Protecting Groundwater for Health

Managing the Quality of Drinking-water Sources

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11

Industry, mining and military sites: Potential hazards and information needs

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Many similarities exist between aspects of site characterization and facility evaluation that are applicable for industrial and mining activities as well as military facilities, as a result of the wide range of activities conducted there. This includes use of fuels, solvents and other chemicals, as well as large storage volumes for some raw materials and wastes. Many elements of planning and preventive measures can be developed based on knowledge of site attributes, processes that are conducted, waste management procedures and site closure activities. With the possible exception of high explosives and ammunition, a large number of potential organic and inorganic groundwater impacts for these types of facilities are coincident.

As illustrations of the principles and strategies for site characterization, this chapter provides case studies. Some of the elements of these case studies are immediately evident, while others emphasize the need for careful collection and interpretation of the data. While they focus on groundwater contamination by one type of human activity,

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they also highlight that settings are often influenced by a more complex mixture of multiple pollution sources to be identified in situation assessment.

NOTE ▶ *Industrial, mining and military activities as well as the environment in which they take place vary greatly. Health hazards arising from industrial, mining and military activities and their potential to pollute groundwater therefore needs to be analysed specifically for the conditions in a given setting. The information in this chapter supports hazard analysis in the context of developing a Water Safety Plan for a given water supply (Chapter 16). Options for controlling these risks are introduced in Chapter 23.*

11.1 INDUSTRIAL ACTIVITIES

Industrial activities in groundwater recharge zones have significant potential to affect large areas of local or regional groundwater as a result of normal operations (e.g. waste disposal, materials storage) as well as short term adverse events (e.g. spills, leaks). Activities defined as industrial may include a wide variety of large scale or small scale commercial, public, governmental or military facilities that are engaged in manufacturing, chemical processing, power generation or ancillary services (US EPA, 1999). In many instances, the aggregate effect of several small local industrial facilities, or even the effects from a single small facility, have severely affected groundwater quality, with impacts on drinking-water supplies.

Although it is an important consideration, apparent industrial facility size may not be the sole or even the principal determinant of risk to groundwater. The degree to which a facility poses risks to aquifers can be related to many factors, including:

- the specific industrial processes and chemicals in use;
- the age and size of the facility;
- corporate ‘housekeeping’ or environmental management practices;
- local geological and hydrological characteristics.

In addition to contaminant release issues, industrial activities in drinking-water catchment areas may exert other non-chemical influences which change the vertical or horizontal flow regime of contaminants (e.g. changes in recharge inflow quantity or percolation rate), or which serve to reduce the overall capacity of the recharge area (e.g. groundwater withdrawal). Thus as discussed further in Chapter 23, the most effective preventive or management strategies for drinking-water catchments from an engineering and cost perspective are those which seek to eliminate, minimize or carefully control potential contaminant sources (Zektser *et al.*, 1995; Berg *et al.*, 1999).

11.1.1 Types of industrial facilities and potential impacts to groundwater

Many industrial facilities employ practices that historically have been associated with groundwater contamination, such as the production, treatment or handling of metals, petroleum, paints and coatings, rubber and plastics, electrical components, pharmaceuticals, pesticides, non-chlorinated and chlorinated solvents, paper, inks and dyes, fabrics, adhesives, fertilizers, wood preservatives, laundry/dry cleaning and explosives. In addition, complex facilities may have a significant component of vehicular traffic, power production, water withdrawal/treatment and grounds maintenance, all of which may be associated with problems related to non-process use of fuels and lubricants. As a result of the extreme industrial diversity in many regions of the world, it is important to identify the types and sizes, as well as numbers of facilities, that may be potential contributors to groundwater pollution. Table 11.1 illustrates categories of industrial plant processes and ancillary processes that may be potential groundwater pollution sources.

Table 11.1. Typical industrial plant processes and ancillary processes

Industrial plant processes	Ancillary processes
Transfer and storage of raw materials	Transfer, storage and use of fuels and lubricants
Production process	Power production
Storage and management of waste products	Water withdrawal and treatment
Storage, transfer and transportation of final product	Run-off management
	Grounds maintenance employing fertilizers and pesticides

Recognition of potential classes of groundwater contaminants for specific types of industries serves as an aid in the development of appropriate plans for the monitoring of ongoing activities (US EPA, 1999), as well as guiding the investigation of impacts that may be associated with past site operations (see Chapter 23).

Table 11.2 presents a number of examples of chemicals commonly associated with important industrial processes that historically have caused groundwater contamination. Substances marked bold are both toxic to humans and frequently found in groundwater. Their behaviour and attenuation in groundwater is discussed in more detail in Chapter 4.

Some of the substances listed in Table 11.2 are raw materials or production intermediates for chemical manufacturing, while some are typical of waste streams from the indicated industrial process. Yet others, however, may not be released from the facility, but rather are formed as natural degradation phenomena once the release of a parent chemical has occurred (Canter and Knox, 1987). For example, dichloroethene (DCE) or vinyl chloride (VC) may in rare instances be released directly but, more commonly, they are detected in groundwater as breakdown products in anaerobic conditions related to the release of perchloroethylene/tetrachloroethene (PCE) or trichloroethene (TCE) in the presence of specific subsurface bacterial populations. Similar changes may be observed in the progressive, sequential reductive dehalogenation of polychlorinated biphenyls (PCBs), which can result in the formation of lower chlorinated homologues from the parent PCBs. Presence of the new analytes, e.g. in groundwater samples, may create uncertainty regarding the source of the contaminants and, hence, may complicate decisions concerning the appropriate response measures.

Table 11.2. Potential groundwater contaminants from common industrial operations (substances marked bold are both toxic to humans and frequently found in groundwater)

Industry type or industrial process	Representative potential groundwater contaminants
Adhesives	acrylates, aluminium, **chlorinated solvents**, formaldehyde, isocyanates, mineral spirits, naphthalene, phenol, phthalates, **toluene**
Electrical components	acids, aluminium, arsenic, beryllium, **cadmium**, caustics, **chlorinated solvents**, cyanides, **lead**, mercury, **nickel**, **selenium**
Explosives	ethyl acetate, HMX, methanol, **nitrobenzenes**, nitroglycerine, **nitrotoluenes**, pentaerythritol tetranitrate, RDX, tetrazene, tetryl, 1,3-DNB
Fabrics	acetic acid, acetone, acrylates, ammonia, **chlorinated solvents**, **copper**, formaldehyde, naphthalene, **nickel**, phthalates
Fertilizers	ammonia, **arsenic**, chlorides, **lead**, phosphates, potassium, **nitrate**, sulphur
Foods and beverages	chlorine, chlorine dioxide, **nitrate**/nitrite, **pesticides**, biogenic amines, methane, dioxins, general organic wastes
Inks and dyes	acrylates, ammonia, anthraquinones, **arsenic**, benzidine, **cadmium**, chlorinated solvents, chromium, ethyl acetate, hexane, **nickel**, oxalic acid, phenol, phthalates, **toluene**
Laundry and dry-cleaning	calcium hypochlorite, **DCE**, **PCE**, Stoddard solvent, **TCE**, **VC**
Metals production and fabrication	acids, **arsenic**, beryllium, **cadmium**, **chlorinated solvents**, **chromium**, **lead**, mercury, mineral oils, napthtalene, **nickel**, sulphur
Solvents (chlorinated)	carbon tetrachloride/tetrachloromethane **(CTC)**, chlorofluoroethanes, **DCE**, methylene chloride, **PCE**, **TCE**, **VC**, 1,1,1-trichloethane
Solvents (non chlorinated)	acetates, alcohols, **benzene**, **ethylbenzene**, ketones, napthtalene, **toluene**, **xylene**
Paints and coatings	acetates, acrylates, alcohols, aluminium, **cadmium**, **chlorinated solvents**, chromium, cyanides, glycol ethers, ketones, **lead**, **mercury**, methylene chloride, mineral spirits, **nickel**, phthalates, styrene, terpenes, **toluene**, 1,4-dioxane
Paper manufacturing	acrylates, **chlorinated solvents**, dioxins, mercury, phenols, styrene, sulphur
Pesticides	**arsenic**, carbamates, **chlorinated insecticides**, cyanides, **ethylbenzene**, **lead**, naphthalene, organophosphates, phenols, phthalates, **toluene**, **xylene**
Petroleum refining	alkanes, **benzene**, **ethylbenzene**, **nickel**, polynuclear aromatic hydrocarbon (PAHs), napthtalene, sulphur, **toluene**, **xylene**
Pharmaceuticals	alcohols, benzoates, bismuth, dyes, glycols, mercury, mineral spirits, sulphur
Rubber and plastics	acrylonitrile, antimony, **benzene**, butadiene, **cadmium**, **chloroform**, **chromium**, **DCE**, **lead**, phenols, phthalates, styrene, **VC**
Wood preserving	ammonia, **arsenic**, **chromium**, **copper**, creosote, dioxins, pentachlorophenol (PCP), phenol, tri-n-butyltin oxide

In the example of both the chlorinated solvents and PCBs, the result may be that Chemical A is disappearing, when in parallel the concentration of the corresponding Chemical B is increasing. This seeming benefit of the reducing concentration of Chemical A can mask marked increases in the significance of potential risk when the degradation product (Chemical B) is more toxicologically potent than the parent molecule (e.g. VC >> DCE).

11.1.2 Types of industrial practices potentially impacting on groundwater quality

Virtually any aspect of industrial operations has the potential to release chemicals, though some processes are more likely than others to be of consequence when considering the vulnerability of groundwater. Organic and inorganic contaminants may reach groundwater most readily as a result of discharge to the ground surface and subsequent leaching through and from soils, or through subsurface releases from tanks, ponds, underground pipelines, injection wells, and similar structures (Canter and Knox, 1987; US EPA, 1999). Problems and characteristics of contamination that are related to individual chemicals may be compounded by events such as fires or explosions which often cause major changes in the chemical structures, chemical properties and distribution of industrial releases.

The withdrawal of groundwater, though not a waste-related or discharge-related matter, may dramatically affect the subsurface movement and distribution of chemicals, especially if the withdrawal is of large volume such as for single pass cooling water. In many parts of the world, permits are required for such withdrawal. Therefore, permits may represent one source of valuable information during reviews of potential industrial impacts in a drinking-water catchment area. Similarly, discharge permits may provide a valuable source of data on potential contamination origins.

Releases of small or large magnitude to surface soils may occur from raw material piles, aboveground tanks, drums and other containers, as well as from process leaks that may occur within the plant, and which may subsequently reach the ground from improper routing of wash waters or process overflow volumes. Industrial material handling operations, including incoming and outgoing shipments, as well as in-house transfers of materials, are often associated with episodic releases of chemicals over time (Canter and Knox, 1987). While each individual event is not necessarily significant, the cumulative effects can be severe.

Factors such as ground cover type (e.g. paved vs. unpaved), interceptor drains, local precipitation rate, soil types and aquifer vulnerability (see Chapter 8) as well as water solubility, vapour pressure, soil microbial activity and the mobility of the chemicals of interest (see Chapter 4) will influence how rapidly and in what form they move toward groundwater through the soil column once released at the surface. Non-production related activities on a site, such as grounds maintenance, may represent potential groundwater impacts from use of chemicals such as fertilizers, pesticides and herbicides (US EPA, 1999). Table 11.3 illustrates a number of acute and chronic release possibilities that have the potential to contaminate groundwater.

Table 11.3. Potential release points and mechanisms

Chronic releases	Acute releases
Direct discharge: ground surface or surface water	Explosion
Subsurface discharge: injection wells	Fire
Leaks: tanks, pipes or impoundments	Catastrophic failure: storage site or transfer system
Transfer loss: pipelines, transfer points, storage facilities	
Non-process activities: herbicides, fertilizers, pesticides	

Once released, low water solubility and strong binding behaviour cause some materials to move slowly in the subsurface environment, in comparison to substances that are highly water soluble and that do not attach to soil particles (see Chapter 4). In addition, high vapour pressure indicates that a chemical will favour volatilization, and spilled materials may be lost to air from water or soils, as opposed to leaching to groundwater. Local and regional meteorology will exert effects on whether or to what extent these or other airborne materials may be subject to later atmospheric ‘washout’ by precipitation, and subsequent re-deposition on the ground in complexed form, which then is available for future soil leaching processes that may contaminate groundwater.

Subsurface releases often represent the most direct pathway by which industrial contaminants may reach groundwater. These occur most commonly as a result of storage or disposal of liquids to pits, ponds, basins and underground tanks (Canter and Knox, 1987), as highlighted in Box 11.1. Such structures often are designed to act principally as evaporation or holding structures; however, as a practical matter, those that are not lined with clay or synthetic materials frequently exhibit a percolation component through the floor and walls of the structure, or through cracks in theoretically impervious tank materials (e.g. concrete, metal). The type, age, burial depth of the structure, soil type, proximity to (or contact with) the groundwater interface, the care with which it was constructed or installed, and the regularity of maintenance procedures, all are important influences on the likelihood that such holding structures may serve as sources to long term groundwater contamination potentially to be addressed in situation assessment.

