more distant coring location, lower amount of tests, and the domination of the eutrophic species *C. tricuspis* in the faunal assemblages cannot mask the faunal signal derived from the mine water input. The natural species composition in HAV4 is poorer than in HAV2, probably due to the greater water depth. Despite this lower species diversity, the distant location from the tailings area appears to dampen the noise in the data and to amplify rather than reduce the mine water signal. In particular, the peaking of *C. constricta* 'aerophila' and *C. aculeata* 'species1' at the same depth as the highest metal enrichment is more conspicuous in HAV4 than in HAV2.

Faunal and geochemical features of the more distant HAV4 were in many ways similar to those in HAV2, even though the metal concentration peaks and faunal changes occurred closer to the sediment surface, at a depth of 10–12 cm, due to the lower sedimentation rate. The results from HAV4 demonstrate the sensitivity of arcellaceans as indicators of mine waters because the faunal signal was still detectable, even though the geochemical peaks had lower concentrations. Furthermore, the species composition indicated possible changes in profundal pH, as *D.protaeiformis* strain 'multicornis' increased in numbers at 5–7 cm and the proportion of *L. vas*, likely to be sensitive to pH, decreased.

Diatom results suggest that the mine waters also affected algae in the Viljakkalanselkä basin, mainly during the post-mining metal input phases. In contrast, the slight changes in diatoms during the mining phase are more likely related to nutrient inputs than metals, because they involve increases in certain planktonic species, even though the diatom-based nutrient reconstruction shows no significant increases in TP. The increase in the eutrophic diatom species *S. parvus* at the end of the mining section corresponds to the increase in the arcellacean form *C. tricuspis*, which also prefers eutrophic conditions. These results indicate that nutrient enrichment proceeded in the Viljakkalanselkä basin during the mining period.

The post-mining metal inputs also caused changes in diatom algae in Viljakkalanselkä. While some of the species that increase in abundance in the peak metal phase are identical to those in the HAV2 core (*F. tenera, S. familiaris, A. minutissima*), taxa such as *Anomoeoneis vitrea* and *F. construens* f. *binodis* are unique to HAV4, indicating that the observed ecological changes in Viljakkalanselkä are not artefacts caused by the transport of both diatom frustules and metals from Kirkkojärvi Bay. Furthermore, effects were also seen in arcellaceans that mostly dwell in the sediment, and are thus less prone to transport with currents than diatoms.

The palaeobiological results further suggest that the ecological changes in Viljakkalanselkä were indeed related to the trace metal content of the mine waters because these were the main variables with statistically significant effects on both diatoms (Ag, Cu, Zn, As, Ni, Mo, Bi, S, Cd, Na, U, Tl) and arcellaceans (Ag, Cu, As, Mo, Zn) in HAV4. The heavily impacted HAV2 core was apparently taken from so close to the mine site that the effects of different groups of elements could not be separated equally well. In contrast, due to the merging of the metal peaks in HAV4, Cu and Ni were also significantly related to changes in diatoms in this background core. Further indications of the importance of metals in the ecological change are the stable DI-pH values and the poor fit of the diatom assemblages to the nutrient gradient.

The changes in diatom taxa during the peak metal input phase in Viljakkalanselkä again correspond to previous records of metal impacted diatom communities. Cattaneo et al. (2004) recorded an increase in *Fragilaria* cf. *tenera*, *Fragilaria capucina* var. *rumpens*, *Achnanthes minutissima*, and *Brachysira (Anomoeoneis) vitrea* in the metal contaminated sediment sections from Lac Dufault in Quebec, which has several mine sites in its catchment. Salonen et al. (2006) documented an increase in the *Fragilaria capucina* group and *A. vitrea*, followed by a massive increase in *A. minutissima* in the mining-impacted Lake Orijärvi in Southern Finland. In Lake Orta in Italy, polluted with Cu and N from industrial activities rather than mining, the diatoms that were unaffected by the pollution (abundances did not decline) included species such as *Synedra tenera*, while *Achananthes minutissima, A. exigua*, *A. lanceolata*, *A. kryophila*, and *Pinnularia subcapitata* thrived during the peak pollution phase (Ruggiu et al. 1998).

