4

Chemicals: Health relevance, transport and attenuation


The presence of substances in groundwater may be affected by naturally occurring processes as well as by actions directly associated with human activities. Naturally occurring processes such as decomposition of organic material in soils or leaching of mineral deposits can result in increased concentrations of several substances. Those of health concern include fluoride, arsenic, nitrate, selenium, uranium, metals, and radionuclides such as radon. Problems of aesthetic quality and acceptance may be caused by iron, manganese, sulphate, chloride and organic matter.

Sources of groundwater contamination associated with human activities are widespread and include diffuse as well as point source pollution like land application of animal wastes and agrochemicals in agriculture; disposal practices of human excreta and wastes such as leaking sewers or sanitation systems, leakage of waste disposal sites, landfills, underground storage tanks and pipelines; and pollution due to both poor practices and accidental spills in mining, industry, traffic, health care facilities and military sites.

The exploitation of petroleum products and the development of industrial chemistry has given rise to a large number of organic chemicals, many of which can be found in the environment. Many organic chemicals are known to have potential human health impacts, and some of these may occur in drinking-water in health-relevant concentrations. In consequence, the list of those for which guideline values and national quality standards have been developed has been continually added to and revised as data on the occurrence of chemicals in water and new toxicological data emerge. Organic chemicals commonly used by industry with known or suspected human health impacts that are often encountered in groundwaters include, for example, aromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylenes (BTEX) as well as volatile chlorinated hydrocarbons such as tetrachloroethylene (PCE) and trichloroethylene (TCE). A diverse range of pesticides is also found in groundwaters. These are primarily, but not exclusively, ascribed to agricultural activities. Typically pesticide concentrations encountered are low. In some cases they have exceeded regulatory limits for drinking-water supplies, although often the regulatory levels exceeded were often much lower than those based on public health considerations.

This chapter concentrates on the groups of chemical substances that are toxic to humans and have reasonable potential to contaminate drinking-water abstracted from groundwater. It provides foundational knowledge of natural groundwater constituents and anthropogenic groundwater contaminants and discusses their relevance to human health, origin, and transport and attenuation in groundwater systems. The chapter is subdivided as follows: Section 4.1 provides introductory theory on the transport and attenuation of chemicals in the subsurface; Sections 4.2 to 4.4 focus upon inorganic chemicals – natural inorganic constituents, nitrogen species and metals respectively; Sections 4.5 to 4.8 focus upon organic chemicals including an introductory section on conceptual contaminant models and transport and attenuation theory specific to organic contaminants followed by sections on some organic chemical groups of key concern – aromatic hydrocarbons, chlorinated hydrocarbons and pesticides respectively; finally, the chapter closes with a brief consideration of currently emerging issues (Section 4.9). Further information on the individual chemicals discussed in this chapter is available in the WHO Guidelines for Drinking-water Quality, Volume 1 (WHO, 2004a), as well as in detailed background documents on WHO’s Water, Sanitation and Health website (http://www.who.int/water_sanitation_health/dwq/chemicals/en/index.html).

4.1 SUBSURFACE TRANSPORT AND ATTENUATION OF CHEMICALS

Understanding of the transport and attenuation of chemicals in the subsurface is fundamental to effective management of risks posed by chemicals and their possible impact on groundwater resources. A risk assessment approach to groundwater protection incorporates the three-stage combination of source, pathway and receptor. All three must be considered and understood to arrive at a balanced view of the risks to health of groundwater users. Informed consideration of the pathway, which in the context of this monograph means transport through the groundwater system, is vital. This not only includes consideration of the general and local hydrogeologic characteristics covered in
Chapters 2 and 8, but also the transport and attenuation of chemicals within that pathway. The latter depend upon the properties of the chemical itself, particularly those properties that control interactions of the chemical with the subsurface regime, a regime that includes not only the host rock and groundwater, but other natural and anthropogenic chemical constituents present as well as microbial life.

Within the overall transport process, attenuation processes may cause movement of the chemical to differ from that of the bulk flowing groundwater, for example dispersion, sorption and chemical or biological degradation of the chemical. Such attenuation processes potentially act to mitigate the impact of chemicals and are a function of both the specific chemical and geologic domain. Indeed, attenuation may vary significantly between individual chemicals and within different geological settings. In recent years natural attenuation of organic contaminants has been increasingly recognized to play an important role in many aquifer systems leading to monitored natural attenuation becoming a recognized remedial strategy to manage risks to groundwater at some contaminated sites (EA, 2000).

This section provides an overview of the key processes that control the transport and attenuation of chemicals in groundwater. Elaboration of some of the more specific attenuation processes is also included in later sections. Further details may be found in the following texts and references therein: Freeze and Cherry (1979), Appelo and Postma (1993), Stumm and Morgan (1996), Domenico and Schwartz (1998), Bedient et al. (1999), Fetter (1999) and Schwartz and Zhang (2003).

### 4.1.1 Natural hydrochemical conditions

It is important to understand at the outset the natural hydrochemical conditions that exist in a given aquifer system, as these provide the baseline from which quality changes caused by human impacts can be determined. The natural hydrochemical conditions may also affect the behaviour of some pollutants. Because groundwater movement is typically slow and residence times long, there is potential for interaction between the water and the rock material through which it passes. The properties of both the water and the material are therefore important, and natural groundwater quality will vary from one rock type to another and within aquifers along groundwater flow paths. Water is essentially a highly polar liquid solvent that will readily dissolve ionic chemical species. Rock material is predominantly inorganic in nature and contact of flowing groundwater with the rock may dissolve inorganic ions into that water, i.e. dissolution of the rock occurs. ‘Major ions’ present are the anions nitrate, sulphate, chloride and bicarbonate and the cations sodium, potassium, magnesium and calcium. Ions typically present at lower concentration, ‘minor ions’, include anions such as fluoride and bromide and a wide variety of metal ions that are predominantly cations. Combined, the total inorganic concentration within the water is referred to as the total dissolved solids (TDS).

Natural groundwater quality changes start in the soil, where infiltrating rainfall dissolves carbon dioxide from biological activity in the soil to produce weak carbonic acid that may assist removal of soluble minerals from the underlying rocks, e.g. calcite cements. At the same time, soil organisms consume some of the oxygen that was dissolved in the rainfall. In temperate and humid climates with significant recharge,
groundwater moves relatively quickly through the aquifer. Contact time with the rock matrix is short and only readily soluble minerals will be involved in reactions. Groundwater in the outcrop areas of aquifers is likely to be low in overall chemical content, i.e. have low major ion contents and low TDS, with igneous rocks usually having less dissolved constituents than sedimentary rocks (Hem, 1989). In coastal regions, sodium and chloride may exceed calcium, magnesium and bicarbonate and the presence of soluble cement between the grains may allow major ion concentrations to be increased. Groundwaters in carbonate rocks have pH above 7, and mineral contents usually dominated by bicarbonate and calcium.

In many small and shallow aquifers the hydrochemistry does not evolve further. However, the baseline natural quality of groundwater may vary spatially within the same aquifer if the mineral assemblages vary, and also evolves with time as the water moves along groundwater flow lines. If an aquifer dips below a confining layer (Figure 2.5), a sequence of hydrochemical processes occurs with progressive distance downgradient away from the outcrop, including precipitation of some solids when relevant ion concentrations reach saturation levels for a solid mineral phase. These processes have been clearly observed in the United Kingdom, where the geological history is such that all three of the major aquifers exhibit the sequence shown in Figure 4.1, which has been characterized by sampling transects of abstraction boreholes across the aquifers (Edmunds et al., 1987).

Figure 4.1. Schematic representation of downgradient hydrochemical changes

In the recharge area, oxidizing conditions occur and dissolution of calcium and bicarbonate dominates. As the water continues to move downgradient, further modifications are at first limited. By observing the redox potential (Eh) of abstracted groundwater, a sharp redox barrier is detected beyond the edge of the confining layer, corresponding to the complete exhaustion of dissolved oxygen. Bicarbonate increases and the pH rises until buffering occurs at about 8.3. Sulphate concentrations remain stable in the oxidizing water, but decrease suddenly just beyond the redox boundary due to sulphate reduction. Groundwater becomes steadily more reducing as it flows downgradient, as demonstrated by the presence of sulphide, increase in the solubility of iron and manganese and denitrification of nitrate. After some further kilometres, sodium begins to increase by ion exchange at the expense of calcium, producing a natural softening of the water. Eventually, the available calcium in the water is exhausted, but sodium continues to increase to a level greater than could be achieved purely by cation exchange. As chloride also begins to increase, this marks the point at which recharging
water moving slowly down through the aquifer mixes with much older saline water present in the sediments (Figure 4.1). The observed hydrochemical changes can thus be interpreted in terms of oxidation/reduction, ion exchange and mixing processes. In arid and semi-arid regions, evapotranspiration rates are much higher, recharge is less, flow paths longer and residence times much greater and hence much higher levels of natural mineralization, often dominated by sodium and chloride, can be encountered. Thus the major ion contents and TDS are often high. In some desert regions, even if groundwater can be found it may be so salty (extremely high TDS) as to be undrinkable, and the difficulty of meeting even the most basic domestic requirements can have serious impacts on health and livelihood.

Natural variations in pH and oxygen status are also important and are not restricted to deep environments. Many groundwaters in tropical regions in weathered basement aquifers and alluvial sequences have low pH, and the reducing conditions which prevail can promote the mobilization of metals and other parameters of health significance such as arsenic. Thus prevailing hydrochemical conditions of the groundwater that are naturally present and develop need to be taken into account when: (i) developing schemes for groundwater abstraction for various uses and in protecting groundwater; and (ii) considering the transport and attenuation of additional chemicals entering groundwaters due to human activity.

4.1.2 Conceptual models and attenuation processes

Effective prediction of transport of chemical pollutants through a subsurface groundwater system and associated assessments of risk requires a valid conceptual model of the contaminant migration scenario. The classical contaminant conceptual model is one of a near-surface leachable source zone where chemical contaminant is leached, i.e. dissolved/solubilized, into water infiltrating through the source (Figure 4.2). A dissolved-phase chemical solute plume subsequently emerges in water draining from the base of the contaminant source zone and moves vertically downward through any unsaturated zone present. The dissolved solute plume ultimately penetrates below the water table to subsequently migrate laterally in the flowing groundwater. Many sources, e.g. a landfill, chemical waste lagoon, contaminated industrial site soils, pesticide residues in field soils, may have sufficient chemical mass to enable them to act as long-term generators of dissolved-phase contaminant plumes; potentially such sources can last decades. This will lead to continuous dissolved-phase plumes extending from these sources through the groundwater pathway that grow with time and may ultimately reach distant receptors unless attenuation processes operate. This near-surface leachable source – dissolved-plume conceptual model is the model most frequently invoked and the one to which groundwater vulnerability and protection concepts and groundwater risk-assessment models are most easily applied. It is important to note, however, that the above conceptualization may be too simplified and alternative conceptual models need to be invoked in some cases, most notably for non aqueous phase liquids (NAPLs) as discussed in Section 4.5.
Attenuation processes operative in the groundwater pathway, both for unsaturated and saturated zones, are summarized below and briefly described in the text that follows. Further details may be found in the texts referenced in other sections of this chapter.