Subsurface releases also may be caused by leakage from underground pipes at connections and valve locations, or as a result of rupture related to pressurization, corrosion and mechanical damage. Such releases frequently go unnoticed and over time may contribute to significant subsurface contamination. The oil refinery case study in Box 11.1 is an example of this type of situation. The frequency, duration and volume of such events, as well as the mobility and toxicity characteristics of the materials that are released will determine the potential risks within drinking-water catchment areas. Some important factors to consider with regard to storage structures are shown in Table 11.4.

Box 11.1. Groundwater pollution with aromatic hydrocarbons and metals caused by a petroleum refinery site in Czechowice, Poland

The process of refining hydrocarbons carries with it potential problems of raw materials transport, handling/storage in large volumes, and chemical production processes. These activities represent points at which chemical substances may be lost to the environment as a result of leaks, spills or other short and long term events. Many thousands of such facilities globally have been the source of local or regional groundwater contamination, particularly in the case of the more water soluble, aromatic hydrocarbon components (e.g. benzene, toluene) and of some historically common additives (e.g. lead).

This phenomenon is well-illustrated by the case of a 100-year old refinery located in an urban industrialized area of Poland. Capacity has more than doubled from early production rates of 40 000 tons of paraffinic crude oil a year producing gasoline, engine oil and fuel oil, as well as specialty oil products. Disposal from by-products of the historical sulphuric acid-based oil refining resulted in the deposition of more than 140 000 tons of acidic petroleum sludges in a series of open, unlined waste lagoons.

The refinery site is underlain predominantly by silty sands, interspersed with several thin discontinuous subsurface clay layers that do little to retard vertical movement of contaminants. Groundwater was located at about 10 m below the ground level in most areas on-site. There is a nearby water supply well, used for commercial and industrial purposes, where increasing levels of petroleum substances have been observed in recent years. Nearby residences are connected to a public water supply system.

A comprehensive refinery site investigation was conducted to assess the extent, degree and potential migration of site contamination, focusing on several principal indicator chemicals, including BTEX, PAHs and heavy metals. These were selected on the basis of their concentrations, mobilities and toxicological properties, as well as their known linkage to historical facility operations. These typically are ‘sentinel compounds’ for the evaluation of potential risks at facilities such as the Polish site.

Soil and groundwater sampling data indicated broadly variable contaminant levels at the refinery site, with a definite ‘hot spot’ within the large lagoon area. Groundwater was found to be heavily impacted mainly by benzene and toluene, though these substances often were at low levels in the lagoon sludges, due to their volatility and the long residence time of sludges in the lagoon. It was concluded from the observed distribution of contamination that the lagoons represent at least localized long-term sources to groundwater for hydrocarbons and some metals, largely limited by the viscosity and low water solubility of their contents. However, more recent plumes of volatile chemicals (e.g. benzene, toluene) are likely a result of ongoing refinery operations, probably related to pipeline leaks, spills associated with product transfer and product losses in other areas of the site. It was recommended that remedial action should be undertaken at the refinery site, strategies be implemented for the prevention of releases and that efforts be initiated to contain the expanding groundwater plume (see Chapter 23, Box 23.1).

Table 11.4. Information needs for storage vessels

Type	Tank, lagoon, pit, pipeline
Age	Years in service, planned life span
Contents	pH, water content, corrosivity
Construction material	Native soils, concrete, metal, clay, plastic
Containment	Type, volume and security of secondary containment structures
Location	Above/below ground surface Proximity to groundwater Location and nature of pipes and valves

As an example, some metal manufacturing and finishing processes generate large volumes of liquid, semisolid and solid wastes that historically have required at least some element of on-site storage and/or disposal. These same facilities often have extensive above ground and underground piping systems that may be sources of groundwater contaminants. The historical use of pits, ponds, lagoons and tanks to store oil or hydrocarbon wastes, as well as solvent-contaminated washwaters and acidic (low pH) or caustic (high pH) sludges, has resulted in many instances of broad scale aquifer contamination. Such contamination includes water-soluble substances of health significance (e.g. arsenic, lead, mercury, chlorinated solvents, fuel components, acidic solutions), as well as those with minimal solubility (e.g. PAHs and PCBs). The large facility size and long operational time frames for many smelters and metal production plants pose specific concerns in terms of clearly identifying and characterizing releases, as well as in terms of implementing effective containment or remedial measures to address the problems.

The use of injection wells for the purpose of liquid industrial waste disposal has the capacity to introduce large volumes of chemical constituents, often of poorly understood composition, into deep groundwater. Well type, construction and integrity, as well as injection depth, chemical composition and duration/volume of injection events all will influence the likelihood that an injection well serves as a source of groundwater contamination.

Impacted streams and rivers are often overlooked as potential sources of groundwater contamination, though they may serve as significant contributors to local groundwater quality if the surface water body recharges local groundwater. Thus the detailed understanding of local and regional surface water quality and/or quantity may play a role in assessing the impact of industrial facilities in areas where upstream discharges to or withdrawal of river volumes affects the downstream recharge characteristics.

Aside from the industrial releases themselves, environmental transport of contaminants from soil to groundwater or within groundwater may be enhanced greatly by the presence of conditions which act to mobilize otherwise recalcitrant chemicals. For example, many organic substances may be bound well to soil if they are present alone, but may become quite mobile if they are present concurrently with another chemical that acts as a cosolvent (e.g. fuels mobilize organic chemical residues in soil). Similarly, mobility of a number of metals in soils (e.g. lead) is dramatically enhanced by low pH conditions in the soil or in local precipitation (Mather *et al.*, 1998). Thus site-specific geological, physicochemical, and land cover or land use considerations often are the dominant features in determining the likelihood that a facility may contribute to groundwater contamination.

Box 11.2. Groundwater pollution with chlorinated solvents caused by leather tanning industry in the United Kingdom

As with refinery sites, large and small chlorinated solvent sites around the world have been associated with groundwater contamination. This is as a result of their historical widespread use for degreasing, metals cleaning, textile treatments and other applications. Although these solvents exhibit comparatively low water solubility, their environmental behaviour and their ability to act as dense non-aqueous phase liquids (DNAPLs) (see Chapter 4) often cause disproportionate problems in developing engineered remediation solutions. In addition, many countries have established quite restrictive water quality protection criteria for chlorinated solvents (e.g. TCE, PCE) or potential environmental degradation products (e.g. VC). A case which has elements reminiscent of many others involved the Cambridge Water Company and several local tanneries in the United Kingdom during the 1950s through to the 1990s.

TCE and PCE are among the most common chlorinated solvents encountered, and were used in the leather tanning process. On-site handling practices, as well as spills and other releases, caused soil contamination at this industrial site. The complex geology in the area (multilayered Chalk composition) complicated several efforts to model the contaminant flow in the vertical and horizontal direction. However, it was concluded that the releases likely occurred in the early years of chlorinated solvent usage at the facility (i.e. the late 1950s). Discovery of contamination of a local water supply well in the early 1980s triggered an extensive investigation by the local Water Authority and the British Geological Survey (BGS), which ultimately demonstrated that significant contamination was broadly distributed in the area at concentrations exceeding 1000 micrograms per litre. Despite conversion of the local water supply well to a pump-and-treat recovery well (which recovered over 3600 litres of PCE in 5 years), a substantial quantity was unrecoverable, as is often the case with the chlorinated solvents.

Although there is a tendency to focus on large industries as most likely to cause large groundwater impacts, the judicial actions surrounding this case emphasized the potential for contributions to local groundwater pollution by many small industries in an area, as well as the valuable benefits of planning and proper chemical handling, as opposed to attempting remedial actions decades after the release has occurred. Of course this observation can be made for other industries as well including, for example, textile operations, tanneries, motor vehicle fuel stations, electroplating shops, etc.

Implementation of rigorous management practices at individual facilities may provide an excellent organizational structure for maintaining good control of raw materials and wastes that have the potential to contaminate groundwater. Recycling, waste minimization and good materials balance accounting have the potential to reduce energy requirements, transportation requirements, chemical demands, water demand and waste disposal needs (see Chapter 23). Situation assessment therefore needs to identify the extent to which such practices are operating.

Furthermore while in many regions of the world practices in production, transport and containment of hazardous chemicals has substantially improved during the past two decades, historical contamination may be substantial. The case study in Box 11.2 shows how discovery of contamination in drinking-water may lead to detection of large-scale contamination of historic origin, particularly also from a high number of small-scale enterprises.

Effective documentation of the hazards that may be posed to groundwater by any particular facility will be a function of the ability to show that good management practices and responsible chemical stewardship are in place and working (Ekmekci and Gunay, 1997). Further evaluation of the existing impacts to groundwater (or lack thereof) can be assisted by access to historical groundwater data for the facility, adjacent facilities or the region in which the facility is located. Based upon that information, it should be possible to expand existing programmes of monitoring or develop new programmes to more effectively detect industrial contamination.

11.2 MINING ACTIVITIES

A number of activities associated with mining operations have a significant potential to pollute groundwater resources. With the exception of some deep mining areas, mines tend to be at higher elevation in the catchment areas where rocks are closer to the surface. Thus impacts from these mining activities may affect downgradient groundwater resources as well.

The broad term mining includes both open pit (surface mines) and underground mines, as well as oil and gas mining (via wells), solution mining, in situ leaching (ISL), heat (geothermal) mining and even gas hydrate mining or ocean dredging. Open pit mining includes not only ore and lignite mining, but also excavation of gravel, sand and clay for the construction industry. While the latter may be less intrusive, they can result in severe environmental effects if not properly managed. Historically, mining was chiefly conducted as underground mining following veins of e.g. ore and coal, whereas more recently the availability of large machinery has promoted a tendency towards open pit mining. Today, criteria determining which option is preferred include economic considerations such as costs for labor (which is substantially more intensive in deep mining) and investment into machinery (which is high for open pit mining), as well as aspects of occupational safety (deep mining tends to be more hazardous) and the acceptability of sacrificing large areas for devastation as open mine pits. ISL is a high-tech option chiefly employed for mining copper and uranium.

Impacts on groundwater quality from mining operations include but are not restricted to:

- mobilization of metals and metalloids due to low pH values in acid mine drainage;
- leaching of substances from rock formations ISL;

- leaching from inadequately designed or operated mining waste dumps or tailing piles (i.e. overburden soil and rock);
- activities directly linked to mining operations, often in their direct vicinity, such as inappropriate usage, handling, storage or spillage of chemicals employed in ore treatment, underground or surface traffic, heavy mining machinery, workshop or refining work operations as well as wood strut preservation in underground mines.

Figure 11.1 provides a general overview of activities associated with the operation of underground mines.

Mining activities may directly impact on groundwater quantity. Both open pit mines and underground mines are often associated with groundwater withdrawal which creates a cone of depression during the operating lifetime of the mine. Thus the unsaturated zone (zone of aeration) is significantly enlarged, leaving rocks and sediments exposed to oxygen for a long time, which may cause the oxidation of sulphides and other minerals. This phenomenon also may occur with 'heaps' or tailing piles from milling sites where minerals can be oxidized.

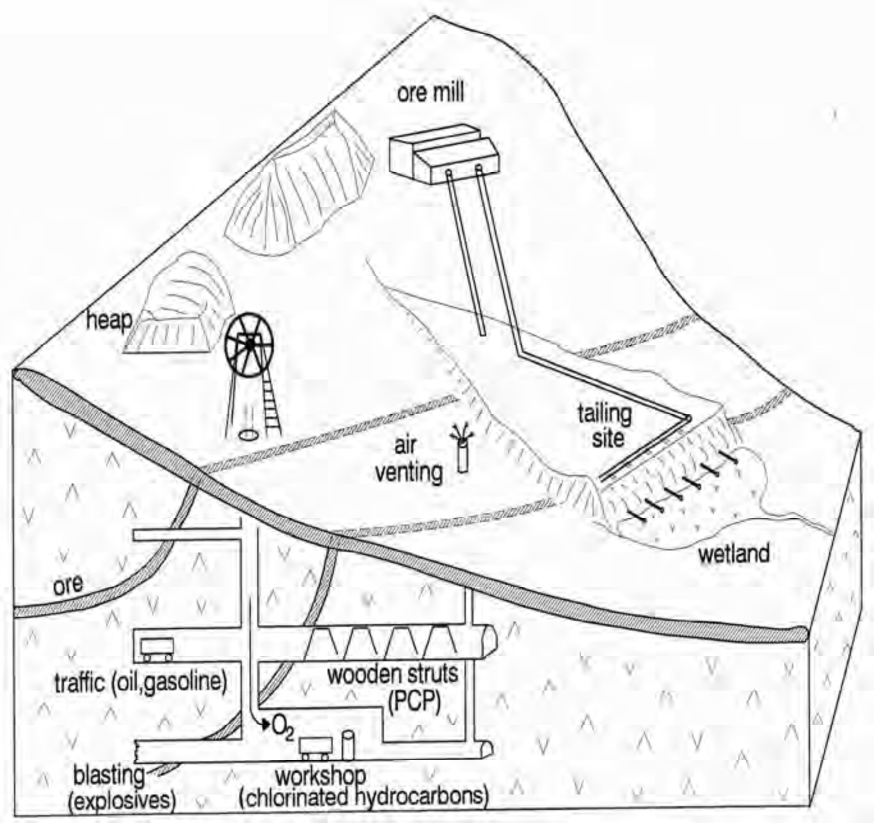

Figure 11.1. Sources of groundwater contamination linked to mining activities

Additional and different problems occur when mines are closed down, as discussed in more detail in Sections 11.2.2 and 11.2.3. Open pit mines may be left open or refilled with waste rock, tailings, industrial by-products and/or they become landfills for municipal waste. Cessation of groundwater withdrawal that is associated with normal mine operations typically leads to a rise in groundwater levels, which may form a lake or may infiltrate the backfill materials and flood former mine shafts. As underground mining changes rock permeability significantly, it is unlikely that natural groundwater conditions will recover to previous levels after mine closure. Mining at the West Rand Goldfields in South Africa, for example, created links through underground penetration of original dykes which originally had separated different groundwater reservoirs in dolomitic areas.