Similarly to the severely impacted core from Lake Kirkkojärvi, the recovery of the diatom assemblages in the Viljakkalanselkä Basin proceeded via an intermediate species composition rich in *A. formosa*, *C. pseudostelligera*, and certain *Nitzschia* species (e.g., *N. pusilla* in HAV4). Here as well, the ecological changes caused by mining have largely disappeared but the assemblages no longer correspond to the pre-mining stage due to the effects of eutrophication (appearance of e.g., *Aulacoseira ambigua, Fragilaria crotonensis*, and *Aulacoseira subarctica* f. *recta*). This is not a mining-related issue but is caused by agriculture, forest management, and human settlement in the catchment. Arcellacean results confirm this pattern of nutrient enrichment.

Similar to HAV2, subtle differences were observed between the planktonic and non-planktonic diatom signals in HAV4. At this pelagial site, planktonic and tychoplanktonic diatoms produced a PCA plot nearly identical to the original data set, while the pre-mining and post-disturbance samples differed in the plot based on non-planktonic taxa, suggesting that especially the non-planktonic species compositions have not returned to their original state.

Conclusions

- Short-term peaks in sediment metal concentrations were observed both in the near-mine sediment core and in the more distant Viljakkalanselkä Basin core, indicating that considerable metal release events occurred and that the metals spread over a large area in the lake system. These events date to the post-mining period, most likely due to a delay in AMD generation after the cessation of tailings deposition. They also show that the period with the most intensive metal inputs was fairly short lived and that the composition of mine waters changes over time.
- The main taxonomic trend in both cores is most likely caused by nutrient enrichment in the water bodies. However, the mine impact was clearly detectable in both arcellaceans and diatoms. The statistically significant relationships between biological indicators and metals imply that metal inputs from the mine site have probably caused the observed ecological changes. The diatom record further suggests that the shifts in algae during the peak metal input were not caused by the effects of pH or phosphorus (nutrients). In contrast, arcellacean results indicated possible short-term decreases in profundal pH levels immediately after the peak metal inputs.
- The ecological effects were relatively minor during the actual metal mining period, especially in the Viljakkalanselkä basin, despite the detectable chemical changes in the sediment cores. This suggests that mining and mineral concentration processes do not always cause significant environmental impacts. Instead, most of the mining-related ecological effects occurred after the actual mining period, coincident with the metal input peaks, implying that the environmental effects of mining can be significantly reduced by the careful design, operation, and maintenance of waste facilities.
- Regardless of the proxy used, the general view of the changes in the lacustrine environment surrounding the Haveri mine was largely similar. However, there were also certain differences between the records: arcellaceans appeared to react more strongly to the early Ni and Cu peaks in Lake Kirkkojärvi than diatoms; the responses also differed after the main metal input. Both records showed that the details of the ecological responses depend on the composition of the mine water inputs, with different taxonomic changes during different stages. Because arcellaceans and diatoms document changes in different habitats, taxonomic groups, and ecosystem levels; this combination provides a more comprehensive picture of the ecological changes than either of the proxies alone.
- The study demonstrated the sensitivity of arcellaceans as indicators of mine water impacts on lacustrine sediments. New insights were gained in the responses of individual arcellacean forms to different stressors with improvements in our ability to differentiate

between the effects of pH and metals in mining environments. *Centropyxis constricta* ‘aerophila’ was identified as a potential indicator of metal pollution in sediments.
- For readers who desire it, an abbreviated taxonomy of the organisms referred to in this document is provided as an electronic supplement.

Acknowledgments The authors wish to thank the K. H. Renlund Foundation for the financial support that made this research possible, Mikael Eklund for his contribution to the field operations, and Hannu Seppänen for the ^{137}Cs analyses. This study was conducted in conjunction with the EU Life-funded RAMAS project and we extend our thanks to the RAMAS team.