DEF

**Advection and dispersion**

Advection is the transport of dissolved solute mass present in groundwater due to the bulk flow (movement) of that groundwater. Advection alone (with no dispersion or reactive processes occurring) would cause a non-reactive solute to advect (move) at the mean groundwater pore velocity. All solutes undergo advection, however, reactive solutes are subject to influences by other processes detailed below.

Molecular diffusion is the movement of solute ions in the direction of the concentration gradient from high towards low concentrations. It affects all solutes.

Mechanical dispersion causes spreading of solute and hence dilution of concentrations, it arises from the tortuosity of the pore channels in a granular aquifer and of the fractures in a consolidated aquifer and the different speeds of groundwater within flow channels of varying width. It affects all solutes.
**Retardation**
Sorption is a process by which chemicals or organisms become attached to soils and/or the geologic rock material (aquifer solids) and removed from the water. Often the sorption process is reversible and solutes desorb and hence dissolved-solute plumes are retarded, rather than solutes being permanently retained by the solids.

Cation exchange is the interchange between cations in solution and cations on the surfaces of clay particles or organic colloids.

Filtration is a process that affects particulate contaminants (e.g. organic/inorganic colloids or microbes) rather than dissolved solutes. Particles larger than pore throat diameters or fracture apertures are prevented from moving by advection and are therefore attenuated within the soil or rock.

**Reactions and transformations of chemicals**
Chemical reactions (abiotic reactions) are classical chemical reactions that are not mediated by bacteria. They may include reaction processes such as precipitation, hydrolysis, complexation, elimination, substitution, etc., that transform chemicals into other chemicals and potentially alter their phase/state (solid, liquid, gas, dissolved).

Precipitation is the removal of ions from solution by the formation of insoluble compounds, i.e. a solid-phase precipitate.

Hydrolysis is a process of chemical reaction by the addition of water.

Complexation is the reaction process by which compounds are formed in which molecules or ions form coordinate bonds to a metal atom or ion.

Biodegradation (biotic reactions) is a reaction process that is facilitated by microbial activity, e.g. by bacteria present in the subsurface. Typically molecules are degraded (broken down) to molecules of a simpler structure that often have lower toxicity.

**Advection**
As described in Chapter 2, groundwater moves due to the presence of a hydraulic gradient and may be characterized by the Darcy velocity q (alternatively named the specific discharge). The Darcy velocity may be calculated via Darcy’s law and is the product of the geologic media hydraulic conductivity K and the groundwater hydraulic gradient i. The actual mean groundwater pore (linear) velocity of groundwater, henceforth referred to as the ‘groundwater velocity’ v differs from the Darcy velocity as flow can only occur through the effective porosity n_e of the formation. The groundwater velocity may be quantified by modifying the Darcy equation:

\[ v = \frac{-Ki}{n_e} \] (Eqn. 4.1)
Advection is the transport of dissolved solutes in groundwater due to the bulk movement of groundwater. The mean advective velocity of non-reactive solutes is equal to the groundwater velocity, \( v \) (Eqn. 4.1) and is normally estimated by knowledge of the Equation 4.1 hydrogeological parameters. Occasionally \( v \) may be estimated from the mean position of a solute plume, typically within a groundwater tracer test (Mackay et al., 1986). Reactive solutes also advect with the flowing groundwater, however, their velocities are modified due to co-occurrence of attenuation processes.

**Dispersion**

All reactive and non-reactive solutes will undergo spreading due to dispersion, causing dissolved-phase plumes to broaden both along and perpendicular to the groundwater flow direction (Figure 4.3). Dispersion is most easily observed for ‘conservative’ non-reactive solutes, such as chloride, as these only undergo advection and dispersion. Dispersion causes mixing of the dissolved-solute plume with uncontaminated water and hence concentration dilution as well as plume spreading. Longitudinal dispersion, spreading in the direction of predominant groundwater flow, is greatest causing solutes to move at greater or less than the mean advective velocity \( v \). Solute spreading is due to mechanical dispersion that can arise at the pore-scale due to (Fetter, 1999): (i) fluids moving faster at pore centres due to less friction; (ii) larger pores allowing faster fluid movement; (iii) routes of varying tortuosity around grains. At a larger scale, macro-dispersion is controlled by the distribution of hydraulic conductivities in the geologic domain; greater geological heterogeneity resulting in greater plume spreading. The above processes cause increasing dispersion with plume travel distance, i.e. dispersion is scale dependent (Gelhar, 1986; Fetter, 1999).

![Figure 4.3. Dispersion of a pulse release of dissolved-solute plume](image-url)

Plume dispersion in other directions is much reduced. Transverse horizontal spreading may arise from flowpath tortuosity and molecular diffusion due to plume...
transverse vertical spreading occurs for similar reasons, but is generally more restricted due to predominantly near-horizontal layering of geologic strata. Overall, a hydrodynamic dispersion coefficient \( D \) is defined for each direction (longitudinal, transverse horizontal, transverse vertical):

\[
D = \alpha v + D^* \quad \text{(Eqn. 4.2)}
\]

which is seen to depend upon \( D^* \), the solute’s effective diffusion coefficient and \( \alpha \) the geologic media dispersivity. Dispersion parameters are most reliably obtained from tracer tests or, less reliably, at the larger (>250 m) scale, by model fitting to existing plumes. Collated values have yielded simple empirical relationships to estimate dispersion, e.g. the longitudinal dispersivity is often approximated to be 0.1 (10 per cent) of the mean plume travel distance (Gelhar, 1986). However, such relationships are very approximate.

**Retardation**

The processes that cause retardation (slowing down) of dissolved-solute plume migration include filtration, sorption and cation exchange. Filtration is a process that affects particulate contaminants (e.g. organic/inorganic colloids or microbes) rather than dissolved solutes, the key focus here. Sorption is a process by which chemicals or organisms become attached to soils and/or the geologic rock material (aquifer solids) and are removed from the water. Often the sorption process is reversible and solutes desorb back into the water phase and hence dissolved-solute plumes are retarded, rather than solutes being permanently retained by the solids. Preferred sorption sites depend upon the chemical solute properties, in general clay strata or organic matter within the geologic solid media are key sorption sites. Such sites may, however, be limited and sorption to other mineral phases, e.g. iron oxyhydroxides, may become important in some cases. Sorption processes normally lead to a Retardation Factor, \( R_i \), being defined that is the ratio of the mean advective velocity (conservative solute velocity) \( (v) \) to the mean velocity of the retarded sorbing solute plume \( (v_i) \):

\[
R_i = v / v_i \quad \text{(Eqn. 4.3)}
\]

Typically \( R_i \) is not estimated from Equation 4.3, rather various methods may be used to estimate \( R_i \) relating to the specific chemical nature of the sorption interaction and a relevant sorption coefficient (e.g. see Section 4.5.2). Sorption-related processes can be sensitive to the environmental conditions. For example, relatively small pH changes may cause significant changes to the mobilization of metals or perhaps organic contaminants that are themselves acids or bases, e.g. phenols or amines.

**Reactions and transformations of chemicals**

Many chemicals undergo reaction or transformation in the subsurface environment. In contrast to retardation, contaminants may be removed rather than simply slowed down. Reactions of harmful chemicals to yield benign products prior to arrival at a receptor are the ideal, e.g. many toxic hydrocarbons have potential to biodegrade to simple organic acids (of low health concern and themselves potentially degradable), carbon dioxide (bicarbonate) and water. Transformation often causes a deactivation (lowering) of
toxicity. Reactions and/or transformations incorporate processes such as chemical precipitation, complexation, hydrolysis, biodegradation (biotic reactions) and chemical reactions (abiotic reactions).

Chemical precipitation and complexation are primarily important for the inorganic species. The formation of coordination complexes is typical behaviour of transition metals, which provide the cation or central atom. Ligands include common inorganic anions such as Cl-, F-, Br-, SO4\(^{2-}\), PO4\(^{3-}\) and CO3\(^{2-}\) as well as organic molecules such as amino acids. Such complexation may facilitate the transport of metals.

Biodegradation is a reaction process mediated by microbial activity (a biotic reaction). Naturally present bacteria may transform the organic molecule to a simpler product, e.g. another organic molecule or even CO\(_2\). Biodegradation has wide applicability to many organic chemicals in a diverse range of subsurface environments. Rates of biodegradation vary widely, some compounds may only degrade very slowly, e.g. high molecular weight polynuclear aromatic hydrocarbons (PAHs) that are relatively recalcitrant (unreactive). Rates are also very dependent upon environmental conditions, including redox, microbial populations present and their activity towards contaminants present.

Abiotic reactions, classic chemical reactions not mediated by bacteria, have been found to be of fairly limited importance in groundwater relative to biodegradation. For example, a few organics, e.g. 1,1,1-trichloroethane (1,1,1-TCA) and some pesticides, may readily undergo reaction with water (hydrolysis), others such as the aromatic hydrocarbon benzene are essentially unreactive to water and a range of other potential chemical reactions.

Potential for attenuation
Potential for attenuation processes to occur varies within the various subsurface zones, i.e. soil, unsaturated and saturated zone. Attenuation processes can be more effective in the soil rather than aquifers due to higher clay contents, organic carbon, microbial populations and replenishable oxygen. This makes the soil a very important first line of defence against groundwater pollution, often termed ‘protective layer’. Consideration of the soil and its attenuation properties is a key factor in assessing the vulnerability of groundwater to pollution (Chapter 8). This also means that where the soil is thin or absent the risk of groundwater pollution may be greatly increased. Many human activities that give rise to pollution by-pass the soil completely and introduce pollutants directly into the unsaturated or even saturated zones of aquifers. Examples include landfills, leaking sewers, pit latrines, transportation routes in excavated areas and highway drainage.

4.2 NATURAL INORGANIC CONSTITUENTS
The occurrence of natural constituents in groundwater varies greatly depending on the nature of the aquifer. In general, aquifers in magmatites and metamorphic rocks show lower dissolved contents than in carbonate or sedimentary rocks. The mobility and thus the concentration of nearly all natural groundwater constituents can be significantly
influenced by changes of physical and chemical conditions in groundwater through human activities.

Fluoride and arsenic are now recognized as the most serious inorganic contaminants in drinking-water on a worldwide basis. Further natural constituents that can cause a public health risk addressed in this chapter (in alphabetical order) are selenium, radon and uranium. Although nitrate has occasionally been found naturally in health-relevant concentrations, in most cases these are caused anthropogenically, and therefore nitrate is addressed in Section 4.3.