Rewatering after closure of the mines may be a very complicated process with great uncertainty as to the eventual outcome to groundwater quality. Re-establishment of local natural flow conditions can allow polluted waters to contaminate hitherto pollution-free areas. To protect the aquifer against negative impacts after mine closure, a sustainable groundwater management system in the vicinity of abandoned mines is required (see Chapter 23.2). Thus situation assessment in settings with mine closure would address how well such processes are controlled, which often has not been the case in the past.

The scale of mining activities is an important factor to the potential for groundwater pollution since small-scale mining activities are more difficult to monitor and control. On the other hand, large-scale mining operations typically have a greater impact on local groundwater resources. Many countries have environmental legislation to address impacts from mining operations or to guide closure and reclamation of individual newer mines; however old mines often are not considered. There is a lack of definition for controls on mine water quality and mine water in excess of maximum contamination levels being allowed to spill into groundwater or surface water in many instances.

11.2.1 Operation of mines: Chemical processes and potential impacts to groundwater

Of all the processes which occur during mining activities, sulphide oxidation is one of the most severe pollution problems where sulphide minerals (e.g. pyrite) occur geologically. It can lead to acid mine drainage that is often enriched with metals such as iron, aluminum, arsenic, cadmium, lead, mercury and uranium. In this respect, the Boshan case study given in Box 11.3 is typical for groundwater contamination through mining, though contaminants from industrial activity more or less strongly linked to mining were found as well.

Sulphide oxidation happens when sulphidic minerals (e.g. pyrite) are exposed to air and water. This process is complex because it involves chemical, microbiological, and electrochemical reactions. The rate of oxidation is controlled by a number of parameters including water pH, partial pressure of oxygen, mineral surfaces and the presence or absence of bacteria.

Geologically, sulphidic minerals (e.g. pyrite) are formed in a reducing environment when sulphate and iron or other inorganics are supplied by water in the presence of decomposable organic matter. Depending upon the boundary conditions and time, the formation of sulphide can be quite variable resulting in different crystal structures of sulphides and pyrite (e.g. framboid, polyframboid, conglomerates and massive octahedron). A limited supply of organic matter in marine sediments is assumed to result in low sulphate reducing rates, and thus formation, of framboidal pyrite (Evangelou, 1995).

Framboidal pyrite is believed to be the major contributor to acid mine drainage due to its large surface area and resulting rapid rates of reactivity. Pyrite in waste piles and tailings is of finer grain and therefore much more reactive than forms that may be present in the original bedrock (Langmuir, 1997). In the absence of buffering material, such drainage is extremely acidic with pH values approaching zero and even negative pH values (Nordstrom *et al.*, 2000).

Box 11.3. Mining and industrial contamination of groundwater in Boshan, Shandong Province, China

Boshan is located in the centre of Shandong Province in China, and is an important mining, industrial and manufacturing centre known particularly for the production of ceramics. Although Boshan only has a population of a few hundred thousand people, the surrounding District is densely populated and industrialized, close to the industrial centre of Zibo City, which has a population in excess of 3.5 million. Like many towns and cities in densely populated regions, it is difficult to distinguish a clear boundary between the urban centre of Boshan and the surrounding semi-rural or rural areas, which in effect form an extensive peri-urban region.

The City of Boshan and the Boshan District are totally dependent on groundwater for water supplies, because surface streams have become seriously contaminated through the disposal of mine water, sewage and industrial wastes. Currently more than 80 000 m^3 per day is pumped from the Tianjinwan well-field located to the east of Boshan. Another well field, the Liangzhuang well field, was abandoned in 1986 due to contamination.

There is widespread contamination of the limestone aquifers near Boshan, which has greatly reduced the amount of groundwater that is available for potable supplies. Possibly the single largest source of contamination in the District is acid mine drainage containing high concentrations of dissolved iron and sulphate from nearby coal mines. Currently about 40 000 m^3 per day of acid mine water is drained from mines, and this has caused progressive increases in the sulphate concentration in local groundwater, with concentrations commonly exceeding 500 mg/l.

In addition to pollution from mining, a major pathway for groundwater pollution in Boshan is seepage from recharge basins and surface streams, particularly from the Xiaofu Stream that passes through urban areas of Boshan. These are heavily contaminated with industrial wastewater containing a variety of chemicals including sulphate, petroleum hydrocarbons, phenols, cyanide, arsenic and other metals.

Sulphate and iron are the most common inorganic contaminants in acid mine water. In addition, chloride, sodium and potassium are increased significantly if halite is present. Several metals and metalloids of public health importance that are associated with increased concentrations due to mining activities include arsenic, manganese, lead, cadmium, nickel, copper, zinc, aluminum, mercury and uranium. For selected elements, Table 11.5 shows ranges of typical background concentrations in relation to increased concentration ranges induced through mining and thus helps in assessing whether concentrations found in groundwater potentially affected by mining might indeed be elevated through this activity.

Uranium, radium, radon and thorium are radioactive elements which are encountered not only in uranium mining, but also in metal ore, lignite and coal mining, where they commonly occur in increased concentrations. In the case of ISL mining, chemicals (e.g. acids or alkaline brines) are pumped into injection wells in large quantities and may remain to some extent in the underground. Oil and gas exploration may be associated with the presence of groundwater and brines with elevated concentrations of potentially hazardous elements (e.g. boron, lithium, selenium, arsenic, bromine, barium and thallium). Mining of evaporites (e.g. halite) is of special concern owing to the extremely high solubility of the salt. Waste rock piles from halite mining commonly contain large amounts of easily dissolved salt. Therefore, groundwater and surface water bodies are commonly impacted by salty waste water during active mine operations.

Table 11.5. Element concentrations from oilfield groundwater and from metal mining in comparison to WHO guidelines values and ranges of background concentrations observed in groundwater under natural conditions (adapted from Merkel and Sperling, 1998; WHO, 2004)

Element	**Oilfield groundwater *(mg/l)***	**Metal mining**	**Background (extreme values)**	**WHO guideline value *(µg/l)***
Arsenic	0.05-0.8	0.1-50	0.0001-0.01 (>1.0)	0.01 (P)
Barium	20-180	1-90	0.005-0.1	0.7
Boron	120-400	No data	0.005-0.070	0.5 (P)
Cadmium	0.001-0.10	0.001-0.4	<0.001-0.005 (0.07)	0.003
Lead	0.001-0.03	0.01-1.5	<0.001-0.01	0.01
Manganese	2-30	0.1-220	0.02-8.0	0.4
Mercury	No data	0.01-0.5	0.00001-0.0005	0.001
Nickel	0.001-0.5	0.001-100	0.001-0.17	0.02 (P)
Selenium	0.5-4.0	1-30	0.0001-0.14	0.01
Uranium	<0.001	0.1-200	<0.001-0.02 (>0.1)	0.015 (P)

P = provisional

Different chemicals, some of health relevance, are used for ore treatment which is commonly conducted close to the mine to reduce transport costs. Cyanide is used, for example, during the extraction of gold. Another problem is the fixation of unwanted by-products, for example in the case of uranium ore treatment where radium is fixed by adding barium chloride to the tailing water in order to precipitate the solid solution mineral Ba(Ra)-sulphate in the tailings. These precipitates may represent long term concerns as potential sources of groundwater contaminants.

During mining activities, precipitation of mineral phases termed secondary minerals may occur. In addition to clay minerals being a common weathering by-product, some minerals such as $KAl_3(SO_4)_2(OH)_6$ (Alunite) and $KFe_3(SO_4)_2(OH)_6$ (Jarosite), can form solid solution complexes with Fe^{3+} and Al^{3+} by evaporation in deep mines and at depth in saturated tailings or in heaps under acid sulphate conditions. Their solubility is relatively low under pH conditions greater than 3. Also, gypsum can be formed in the presence of sulphate and calcium and melanterite ($FeSO_4{\cdot}7H_2O$) in the presence of iron. Most secondary minerals have low solubility which is important in the case of mine flooding because it limits the rate of their re-solution. Thus secondary minerals may act as temporary or permanent sinks for groundwater contaminants making their investigation important.

Large quantities of hydrocarbonsare used in the mining industry for trucks and heavy mining machinery, and chlorinated hydrocarbons may be used for equipment cleaning purposes. PCP, γ-HCH and creosote are commonly used for the preservation of wood which may be of special concern in deep mines using wood struts. When a mine is closed down quantities of hydrocarbons and chlorinated hydrocarbons may be left in the subsurface or in surface contaminant areas and may act as long-term sources for potential contamination. Wood treatment agents like PCP will be leached slowly from remaining wood struts and may contaminate the groundwater in the mine vicinity over a long period. During open pit mining (e.g. lignite mining) spills of fuel and oil may occur regularly. Also, pipelines from oil and gas fields often run over hundreds or thousands of kilometres and leaks and spills can occur (see Chapter 13). Further, explosives from mining activities were suspected to be the chief source of nitrate contamination at the Orapa diamond mine in Botswana (Box 11.4).

Box 11.4. Diamond mining as potential nitrate source in groundwater at the Orapa diamond mine in Botswana

Mining of the kimberlite pipe at Orapa began in 1971. This is the second largest kimberlite pipe in the world in terms of area, covering 117 ha. Mining operation is in a conventional open pit with the pit bottom now at approximately 110 m below surface.

Although no contamination of the groundwater is to be expected from diamond mining, a study by the Debswana Diamond Company (Pty) Ltd revealed elevated levels of nitrate (generally >50 mg/l), in particular for wellfield 2 and 5 (Mokokwe, 1999). In addition, the available data revealed a strong spatial and temporal variability of the observed nitrate levels. The latter was surprising since the main aquifer, the Ntane sandstone, is largely confined and features water of an old age. Thus one would expect nitrate levels to be rather uniform and of natural origin.

A potential anthropogenic source of nitrate, even if only at a limited scale, is the 240 t of ammonium nitrate-based explosives that are used in the pit monthly. Although most of the explosives will be converted to nitrogen and other gases, and be vaporized during the explosion, pollution of the groundwater in the overlying Kalahari Group sediments may occur, in particular through leachates from the slimes and slurry dams (Tredoux, 2000). Because high nitrate levels constitute a health risk to infants, the Federal Institute for Geosciences and Natural Resources, Germany and the Technical University of Berlin and the Debswana Diamond Company (Pty) Ltd carried out a survey in Orapa in January 2000 of 60 boreholes and wells.

The results of this survey again highlighted that nitrate concentrations in Orapa almost always exceeded the WHO guideline level (Figure 11.2). The highest concentration of 199 mg/l was found to the east of the old mining dumps. Concentrations decreased in the direction of the surrounding production boreholes which indicates that this very high nitrate concentration is caused by leachate from the old refuse dumps.

In contrast, groundwater samples from the observation boreholes around the new township landfill site displayed neither significant ion concentration nor changes of ion ratios. Hence, this waste disposal site does not seem to be a source of groundwater pollution yet.

Nitrate was also high at a borehole north of the Orapa Township, probably due to ingress of excreta from households that are not connected to the sewage system. This case highlights the complexity of potential sources of nitrogen.

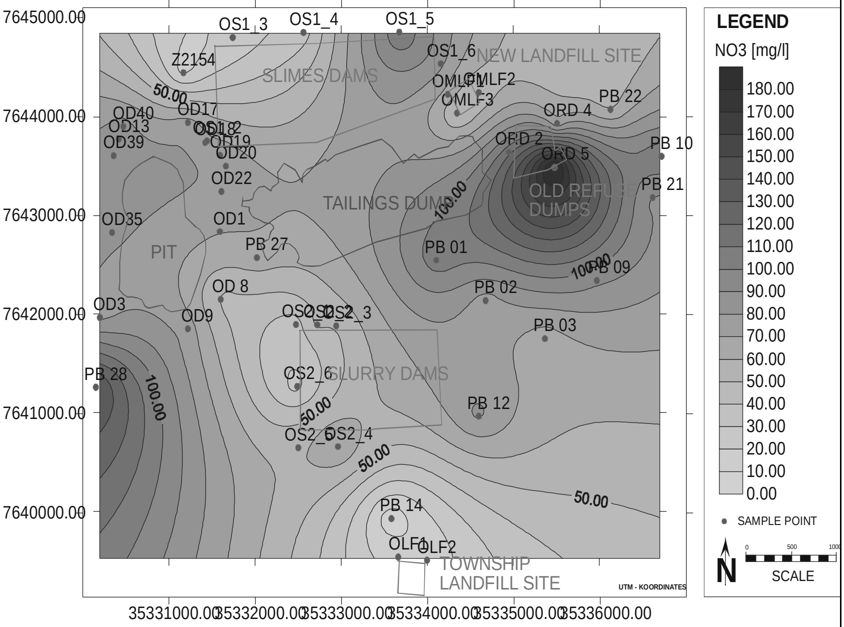

Figure 11.2. Nitrate distribution at the Orapa diamond mine and at wellfield 5

11.2.2 Closure of deep mines

Deep mining is often conducted in hard rock environments with a small degree of total porosity. In the large majority of settings, their operation requires continuous dewatering of the mine shafts. Thus the recovery rate to refill a cone of depression caused by long term dewatering operations can be very slow. However, if the bedrock is more porous, as in the case of sandstone with both fracture flow and pore flow (Chapter 2), the artificial and natural fracture cavities will refill quickly, while the pores will refill much more slowly. This may cause entrapment of air in some parts of the mine. This entrapped air can be removed only by diffusion over a long period of time, until the whole mine area is saturated.