References

Äikäs O, Seppänen H, Yli-Kyyny K, Leino J (1994) Young uranium deposits in peat, Finland: an orientation study. Geological survey of Finland report of investigation 124, Espoo, 21 pp

Asioli A, Medioli FS, Patterson RT (1996) Thecamoebians as a tool for reconstruction of paleoenvironments in some Italian lakes in the foothills of the southern Alps (Orta, Varese and Candia). J Foramin Res 26:248–263

Beyens L, Chardez D, De Baere D, Verbruggen C (1995) The aquatic testate amoebae fauna of the Strømness Bay are, South Georgia. Antarct Sci 7:3–8

Booth RK (2002) Testate amoebae as paleoindicators of surface-moisture changes on Michigan peatlands: modern ecology and hydrological calibration. J Paleolimnol 28:329–348

Boudreau REA (1999) Foraminifera and Arcellaceans from non-marine environments in northern Lake Winnipegosis, Manitoba. M.Sc. Thesis, Carleton University, Ottawa, 113 pp

Boudreau REA, Galloway JM, Patterson RT, Kumar A, Michel FA (2005) A paleolimnologic record of Holocene climate and environmental change in the Temagami region, northeastern Ontario. J Paleolimnol 33:445–461

BRMG (Bureau de Recherches Géologiques et Minières) (2001) Management of mining, quarrying and ore-processing waste in the European Union, BRMG. Orleans, France, p 79

Burbidge SM, Schröder-Adams CJ (1998) Thecamoebians in Lake Winnipeg: a tool for Holocene paleolimnology. J Paleolimnol 19:309–328

Cattaneo A, Couillard Y, Wunsam S, Courcelles M (2004) Diatom taxonomic and morphological changes as indicators of metal pollution and recovery in Lac Dufault (Québec, Canada). J Paleolimnol 32:163–175

Cattaneo A, Couillard Y, Wunsam S (2008) Sedimentary diatoms along a temporal and spatial gradient of metal contamination. J Paleolimnol 40:115–127

Charman DJ, Hendon D, Woodland WA (2000) The identification of testate amoebae (Protozoa: Rhizopoda) in peats. QRA technical guide #9, Quaternary Research Association, London, 147 pp

Charman DJ, Roe HM, Gehrels WR (2002) Modern distribution of saltmarsh testate amoebae: regional variability of zonation and response to environmental variables. J Quat Sci 17:387–409

Collins ES, McCarthy RM, Medioli FS, Scott DB, Honig CA (1990) Biogeographic distribution of modern thecamoebians in a transect along the eastern North American coast. In: Hemleben C, Kaminski MA, Kuhnt W, Scott DB (eds) Paleoecology, biostratigraphy, paleoceanography and taxonomy of agglutinated foraminifera. NATO ASI Ser Ser C Math Phys Sci 327, Klüwer, Dordrecht, pp. 783–791

Couillard Y, Courcelle M, Cattaneo A, Wunsam S (2004) A test of the integrity of metal records in sediment cores based on the documented history of metal contamination in Lac Dufault (Québec, Canada). J Paleolimnol 32:149–162

Cunningham L, Raymond B, Snape I, Riddle MJ (2005) Benthic diatom communities as indicators of anthropogenic metal contamination near Casey Station, Antarctica. J Paleolimnol 33:499–513

Dalby AP, Kumar A, Moore JM, Patterson RT (2000) Preliminary survey of arcellaceans (thecamoebians) as limnological indicators in tropical Lake Sentani, Irian Jaya, Indonesia. J Foramin Res 30:135–142

Dallimore A, Schröder-Adams CJ, Dallimore SR (2000) Holocene environmental history of thermokarst lakes on Richards Island, Northwest Territories, Canada: thecamoebians as paleolimnological indicators. J Paleolimnol 23:261–283

Dixit SS, Cumming BF, Birks HJB, Smol JP, Kingston JC, Uutala AJ, Charles DF, Camburn KE (1993) Diatom assemblages from Adirondack lakes (New York, USA) and the development of inference models for retrospective environmental assessment. J Paleolimnol 8:27–47