4.2.1 Arsenic

Health aspects

The International Agency for Research on Cancer (IARC) has classified arsenic (As) as a Group 1 human carcinogen (IARC, 2001). The health effects of arsenic in drinking-water include skin cancer, internal cancers (lung, bladder, kidney) and peripheral vascular disease (blackfoot disease). Evidence of chronic arsenic poisoning includes melanosis (abnormal black-brown pigmentation of the skin), hyperkeratosis (thickening of the soles of the feet), gangrene and skin and bladder cancer (WHO, 2003a). Arsenic toxicity may not be apparent for some time but the time to appearance of symptoms and the severity of effects will depend on the concentration in the drinking-water, other sources of exposure, dietary habits that may increase arsenic concentrations in staple dishes and a variety of other possible nutritional factors.

While earlier maximum allowable concentrations recommended by WHO for arsenic in drinking-water were higher, in 1993 the provisional WHO guideline value for arsenic in drinking-water was reduced to 10 µg/l based on concerns regarding its carcinogenicity in humans (WHO, 2004a). Regulations in some countries, e.g. the European Union (EU), Japan and the USA follow this guideline value and Australia has established a drinking-water standard for arsenic of 7 µg/l. A number of countries operate at present at a 50 µg/l standard, which corresponds to the provisional WHO guideline value before 1993. Some national authorities are currently seeking to reduce their own limits in line with the WHO guideline value. It is important to realize that the WHO Guidelines emphasize the need for adaptation of national standards to local health priorities, social, cultural, environmental and economic conditions and also advocate progressive improvement that may include interim standards. Furthermore, the WHO Guidelines emphasises the scientific uncertainty of the dose-response curves at low intakes and thus in deriving the guideline value of 10 µg/l. For improving public health benefits, other issues may therefore take priority over upgrading the sensitivity of analytical facilities for
detecting lower concentrations or investing in upgrading drinking-water supplies to reduce arsenic concentrations to levels below 50 µg/l.

In recent years both the WHO guideline value and current national standards for arsenic have been found to be frequently exceeded in drinking-water sources. The scale of the arsenic problem in terms of population exposed to high arsenic concentrations is greatest in Bangladesh with between 35 and 77 million people at risk (Smith et al., 2000). However, many other countries are also faced with elevated arsenic concentrations in groundwater, such as Hungary, Chile, Mexico, northeast Canada, the western USA and many countries in South Asia. More detailed information on occurrence and health significance of arsenic can be found in ‘Arsenic in Drinking-water’ (WHO, In Press).

Occurrence
Arsenic is an ubiquitous element found in soils and rocks, natural waters and organisms. It occurs naturally in a number of geological environments, but is particularly common in regions of active volcanism where it is present in geothermal fluids and also occurs in sulphide minerals (principally arsenopyrite) precipitated from hydrothermal fluids in metamorphic environments (Hem, 1989). Arsenic may also accumulate in sedimentary environments by being co-precipitated with hydrous iron oxides or as sulphide minerals in anaerobic environments. It is mobilized in the environment through a combination of natural processes such as weathering reactions, biological activity and igneous activity as well as through a range of anthropogenic activities. Of the various routes of exposure to arsenic in the environment, drinking-water probably poses the greatest threat to human health.

Background concentrations of arsenic in groundwater in most countries are less than 10 µg/l. However, surveys performed in arsenic-rich areas showed a very large range, from <0.5 to 5000 µg/l (Smedley and Kinniburgh, 2001). Cases of large scale naturally occurring arsenic in groundwater are mainly restricted to hydrogeological environments characterized by young sediment deposits (often alluvium), and low-lying flat conditions with slow-moving groundwater such as the deltaic areas forming much of Bangladesh. Investigations by WHO in Bangladesh indicate that 20 per cent of 25 000 boreholes tested in that country have arsenic concentrations that exceed 50 µg/l. High concentrations of arsenic in groundwater also occur in regions where oxidation of sulphide minerals (such as arsenopyrite) has occurred (Alaerts et al., 2001).

Arsenic concentration in German groundwater downstream of abandoned waste disposal sites was found to have a mean concentration of 61 µg/l (n = 253 sites) due to arsenic leaching from domestic coal ashes deposited with household wastes. In contrast, the mean arsenic concentration in uncontaminated aquifers is 0.5 µg/l (n = 472 sites) (Kernsdorff et al., 1992).

Transport and attenuation
The concentration of arsenic in natural waters is normally controlled by solid-solution interactions, particularly in groundwater where the solid/solution ratio is large. In most soils and aquifers, mineral arsenic interactions are likely to dominate over organic matter-arsenic interactions, although organic matter may interact to some extent through its reactions with the surfaces of minerals (Smedley and Kinniburgh, 2001). One of the
best correlations between the concentration of arsenic in sediments and other elements is with iron. These interactions have also been the basis for the use of iron, aluminium and manganese salts in water treatment for arsenic removal.

Arsenic shows a high sensitivity to mobilization at the pH values typically found in groundwater (pH 6.5-8.5) and under both oxidizing and reducing conditions. Arsenic can occur in the environment in several oxidation states (-3, 0, +3 and +5) but in natural waters is mostly found in inorganic oxyanion forms as trivalent arsenite (As(III)) or pentavalent arsenate (As(V)). Redox potential (Eₚ) and pH are the most important factors controlling arsenic speciation. Relative to the other oxyanion-forming elements, arsenic is among the most problematic in the environment because of its mobility over a wide range of redox conditions (Smedley and Kinniburgh, 2001). Under oxidizing conditions, H₂AsO₄⁻ is dominant at low pH (less than ~pH 6.9), while at higher pH, HAsO₄²⁻ becomes dominant (H₃AsO₄ and AsO₄³⁻ may be present in extremely acidic and alkaline conditions, respectively). Under reducing conditions at less than ~pH 9.2, the uncharged arsenate(III)-species (H₃AsO₃) will predominate.

Transport is largely controlled by the aquifer conditions, particularly by adsorption on ferric oxohydroxides, humic substances and clays. Arsenic adsorption is most likely to be non-linear, with the rate of adsorption disproportionally decreasing with increasing concentrations in groundwater. This leads to reduced retardation at high concentrations. Since different arsenic species exhibit different retardation behaviour, arsenate (V) and arsenite (III) should travel through an aquifer with different amounts of interactions resulting in different velocities and increased separation along a flow path. This was demonstrated by Gulens et al. (in Smedley and Kinniburgh, 2001) using controlled soil-column experiments and various groundwaters. They showed that: (i) As(III) moved five to six times faster than As(V) under oxidizing conditions (at pH 5.7); (ii) with a ‘neutral’ groundwater (pH 6.9) under oxidizing conditions, As(V) moved much faster than under (i) but was still slower than As(III); (iii) under reducing conditions (at pH 8.3), both As(III) and As(V) moved rapidly through the column; (iv) when the amount of arsenic injected was substantially reduced, the mobility of the As(III) and As(V) was greatly reduced.

There is no process in the subsurface that alters arsenic species beside precipitation and adsorption. If groundwater with elevated arsenic levels is used for drinking-water supply, then treatment should be applied. There has been increasing research into this area and a number of low-cost household treatment technologies are available. Data from studies in Bangladesh suggest that low-cost technologies can remove arsenic to below 0.05 mg/l and sometimes lower (Ahmed et al., 2001). Technologies are also available for system treatment including activated alumina, chemical precipitation and reverse osmosis (for arsenate). However, in some situations, source substitution or mixing is preferable to arsenic removal (Alaerts et al., 2001).

4.2.2 Fluoride

Health aspects

Because fluoride is widely dispersed in the environment, all living organisms are widely exposed to it and tolerate modest amounts. In humans, fluoride has an affinity for
accumulating in mineralizing tissues in the body, in young people in bone and teeth, in older people in bone, and incorporation of fluoride into the matrix of teeth during their formation is protective against dental caries.

Health problems associated with the condition known as fluorosis may occur when fluoride concentrations in groundwater exceed 1.5 mg/l: staining of the tooth enamel may become apparent (dental fluorosis) and, with continued exposure, teeth may become extremely brittle. The incidence and severity of dental fluorosis, and the much more serious skeletal fluorosis, depend on a range of factors including the quantity of water drunk and exposure to fluoride from other sources, such as from high fluoride coal in China. Nutritional status may also be important. Estimates based on studies from China and India indicate that for a total intake of 14 mg/day there is a clear excess risk of skeletal adverse effects, and there is suggestive evidence of an increased risk of effects on the skeleton at total fluoride intakes above about 6 mg/day (WHO, 2004b). In its most severe form, this disease is characterized by irregular bone deposits that may cause arthritis and crippling when occurring at joints.

The WHO guideline value for fluoride is 1.5 mg/l since 1984 (WHO, 2004a). The EU maximum admissible concentration for fluoride in drinking-water is 1.5 mg/l. The US Environmental Protection Agency (US EPA) set an enforceable primary maximum contaminant level of 4 mg/l in water systems to prevent crippling skeletal fluorosis. A secondary contaminant level of 2 mg/l was recommended by US EPA to protect against objectionable dental fluorosis. In setting national standards for fluoride, it is particularly important to consider volumes of water intake (which are affected by climatic conditions) and intake of fluoride from other sources (e.g. food, air). Where higher fluoride concentrations occur in groundwater used as drinking-water source, treatment and/or change or mixing with other waste sources containing lower fluoride levels is necessary in order to meet drinking-water standards. In areas with high natural fluoride levels, the public health benefits of investments in the treatment necessary to meet the WHO guideline value may need to be balanced against other priorities for optimising public health benefits.

More detailed information on occurrence and health significance of fluoride can be found in ‘Fluorides in Drinking Water’ (Bailey et al., In Press).

**Occurrence**

Fluoride (F-) naturally occurs in rocks in many geological environments (Hem, 1989) but fluoride concentrations in groundwater are particularly high in groundwater associated with acid volcanic rocks, e.g. in Sudan, Ethiopia, Uganda, Kenya and Tanzania (Bailey et al., In Press). High concentrations of fluoride also occur in some metamorphic and sedimentary rocks that contain significant amounts of fluoride-bearing minerals such as fluorspar and apatite. Fluoride in water supply based on groundwater is a problem in a number of countries and over 70 million people worldwide are believed to be at risk of adverse health effects from consumption of water containing high levels of fluoride. India and China have particular problems and estimates suggest up to 60 million are affected in these two countries alone.

Exposure to fluoride from drinking-water depends greatly on natural circumstances. Levels in raw water are normally below 1.5 mg/l, but groundwater has been found to
contain >50 mg/l in some areas rich in fluoride-containing minerals. For example, in Kenya, 61 per cent of groundwater samples collected nationally from drinking-water wells exceeded 1 mg/l (Bailey et al., In Press). In general high fluoride concentrations in groundwater show a strong positive correlation with dissolved solids, sodium, and alkalinity, and a strong negative correlation with hardness.