Effective flooding of deep mines will vary according to local conditions. The simplest way is to switch off the pumps used for dewatering. Groundwater levels will then recover at rates dependent upon the hydrogeology of the area. However, due to the higher permeability of adits (drainage tunnels) and shafts, water levels and flow directions are unlikely to recover to natural pre-mining conditions (Figure 11.3). When the cone of depression is refilled, groundwater will resume flow towards the natural drainage and may transport potential contaminants in a downgradient direction. This process of mine closure is referred to as uncontrolled flooding.

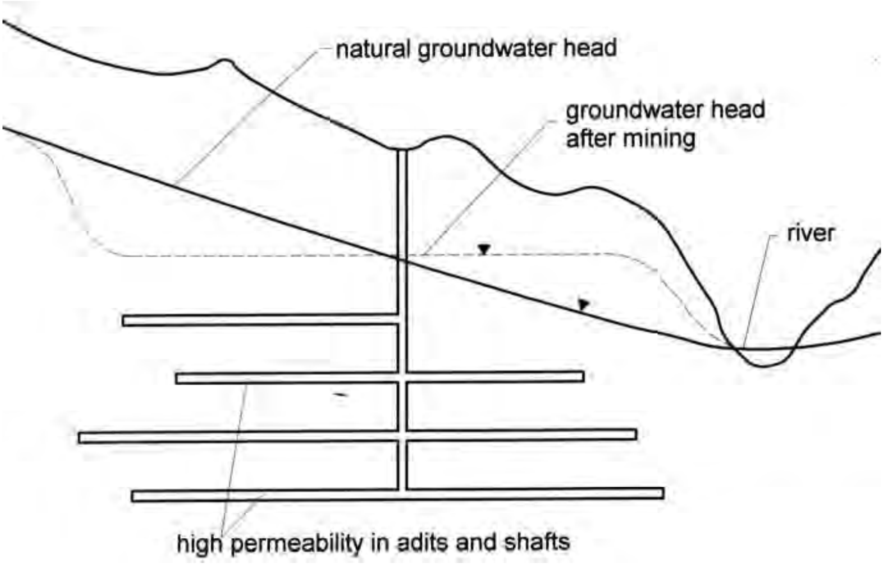

Figure 11.3. Changes in groundwater hydraulic heads due to increased conductivity caused by adits and shafts in mined areas

The rapid solution of minerals on first contact with water (‘first flush’) often results in a maximum of inorganic contaminants during the initial flushing of the mine at closure. Groundwater quality from a flooded mine may recover to background concentrations after some years or concentrations may remain increased for decades or centuries if pyrite oxidation is still taking place in the unsaturated zone. Some of the secondary minerals that have been precipitated during the mine operational time are also dissolved during the mine flooding process. Thus groundwater often contains significantly increased concentrations of various contaminants at the very beginning of groundwater recovery; however, they may decrease with time due to dissolution of secondary minerals like gypsum or melanterite ($FeSO_4$).

It is quite common in mountainous areas to manage groundwater withdrawal passively from an active mine by means of drainage tunnels known as adits. Construction of such tunnels is expensive; however they are comparatively inexpensive to operate (no need for pumps, no electrical power consumption). If such tunnels are not sealed by concrete dams at or during mine closure, groundwater drainage will continue as long as the tunnel remains open. Thus groundwater levels will not return to pre-mining conditions. In consequence, pyrite oxidation may continue to take place until all sulphide minerals are consumed. Low pH and elevated metal concentrations associated with pyrite oxidation may make the water unsafe for drinking purposes both locally and downgradient.

11.2.3 Closure of open pit mines

Closing surface mines is related to the refilling of excavations with overburden and the recovery of groundwater levels. If other wastes (e.g. industrial wastes, municipal wastes) are deposited together with waste rock during mine closure, additional contamination problems may occur (Chapter 12). Waste rock which was backfilled into the open pit mine may have a high potential to produce acid mine drainage due to oxygen contact over long time periods and thus the formation of secondary minerals which can be easily dissolved with the recovering water table.

Depending on the amount of ore or coal/lignite mined, it is quite common that the deficit volume of an open pit mine is filled largely with groundwater, forming a lake. This lake formation may result in a deformation of local groundwater elevations. At the in-flowing (upgradient) end of the lake the depth-to-groundwater elevation will be increased and will be decreased at the out-flowing lakeshore. If the lake is elongated this impact is more severe.

Whereas during mine operation dewatering chiefly transports contaminants into surface waters, post-mining lakes often become highly acidic and contain high concentrations of metals. As they are integral elements of the local groundwater system, these pollutants will be transported downgradient and impact the aquifer. This is a large-scale quality problem in the Lausitz Region of Germany, as highlighted in Box 11.5.

In arid and semiarid areas with low flow groundwater conditions, which are linked with a low gradient of the groundwater table, any open pit mine lake which forms will be subject to intensive evaporation from the open water surface. Thus the mine lake actually may become a depression in the regional groundwater system even without downgradient outflow. Consequently, the salinity of groundwater or concentrations of other inorganic constituents may increase with time, making the resource unusable for drinking-water or other purposes.

Box 11.5. Consequences of the closure of open pit mines in the Lausitz region, Germany

When groundwater withdrawal occurs over long periods, many mining areas suffer from the effects of the export of groundwater long after mine closure, as illustrated by the Lausitz lignite open pit mining district in Germany. Since the beginning of the 20th century lignite mining took place in an area of approximately 2100 km^2. Groundwater withdrawal initially was conducted at a rate of 2 to 3 m^3/s, increasing to a maximum of 33 m^3/s in 1989. The water was largely pumped to the rivers Spree and Schwarze Elster. This dewatering activity accumulated to a groundwater deficit of 13 billion m^3 in 1990, at which time lignite mining was reduced dramatically following the unification of western and eastern Germany. Natural recharge is not locally sufficient to replace these massive deficits within a short time and measures have been set in operation to ensure a minimum base flow in the rivers. Thus a river catchment and groundwater management system was implemented, which is expected to remain in operation for at least two to three decades, until nearly natural conditions have been re-established in groundwater and surface water levels. The process of filling the open pit lakes created by the mining activities with river water has the potential to result in infiltration into oxidized waste rock piles, thereby creating strong potential for development of acid mine drainage. An acidic plume can already be observed migrating downstream of these lakes. The concern is that even after two to three decades when the groundwater deficit is reversed the interconnected lakes will result in severe problems of acid groundwater. Further, these pH impacts, with associated toxic metals, are likely to affect the local lakes and rivers, rendering them also unusable for abstracting drinking-water for several decades at minimum.

11.2.4 Predicting post-mining groundwater quality

Mine operators and local authorities need to understand water quality both during and after mining operations. A first step in prediction is to consider water quality at operating or abandoned mines in similar geological and hydrogeological conditions. A second step is the analysis of rock samples from the site to determine both alkaline-producing potential and acid potential (Brady and Cravotta, 1992). In addition to such static tests, kinetic leaching tests have been developed as measures of water quality effects; however, long term field verification is lacking for these kinetic tests. In some cases, the prediction of post-mining hydrochemical conditions can be accomplished by the use of regression analyses.

In order to understand complex chemical processes and/or to predict post-mining water quality, a variety of hydrogeochemical models are available, such as PhreeqC2, Phrqpitz or EQ3/6 (Plummer *et al.*, 1988; Wolery, 1992; Parkhurst and Appelo, 1999). Where acid neutralization reactions can have a strong effect on the transport of dissolved metals, models based on the coupled solute-transport/hydrogeochemical mass-transfer like MINTRAN (Walter *et al.*, 1994) or TREAC are preferable. They predict pH buffering sequences and metal attenuation mechanisms that are similar to those observed at field sites.

11.3 MILITARY FACILITIES AND ACTIVITIES

Regional and international conflicts or military occupations, coupled with day-to-day operations of military bases and support facilities, have resulted in environmental degradation and long-term contamination of soil and groundwater at both former and active military sites. An example of severe contamination from day-to-day operations is given in the Valcunai case study in Box 11.6. For assessing impact on groundwater, a distinction can often be drawn between direct military actions or conflicts on one hand and the (often longer term) use history of military sites and manufactories on the other. Depending upon the nature of the site, contamination to be addressed by situation assessment will include non-ordnance-related chemicals that are associated with typical ancillary military operations (e.g. fuels, pest control chemicals and municipal wastes). Because military bases often resemble towns or small cities in their breadth of activities (Teaf, 1995), many of the considerations that are presented in Chapters 10, 11.1 and 12 regarding municipal and industrial risks to groundwater recharge areas also are relevant here.

Box 11.6. Impacts on groundwater quality by a former military base in Lithuania

The Valcunai Oil Product base, which is located 14 km south of Vilnius, was a site of underground storage of light oils and rocket propellants (nitrogen tetroxide) from 1963 until 1993. Over 33 000 m^3 of storage in leaky underground tanks was in service (27 500 m^3 for light oils and over 3000 m^3 for rocket fuels). A three year monitoring study (Seirys and Marcinonis, 1999) determined that groundwater has been impacted both by pure oil product (3000 to 3500 m^2 at a depth of 5.5-7.5 m), chlorinated solvents (e.g. TCE, PCE, carbon tetrachloride) as well as dissolved aqueous phase constituents from oils and other organics and inorganics (nitrates, metals). While a glacial till confining unit of approximately 60 m thickness separates the shallow aquifer from the productive deeper aquifer beneath the oil storage areas, this confining unit is absent beneath the rocket fuel storage areas, rendering the deep aquifer very vulnerable. This aquifer supplies the Pagairai Wellfield, the largest potable water supply for the City of Vilnius. Subsurface ravines representing historical glacial features act as drainage channels for groundwater. Contamination has been observed to be mobile both vertically and horizontally in groundwater. The study reported contaminated shallow groundwater to be discharging to the Rudamina River approximately 0.8 km distant. Thus the Valcunai site represents an example of complex subsurface characteristics with high levels of contamination affecting soils, groundwater and surface water, all of which illustrate the difficult technical aspects of remediation. Removal of free phase hydrocarbons is addressed with extraction wells and oil separation units treating very large volumes of groundwater. The estimated goal of recovery is in the range of 400 to 500 m^3 per two years.

Groundwater pollution resulting from deployment of explosives in military conflict includes the impact of damage or destruction of industry, traffic facilities and municipal sewage that may lead to pollutant release. This is similar to spills in 'extreme events' as discussed in Chapters 10, 11.1 and 12, but may additionally include combustion products and their transformation products. Further aspects of groundwater pollution through military conflict are physical damage to water supply infrastructure, and the direct contamination of water by residues of many types of explosives, for most of which health and environmental impacts as well as their behaviour in groundwater are poorly understood. The discussion below focuses on the potential for groundwater contamination released from warfare agents' production and military operation sites.

In historical review, as with many other human activities potentially polluting groundwater, the scale of deployment and the variety of warfare agents increased dramatically during the 20th century. The additional use of chemical warfare (CW) agents introduced a potential for environmental damage. After conflicts, entire armament production plants and military facilities have been dismantled or destroyed and ordnance buried or dumped without any environmental safety precautions.

The groundwater pollution potential from military operations became apparent and subject of scientific research only in the early 1990s. The results disproved the often-expressed hope that many of the military chemicals which are classified as dangerous would quickly be degraded in soil to non-hazardous concentrations (Mulisch *et al.*, 1999a; 1999b).

The specific difficulty in assessing the potential for chemical impairments to groundwater from military sites is that substances used are often subject to secrecy, while their identification in a historical review of site-specific activities would greatly support situation assessment. Only if the substances to be expected are known can their hazard potential be determined for a given site on the basis of substance-specific data. Investigations of the complex biophysical, chemical and biochemical transfer processes as well as of microbial metabolism of organics further supplement the basis for a prognosis of the likely groundwater impacts in the recharge area, including contaminant fate, distribution, bioavailability and degradation in the subsurface (Mulisch *et al.*, 1996; 2000). Historical research to identify military chemical production sites and the areas in which these products were used can substantially help to identify possible risks to groundwater in a region.