Ek AS, Löfgren S, Bergholm J, Qvarfort U (2001) Environmental effects of one thousand years of copper production at Falun, central Sweden. Ambio 30:96–103

Ellison RL (1995) Paleolimnological analysis of Ullswater using testate amoebae. J Paleolimnol 23:51–63

Escobar J, Brenner M, Whitmore TJ, Kenney WF, Curtis JH (2008) Ecology of testate amoebae (thecamoebians) in subtropical Florida lakes. J Paleolimnol 40:715–731. doi:10.1007/s10933-008-9195-5

Gehrels WR, Roe HM, Charman DJ (2001) Foraminifera, testate amoebae and diatoms as sea-level indicators in UK saltmarshes: a quantitative multi-proxy approach. J Quat Sci 16:201–220

Hammer Ø, Harper DAT, Ryan PD (2001) PAST: paleontological statistics software package for education and data analysis. Palaeontologia Electronica 4. http://palaeo-electronica.org/2001_1/past/issue1_01.htm

Heikkinen PM, Noras P, Salminen R, Mroueh UM, Vahanne P, Wahlström M, Kaartinen T, Juvankoski M, Vestola E, Mäkelä E, Leino T, Kosonen M, Hatakka T, Jarva J, Kauppila T, Leveinen J, Lintinen P, Suomela P, Pöyry H, Vallius P, Nevalainen J, Tolla P, Komppa V (2008) Mine closure handbook. Environmental techniques for the extractive industries. GTK, VTT, Outokumpu Oyj, Finnish Road Enterprise, Soil and Water Ltd, Espoo. Available at: http://arkisto.gtk.fi/ej/ej74.pdf

Karvinen WO (1997) The Haveri copper-gold mine property, southern Finland. In: Ehlers C (ed) Research and exploration—where do they meet? 4th biennial SGA meeting, Turku, Finland, Excursion guidebook B3 Guide 44 Geological Survey of Finland. Espoo, Finland, pp 20–22

Kauppila T (2006) Sediment-based study of the effects of decreasing mine water pollution on a heavily modified, nutrient enriched lake. J Paleolimnol 35:25–38

Kauppila T, Moisio T, Salonen V-P (2002) A diatom-based inference model for autumn epilimnetic total phosphorous concentration and its application to a presently eutrophic boreal lake. J Paleolimnol 27:261–273

Kauppila T, Kihlman S, Mäkinen J (2006) Distribution of arcellaceans (testate amoebae) in the sediments of a mine water polluted bay of Lake Retunen, Finland. Water Air Soil Pollut 172:337–358

Kihlman S, Kauppila T (2009) Mine-water-induced gradients in sediment metals and arcellacean assemblages in a boreal freshwater bay (Petkellahti, Finland) J Paleolimnol. doi 10.1007/s10933-008-9303-6

Krammer K, Lange-Bertalot H (1986) Bacillariophyceae 1, Naviculaceae. In: Ettl H, Gerloff J, Heynig H, Mollenhauer D (eds) Süsswasserflora von Mitteleuropa, Band 2. Gustav Fisher, Stuttgart

Krammer K, Lange-Bertalot H (1988) Bacillariophyceae 2, Bacillariaceae, Epithemiaceae, Surirellaceae. In: Ettl H, Gerloff J, Heynig H, Mollenhauer D (eds) Süsswasserflora von Mitteleuropa, Band 2. Gustav Fisher, Stuttgart

Krammer K, Lange-Bertalot H (1991a) Bacillariophyceae 3, Centrales, Fragilariaceae, Eunotiaceae. In: Ettl H, Gerloff J, Heynig H, Mollenhauer D (eds) Süsswasserflora von Mitteleuropa, Band 2. Gustav Fisher, Stuttgart

Krammer K, Lange-Bertalot H (1991b) Bacillariophyceae 4, Achnanthaceae, Kritishe Ergänzungen zu Navicula (Lineolatae) und Gomphonema. In: Ettl H, Gärtner G, Gerloff J, Heynig H, Mollenhauer D (eds) Süsswasserflora von Mitteleuropa, Band 2. Gustav Fisher, Stuttgart