Transport and attenuation
The concentration of fluoride ions in groundwater is driven by the presence of calcium ions and the solubility product of fluorite (CaF$_2$). In equilibrium, a calcium concentration of 40 mg/l equates to a concentration of 3.2 mg/l fluoride. In groundwater with a high concentration of calcium ions, fluoride concentrations rarely exceed 1 mg/l. Substantially higher fluoride concentrations in groundwater are usually caused by a lack of calcium. During high percolation rates, Flühler et al. (1985) observed increased fluoride concentration in the leachate of fluoride-enriched soils due to a limited additional delivery of calcium.

In groundwater with a high pH (>8) and dominated by sodium ions and carbonate species, fluoride concentrations commonly exceed 1 mg/l, and concentrations in excess of 50 mg/l have been recorded in groundwater in South Africa, and in Arizona in the USA (Hem, 1989). Moreover, the fluoride-ion (F$^-$) can interact with mineral surfaces, but is substituted by hydroxyl-ions at high pH values. Hem (1989) observed a fluoride concentration of 22 mg/l in a caustic thermal groundwater (pH 9.2, 50 ºC) in Owyhee County, Idaho. Fluoride ions form strong complexes especially with aluminium, beryllium and iron (III).

### 4.2.3 Selenium

Health aspects
Selenium is an essential trace element with a physiologically required intake of about 1 µg per kg body weight and day for adults. Deficiencies of selenium in diets may cause a number of health effects, although few reports of clinical signs of deficiency are available. However, the range of concentrations of this element in food and water that provide health benefits appears to be very narrow. When ingested in excess of nutritional requirements in food and drinking-water, selenium can cause a number of acute and chronic health effects including damage to or loss of hair and fingernails, finger deformities, skin lesions, tooth decay and neurological disorders (WHO, 2003b).

Although drinking-water generally accounts for less than 1 per cent of the typical dietary intake of selenium, in some circumstances naturally-occurring concentrations of selenium in groundwater may be sufficiently high to cause health problems. The WHO guideline value for selenium in drinking-water is 0.01 mg/l (WHO, 2004a).

Occurrence
Selenium has similar chemical properties and behaviour to sulphur (Hem, 1989), and is commonly associated with metal sulphide minerals in mineral deposits in a wide range of igneous rocks and with sulphur-rich coal. Sedimentary rocks and overlying soil in some regions may have high background concentrations of selenium. In the western part of the USA, these are associated with uranium and vanadium mineralization in shales.
and sandstones. In some semi-arid areas in China and India, selenium reaches high concentrations in soil and accumulates in plant tissue. Runoff from irrigated agriculture on seleniferous soil may contain dissolved selenium concentrations of up to 1 mg/l (Hem, 1989), and groundwater in these areas also typically contains high concentrations of leached selenium (Barceloux, 1999). Groundwater concentrations of selenium rarely exceed 1 µg/l (Hem, 1989), but up to 6000 µg/l have been reported (WHO, 2003b), and high concentrations (tens to hundreds of micrograms per litre) may occur in surface water and groundwater near metal-sulphide mine sites.

Selenium concentrations are often particularly high in surface waters and groundwater in coal mining areas where solid wastes and wastewater from coal power stations are disposed to the environment (Barceloux, 1999; US EPA, 2000).

**Transport and attenuation**

Selenium can exist in nature in four oxidation states: 0 (elemental selenium), -2 (selenide), +4 (selenite) and +6 (selenate). Under oxidizing conditions, the selenium occurs predominantly as selenite \( \text{SeO}_3^{2-} \) and selenate \( \text{SeO}_4^{2-} \) ions in natural waters. These ions have a very high solubility, and can reach very high concentrations in conditions when water is being subjected to high rates of evapotranspiration such as in regions with semi-arid or arid climates. Selenate and selenite minerals can accumulate with sulphates in soils in regions with semi-arid or arid climates.

High concentrations of selenium may also occur in groundwater beneath areas where intense irrigated agriculture flushes selenium compounds through the soil profile, and if groundwater pumping rates are high, the concentration of selenium may be progressively increased by the recycling of salts by the process of pumping, evaporation and recharge of pumped effluent. Consequently, selenium concentrations in shallow groundwater and in drainage from irrigated agriculture on seleniferous soils are often highly toxic to wildlife that ingests the water, as in the widely studied case of the Kesterson National Wildlife Refuge in the San Joaquin Valley of California (NRC, 1989). This water is also potentially toxic to humans who might use shallow groundwater as a drinking-water source, although water contaminated with high selenium concentrations is often too saline for potable use.

Under reducing conditions in groundwater or in marshes, selenium can also be removed from water through co-precipitation with sulphide minerals such as pyrite \((\text{FeS}_2)\) or the precipitation of ferroselite \((\text{FeSe}_2)\); through volatilization as dimethyl selenide or hydrogen selenide, or through the uptake of organo-selenium compounds by plants. Consequently, anaerobic bioreactors or artificial wetlands are being used for selenium removal from water, predominantly to protect receiving environments from the discharge of wastewater contaminated by selenium.

Selenium can be removed from water by adsorption onto iron oxyhydroxide minerals (especially ferricydrite) and this is one of the preferred water treatment methods. Selenium can also be removed from drinking-water by reverse osmosis and through the use of anion-exchange resins.
4.2.4 Radon

Health aspects
Radon is a radioactive gas emitted from radium, a daughter product of uranium that occurs naturally in rocks and soil. The main health effect of radon is to cause lung cancer. Radon, together with its decay products, emits alpha particles that can damage lung tissue. Although most radon is exhaled before it can do significant damage, its decay products can remain trapped in the respiratory system attached to dust, smoke and other fine particles from the air.

The global average human exposure to radiation from natural sources is 2.4 mSv per year with an average dose from inhalation of radon of 1.2 mSv per year. There are large local variations in this exposure depending on a number of factors, such as height above sea level, the amount and type of radionuclides in the soil, and the amount taken into the body in air, food, and water (WHO, 2004a). Unlike most other naturally occurring groundwater contaminants, most of the health effects of radon in groundwater are considered to be due to its contribution to indoor air quality rather than due to effects caused by direct ingestion of water. UNSCEAR has calculated the average doses from radon in drinking-water as low as 0.025 mSv/year via inhalation and 0.002 mSv/year from ingestion as compared to the inhalation dose from radon in the air of 1.1 mSv/year (UNSCEAR, 2000). The WHO has recommended a reference level of committed effective dose of 0.1 mSv from 1 year’s consumption of drinking-water (WHO, 2004a).

Stirring and transferring water from one container to another will liberate dissolved radon. Water that has been left to stand will have reduced radon activity, and boiling will remove radon completely. As a result, it is important that the form of water consumed is taken into account in assessing the dose from ingestion. Moreover, the use of water supplies for other domestic purposes will increase the levels of radon in the air, thus increasing the dose from inhalation. This dose depends markedly on the form of domestic usage and housing construction (NCRP, 1989). The form of water intake, the domestic use of water and the construction of houses vary widely throughout the world. It is therefore not possible to derive an activity concentration for radon in drinking-water that is universally applicable.

WHO recommends implementing controls if the radon concentration of drinking-water exceeds 100 Bq/litre (WHO, 2004a), and the EU likewise recommends assessing the need for protective measures at concentrations above this level (Euratom 2001/928; CEC, 2001).

Occurrence
Radon (Rn) is a naturally occurring, colourless, odourless gaseous element that is soluble in water. It occurs naturally only as a product of the radioactive decay of radium, itself a radioactive decay product of uranium. As is the case for uranium, concentrations of radon are directly related to the local geology, and are particularly high in granitic rocks and pegmatites and sediments with phosphate nodules or heavy mineral sand deposits.

Radon-222 is a frequently encountered radioactive constituent in natural waters and typically exceeds the concentration of other radionuclides, including uranium, thorium and radium, by orders of magnitude. High radon emanation, especially along fracture surfaces, contributes significantly to radon concentrations in groundwater. Data from
sampling campaigns indicate that there is a great degree of variability in the radon-222 concentration of samples drawn from any given rock type. The United States Geological Survey (USGS) conducted a study on occurrence of dissolved radon in groundwater in Pennsylvania (Senior, 1998). Findings of this study indicated that rock types with the highest median radon concentrations in groundwater include schist and phyllite (2400 pCi/l) as well as quartzite (2150 pCi/l). The geohydrologic groups with lowest median radon concentrations in ground water include carbonate rocks (540 pCi/l) and other rocks (360 pCi/l). Water from wells in gneiss had a median radon concentration of 1000 pCi/l, and water from wells in Triassic-age sedimentary rocks had a median radon concentration of 1300 pCi/l. Radon concentrations generally do not correlate with well characteristics, the pH of water or concentrations of dissolved major ions and other chemical constituents in the water samples.

Transport and attenuation
The rate of radon’s radioactive decay is defined by its half-life, which is the time required for one half of the amount of radon present to break down to form other elements. The half-life of radon is 3.8 days. Several factors probably control the concentration of radon-222 in a water supply. The flux of radon-222 within the ground may be controlled by the radium-226 concentration in the surrounding rocks, the emanation fraction for the radon-222 from the rock matrix and the permeability of the rock to radon-222 movement. For a given flux, the concentration of radon-222 in a water supply would then also be controlled by the ratio of aquifer surface area to volume.

4.2.5 Uranium

Health aspects
Uranium is a heavy metal of toxicological rather than radiological relevance in drinking-water. In particular, it is of concern because of its impact on kidney function following long-term exposure. Because of uncertainties regarding the toxicity of uranium for human beings the WHO has proposed a provisional drinking-water guideline value of 15 µg/l (WHO, 2004a; 2005a). The US EPA maximum contaminant level for uranium in drinking-water is 30 µg/l.

Occurrence
Uranium (U) is widely distributed in the geological environment, but concentrations in groundwater are particularly high in granitic rocks and pegmatites, and locally in some sedimentary rocks like sandstones. Uranium often occurs in oxidizing and sulphate-rich groundwater. There are three naturally occurring isotopes of uranium: \(^{234}\text{U}\) (<0.01 per cent), \(^{235}\text{U}\) (0.72 per cent), and \(^{238}\text{U}\) (99.27 per cent). All three isotopes are equally toxic.

Concentrations of uranium in natural waters usually range between 0.1 and 10 µg/l (Hem, 1989), but are often up to 100 µg/l in groundwater in areas underlain by granitic rocks, and may exceed 1 mg/l near uranium mineral deposits.

Transport and attenuation
The transport of uranium in groundwater varies widely according to the aquifer conditions. In anoxic conditions, uranium is reduced to U(IV) which is relatively
insoluble and precipitates. In oxidizing environments, uranium exists mainly as \( \text{UO}_2X_2^- \) (= uranyl)-compounds with U(VI) which is considerably more soluble. Even with the higher solubility of U(VI), transport of U(VI) can be limited as it sorbs strongly to solid surfaces at circum-neutral pH. Very low and very high pH conditions limit sorption as does the presence of certain complexing ligands such as natural organic matter, organic chelating agents and carbonate, all of which can significantly enhance the transport of uranium.