The description of potential groundwater contaminant problems, as given in the following section, follows the basic categorization of sites into armament production sites (manufactories) and areas/sites at which the products are used (military operation sites). The latter may include base facilities as well as deployment areas (e.g. shooting ranges, test sites). Potential control and remediation measures for settings in which military sites are suspected sources of groundwater contamination are similar to those for industrial sites and are discussed together with these in Chapter 23.

11.3.1 Potential groundwater contaminants from military production sites

Both active and abandoned military production and manufactory sites may comprise explosives and powder factories, plants for the production of CW and smoke agents, armament filling plants and munitions factories, as well sites at which munitions were stored, disposed of or buried. For production-related reasons (e.g. need for large volumes of groundwater), these armament complexes are often located in areas that are rich in groundwater resources, which potentially elevates risks of large-scale pollution. In particular, contamination has been reported from sites where loading/unloading and filling operations took place, as well as cleaning and maintenance work on machinery or the cleaning/refurbishment of containers and ammunition. Wastewater from cleaning operations was generally highly contaminated by explosives, such as trinitrotoluene (TNT) isomers. Blasting operations can result in widespread contamination by explosives especially at large plants. Areas of suspected contamination also include, in particular, sites at which residues of explosives and off-specification batches of munitions were burned or buried.

The groups of products generally referred to as military warfare agents mainly comprise explosives and a number of chemical agents. Of the categories of explosives, the high-brisance (very powerful) explosives are of greatest interest, largely because they typically are safer to handle on a regular basis and have very high detonation velocities. Major representatives are 2,4,6-TNT, 2,4 or 2,6-DNT, 1,3-DNB, hexogen (cyclotrimethylenetrinitramine) and picric acid (2,4,6-trinitrophenol), but also nitropenta and tetryl. To detonate the high-brisance explosives, it is necessary to ignite them with highly sensitive initiating explosives (e.g. nitropenta and tetryl as well as lead azide, mercury fulminate, thallium azide, and tetrazene). Other important explosives include cyclotrimethylenetetranitramine (RDX), cyclotetramethylenetetranitramine (HMX), ammonium picrate, ammonium nitrate, nitroguanidine, nitroglycerin and dinitrophenols.

Several of the military explosives are of more dominant interest than others because of the large volume of their use, their potential to migrate to groundwater, persistence and toxicity characteristics. For example, 2,4,6-TNT has been very widely used as filling for bombs, mines and shells, readily dissolves in water and can move to groundwater with ease, is persistent (though microbial degradation to aminodinitrotoluolene occurs), and has a high degree of toxicity. It also is classified by US EPA as a possible human carcinogen. Dinitrotoluene (DNT) is mobile in groundwater, is scarcely oxidized biochemically, and not hydrolysed under environmental conditions. Many examples of TNT and DNT contamination have been identified in European and USA military facilities or support industries. Tetryl slowly hydrolyses to picric acid, which does not degrade biochemically under aerobic conditions and only slowly to picramic acid under anaerobic conditions.

Some military ordnance chemicals (e.g. amines, nitro compounds and nitroso compounds) are of interest also because their degradation products (e.g. nitrates) represent significant groundwater contamination sources. Table 11.6 identifies a number of the most common explosive or other military substances with notes on their environmental and health concerns.

Table 11.6. Health-relevant military ordnance chemicals in groundwater (ATSDR, 1995-2001; NIOSH, 1997; US EPA, 2002)

Chemical	Potential migration	Non-cancer toxicity	Cancer potential
Explosives			
2,4,6-TNT	High	High	Yes
2,4 or 2,6-DNT33	High	High	Yes
Nitroglycerin	High	High	Unknown
Dinitrophenols	High/moderate	High	Unknown
RDX	High	Moderate	Yes
HMX	High	Moderate	Unknown
Tetryl	High	Moderate	Unknown
1,3-DNB	Moderate	Moderate	Unknown
CW agents			
Phosgene	High	High	No
HD	High	High	No
Organophosphates (e.g. sarin)	High	High	No
Hydrocyanic acid	High	High	No

The human health relevance of most of these compounds is a result of the specific metabolic transformations (mostly reductions) of their nitrogroup(s) by the intestinal microorganisms and by hepatic metabolism. Many intermediates are strongly electrophilic compounds. They have the potential to damage DNA either directly or by disturbing its regulation and expression by epigenetic mechanisms up to the protein and cellular level. High intakes of some compounds are also acutely dangerous by inhibiting the transport of oxygen by oxidizing Hb to metHb. The in vivo toxicologic database, especially for some environmental and microbial metabolites, is very poor.

Chemical weapons

About 70 different chemicals were used or stockpiled as CW agents during the 20th century. Now banned worldwide, CW agents can still be found at former manufactories or at clandestine production and storage facilities. They may be categorized according to their main effects on the human organism, and include but are not restricted to blood agents (e.g. hydrocyanic acid), nerve agents (e.g. sarin), skin agents (e.g. mustard gas; HD), or respiratory agents (e.g. phosgene).

CW agents are frequently called ‘war gases’ though this historic term is no longer correct, since many effective CW agents are liquids or solids and only gases in specialized circumstances. As with other chemicals, the relevance of CW agents to potential groundwater contamination depends primarily on their water solubility and their hydrolytic stability (see Chapter 4). Table 11.6 gives examples of warfare agents in relation to their potential to migrate in groundwater.

11.3.2 Potential groundwater contaminants from military operation sites

For assessing pollution potential of military bases and operation sites, both the military-specific substances discussed above and contaminants from other activities on the site may be relevant. In times of peace, warfare agents are used only for training purposes, though such activities may pose contamination risks for groundwater as well. Abandoned sites are categorized according to their main original uses (e.g. training grounds, barracks, facilities for maintenance of technical equipment, airfields and missile sites). Even at locations that, based on their use history, initially are not suspected of encompassing contaminated areas (e.g. administrative buildings, dwellings), considerable contamination including that extending into the groundwater has been found in many cases, and this contamination can threaten the local drinking-water supply if it occurs in recharge areas (Teaf, 1995).

In contrast, training grounds can be expected to exhibit widespread contamination from munitions, as a result of non-point inputs caused directly by military activities (e.g. bomb-dropping grounds, shooting ranges for tanks). Likewise refueling activities in the field or at base support facilities have caused widespread contamination of soil and groundwater by hydrocarbons. Contamination from point sources arises within individual operational areas such as areas in which military equipment is maintained or cleaned, burning sites, or as a result of exceptional events (hazardous release incidents). All of these activities have resulted in groundwater contamination with metals, solvents, hydrocarbons, explosives and other substances.

Many substances used in the military sector are also used in the civilian sector, including petroleum products from fuel depots for motor vehicles and aircraft. According to results obtained from numerous exploratory investigations into contaminated military sites, contamination by petroleum hydrocarbons ranks first, in quantitative terms. Other contaminants found are mainly organic solvents (e.g. chlorinated hydrocarbons) such as were used in large quantities in maintenance facilities and tank-washing installations. Plant treatment, agricultural and pest control products were used in large quantities as defoliants or to keep strategic or militarily sensitive areas free of vegetation or nuisance insects. Large residential facilities (e.g. base housing and daily military operations) also generated the equivalent of municipal waste which, if improperly disposed (see Chapter 12), has the potential to affect groundwater (Herndon *et al*., 1995).

At training grounds known as ABC facilities (training in defense against Atomic, Biological and Chemical weapons), contamination has occurred mainly from the use of CW agents, from decontamination activities and from the use of incendiaries and smoke agents. Original warfare agents were used for training purposes at these facilities only in very small quantities. Today, CW agents may be found buried on training grounds or in disposal areas at active as well as closed military bases.

On many military properties, illegal and/or uncharacterized waste dumps were established, so that no information is available about the chemical composition of the waste dumped or the length of time the dumps were in use. The special conditions that typically govern the establishment of landfills, and the associated use restrictions (e.g. restrictions on abstraction of drinking-water in the catchment area), tend to have been disregarded by military forces. The variability and site-specificity of these conditions has made chemical characterization, site investigation and groundwater pollution assessment difficult (Herndon *et al*., 1995).

11.4 CHECKLIST

NOTE ▶ *The following checklist outlines information needed for characterizing industrial, mining and military activities in the drinking-water catchment area. It supports hazard analysis in the context of developing a Water Safety Plan (Chapter 16). It is neither complete nor designed as a template for direct use but needs to be specially adapted for local conditions. The analysis of the potential of groundwater pollution from human activity requires combining the checklist below with information about socioeconomic conditions (Chapter 7), aquifer pollution vulnerability (Chapter 8), and other specific polluting activities in the catchment area (Chapters 9-10 and 12-13).*

ⓘ **Are active or abandoned industrial, mining and military sites located in the drinking-water catchment area?**

- ✓ Compile inventory of registered large-scale facilities and operations, and check their locations
- ✓ Compile inventory of small-scale enterprises, production sites, mining sites or military operations, and check their locations
- ✓ List operations at these sites for
    - <u>Industry</u>: processes employed and goods produced
    - <u>Mining</u>: products mined (e.g. ore, coal, lignite, gravel, sand) and mine type (e.g. deep or open pit mining, ISL)
    - <u>Military</u>: type (e.g. ordinance testing, troop training, logistic support)
- ✓ Compile inventory of abandoned industrial sites, mines, military facilities and disposal areas that may still be leaching pollutants to groundwater
- ✓ Check data about past accidents (e.g. fires, explosions, spillages) which may have left potential ‘hot spots’ on historic or active facilities
- ✓ …

ⓘ **What kind and which amounts of materials are used, transported and stored at individual facilities?**

- ✓ Compile inventory of raw materials needed for production or operation at individual industry, mining or military facilities (including potentially hazardous degradation products if known)

- ✓ Classify site-related goods and materials according to their potential hazard to groundwater
- ✓ Compile inventory of permits for discharging effluents to soils, water bodies, injection wells (including predisposal treatment if known)
- ✓ Compile information on transportation to and from the facility, i.e. on raw materials, ore, potentially hazardous products and wastes
- ✓ Compile inventory of number, size, type, age and materials held in pipelines, storage ponds, lagoons and tanks for liquids, with particular consideration given to subsurface structures
- ✓ Check for indication of episodic releases accumulating contaminants over time
- ✓ Estimate amount of groundwater withdrawn by industries, mines or military sites, including uses if known (e.g. process water, cooling water)
- ✓ …

Are the individual facilities in good condition and safe locations?

- ✓ Check existence of containment structures for storage, production and transportation of hazardous goods and materials (e.g. pipelines, storage ponds, lagoons, tanks for liquids)
- ✓ Evaluate siting, design, construction and technical condition of individual structures and facilities in relation to aquifer vulnerability and physical conditions in the catchment area (e.g. water table, soil, hydrogeology): consider checklist for Chapter 8
- ✓ For mining: Evaluate location of heaps and tailings in relation to aquifer vulnerability
- ✓ Check type of grounds maintenance and use of chemicals (e.g. herbicides, explosives, pesticides, fertilizers, combustible hydrocarbons)
- ✓ …

Are good management practices implemented at individual sites and facilities to protect groundwater?

Note: See Chapter 23 for the information background for these items.

- ✓ Check availability and implementation of environmental management concepts, and whether there are audits for best management practice and operational precautions in relation to groundwater protection
- ✓ Check closure plans and maintenance of decommissioned sites:
  - For industrial and military sites: adequate dismantling of facilities and removal of potential groundwater contaminants from sites
  - For mining: adequate management of acid mine drainage to prevent acidification and mobilization of metals
- ✓ Check availability and implementation of emergency response plans, particularly in relation to groundwater protection
- ✓ Check availability and implementation of waste management concepts

- ✓ Check whether there is accounting for materials brought in, materials processed, wastes requiring disposal and long term closure procedures
- ✓ Evaluate operation and management practices at individual facilities in relation to aquifer vulnerability and physical conditions in the catchment area (e.g. water table, soil, hydrogeology): consider checklist for Chapter 8
- ✓ …

ⓘ **Are side effects of production processes also relevant to groundwater contamination?**

- ✓ Identify vehicular traffic, power production, water withdrawal/treatment, and grounds maintenance
- ✓ Evaluate emission of substances that act as cosolvents (e.g. fuel, acids) and are likely to mobilize other hazardous chemicals
- ✓ Identify construction activities on industrial, mining or military sites that may physically affect the aquifer or cause contaminant emissions
- ✓ …

ⓘ **Are hazardous events likely to increase groundwater pollution potential?**

- ✓ Evaluate whether and how storm water events would enhance transport of pollutants to the aquifer
- ✓ Evaluate which spills and accidents are likely to cause groundwater pollution
- ✓ …

ⓘ **Is drinking-water abstracted in proximity to industry, manufacturing, mining or military sites?**

- ✓ Assess distance between such sites and drinking-water abstraction (see Chapter 8)
- ✓ Check adequacy of wellhead protection measures, wellhead construction and maintenance as well as sanitary seals used (see Chapter 18) to prevent ingress of contaminants from production, mining or military sites
- ✓ …

ⓘ **Are groundwater quality data available to indicate pollution from industrial, mining or military activities?**

- ✓ Compile historic data from the areas and facilities of interest, e.g. from local or regional surveys, research projects or previous monitoring programmes

- ✓ Check need and options for implementation of new or expanded monitoring programmes likely to detect contamination from industrial, mining or military operations
- ✓ …

What regulatory framework exists for industrial, mining and military activities?