Kumar A, Dalby AP (1998) Identification key for Holocene lacustrine arcellacean (thecamoebian) taxa. Palaentol Electron 1: http://palaeo-electronica.org/1998_1/dalby/issue1.htm

Kumar A, Patterson RT (2000) Arcellaceans (thecamoebians): new tools for monitoring long and short-term changes in lake bottom acidity. Environ Geol 39:689–697

Lahermo P, Väänänen P, Tarvainen T, Salminen R (1996) Geochemical atlas of Finland, part 3. Environmental geochemistry—stream waters and sediments. Geological survey of Finland, Espoo

Laperrière L, Fallu M-A, Hausmann S, Pienitz R, Muir D (2008) Paleolimnological evidence of mining and demographic impacts on Lac Dauriat, Schefferville (subarctic Québec, Canada). J Paleolimnol 40:309–324

Loukola-Ruskeeniemi K, Uutela A, Tenhola M, Paukola T (1998) Environmental impact of metalliferous black shales at Talvivaara in Finland, with indication of lake acidification 9000 years ago. J Geochem Explor 64:395–407

Mäkelä K (1980) Geochemistry and origin of Haveri and Kiipu, Proterozoic strata-bound volcanogenic gold-copper and zinc mineralizations from southwestern Finland. Geological Survey of Finland Bull, vol 310, 79 pp

Mathur AK, Asthana R, Ravindra R (2006) Arcellaceans (thecamoebians) from core sediments of Priyadarshini Lake, Schirmacher Oasis, Eastern Antarctica. Curr Sci 90:1603–1605

Mattheeussen R, Ledeganck P, Vincke S, Van der Vijver B, Nijs I, Beyens L (2005) Habitat selection of aquatic testate amoebae communities on Qeqertarsuaq (Disko Island), West Greenland. Acta Protozool 44:253–263

McCarthy FMG, Collins ES, McAndrews JH, Kerr HA, Scott DB, Medioli FS (1995) A comparison of postglacial arcellacean ('thecamoebian') and pollen succession in Atlantic Canada, illustrating the potential of arcellaceans for paleoclimatic reconstruction. J Paleontol 69:980–993

Medioli BE, Brooks GR (2003) Diatom and thecamoebians signatures of Red River (Manitoba and North Dakota) floods: data collected from the 1997 and 1999 spring freshets. J Paleolimnol 29:353–386

Medioli FS, Scott DB (1983) Holocene Arcellacea (thecamoebians) from eastern Canada. Cushman Found Foraminifer Res Spec Publ, vol 21, 63 pp

Michelutti N, Laing TE, Smol JP (2001) Diatom assessment of past environmental changes in lakes located near the Noril'sk (Siberia) smelters. Water Air Soil Pollut 125:231–241

Ogden CG, Hedley RH (1980) An Atlas to freshwater testate amoebae. British Museum of Natural History, Oxford University Press, Oxford 222 pp

Parviainen A, Eklund M (2007) Tailings oxidation and mineralogy of Haveri Au-Cu mine, SW Finland—preliminary results. Abstracts, 17th annual VM goldschmidt conference, Cologne. Geochim Cosmochim Acta 71(15S): A761

Parviainen A, Vaajasaari K, Loukola-Ruskeeniemi K, Kauppila T, Bilaletdin Ä, Kaipainen H, Tammenmaa J, Hokkanen T (2006) Anthropogenic arsenic sources in the Pirkanmaa region in Finland. Geological survey of Finland, Espoo, available at: http://projects.gtk.fi/export/sites/projects/ramas/reports/TASK2web.pdf

Patterson RT, Kumar A (2000) Assessment of arcellaceans (thecamoebian) assemblages, species, and strains as contaminant indicators in James Lake, Northeastern Ontario, Canada. J Foramin Res 30:310–320

Patterson RT, Kumar A (2002) A review of current testate rhizopod (thecamoebian) research in Canada. Palaeogeogr Palaeoclimatol Palaeoecol 180:225–251