4.3 NITROGEN SPECIES

Ammonia, nitrate and nitrogen containing organic compounds of humic type are the dominating nitrogen compounds in groundwater. Though nitrite is highly toxic, it usually occurs only in very low concentrations in groundwater and these are not relevant to human health. However, nitrite can become relevant from conversion of ammonia or nitrogen in the drinking-water supply system or human body.

**NOTE**

Though nitrogen may occur naturally in groundwater, the main sources of groundwater pollution are human activities such as agriculture and sanitation (see Chapters 9 and 10).

*Health aspects*

Ammonia in drinking-water is not of direct health relevance, and therefore WHO have not set a health-based guideline value. However, ammonia can compromise disinfection efficiency, can cause the failure of filters for the removal of manganese, and can cause taste and odour problems. Also in distribution systems it can lead to nitrite formation which is of health relevance.

The toxicity of nitrate to humans is mainly attributable to its reduction to nitrite. Nitrite, or nitrate converted to nitrite in the body, causes a chemical reaction that can lead to the induction of methaemoglobinaemia, especially in bottle-fed infants. Methaemoglobin (metHB), normally present at 1-3 per cent in the blood, is the oxidized form of haemoglobin (Hb) and cannot act as an oxygen carrier in the blood. The reduced oxygen transport becomes clinically manifest when the proportion of metHB concentration reaches 5-10 per cent or more of normal Hb values (WHO, 1996a). Nitrate is enzymatically reduced in saliva forming nitrite. Additionally, in infants under one year of age the relatively low acidity in the stomach allows bacteria to form nitrite. Up to 100 per cent of nitrate is reduced to nitrite in infants, as compared to 10 per cent in adults and children over one year of age. When the proportion of metHB reaches 5-10 per cent, the symptoms can include lethargy, shortness of breath and a bluish skin colour ("blue baby syndrome"). Anoxia and death can occur at very high uptakes of nitrite and nitrate from drinking-water.

Methaemoglobinaemia is observed in populations where food for infant formula in prepared with water containing nitrate in excess of around 50 mg/l, but other factors are also involved in disease causation. The risk is enhanced by sewage contamination. This
contributes nitrate and renders chemical conditions in the water to be reducing, thus
supporting the presence of nitrate reducing bacteria. Moreover, ingestion of microbially
contaminated water causes gastroenteritis infection which would also predispose the
infant to a nitrate reducing conditions and thereby more nitrite exposure (WHO, 2004a).
A review of numerous case studies of water-related infant methaemoglobinemia in the
1980s indicated high correlation with microbial contamination of the water (US EPA,

The weight of evidence is strongly against an association between nitrite and nitrate
demonstrate increased tumour incidence only after exposure to extremely high levels of
nitrite in the order of 1000 mg/l in drinking-water and simultaneously high levels of
nitrosatable precursors (WHO, 1996b). At lower nitrite levels, tumour incidence
resembled those of control groups treated with the nitrosatable compound only. On the
basis of adequately performed and reported studies, it may be concluded that nitrite itself
is not carcinogenic to animals (WHO, 1996a).

Based on methaemoglobinemia in infants (an acute effect), the WHO has established
a guideline value for nitrate ion of 50 mg/l as NO$_3^-$ and a provisional guideline value for
nitrite of 3 mg/l as NO$_2^-$ (WHO, 2004a). Because of the possibility of simultaneous
occurrence of nitrite and nitrate in drinking-water, the sum of the ratios of the
concentrations ($C_{nitrate}$ or $C_{nitrite}$) of each to its guideline value ($GV_{nitrate}$ or $GV_{nitrite}$) should
not to exceed one.

**Sources and occurrence**

Nitrogen is present in human and animal waste in organic form, which may then
subsequently be mineralized to inorganic forms. Ammonia (ionized as NH$_4^+$, non-
ionized as NH$_3$) as well as urea (NH$_2$)$_2$CO is a major component of the metabolism of
mammals. Ammonia in the environment mainly results from animal feed lots and the use
of manures in agriculture (Chapter 9), or from on-site sanitation or leaking sewers
(Chapter 10). Thus ammonia in water is often an indicator of sewage pollution. The
nitrite ion (NO$_2^-$) contains nitrogen in a relatively unstable oxidation state. Nitrite does
not typically occur in natural waters at significant levels, except temporarily under
reducing conditions. Chemical and biological processes can further reduce nitrite to
various compounds or oxidize it to nitrate. The nitrate ion (NO$_3^-$) is the stable form of
combined nitrogen for oxygenated systems. Nitrate is one of the major anions in natural
waters, but as for ammonia, concentrations can be greatly elevated due to agricultural
activities (Chapter 9), and sanitation practices (Chapter 10).

Natural levels of ammonia in ground and surface waters are usually below 0.2 mg/l,
and nitrate concentrations in groundwater and surface water typically range between 0-
18 mg/l as NO$_3^-$. Although elevated concentrations of nitrate in groundwater are mostly
caued by agricultural activity or sanitation practices, natural nitrate concentrations can
also exceed 100 mg/l as NO$_3^-$ as observed in some arid parts of the world such as the
Sahel and north Africa (Edmunds and Gaye, 1994) and the arid interior of Australia
(Box 4.1).
Box 4.1. Naturally-occurring high nitrate in Australia

High groundwater nitrate concentrations have been observed in the arid interior of Australia, commonly exceeding 45 mg/l, and often exceeding 100 mg/l in groundwater which otherwise meets national and international drinking-water guidelines (Lawrence, 1983; Barnes et al., 1992). The nitrate in this region is partially derived from nitrogen fixing by native vegetation, and by cyanobacteria crusts on soils. Termite mounds appear to be a significant contributory source of the nitrate (Barnes et al., 1992), possibly due to the presence of nitrogen fixing bacteria in many termite species, and the nitrogen-rich secretions used to build the walls of the mounds. Nitrate is leached to the water table in arid Australia after periodic heavy rainfall events, particularly after bush fires that allow soluble nitrate salts to accumulate in soils. Denitrification in these soils appears to be inhibited by low carbon levels.

Transport and attenuation

Ammonium (NH$_4^+$) shows a high tendency for adsorption to clay minerals, which limits its mobility in the subsurface (saturated and unsaturated zones). In contrast, interactions between minerals and nitrate or nitrite are usually negligible and both ions are mobile in the subsurface.

Under aerobic conditions in the subsurface oxidation of ammonium through nitrite to nitrate by microorganisms is the only process where nitrate is formed in natural systems.

**DEF**

*Nitrification* is the biological conversion of ammonium through nitrite to nitrate. *Denitrification* is the biological process of reducing nitrate to ammonia and nitrogen gas.

Despite the natural high concentrations of nitrate in groundwater in much of inland Australia, there have been no verified cases of MetHb in Aboriginal people (Hearn et al., 1993), who are the main users of groundwater in this part of the country. Because potable quality groundwater is scarce in the interior of Australia, and because the use of water is vital for maintaining hygiene in the region, the National Health and Medical Research Council revised the national water quality guidelines in 1990. The revised guidelines allow the use of groundwater with concentrations of nitrate exceeding 100 mg/l for all non-potable needs, up to 100 mg/l for potable use except for infants under 3 months old, and up to 50 mg/l for infants under 3 months old. Although technologies exist to remove nitrate from drinking-water using microbial denitrification, the equipment is difficult to maintain in remote aboriginal settlements, and it was considered in this case that changing guideline concentrations would produce better health outcomes. These changes were incorporated into the Australian drinking-water guidelines in 1996. The autotrophic conversion of ammonia to nitrite and nitrate (nitrification) requires oxygen. The discharge of ammonia nitrogen into groundwater and its subsequent oxidation can thus seriously reduce the dissolved oxygen content in
shallow groundwater, especially where high ammonia loads are applied and re-aeration of the soil is limited.

In the absence of dissolved oxygen (such as in some deep or confined groundwaters), denitrification can occur, driven by denitrifying bacteria. Under fully anaerobic conditions, in an aquifer where predominantly sulphides serve as reduction agents, the microbial oxidation of sulphides into sulphate and simultaneous reduction of nitrate to nitrogen gas can occur which also reduces the nitrate content.

As microbial processes, both nitrification and denitrification are affected by many factors that are of importance to microbial activity. Nitrification and denitrification are optimal at about 25°C and are inhibited at 10°C or less. Other regulating factors are pH and all factors affecting the diffusion of oxygen such as soil density, grain structure, porosity and soil moisture. Warm, moist and well aerated soils provide ideal conditions for nitrification. Denitrification occurs only under anoxic or almost anoxic conditions. Beside the presence of nitrate, the denitrifying bacteria require a carbon source. A soil moisture of more than 80 per cent has been found to be essential for denitrification. Thus in many settings natural attenuation can substantially reduce nitrate concentrations in groundwater over time, but rates of attenuation strongly depend on conditions in the aquifer.

4.4 METALS

The following focuses on those metals which are toxic to humans and which have frequently been observed as groundwater contaminants in connection with human activities and/or have physical and chemical properties which make them potential groundwater contaminants, i.e. cadmium (Cd), lead (Pb), nickel (Ni), chromium (Cr), and copper (Cu).

Health aspects

Cadmium has a high renal toxicity, which is not only due to its mode of action but also to its irreversible accumulation in the kidney. The health based guideline value for cadmium in drinking-water is 3 µg/l (WHO, 2004a).

Lead is a strong neurotoxin in the unborn, newborn and young children. It crosses the placenta easily and is toxic to both the central and the peripheral nervous system, thus causing cognitive and behavioural effects (WHO, 2004a). The threshold of neurotoxicological concern, defined as a group based mean blood lead level, has decreased continually during the last 10 to 20 years, and epidemiological evidence indicates lead levels above 30 µg of lead per litre of blood to be associated with intelligence quotient deficits in children (WHO, 2004a). The use of lead in antiknock and lubricating agents in petrol is being phased out in many countries, thus decreasing this source of contamination. However, a major main source of exposure to lead through water is household plumbing systems, i.e. pipes, fittings, solder and connections from the mains to homes. Dissolution from such materials strongly depends on chemical properties of the drinking-water, with soft, acidic water dissolving the largest amount. The WHO guideline value for lead in drinking-water is 10 µg/l (WHO, 2003c; 2004a).
The significance of Nickel from the health point of view is mainly due to its high allergenic potential. The WHO drinking-water guideline value for the protection of sensitive persons is 20 µg/l (WHO, 2004a).