- ✓ Compile information on national, regional, local, or catchment area specific legislation, regulations, recommendations, voluntary agreements or common codes of good practices on siting, construction, operation, maintenance of sites, and on restrictions, ban or prohibition of substances produced, processed or generated as wastes
- ✓ Check whether the regulatory framework adequately addresses environmental and specifically groundwater protection
- ✓ Identify gaps and weaknesses known which may encourage specific pollution problems
- ✓ …

Documentation and visualization of information on practices at industry, manufacturing, mining and military sites and operations.

- ✓ Compile summarizing report and consolidate information from checklist points above
- ✓ Compile summary of types and amounts of substances produced, processed or generated as wastes and which are potentially hazardous if they leach into the aquifer
- ✓ Map industrial and mining production sites and military facilities (in-use and abandoned), preferably including suspected ‘hot spots’ of contamination (use GIS if possible)
- ✓ …

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23

Industry, mining and military sites: Control and protection

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A range of hazardous substances may be released to the environment from industrial sites, depending on specific industrial processes (see Table 11.2). Among these, the mobile compounds reach groundwater (see Chapter 4). Less mobile compounds may also contaminate groundwater where process wastewaters are discharged through soakage pits. The most common contaminants to reach groundwater in significant quantities from industrial sites are the chlorinated solvents such as trichloroethene (TCE) and perchloroethylene/tetrachloroethene (PCE) but, in specific circumstances, concentrations of many others such as chromium and petroleum constituents may be elevated. Mining can give rise to a range of inorganic contaminants and acid waters, in particular, can result in the accelerated leaching of metals into groundwater. Stored, disposed and deteriorating explosives have been found in some groundwaters below military sites. In Germany and in the USA, perchlorate used in rocket fuel has given rise to major problems. However, the most common contaminant for both military and industrial sites is probably oil from machinery and vehicles, particularly in the case of military sites.

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In contrast to groundwater contamination from agriculture and off-site sanitation, larger industrial operations tend to be localized point sources of pollution. This is not the case for small-scale enterprises, particularly where these are not connected to centralized sewerage. Nevertheless, the control and protection measures proposed in this chapter for industry can in principle be applied to small-scale enterprises as well.

Military bases often resemble both industrial facilities and small cities regarding the use, storage, and disposal of a variety of chemicals, heavy metals and waste materials. Many planning and operational control measures to prevent the contamination of groundwater by chemicals used in routine military operation are the same as those for industrial sites, and they are therefore discussed together in this chapter.

A variety of effective control measures can be implemented to minimize the likelihood and the magnitude of groundwater impacts from industrial, mining and military activities in groundwater recharge zones. These measures fall into broad categories of: (i) planning, including principal site selection; (ii) engineering approaches which can be implemented in the phase of planning and designing of facilities; and (iii) operational/procedural controls which can be administrated for both new and existing facilities. Some control measures may have both engineering implications (process design) and administrative elements (modification of employee practices), e.g. efforts to substitute with less hazardous process chemicals or development of a corporate recycling plan to reduce waste volumes. Operational monitoring of control measures is important to ensure the ongoing safe storage, handling and disposal of process chemicals, maintenance supplies and waste materials (see Table 23.1). Good practice to support this includes training of personnel in proper safety and handling of these materials under routine conditions as well as in the case of spills or leaks.

All of these measures are typically directed at preventing or limiting the quantity and significance of releases. They include monitoring for early detection of releases and improvement of available containment or remedial capabilities in the event that accidental or intentional contaminant releases occur. In terms of resource allocation, there is a clear benefit to avoidance of releases or accidents. Plans and procedures for avoidance of releases are usually less costly in terms of time and money than remedial measures (i.e. the cleanup of contaminated media such as soils and groundwater) once contamination has spread over a broader area, perhaps even throughout a watershed or aquifer.

Implementing control measures for industry, mining and military sites in drinking-water catchments can be triggered by water suppliers and/or the public authority responsible for drinking-water safety, e.g. in the context of designating protection zones (see Chapter 17), or in the context of developing a WSP (see Chapter 16).

NOTE ▶ *In developing a Water Safety Plan (Chapter 16), system assessment would review the efficacy of control measures and management plans for protecting groundwater in the drinking-water catchment from contamination by industrial, mining and military activities. Chapter 11 provides the background information about the potential impact of these activities on groundwater and provides guidance on the information needed to analyse these hazards.*

This chapter introduces options for controlling risks from these activities. As the responsibility for them usually falls outside that of drinking-water suppliers, close collaboration of the stakeholders involved, including the authorities responsible for the surveillance of industry, mining and military activities, is important to implement, upgrade and monitor these control measures. This may be initiated by the drinking-water sector, e.g. in the context of developing a Water Safety Plan or of designating protection zones (see Chapter 17).

23.1 INDUSTRIAL AND MILITARY SITES

As discussed in Chapter 11, the main concern at industrial facilities as well as at smaller enterprises typically is the improper containment and handling, management or disposal of chemicals, which can lead to soil, surface water and groundwater contamination. This may be the result of active contamination routes, such as intentional dumping or inappropriate disposal activities, or may occur via passive contamination routes such as leaking tanks or broken transfer pipes. Both for industrial and for military sites, groundwater protection usually involves improvement of design and construction of facilities, modification of current practices, as well as remediation of past contamination.

23.1.1 Strategies for pollution prevention and environmental management

The protection of groundwater from industrial and military contaminants is facilitated if this can be managed within general environmental controls, i.e. in environmental management systems such the international ISO 14001 standard or pursuant to EU Regulation 761/2001. One example of a comprehensive strategy to address site-specific control measures at industrial facilities is embodied in the 1991 Integrated Pollution Prevention and Control approach of the Organisation for Economic Co-Operation and Development in Europe (Recommendation on Integrated Pollution Prevention and Control; C/90/164/Final/ 1991). This approach recommends means by which to anticipate and manage chemical handling and process-related activities that may potentially contaminate the environment, including groundwater. Recommendations include those of an engineering nature, as well as an administrative or institutional nature. The approach calls for:

- identification of existing contamination;
- design of mechanisms to detect potential future releases;
- development of plans to minimize the impacts of such releases.

Various cradle-to-grave or catchment-to-consumer management strategies similar to the Organisation for Economic Co-Operation and Development approach for chemicals, especially directed at protection of groundwater resources, have been implemented in a number of countries. Such management systems help to achieve the objective of establishing environmentally safe and groundwater-conserving practices in dealing with industrial chemicals through policy and administrative measures as well as through an appropriate management of material flows based on life cycle analysis. Active military installations, for example, are well suited for such management systems due to the controlled nature of site personnel and activities. Environmental management systems can, in the long term, replace some monitoring and control tasks, resulting in cost saving.

Audits and evaluations of products are one way in which manufacturers, distributors and users of chemicals can contribute to production and use of substances with less pollution potential (HERA, 2002). Environmental and regulatory compliance audits have been common practice in industrial and commercial settings for a decade or more under international programs of environmental management and consumer product safety such as ISO 14000 (Fredericks and McCallum, 1995; ISO, 2001). In addition, responsible and detailed labelling of consumer products is a method for linking information from the manufacturers with consumers and users to optimize environmentally sound disposal practices (US EPA, 2002b).

Similarly, the encouragement or institution of procedures for re-using waste materials can be an economically and technically sound means to reduce waste volumes and limit potential contamination by process wastes. The use of internal process modifications, or business contacts with an external waste exchange programme which converts one plant’s waste output into another plant’s resources are proven methods for achieving these goals. Industrial waste treatment and recovery strategies to convert or to process wastes into profitable materials have been effective in worldwide applications since at least the 1970s. These strategies are most effective where large volume wastes of specific types (e.g. spent solvents with low residual contaminants) are available from a plant, and low cost transportation is available to a plant with distillation or purification facilities.

Waste exchange, defined as the use of discarded, surplus or off-specification materials for beneficial purposes, represents one potential component of waste management options. While some materials are easily amenable to such exchanges (e.g. solvents for reclamation, metals dusts for refining), other waste sources require innovative approaches to identify users. Examples such as the oil refinery in Poland discussed in Box 23.1 illustrate the double benefit associated with the waste exchange concept. This growing trend in waste management benefits both parties and is typically facilitated by a non-profit intermediary.

Box 23.1. Waste exchange at a petroleum refinery site in Czechowice, Poland

The oil refinery case example described in Chapter 11 (Box 11.1) illustrates the potential for waste exchange as an avoidance strategy: Final disposition of the acidic petroleum sludges currently stored in the refinery's waste lagoons is an issue of concern for the refinery as it seeks to modernize its operations. With advice and guidance from an American waste exchange, the refinery sought to find a potential user for these sludges. A nearby cement manufacturer was identified as having the capabilities to co-fire the sludge in their cement curing/drying kilns, strictly for its energy value. Negotiations between the two parties led to a series of test burns using varying amounts of refinery sludge. The process was proven to be feasible and negotiations began for full-scale implementation. Successful consummation of this arrangement provided a low- or no-cost source of supplemental fuel to the cement manufacturer while providing a disposal mechanism and, potentially, income to the oil refinery. Existing waste materials will be removed from the urban area in which the refinery is located, reducing the potential for groundwater contamination, and the cement manufacturer will reduce their use of external fuel.

A further important strategy to avoid contaminating groundwater is transition to production processes that substantially reduce or totally replace the use of hazardous chemicals and/or the use of water. Such developments have been successful in many branches of production and include effluent-free steel industry, mercury free chlor-alkali electrolysis, AOX-free propendioxide production, or wastewaterless flue gas washers and cooling systems. Instalment of such production technologies often proves cost-effective for the enterprise within fairly short time spans, particularly in settings where water prices are an issue, or where the enforcement of pollution restriction legislation renders polluting practices costly.

Avoidance strategies are also important for a wide variety of substances used in industry and with the potential to adversely affect groundwater which are also are present in common household products (e.g. alcohols, petroleum hydrocarbons, chlorinated solvents, soaps/surfactants, ammonia, phthalates, paints, batteries, pesticides, adhesives). While individual quantities per household may seem small in comparison to those generated by industrial facilities, a large number of households disposing such products in landfills and/or septic systems may represent an equal or greater potential hazard (EC, 2002; Health Canada, 2002; US EPA, 2002a). In some areas, incentives encourage the production, marketing and use of less toxic and less environmentally hazardous alternatives. However, the costs and time necessary to effect changes in established behaviours can be large (EC, 2002).

23.1.2 Choice of site

A fundamental element of any strategy for prevention or avoidance of adverse impacts in groundwater recharge areas is appropriate choice of the site for a facility, including the option of relocating existing facilities. Consideration of groundwater vulnerability is invaluable in assessing the suitability of locations for new operations, and may be used in conjunction with site development plans and engineering precautions to design a facility with minimum potential aquifer impacts. An important measure in planning and choice of site is to require permits for construction and operation which specify activities, production processes and management plans. Legislation and local land use controls or zoning requirements can be effective tools to guide industrial development for achievement of minimum impact in drinking-water catchment areas. Limitations on siting in flood prone or low areas, areas of karstic terrain, close proximity to water bodies or within current or potential future drinking-water protection zones recognize that accidental releases or ongoing industrial operations in these areas rapidly affect groundwater.

Where facilities already exist in vulnerable drinking-water catchments and relocation is not an option, control measures to prevent releases of hazardous substances become particularly important, and specific controls may be required in permits for their operation to limit their hazard potential. Such requirements may include use of environmentally improved technology and products, more intensive monitoring systems, emergency response plans and prohibiting the use of specifically identified hazardous substances in their processes.

Issues of site-specific relevance include: surface topography and features; soil type and local variability; aquifer vulnerability (see Chapter 8); proximity to rivers and other water bodies; chemical type, physical form and quantity of materials handled; degree to which plant construction will require major changes to existing conditions and thus impact on aquifer vulnerability (e.g. extensive excavation, backfilling or soil relocation, pipeline installation, well construction, paving or building cover for substantial areas).

23.1.3 Design and construction for prevention of spills and leakage

A wide range of engineering measures can be applied in the design and construction of a facility as an effective defence to prevent or avoid releases of hazardous substances. These include approaches such as impermeable surfaces and secondary containment structures around tanks, double-walled pipes, alarm devices indicating overfilling of tanks or other vessels, and knock-down barriers to protect tanks or pipes from damage by vehicles (see also Box 23.2 for examples). They also include using natural (e.g. clay) or synthetic (e.g. geotextile) liners to prevent percolation from ponds or storage areas, and capturing in-plant process residues or surface run-off in properly designed and constructed holding areas prior to treatment. Often, structures to retain spilled and/or leaking fluids are important particularly for unloading stations where hazardous fluids are transferred from railway or truck tanks to on-site containers (see Figure 23.4 in Box 23.2). Prevention and mitigation of releases can also be accomplished by neutralizing, encapsulating, stabilizing or solidifying materials (e.g. process wastes, soils, sludges) to prevent or control mobility.