Patterson RT, MacKinnon KD, Scott DB, Medioli FS (1985) Arcellaceans (Thecamoebians) in small Lakes of New Brunswick and Nova Scotia: modern distribution and Holocene stratigraphic changes. J Foramin Res 15:114–137

Patterson RT, Barker T, Burbidge SM (1996) Arcellaceans (thecamoebians) as proxies of arsenic and mercury contamination in northeastern Ontario lakes. J Foramin Res 26:172–183

Patterson RT, Dalby A, Kumar A, Henderson LA, Boudreau REA (2002) Arcellaceans (thecamoebians) as indicators of land use change: settlement history of the Swan Lake area, Ontario as a case study. J Paleolimnol 28:297–316

Puustinen K (2003) Suomen kaivosteollisuus ja mineraalisten raaka-aineiden tuotanto vuosina 1530–2001, historiallinen katsaus etenkin tuotantolukujen valossa. Archive report M 10.1/2003/3, Geological Survey of Finland, Finland, available at: http://www.gsf.fi/aineistot/kaivosteollisuus/index.htm (Finnish)

Reinhardt EG, Dalby AP, Kumar A, Patterson RT (1998) Arcellaceans as pollution indicators in mine tailing contaminated lakes near Cobalt, Ontario, Canada. Micropaleontology 44:131–148

Reinhardt EG, Little M, Donato S, Findlay D, Krueger A, Clark C, Boyce J (2005) Arcellacean (thecamoebians) evidence of land-use change and eutrophication in Frenchman's Bay, Pickering, Ontario. Environ Geol 47:729–739

Ripley EA, Redmann RE, Crowder AA (1996) Environmental effects of mining. St Lucie Press, Delray Beach 356 pp

Roe HM, Charman DJ, Gehrels WR (2002) Fossil testate amoebae in coastal deposits in the UK: implications for studies of sea-level change. J Quat Sci 17:411–429

Ruggiu D, Luglié A, Cattaneo A, Panzani P (1998) Paleoecological evidence for diatom response to metal pollution in Lake Orta (N. Italy). J Paleolimnol 20:333–345

Salonen V-P, Tuovinen N, Valpola S (2006) History of mine drainage impact on Lake Orijärvi algal communities, SW Finland. J Paleolimnol 35:289–303

Scott DB, Hermelin JOR (1993) A device for precision splitting of micropaleontological samples in liquid suspension. J Paleontol 67:151–1540

Scott DB, Medioli FS (1983) Testate rhizopods in Lake Erie: modern distribution and stratigraphic implications. J Paleontol 54:809–820

Stoermer EF, Smol JP (eds) (1999) The diatoms—applications for the environmental and earth sciences. Cambridge University Press, Cambridge 469 pp

ter Braak CJF, Šmilauer P (2002) CANOCO reference manual and CanoDraw for windows user's guide: software for canonical community ordination (version 4.5). Microcomputer Power, Ithaca

Tolonen K (1986) Rhizopod analysis. In: Berglund BE (ed) Handbook of Holocene palaeoecology and palaeohydrology. Wiley, New York, pp 645–666

Torigai K, Shröder-Adams CJ, Burbidge SM (2000) A variable lacustrine environment in lake Winnipeg, Manitoba: evidence from modern thecamoebians distribution. J Paleolimnol 23:305–318

US EPA (1994) Method 3051. Microwave assisted acid digestion of sediments, sludges, soils and oils. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3051.pdf

Warner BG, Charman DJ (1994) Holocene changes on a peatland in northwestern Ontario interpreted from testate amoebae (Protozoa) analysis. Boreas 23:270–279

Wolkersdorfer C, Bowell R (eds) (2004) Contemporary reviews of mine water studies in Europe, part 1. Mine Water Environ 23: 162–182

Wolkersdorfer C, Bowell R (eds) (2005a) Contemporary reviews of mine water studies in Europe, part 2. Mine Water Environ 24: 2–37

Wolkersdorfer C, Bowell R (eds) (2005b) Contemporary reviews of mine water studies in Europe, part 3. Mine Water Environ 24: 58–76