Chromium can be found in the environment in two valency states, Cr(III) and Cr(VI). The former predominates in soils, whereas the latter occurs exclusively as chromate (CrO$_4^{2-}$) from anthropogenic sources. Cr(VI) is the form which is of toxicological significance because of its easy uptake into cells together with SO$_4^{2-}$ and PO$_4^{3-}$. Within cells and during its reduction to Cr(III), the chromate ion represents a considerable genotoxic and clastogenic potential (Costa, 2002). However, since even very high doses of Cr(VI) are subjected to rapid chemical reduction in the upper gastrointestinal tract (Kerger et al., 1997), only negligible amounts of Cr(VI) should reach the blood compartment and other body fluids and organs. The health based guideline value for chromium in drinking-water is 50 µg/l (WHO, 2004a), and while higher concentrations have been reported from some drinking-water supplies, most studies indicate the concentration of chromium in groundwater to be low (WHO, 2003d). Cr(III) in drinking-water may eventually be oxidized to Cr(VI) during its ozonation.

Copper is an essential trace element with an optimal daily oral intake of 1-2 mg per person. Naturally occurring copper concentrations in groundwater are without any health significance and scatter mostly around 20 µg/l. If drinking-water drawn from groundwater contains elevated levels, in most situations corrosion of copper pipes is the primary source. Mean concentrations of more than 2 mg/l could lead to liver cirrhosis in babies if their formula is repeatedly prepared using such water (Zietz et al., 2003). The prevalent endpoint of acute copper toxicity by time, concentration and dose is nausea (Araya et al., 2003). The health based guideline value for copper in drinking-water is 2 mg/l (WHO, 2004a; 2004c).

Sources and occurrence
Metals from activities such as mining, manufacturing industries, metal finishing, wastewater, waste disposal, agriculture and the burning of fossil fuels can reach concentrations in groundwater which are hazardous to human health. Chapter 11 lists industry types together with the metals they commonly emit (see Table 11.2.) Metals are natural constituents in groundwaters, having their origin in weathering and solution of numerous minerals. However, natural concentrations of metals in groundwaters are generally low. Typical concentrations in natural groundwaters are <10 µg/l (copper, nickel), <5 µg/l (lead) or <1 µg/l (cadmium, chromium). Even so, the concentrations can locally increase naturally up to levels which are of toxicological relevance and can exceed drinking-water guidelines, e.g. in aquifers containing high amounts of heavy metal bearing minerals (ore). Metal concentrations in groundwater may be of particular concern where it is directly affected by manufacturing and mining as well as downstream of abandoned waste disposal sites. Another anthropogenic cause of elevated metal concentrations in groundwaters is the acidification of rain and soils by air pollution and the mobilization of metals at lower pH values. This problem predominantly appears in forested areas, because the deposition rates of the acidifying anions sulphur and nitrate from the atmosphere are evidently higher in forests due to the large surface of needles.
and leaves, and because soils in forests are generally poor in nutrients and have a low neutralization capacity against acids.

Transport and attenuation
Most of the metals of concern occur in groundwater mainly as cations (e.g. Pb\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\), Cd\(^{2+}\)) which generally become more insoluble as pH increases. At a nearly neutral pH typical for most groundwaters, the solubility of most metal cations is severely limited by precipitation as an oxide, hydroxide, carbonate or phosphate mineral, or more likely by their strong adsorption to hydrous metal oxides, clay or organic matter in the aquifer matrix. The adsorption decreases with decreasing pH. As a consequence, in naturally or anthropogenically acidified groundwaters metals are mobile and can travel long distances. Furthermore, as simple cations there is no microbial or other degradation.

In a soil solution containing a variety of heavy metal cations that tend to adsorb to particle surfaces, there is competition between metals for the available sites. Of several factors that determine this selectivity, ionic potential, which is equal to the charge of an ion over its ionic radius, has a significant effect. Cations with a lower ionic potential tend to release their solvating water molecules more readily so that inner sphere surface complexes can be formed. Selectivity sequences are arranged in order of decreasing ionic radius, which results in increasing ionic potential and decreasing affinity or selectivity for adsorption. As an example the following selectivity sequence of transition elements belonging to group IIb has been determined (Sposito, 1989):

\[
\text{Hg}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}
\]

As a consequence, mercury is the most strongly adsorbed; this being the probable reason for its generally very low concentration occurrence in groundwater.

Metals within the transition group differ in that electron configuration becomes more important than ionic radius in determining selectivity. The relative affinity of some metals belonging to different transition groups is given by:

\[
\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+}
\]

However, this sequence can be more or less changed in groundwater by naturally occurring complexing agents like fulvic acids which is especially true for copper (Schnitzer and Khan, 1972).

In addition, most oxyanions tend to become less strongly sorbed as the pH increases (Sposito, 1989). Therefore, the oxyanion-forming metals such as chromium are some of the more common trace contaminants in groundwater. Chromium is mobile as stable Cr(VI) oxyanion species under oxidizing conditions, but forms cationic Cr(III) species in reducing environments and hence behaves relatively immobile under these conditions. For example, in contaminated groundwater at industrial and waste disposal sites Chromium occurs as Cr\(^{3+}\) and CrO\(_4^{2-}\) species, with CrO\(_4^{2-}\) being much more toxic but less common than Cr\(^{3+}\). In most aquifers chromium is not very mobile because of precipitation of hydrous chromium(III)oxide. In sulphur-rich, reducing environments, many of the trace metals also form insoluble sulphides (Smedley and Kinniburgh, 2001).
### 4.5 ORGANIC COMPOUNDS

Organic compounds in groundwater commonly derive from breakdown and leaching of naturally occurring organic material, e.g. from organic-rich soil horizons and organic matter associated with other geologic strata, or human activity, e.g. domestic, agricultural, commercial and industrial activities.

Natural sources will always contribute some organic compounds to groundwater, often at low levels. Natural organic matter comprises water-soluble compounds of a rather complex nature having a broad range of chemical and physical properties. Typically, natural organic matter in groundwater is composed of humic substances (mostly fulvic acids) and non-humic materials, e.g. proteins, carbohydrates, and hydrocarbons (Thurman, 1985; Stevenson, 1994). While natural organic matter is a complex, heterogeneous mixture, it can be characterized according to size, structure, functionality, and reactivity. Natural organic matter can originate from terrestrial sources (allochthonous natural organic matter) and/or algal and bacterial sources within the water (autochthonous natural organic matter). Dissolved organic carbon (DOC) is considered to be a suitable parameter for quantifying organic matter present in groundwater; however, DOC is a bulk organic quality parameter and does not provide specific identification data and may also incorporate organic compounds arising from human activity. Natural organic matter, although considered benign, may still indirectly influence groundwater quality. For example, contaminants may bind to organic-matter colloids allowing their facilitated transport within groundwater, a process proposed (but not proven) to be of most significance for the more highly sorbing organic compounds. Also, routine chlorination of water supplies containing natural organic matter may form disinfection by-products such as trihalomethanes. However, because of their low direct health relevance, natural organic substances are not addressed further herein.

Human activity has released a vast range of anthropogenic organic chemicals, commonly termed ‘micro-pollutants’, to the environment, some of which may detrimentally impact groundwater quality. This chapter focuses on commercially and industrially derived chemicals which (i) have a high toxicity, (ii) have physical and chemical properties facilitating their occurrence in groundwater and (iii) have been observed to occur frequently as groundwater contaminants. Chapter 11 lists industry types together with substances that may potentially be released to the subsurface from their respective industrial activities. The occurrence of organic pollutants in groundwater is controlled not only by their use intensity and release potential, but also by their physical and chemical properties which influence subsurface transport and attenuation. Discussion of this aspect specific to organic chemicals follows and extends the general concepts covered in Section 4.1.

#### 4.5.1 Conceptual transport models for non aqueous phase liquids

A correct conceptual model of contaminant behaviour is essential for assessing subsurface organic contaminant migration. The classical near-surface leachable source zone – dissolved plume model presented earlier (Section 4.1.2, Figure 4.2) is not applicable for all organic substances. Of key importance is the recognition that organic chemicals have very different affinities for water, ranging from organic compounds that
are hydrophilic (“love” water) to organics that are hydrophobic (“fear” water). Such concepts are used below to develop appropriate contaminant conceptual models followed by discussion of specific transport processes applicable within the models developed.

Water is a highly polar solvent, so polar in fact that it develops a hydrogen-bonded structure and will easily dissolve and solvate ionic species. The vast majority of organic compounds are covalent molecules, rather than ionic species, and most have a limited tendency to partition or dissolve into water. Further, many organic compounds found in groundwater are used as liquids, e.g. hydrocarbon fuels or industry solvents. A focus upon organic liquids is hence relevant. Organic compounds that most easily partition or dissolve into water tend to be small molecules, have a polar structure and may hydrogen-bond with water. Examples include methanol (CH₃OH) and other short-chain alcohols, e.g. ethanol and propanols that may be used as de-icers, and ketones such as methyl-ethyl-ketone and ethers such as dioxane that are used as industrial solvents. Some compounds are so hydrophilic that they form a single fluid phase with the water and are said to be miscible with the water, e.g. methanol, acetone, dioxane.

Most organic compounds are, however, relatively hydrophobic as they are comparatively large molecules of limited polarity with low hydrogen-bonding potential. Most organic liquids are so hydrophobic that they form a separate organic phase to the water (aqueous) phase. They are immiscible with water and a phase boundary exists between the organic phase and the aqueous phase, with the organic phase generally being referred to as the non aqueous phase liquid (NAPL). When a separate organic NAPL exists it is important to consider the density of the NAPL relative to water as this controls whether the NAPL will be upper or lower phase relative to the water phase. Most hydrocarbon-based organic liquids have a density <1 (g/ml), e.g. benzene is 0.88 and pentane is 0.63 and when in contact with water will be the upper phase and “float” upon the water phase of density 1. Such “light” organic compounds are generally referred to as being LNAPLs.

In contrast, other hydrophobic organics have a relatively high density due to incorporation of dense chlorine (or other halogen) atoms in their structure and for example chlorinated solvents such as trichloroethene (TCE) and 1,1,1-trichloroethane (1,1,1-TCA) and polychlorinated biphenyl (PCB) mixtures have densities in the 1.1 to 1.7 range. Due to their density such organic phases will be the lower phase and ‘sink’ below the water phase. Such “dense” organic compounds are generally referred to as DNAPLs.

Although hydrophobic, LNAPL and DNAPL organics still have potential for some of their organic molecules to dissolve into the adjacent aqueous phase. The organics are ‘sparingly soluble’ and will have a finite solubility value in water leading to dissolved concentrations in the water phase. Solubility values achieved by individual organic compounds in water are highly variable between organics and controlled by their relative hydrophobicity. For example, small and/or polar organics have the greatest solubility with for example dichloromethane (DCM) (CH₂Cl₂) being one of the most soluble with a solubility of ca. ~20,000 mg/l, which contrasts with e.g. DDT, a large pesticide molecule that is not easily accommodated in the polar water structure and has a solubility of just about 0.1 mg/l. Similarly benzene, as single aromatic ring hydrocarbon, has a solubility
ca. 1,800 mg/l that is much greater than benzo[a]pyrene, a PAH of solubility ca. 0.004 mg/l that is composed of five adjacent aromatic rings.