Canopies over stored materials, coupled with capping options designed to isolate materials or to protect them from precipitation and to prevent leaching, can also be site-specific source control measures (Figure 23.3 in Box 23.2). The appropriate degree of complexity for a capping option is related to factors including size and configuration of the capped area, toxicity and potential mobility of the materials to be addressed, duration of required isolation, and whether the surface of the capped area is to be used for secondary activities. As indicated in Table 23.1 at the end of this chapter, capping typically will be accompanied by an operational monitoring requirement to ensure that the cap (and/or companion liner system) continues to be effective at isolating the materials. Available capping options vary widely in cost, durability and effectiveness for particular applications. Such options may best be viewed as temporary, albeit long-term, solutions for which subsequent, permanent solutions are desirable.

Levels of sophistication – and thus of costs – can vary for design and construction control measures. Often, fairly simple low-cost measures effectively provide substantial protection against soil and groundwater contamination, and are valuable first steps upon which incremental improvements can build later. In the study shown in Box 23.2, short-term, medium-term and long-term measures were proposed for many of the problems identified. For example, while the long-term measure for protecting tanks against overflow of hazardous chemicals through overfilling would be to fit them with approved devices, overflow can already be quite effectively prevented by installing a simple indicator of filling level and a routine for its regular monitoring. An immediate measure would be to ensure that special care is taken when filling the tank by requiring two staff members to fill the tank together. Likewise, while double bottoms for tanks may be installed in the long run, intensified internal checks and determination of the wall thickness of the tank may improve safety in the meantime.

For all containment structures, regular maintenance and monitoring of their integrity is critical for keeping them functional. Management plans for a facility should include these activities and responsibilities for their regular performance and documentation.

23.1.4 Operational controls

For protecting groundwater from industrial contamination, controlling operations that may lead to spills and leaching is often equally important as safe containment. Operational controls address procedures for handling, using, transferring and storing substances such as properly unloading trucks or railway tankers, using safety couplings and valves, using mobile drip trays, avoiding overfilling containers and providing materials to absorb hazardous chemicals in case of spills. An important aspect is preventing joint storage of substances that may undergo chemical reactions with each other and taking properties such as auto-ignition, combustibility or corrosiveness into account. Also, labelling of tanks, containers and facilities with hazardous chemicals is necessary to allow appropriate emergency responses. A further important operational control is the implementation of emergency response plans which are regularly rehearsed by the staff of the facility.

Operational controls are best developed with operational staff and fixed in writing as standard operating procedures in a facility's management plans. Implementation is supported by checklists and forms to sign after conducting specific routines. Adequate training and qualification of staff, including the aspects of groundwater protection, as well as clear assignment of tasks and responsibilities, are prerequisites to making them work. Often the target of avoiding spills for the sake of groundwater protection is closely linked to the target of avoiding exposure for the sake of occupational health and safety, and both may be addressed within the same control measure.

Box 23.2. Technology transfer for plant-related water protection in Moldavia, Rumania and Ukraine (based on FEA, 2002)

Within the framework of the Environmental Action Program for Central and Eastern Europe which was agreed by the Ministers for Environment of the UNECE, a Technical Assistance Programme launched by the German Ministry of Environment developed a methodology for assessing water pollution hazards by industries with high water pollution potential. This used the recommendations of the International Commissions for the Protection of the Rhine (ICPR) as well as of the Elbe (ICPE) as a basis. From this assessment, short, medium, and long-term measures were identified with which the ICPR and ICPE recommendations can be met. The majority of these measures are equally relevant to the protection of groundwater and surface water. Measures relating to design and structure of facilities include the following:

Short-term measures:

- Repair and seal cracks and damage in existing sealed surfaces
- Perform internal examinations of tanks and containers
- Fill tanks and containers under the supervision of two operating persons
- Examine and prepare a concept for joint storage of hazardous substances (with the potential to react)
- Use mobile collecting basins and detachable connections for plants with transhipment (tank wagon – plant connections)

Medium-term measures:

- Provide a stop valve for open-air collecting basins connected to the wastewater system
- Demonstrate that wastewater pipelines are not leaking (Figure 23.2)
- Renovate sealed surfaces in plants for transhipment and/or storage

Long-term measures:

- Install overfill safety systems for storage containers
- Provide collecting basins for retaining water-polluting substances and fire-fighting water
- Create sealed surfaces and retaining volume for railway tank-car stations (Figure 23.4)
- Establish wastewater treatment facilities that meet quality requirements

Operational control measures include requiring the plant operator to:

- define in-plant responsibilities for taking and checking safety measures which include functional safety, impermeability of containment structures, functionning of safety equipment, documentation (in writing) of regular checks undertaken
- provide detailed reports on accidents and incidents, including causes, consequences and future preventive measures
- report releases of hazardous substances to competent authority
- define equipment for plant monitoring and related instructions for action, including prevention of accidents, water hazard potential, potential for substance release, precautionary measures and protection requirements

- use internal monitoring wherever there is a need to prevent releases of substances hazardous to water, to allow detection on time to implement contingency measures

Checklists were developed for setting up internal alarm and hazard control plans defining actions and responsibilities for types of incidents (e.g. leakage, overfilling of vessels, failures of receptacles, containers, pipelines, fires and fire-fighting water, accidents during transport of hazardous goods) as well as for different plants. This includes exercises to train accident responses at regular intervals.

Figure 23.1. Leakages at a production plant

Action proposals: Technical structures to minimize foaming; venting on a buffer tank for the retention of the foam.

Figure 23.2. Single wall pipe subways through retention room; no knock-down protection

Action proposals: Pipe installation above the retention room wall; constructing knock-down protection (big stones); regular pressure tests; street crossing over ground; double wall pipes installation.

Figure 23.3. Storage of solids

Action proposals: Creation of a reasonable canopy; moving the pipe in the bow area; renovation of the existing sealing area.

Figure 23.4. Unloading station for hazardous fluids from railroad tank cars

Action proposals: Conduct unloading with two people; build adequately sealed retention space.

23.1.5 Decommissioning of contaminated sites

When industrial and military sites are abandoned, hazardous chemicals that may leak into groundwater may unintentionally be left behind. An important control measure in drinking-water catchments therefore is proper decommissioning – potentially involving clean-up – of such sites. Issues of decontamination and remediation of sites formerly used for industrial or military purposes are often complex due to the difficulties of identifying those responsible for the pollution in order to implement the polluter pays principle. This is particularly difficult in the context of abandoned sites. Teaf (1995) and Herndon *et al*. (1995) have described the former military facilities in central and eastern Europe as a large scale example of this and reported that the technical and financial responsibility for mitigation became the burden of the host country. Similar problems occur on abandoned industrial sites. An important control measure to prevent this type of situation is to include the responsibility for decommissioning and potentially necessary remediation in plans and permits for establishing such operations.

23.1.6 Clean-up and remediation of contamination

Once a decision has been made to clean up a given site, an initial site characterization must be performed to determine the type and extent of contamination, it may be possible to use available data for preliminary decision-making. For example, after-care measures in the form of exploratory investigations, containment techniques and remedial actions (Teaf, 1995) were carried out in particular in the early 1990s in Germany for military-contaminated sites located in the vicinity of drinking-water abstraction. This included the toxicological assessment of individual constituents and groups of military chemicals, as well as assessment of their migration behaviour and biochemical, chemical and hydrolytic degradability in subsoil (e.g. to evaluate their potential to leach into groundwater).

The characterization process prior to mitigation of industrial and military sites must consider a cardinal rule: that which is not sought is never found. Although the highest concentrations of contaminant generally will be focused at the source area, the characterization and clean up efforts also must identify and evaluate the extent and continued migration of contaminant plumes in soils, groundwater or surface water. This is critical because degradation often occurs in the areas of lower concentration associated with plume fringe, which may be far from the source.

A variety of technologies exist for the remediation of soil, surface water and groundwater at industrial facilities (e.g. thermal and chemical treatments, biological remediation technologies, soil washing and filtration; see Soesilo and Wilson, 1997; Nyer, 1998; Hyman and Dupont, 2001). Depending on the type of contamination and the threat to drinking-water aquifers, natural attenuation may also be an option (see also Chapter 24). When selecting a remedial technology, the decision will be influenced by potential effectiveness, reliability, implementability, cost and time constraints. Each technology has intrinsic advantages and disadvantages that can be optimized by carefully matching site-specific conditions with a remedial technology or suite of technologies. For example, many organic contaminants (e.g. petroleum hydrocarbons) are readily degraded by microbial communities under appropriate environmental conditions (see Chapter 4). Bioremediation seeks to optimize those conditions through a variety of in situ or constructed on-site mechanisms. Biological technologies such as these take advantage of and facilitate natural processes and, as such, are often favoured and are potentially less expensive, in comparison with more technologically complex approaches. The increased time frames associated with some biological remediation technologies may be more easily accommodated at sites controlled by government entities (e.g. military installations) than at those associated with commercial or industrial enterprises. Contaminants such as petroleum products or chlorinated solvents are amenable to such efforts.

Once a release to soils, waterbody sediments or other elements of a groundwater recharge area has occurred, there are many established and new methods to prevent or limit contaminant migration in soils and to control or reverse plume expansion in groundwater. These methods include physical controls (e.g. sheet piling, trenches/slurry walls/grouting, recovery wells, air sparging), physical separation (to reduce reactions) and chemical methods for contaminant control (e.g. oxidation/aeration, reduction, permeable reactive barrier, dual phase extraction), as well as in situ or ex situ degradation by physical or biological processes. Recent advances in phytoremediation, for example, have resulted in deployments of certain tree species known as phreatophytes (e.g. poplar, willow) to intercept contaminant groundwater plumes (Quinn *et al.*, 2001). Such biological control also may enhance degradation of some organic contaminants. Maintenance and operation costs of such a system are lower than for typical engineered systems (e.g. pump and treat) over the relative lives of the systems. Depending on local and regional hydraulic effects exerted by water bodies, surface water control may be an important element of a comprehensive strategy to prevent industrial impacts in recharge areas.

The most straightforward mechanism for addressing contaminated soil, generally above the saturated zone, involves excavation and off-site disposal. However, the quantity and character of soils, as well as the associated removal, transportation and disposal costs, may limit the utility of this option. In addition, the transport of contaminated materials to another location may not relieve the original landowner of legal liability.

23.2 MINING

As with industrial activities, control measures for mining activities involve prevention as well as remediation and monitoring whether process controls are being implemented. Due to the large scale of many mining activities and milling sites, retrospective mitigation of their environmental impact is often substantially more difficult than prevention. Further, groundwater protection strategies are needed for both the active mining period and the post-mining period, and have to include the mine itself as well as mine waste, milling facilities and atmospheric emissions. Control measures may be equally necessary for small mining sites, particularly where they are numerous and potentially lead to considerable contamination of groundwater (see Chapter 11).

As for industry, choice of site is the first and often most important measure to protect groundwater. Many countries require an environmental assessment study for new mining activities exceeding a certain size (number of employees, amount of ore excavated). Ideally, intersectional collaboration in this planning phase should involve public health authorities and water suppliers to help recognize the potential impact on groundwater resources. Numerical modelling of groundwater flow, hydraulic situation before, during, and after mining activities and the impact of mining on groundwater quality is a state of the art technique and often successfully performed. Groundwater modelling is also an important tool to determine appropriate locations for monitoring wells to be drilled in the region of interest for mining, in order to record groundwater flow and quality parameters. Moreover, an Environmental Impact Assessment (EIA, Chapter 20) should be performed taking into account the vulnerability of the groundwater, the type of ore mined and processed, and other environmental threats in the region. This will lead to a more sustainable mining activity by introducing appropriate treatment and processing techniques. The EIA should cover the entire time frame, i.e. the exploration of an ore body, the mining activity, the remediation measures taken and the post-mining land use.

23.2.1 Deep mines

Constructing and operating a deep mine usually requires groundwater withdrawal. A necessary control measure to prevent water pollution in some cases is water treatment if the water contains toxic elements above a critical level. Monitoring would address on a regular basis whether treatment is in place and properly operating.

A further measure for preventing contamination is limiting the use of hazardous chemicals in ore processing and, where use is inevitable, application and handling with special care. Control measures may involve limiting, budgeting and recording the amounts of such chemicals used. Areas where heaps and tailing ponds will be constructed have to be investigated carefully including geological and hydrogeological aspects; in many cases liners (e.g. geotextile; see also Chapter 24) are useful as additional protection against contaminant leakages.

Before closing a deep mine, potential contaminants (e.g. fuel, oil, machinery) should be removed. In numerous cases where this was not done, considerable amounts of contaminants and waste in the mine have led to groundwater contamination.

Refilling of tunnels and shafts with waste rock or fly ash is a common technique to avoid land subsidence. However, it may also help in establishing lower permeability in the flooded mine and act as reactive material. The chemical nature of such fill materials should also be considered. These materials may be a potential source of contaminants (e.g. metals) in addition to mined materials. On the other hand, they may also be selected to bind contaminants: calcite may buffer low pH values, while iron (Fe^0) acts as a reducing agent, and fly ash or brown coal seem to be effective in sorption. However, little is known about long term behaviour of reactive material in underground mines. Thus the choice of adequate refilling materials is an important groundwater protection measure but long-term surveillance will often be necessary to ensure that contaminants are not released in concentrations above critical levels. Controls to ensure that adequate measures are taken for closure may include the requirement of approval of plans for such measures by government authorities or a catchment protection body.

During controlled flooding of a mine, contaminated groundwater is pumped and treated until the contamination level has decreased to acceptable concentrations. In many cases, this may require an extended period of time, and alternative passive treatment techniques might be preferable. In some cases, hydraulic isolation of the mine area might solve the problem, but this can be expensive as well. Tracer experiments are common tools to investigate the hydraulic flow pattern in a deep mine. Constructed wetlands can be used as effective and inexpensive measures to treat surface water after the first flush has reached an acceptable value of contaminants (Younger, 2000). As long as the contaminated groundwater flows at shallow depths, reactive walls (i.e. subsurface permeable barriers built with reactive materials to degrade or immobilize water-borne contaminants) may be considered as a low cost measure (Blowes *et al*., 2000). Reactive walls or permeable reactive barriers are passive treatment systems: a ditch is excavated in an aquifer downstream of the contaminant source and refilled with permeable and reactive material (e.g. mixture of sand with iron). Since iron in its elemental form is a very strongly reducing agent, metal ions (e.g. uranium, chromium) will be transferred in their reduced redox state and in consequence precipitate. Thus groundwater leaving the permeable reactive barriers is purified by certain metals and organic contaminants efficiently and at low costs. All approaches to treating water from mines will require adequate surveillance of treatment efficacy which would be defined in a management plan.

23.2.2 Open pit mines

Since open pit mining usually destroys aquifer structure, this type of mining often has the most severe impact on groundwater on a regional scale. Legislation and governmental controls on surface mining in relation to groundwater use have been implemented successfully. To control sulphides, waste rock should be covered as soon as possible (see below). Carbonate as alkalinity buffer may be added as additional measure to compensate the pH value due to pyrite oxidation. Calcium phosphate also has been used to control acid generation (Evangelou, 1995).

The design of open pit mining activities must also account for the final shape of a mine lake. Rapid recovery of groundwater to the final level in such a lake is often targeted to minimize erosion and stability problems with the embankment. As discussed in Chapter 11, acid mine drainage may flow from the oxidized zones of aquifers and heaps towards the pit lake resulting in extremely low pH-values in the lake water. If surface water is available to fill the lake, water quality will be no problem in the very beginning as this is usually well buffered. However, hydraulic equilibrium between groundwater and the lake will establish itself with time and water quality may decline when the groundwater in contact with rock is contaminated due to the solution of secondary minerals and/or waste deposits. Therefore management action to protect groundwater from post-mining lakes and vice versa requires both consideration of these processes already in the planning phase for the activity and surveillance for the post-mining phase until new hydrological equilibrium between ground- and surface water, as well as chemical equilibrium between solids and water, have been reached. Acid mine lakes can be treated by means of liming with dolomite quicklime. The pH will rise to about six and high sulphate concentrations will decrease by the formation of gypsum. Time intervals of monitoring should relate to rates of change and may decrease as processes slow down.

23.2.3 Acid mine leachate

As pointed out in Chapter 11, acid mine leachate is one of the most severe potential groundwater impacts from this human activity. Approaches to controlling this involve keeping the oxygen supply to sulphide minerals as low as possible to avoid reactions producing sulphuric acid. This requires careful investigation of the distribution of sulphides in the mine area and its vicinity. Also, minimizing the dewatering cone of depression will reduce leachate. Refilling shafts and adits with material of fine grain size reduces the permeability in these artificial cavities and helps establish more natural groundwater levels during the post-mine period. This material also may act as reactive material, lowering the outflow of contaminants from the mine site (see Section 23.2.1). Where these measures are chosen – alone or in combination – monitoring their proper operation is needed on a regular basis to ensure their implementation. Depending on the setting, monitoring could include regular checks on pH and sulphate concentrations in order to control whether sulphide oxidation is still ongoing; on the depression cone; and on the amounts as well as type of refilling material actually used.

23.2.4 Heaps, piles, mills and tailings

Major sources of pollution from mining often are heaps, piles and tailing ponds. Waste rock and residues from ore milling and ore processing ('tailings') at new or operational mining facilities need to be handled with the same care as municipal or industrial wastes. Control measures to mitigate their impact therefore include many state-of-the-art techniques used for waste deposits, such as drainage and treatment of drainage water to meet the targeted water quality criteria, or placement of spoil heaps and tailings over areas of impermeable sediments such as clay or bedrock that will not allow leachate to reach groundwater. Alternatively a clay lining or a geo-textile fabric can be used to line the site intended for disposal of spoil and tailings, or a foundation pad can be constructed which is impermeable or has reduced permeability. In both cases care must be taken to contain or treat leachate that runs off from the site. Corresponding control measures address the function of such containments and whether they are intact. Control measures for sustainable mining may also include the addition of buffering minerals to heaps, e.g. a certain amount of lime stone or fly ash according to the amount of sulphide in the waste rock. This buffers the formation of acid mine drainage in situ.

Control measures for such approaches involve periodic assessment of whether seals are tight, and monitoring systems for groundwater quality up- and downstream will assist in verifying whether the approach taken is sufficient.

In many settings, earlier construction of heaps, piles and tailings without consideration of their impact on groundwater quality has led to problems now requiring remediation. For example, remediation of the uranium mining and milling sites which were in operation from 1946-1990 in the eastern part of Germany is costing the German Government about US$ 6.5 billion. Treatment of contaminated groundwater as well as surface water from deep mines during ongoing operation may be accomplished by means of classical treatment techniques, though this may be prolonged and costly. Thus alternative treatment techniques such as reactive walls, carbonate drains, and constructed wetlands are increasingly being used. Constructed wetlands have proved to be a promising tool for natural attenuation of mine-related contaminants (Hedin *et al.*, 1994; Younger, 2001).

Physical shaping and capping of heaps and tailings is necessary to avoid erosion, dust transport and reduction of the amount of infiltration. If radioactive ores or waste rock with radioactive components occur on-site, this must be taken into account in designing covers or caps that can act as a radon barrier as well (Merkel *et al.*, 2002). Tailings may be covered with wet or dry caps, the latter being most common. Again, control measures should ascertain that caps are in place and functioning.

Rehabilitation of old heaps and tailings requires a careful investigation of boundary conditions and impact on groundwater. This will show to what extent reshaping and capping of these heaps and tailings may be necessary to achieve slope stability, erosion protection and surface or groundwater protection. Passive water treatment techniques may be applicable for long-term protection of groundwater resources.

23.2.5 In situ leaching

Mining by in situ leaching (ISL) presents special concerns to groundwater quality since hazardous chemicals are used for the in situ extraction of ore by leaching (see Chapter 11). Approval of ISL mining by regulators should therefore require management plans which define control measures with operational monitoring systems as well as maintenance of all installations to ensure that groundwater clean up can be performed at the specific site. Monitoring is critical to ensure that no process chemicals leave the ISL mining site during operation. When ISL mining is terminated, the site should be cleaned until pre-mining or otherwise acceptable conditions have been established.

23.3 MONITORING AND VERIFICATION OF MEASURES CONTROLLING INDUSTRY, MINING AND MILITARY SITES

The control measures for industry, military sites and mining in drinking-water catchments proposed above range from planning tools in the context of broader environmental policy to specific technical measures such as structures, containments and operational controls. Selected examples are summarized in Table 23.1.

NOTE ▶ *The implementation of control measures such as those suggested in Table 23.1 is effectively supported if the stakeholders involved collaboratively develop management plans that define the control measures and how their performance is monitored, which corrective action should be taken both during normal operations and during incident conditions, responsibilities, lines of communication as well as documentation procedures.*

The implementation of control measures protecting drinking-water aquifers from industry, mining and military activities is substantially facilitated by an environmental policy framework (see Chapter 20).

Monitoring of the measures implemented is crucial to ensure that they are in place and effective. Table 23.1 therefore includes options for monitoring and verification of the control measure examples given. Most of these focus on checking whether the controls are functioning as intended, rather than on contaminant concentrations in groundwater. For planning, reviewing will address whether plans exist, are appropriate and are being implemented, particularly in the context of issuing permits for new or extended operations. Periodic auditing of plans is an effective tool for such surveillance. Likewise, reviewing of emergency response plans would assess whether they are appropriate and whether they are occasionally being used for appropriate facility training exercises.

Similarly, for control measures in design and construction, the first step is to assess whether or not they are adequate for achieving the protection target, and whether or not they are in place as indicated in the construction plan. For the day-to-day routine operation of controls, monitoring focuses on assessing whether they are functioning as they should, e.g. whether containments are sealed, mine drainage is being treated or waste management plans are being implemented.

Monitoring of controls for day-to-day operations is particularly important as these tend to slip if not taken seriously. Examples given in Table 23.1 include maintenance routines, specifications on amounts and types of chemicals to be used, safety rules for handling, transferring and storing hazardous chemicals and routines for pumping hazardous leachate from mines. Such rules will be specified in management plans and standard operating procedures. Their implementation can be monitored by checking records, e.g. of maintenance measures taken or amounts of chemicals used in process steps, as well as by occasional inspection of process steps, such as unloading tankers with hazardous chemicals or integrity of storage structures, and by interviewing technical staff on how these steps are normally performed.

NOTE ▶ *Options for monitoring suggested in Table 23.1 rarely include regular groundwater quality monitoring. Where control measures such as structures are poorly accessible, however, monitoring of selected indicator parameters in groundwater is suggested.*

Comprehensive groundwater quality monitoring programmes are a supplementary aspect of monitoring with the purpose of providing verification of the efficacy of the overall drinking-water catchment management.

Where spills and releases are suspected or where the risk that this may happen is elevated, monitoring to provide for early detection is important. Careful evaluation of both the hydrogeology and the facility operations will allow prediction of likely locations and flow patterns of initial releases. Monitoring for key parameters that would readily indicate a leak at these locations can provide early warnings. This may include groundwater sampling and analysis of selected indicator parameters that would readily reflect leakage and potential contamination. Contaminant analyses will also be an important control measure after decommissioning of industrial and military sites and in particular after clean-up and remediation of contamination. Generally, resources expended in monitoring result in reduced remedial costs (and potential enforcement) in the event of a release. In the context of monitoring for overall verification of the catchment management concept, it is often effective to include contaminants anticipated or known to occur from industry, mining and military activities in the catchment, particularly at the sites of these activities, but also at groundwater intakes.

Table 23.1. Examples of control measures for industry, mining or military sites and options for their monitoring and verification

Process step	Examples of control measures for industry, mining and military sites	Options for their monitoring and verification
PLANNING	Require permits for the location, design and operation of industries, manufacturing enterprises, mining and military sites (e.g. EIA)	Review (application for) permit with respect to adequacy of siting, planning and design as well as public consultation
	Require plans for post-operational safety of site as part of the permit for such operations which are likely to need post-closure management (e.g. mining or military training sites)	Require long-term financial commitments and post-operational management plans (e.g. for lakes resulting from open pit mining) for issuing permit
	Require environmental or chemical management plans, including waste management plans when issuing a permit (including e.g. probations or limitations of specific processes or chemicals; treatment for mines using in-situ leaching)	Review existence and adequacy of management plans; audit if possible
	Require emergency response plans for enterprises which operate with hazardous substances	Review or audit emergency response plans
	If drinking-water protection zones are designated, enforce keeping hazardous enterprises out	Conduct periodic site inspections
DESIGN AND CONSTRUCTION	Install and maintain temporary and/or permanent containment structures (tanks, caps, vaults) for storage and handling of hazardous chemicals, explosives, mine heaps, tailings and ponds	Review adequacy of design and compliance with plans and regulations Inspect sites and enterprises for compliance with plans, and structural integrity and function
	Remove or remediate contaminated soil	Analyse residual soil and groundwater samples
	Refill mine tunnels and shafts; remove/stabilize potential contaminants; remove contaminants (e.g. fuel oil), machinery before refilling	Conduct follow-up site inspection and monitoring
	Rehabilitate old heaps and tailings; treat leachate	
OPERATION AND MAINTENANCE	Control/restrict amounts and types of chemicals used in production processes and mining operations	Review records/reports of chemical use, storage of wastes and maintenance of systems Analyse in situ leachate for chemical concentrations
	Control storage, handling and disposal of high risk chemicals and wastes	Inspect compliance to codes of practice, standard operating procedures and/or chemical management plans
	Maintain containment structures for storage and handling of hazardous chemicals and explosives	Check whether maintenance plans have been signed off; occasionally inspect maintenance Monitor downstream groundwater for parameter indicating leakage
	Minimize acid leachate from mines by controlling dewatering cone of depression	Monitor water levels, pH, or sulphide
	Treat contaminated groundwater from (active or closed) mining operations until contaminant concentrations reach acceptable levels	Monitor operational parameters for treatment system chosen (e.g. condition of artificial wetland and water flow) Analyse selected contaminants in treated water
	Conduct post-operational management of sites potentially leaking hazardous substances	Inspect monitoring and maintenance by operators and evaluation of reports required by permit Monitor downstream groundwater for parameter indicating contaminant migration

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