The above provides fundamental understanding for conceptual models of organic contaminant transport in the subsurface and why specific organic compounds have a tendency to occur or not occur in groundwater. Hydrophilic miscible organics behave similarly to the classical leachable source model (Figure 4.2). In essence, a spill of e.g. a de-icer fluid at surface would migrate as a concentrated organic-aqueous fluid through the unsaturated zone and then migrate laterally in the groundwater as a concentrated dissolved-phase plume. Importantly, hydrophobic immiscible organics, i.e. NAPLs, exhibit very different behaviour. Conceptual models for LNAPL releases and DNAPL releases (Mackay and Cherry, 1989) are shown in Figures 4.4 and 4.5.

NAPLs may migrate as a separate NAPL phase and displace air and water from the pores they invade if they have sufficient head (pressure) to overcome the entry pressure to the pores or fractures. This head is controlled by aspects such as the spill volume and rate and the vertical column of continuous NAPL developed in the subsurface. NAPL migration is also controlled by its density and viscosity. Petrol fuel and chlorinated solvents have viscosities lower than water and more easily migrate in the subsurface; in contrast, PCB oils or coal tar (PAH-based) hydrocarbons may be very viscous and perhaps take years for the NAPL to come to a resting position in the subsurface. Chlorinated solvents such as PCE have high densities and may penetrate to significant depths through aquifer systems in very short time periods. Whereas dissolved pesticides may take years to decades to migrate through a 30 m unsaturated zone, DNAPL may migrate through such a zone in the order of hours to days (Pankow and Cherry, 1996). DNAPLs may penetrate discrete sand horizons and hairline fractures in clays and compromise clay units that are normally an effective barrier to dissolved plume migration.

At the water table, LNAPLs, being less dense than water, will form a floating layer of LNAPL on the water table often slightly elongated in the direction of the water table hydraulic gradient. DNAPL, in contrast may penetrate as a separate immiscible DNAPL below the water table. Predominant movement will be vertically downward due to its density, but some lateral spreading will occur as it encounters lower permeability strata. If spilt in sufficient volume and with sufficient driving head, the DNAPL may penetrate the full aquifer depth to the underlying aquitard/bedrock (Kueper et al., 1993). This should not be assumed to occur in all cases. Migrating NAPL leaves a trail of immobile residual NAPL droplets behind its migration pathway held by capillary forces causing NAPL to spread across an aquifer thickness. DNAPL accumulating on low permeability features, often referred to as pools, is potentially mobile. It may ultimately penetrate through discrete sand horizons and hairline fractures in clays and compromise clay units that are normally an effective barrier to dissolved plume migration.
Figure 4.4. Conceptual model of a light non aqueous phase liquid (LNAPL) release

Figure 4.5. Conceptual model of a dense non aqueous phase liquid (DNAPL) release
Often NAPL will remain relatively local to a site, possible exceptions being the migration of LNAPL to a local surface water and perhaps huge NAPL spills, e.g. at a poorly operated oil refinery/distribution facility. Risks posed to groundwater resources and supplies are most often concerned with the migration of the dissolved-phase plume formed by the contact of flowing groundwater with the spilt NAPL. Although the presence of NAPL may impede the flow of groundwater, e.g. in DNAPL pools and central LNAPL body, areas where NAPL residual saturations are lower will still be permeable to water and NAPL dissolution will occur. Often the mass of NAPL is so large and the dissolution (solubilization) of NAPL into water so slow that the entire NAPL body post spill should be regarded as a largely immobile source zone able to continuously generate a dissolved-phase solute plume of organics downgradient for years to decades, even centuries for low-solubility NAPLs. Thus historic spill sites may still constitute major sources of NAPL in the deep subsurface and cause very large dissolved-phase plumes, particularly where dissolved-phase plume attenuation is limited. In general, DNAPLs tend to pose the greatest groundwater threat as they reside deep in groundwater systems and many, being chlorinated, are less susceptible to attenuation. In contrast, LNAPLs are restricted to shallower groundwater-table depths, and are more susceptible to attenuation via biodegradation.

The above provides a basic introduction to NAPLs in groundwater. Much research and field experience has been gained since the pioneering NAPLs research of Schwille (1988) and the reader is referred to Mercer and Cohen (1990) and Pankow and Cherry (1996) and references therein for further details.

4.5.2 General aspects of transport and attenuation of organics

Some of the transport and attenuation processes introduced earlier require specific discussion for organic contaminants. Several physiochemical properties/parameters exert a key control over subsurface organic contaminant migration. A selection of parameters is listed in Table 4.1 for a range of organic chemicals of groundwater-health concern. Values for a specific parameter generally vary over orders of magnitude across the listed chemicals and infer substantial variations in transport and attenuation between organic contaminants. Table 4.1 is not exhaustive: there are many more organic chemicals; values of individual chemical parameters may show significant variability across the literature; and other parameters exist, most notably half-life, that due to their dependency on site conditions display significant variability (see Section 4.5.4 for references to some half-life literature). For more detailed databases and their supporting literature see e.g. US EPA (1996; 1999) and Montgomery (1996).
Table 4.1. Selected physiochemical parameter values for important organic groundwater contaminants at 20-25°C (Mercer and Cohen, 1990; US EPA, 1996; 1999) (see Section 4.5.3 for an explanation of the abbreviations)

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Density (g/ml)</th>
<th>Absolute viscosity (cP)</th>
<th>Aqueous solubility (mg/l)</th>
<th>Vapour pressure (atm.)</th>
<th>Henry's constant (atm. m³/mol)</th>
<th>KOC (ml/g)</th>
<th>KOW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic Hydrocarbons</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>0.87</td>
<td>0.60</td>
<td>175</td>
<td>0.13</td>
<td>0.0056</td>
<td>62</td>
<td>130</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.86</td>
<td>0.55</td>
<td>555</td>
<td>0.037</td>
<td>0.0064</td>
<td>140</td>
<td>540</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.87</td>
<td>0.68</td>
<td>152</td>
<td>0.0092</td>
<td>0.0064</td>
<td>200</td>
<td>1400</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>0.88</td>
<td>0.81</td>
<td>175</td>
<td>0.0087</td>
<td>0.0051</td>
<td>240</td>
<td>890</td>
</tr>
<tr>
<td>Chlorinated Hydrocarbons</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DCM</td>
<td>1.34</td>
<td>0.45</td>
<td>20000</td>
<td>0.48</td>
<td>0.0020</td>
<td>8.8</td>
<td>20</td>
</tr>
<tr>
<td>TCM</td>
<td>1.50</td>
<td>0.60</td>
<td>8200</td>
<td>0.20</td>
<td>0.0029</td>
<td>53</td>
<td>93</td>
</tr>
<tr>
<td>CTC</td>
<td>1.58</td>
<td>0.97</td>
<td>757</td>
<td>0.12</td>
<td>0.024</td>
<td>152</td>
<td>440</td>
</tr>
<tr>
<td>TCE</td>
<td>1.47</td>
<td>0.57</td>
<td>1100</td>
<td>0.076</td>
<td>0.0091</td>
<td>94</td>
<td>240</td>
</tr>
<tr>
<td>PCE</td>
<td>1.63</td>
<td>1.93</td>
<td>150</td>
<td>0.024</td>
<td>0.026</td>
<td>265</td>
<td>400</td>
</tr>
<tr>
<td>VC</td>
<td>Gas</td>
<td>Gas</td>
<td>2760</td>
<td>3.7</td>
<td>0.027</td>
<td>18</td>
<td>14</td>
</tr>
<tr>
<td>1,2-DCA</td>
<td>1.26</td>
<td>0.89</td>
<td>8520</td>
<td>0.084</td>
<td>0.00098</td>
<td>38</td>
<td>30</td>
</tr>
<tr>
<td>1,1-DCE</td>
<td>1.22</td>
<td>0.36</td>
<td>2250</td>
<td>0.79</td>
<td>0.034</td>
<td>65</td>
<td>69</td>
</tr>
<tr>
<td>cDCE</td>
<td>1.27</td>
<td>0.44</td>
<td>3500</td>
<td>0.27</td>
<td>0.0076</td>
<td>49</td>
<td>5.0</td>
</tr>
<tr>
<td>tDCE</td>
<td>1.26</td>
<td>0.40</td>
<td>6300</td>
<td>0.43</td>
<td>0.0066</td>
<td>38</td>
<td>3.0</td>
</tr>
<tr>
<td>1,2-DCB</td>
<td>1.30</td>
<td>1.32</td>
<td>100</td>
<td>0.0018</td>
<td>0.0021</td>
<td>379</td>
<td>2790</td>
</tr>
<tr>
<td>1,4-DCB</td>
<td>1.28</td>
<td>1.04</td>
<td>73</td>
<td>0.0014</td>
<td>0.0028</td>
<td>616</td>
<td>2580</td>
</tr>
<tr>
<td>Others</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>1.16</td>
<td>solid</td>
<td>31</td>
<td>0.00012</td>
<td>0.00048</td>
<td>1190</td>
<td>2290</td>
</tr>
<tr>
<td>Anthracene</td>
<td>1.24</td>
<td>solid</td>
<td>0.043</td>
<td>3.6x10⁻⁸</td>
<td>0.00007</td>
<td>23 500</td>
<td>35 500</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>1.35</td>
<td>solid</td>
<td>0.0016</td>
<td>6.4x10⁻¹⁵</td>
<td>0.000001</td>
<td>969 000</td>
<td>1 260 000</td>
</tr>
<tr>
<td>PCB-1248</td>
<td>1.44</td>
<td>212</td>
<td>0.054</td>
<td>6.6x10⁻⁷</td>
<td>0.0035</td>
<td>437 000</td>
<td>562 000</td>
</tr>
</tbody>
</table>

Volatilization

Although other processes may be enhanced in the unsaturated zone relative to the saturated zone, e.g. biodegradation through the ready availability of oxygen, volatilization is a key process that only occurs in the unsaturated zone. Organic compounds with high vapour pressures (P) (>0.008 atm., i.e. xylene in Table 4.1) are termed (volatile organic compounds (VOCs). The vapour concentration adjacent to a NAPL or organic solid is dictated by its vapour pressure. Although volatilization of subsurface organic contaminants, e.g. NAPL sources, may occur and organic vapours potentially lost to the above ground atmosphere, VOCs are nevertheless very widely encountered in groundwaters; possible reasons include many VOCs are NAPLS of relatively high solubility (S) and low sorbing potential (KOC). Vapours migrate due to diffusion and advection within the air phase and may migrate due to pressure (barometric) and temperature fluctuations, water infiltration and preferential conduit routes (Mendoza et al., 1996). In relation to vapour-phase diffusion, it is emphasized diffusion coefficients in the air phase are ~4 orders of magnitude greater that the water phase. This allows much greater opportunity for lateral (radial) migration of vapour plumes and, due to vapour contact, contamination of underlying groundwaters over a wide area (Rivett, 1995).
Partitioning of dissolved organic solutes between a contaminated water phase and an adjacent air-phase is controlled by the Henry’s Law partition coefficient:

$$H = \frac{C_A}{C_W}$$  \hspace{1cm} (Eqn. 4.4)

where $H$ is the Henry’s Law constant, $C_W$ is the concentration of an organic compound in water and $C_A$ is its vapour concentration in the gaseous phase. It should be noted that similar concentration units will yield a dimensionless (i.e. unitless) $H$ value, however, the air concentration is often expressed in terms of pressure and hence $H$ values may be quoted with units of the type $\text{atmos m}^3 \text{ mol}^{-1}$, e.g. for benzene $H$ (dimensionless) is 0.24 and with units $H$ is $5.5 \times 10^{-3} \text{ atmos m}^3 \text{ mol}^{-1}$ (Table 4.1).

**Solubilization**

As indicated in Section 4.5.1, the differing hydrophobic nature of organic compounds means their solubility in water varies over orders of magnitude (Table 4.1). Solubility values represent maximum concentrations that may be achieved in a dissolved-phase plume. VOC contaminants, e.g. benzene and TCE tend to be small molecules that are moderately soluble, amenable to analysis and hence often detected in groundwater. Although solubilities are relatively low compared to inorganic ions, they may nevertheless achieve concentrations 4-5 orders of magnitude greater than drinking-water standards or guideline values. Larger molecular weight organics will have lower solubilities, hence concentrations e.g. of DDT in groundwater may only reach about 0.1 mg/l (its solubility). Thus DDT at solubility only exceeds the WHO guideline value of 1 µg/l by a factor of approx. 50, hence allowing for dilution and some attenuation, the prospects of exceeding the DDT standard in groundwater are low except in close proximity to a DDT source. DDT’s high hydrophobicity and hence high sorption (see below) tends to cause DDT (and other organic chemicals of similar properties, e.g. high molecular weight PCBs and PAHs) to perhaps be more of a soil rather than a groundwater problem.

**Sorption**

Sorption exerts a key control over the transport of anthropogenic organic contaminants. Organic sorption is a complex topic, a detailed review is provided by Allen-King et al. (2002). Sorption is a function of the properties of both the organic solute and aquifer solid. Hydrophobic non-ionic organic contaminants preferentially sorb to the low-polarity components of geosolids, e.g. any organic material present. Sorption is inversely related to organic compound solubility; the more hydrophobic and less soluble an organic solute, the greater its intrinsic potential for sorption to any organic material present in the aquifer solids. Hence hydrophilic organics have negligible sorption, and mild to moderately hydrophobic organics such as the VOCs show limited sorption. In contrast, hydrophobic, high molecular weight, large organics such as PAHs and PCBs of low solubility exhibit high sorption (Table 4.1).

An additional measure of organic compound hydrophobicity often used in sorption research is the octanol-water partition coefficient ($K_{ow}$) (Table 4.1), that is simply an equilibrium partitioning of the organic solute between the organic octanol phase and
water phase. The higher the $K_{ow}$ value, the more hydrophobic, less soluble and more sorptive the organic compound.

The degree of sorption is also controlled by the sorption potential of the sorbate, i.e. the aquifer material that dissolved concentrations in groundwater contact. Frequently sorption is assumed to be at equilibrium and linear with organic solute concentrations, the magnitude of sorption being expressed by the sorption partition coefficient $K_d$:

$$K_d = \frac{C_s}{C_W} \quad \text{(Eqn. 4.5)}$$

where $C_s$ is the sorbed concentration. The main sorbing phase for organic solutes is any organic material present in the rock phase originating for example from organic detritus, e.g. humic material, deposited at the time of rock deposition. This organic material is referred to as the fraction of organic carbon ($f_{oc}$) within the geologic or soil matrix. Although $f_{oc}$ values may be on the order of one per cent or more in organic-rich soil horizons, many aquifers comprise geologic strata with low $f_{oc}$ values, e.g. an $f_{oc}$~0.02 per cent is recorded for the Borden glaciolacustrine sands, Canada (Rivett and Allen-King, 2003). The $f_{oc}$, even at such low concentrations, may still be the dominant sorption phase rather than poorly sorbing mineral surfaces. Simultaneous laboratory measurements of $f_{oc}$ and $K_d$ have shown that they are approximately linearly related, with the constant of proportionality being termed the organic-carbon partition coefficient ($K_{oc}$) of the specific organic solute (Table 4.1). Typically practitioners assessing sorption controls now obtain $K_{oc}$ values from databases (e.g. US EPA, 1996), measure the aquifer $f_{oc}$ (Heron et al., 1997) and estimate the sorption $K_d$ from the relationship:

$$K_d = f_{oc} K_{oc} \quad \text{(Eqn. 4.6)}$$

where $f_{oc}$ is in mass fraction dimensionless units, e.g. expressed as 0.0002 rather than as 0.02 per cent. Hence the greater the $f_{oc}$ of the aquifer deposits (e.g. higher values are often found in shallow soils or recent sub-river, i.e. hyporheic zone), and greater the $K_d$, which will increase with solute hydrophobicity, the greater the $K_d$ value, i.e. sorption. Assuming ideal linear equilibrium sorption and calculation of $K_d$ from the above, the retardation factor $R_i$ of organic solute $i$ may be estimated from:

$$R_i = 1 + \left(\frac{\rho}{\eta}\right)K_d \quad \text{(Eqn. 4.7)}$$

where $\rho$ and $\eta$ are the bulk density and porosity of the porous media respectively.

The above hydrophobic partitioning ideal sorption approach is an approximation of reality; it provides a reasonable first estimate. It should be recognized, however, that non-ideal sorption processes may be significant (Allen-King et al., 2002); these include slow equilibration of sorbed and dissolved phases, dependence of the degree of sorption on dissolved concentration magnitude and the presence of any competing, also sorbing, solutes within multi-contaminant plumes. Further, the nature of the $f_{oc}$, i.e. ratio of the carbon-hydrogen-oxygen contents, has an important control on the sorption that occurs.

It is often useful to combine some of the above parameters visually to assess how organic contaminants may comparatively behave. Figure 4.6 plots $K_{ow}$, a measure of compound hydrophobicity that will indicate solubility and sorptive retardation trends against vapour pressure, a measure of volatilization tendency. The figure indicates PAHs are unlikely to volatilize and will undergo high sorption, and this would infer that
soil/unsaturated zone solids concentrations of PAHs could often be high (frequently the case) and perhaps there is relatively limited development of PAH plumes to groundwater (often relatively small plumes are encountered). The chlorinated hydrocarbons, in contrast, are volatile but of low sorption potential. It is likely they would vaporize (and potentially be a vapour hazard to receptors at the soil surface) and also leach to groundwater leaving low concentrations in soils and unsaturated samples (quite often the case).

Figure 4.6. Polarity-volatility diagram for selected organic contaminants

Chemical reactions
Although there are a multitude of possible chemical reactions (abiotic reactions, i.e. not mediated by bacteria), reactions of low-concentration organics in a water-based environment tend to be fairly limited. Perhaps the most common reaction is that of slightly positively charged organic compounds ($C^\delta^+$) with negatively charged (nucleophilic) species, such as $\text{HS}^-$, $\text{OH}^-$ or water. The latter is a hydrolysis reaction. Reactive organic solutes tend to be organic halides, particularly brominated compounds and to a lesser extent chlorinated compounds. An example of a chemical reaction is that of the chlorinated solvent 1,1,1-TCA which was commonly used to degrease metals and circuit boards (as a less toxic replacement to TCE, before concerns were raised about its ozone-depletion potential). TCA in water will either undergo an elimination reaction to yield 1,1-DCE, or alternatively a sequential hydrolysis reaction replacing all the chlorine atoms as chloride to yield ethanoic acid. Interestingly it may also biodegrade to predominantly form a different product, 1,1-DCA (Klecka et al., 1990). Further information on chemical reactions in water may be found in Schwarzenbach et al. (1993).
Biodegradation

Bacteria degrade organic contaminants to simpler, often less toxic, products. Biodegradation is perceived to be the primary attenuation process that may mitigate dissolved-plume impacts to receptors by organic chemicals. Monitored natural attenuation (MNA) remedial strategies generally have their main focus upon demonstration of occurrence of biodegradation (Wiedemeier et al., 1999). This not only entails monitoring the disappearance of the organic contaminant, but also the appearance of intermediate organic contaminants that may themselves persist or be further biodegraded, ideally to benign inorganic products, e.g. water, carbon dioxide, chloride.

Monitoring of the inorganic hydrochemistry is also a key requirement to assessing biodegradation occurrence. Sites may be initially aerobic/oxic (containing oxygen), and under these conditions biodegradation of many contaminants is often the most rapid. Dissolved oxygen concentrations in groundwater are usually low, maximally ~10 mg/l. Such levels can easily be depleted by even low to moderate levels of organic contamination present and are not easily renewed as dispersive mixing in groundwaters to allow oxygen re-entry is typically low. Other electron acceptors, for example sulphate, nitrate, iron and manganese, are then used to allow biodegradation to continue under anaerobic conditions. Finally site conditions may become so reducing that biodegradation occurs under methanogenic conditions.

Specific examples of biodegradation are included in the sections that follow. In general, most hydrocarbon-based compounds and most oxygenated-organics are relatively biodegradable under a wide range of conditions, and natural attenuation of such plumes often significant. Chlorinated (halogenated) compounds are generally less biodegradable but evidence has increasingly shown that they do biodegrade under appropriate redox-bacterial conditions. A sequence of reactions under varying redox conditions may be required to allow complete biodegradation to benign products. This means that for some contaminants and sites full biodegradation to benign products is difficult and there may be persistence of both the original contaminants and their intermediate degradation products, both of which may have toxicity.

4.5.3 Organic chemicals of major concern in groundwater

Consideration of the above transport and attenuation processes, together with data on organic chemical toxicity, use of chemicals and associated potential for release to the subsurface, and actual chemical occurrence in groundwater data, enables identification of groups of organic chemicals, as well as individual chemicals, thought to be of major concern in groundwater. Two organic chemical groups of key concern include:

- aromatic hydrocarbons: benzene, toluene, ethylbenzene and xylenes (BTEX);
- chlorinated hydrocarbons (aliphatic and aromatic): dichloromethane (DCM), trichloromethane (TCM, also known as chloroform), tetrachloromethane (also known as carbon tetrachloride, CTC), trichloroethene (TCE), tetrachloroethene (PCE, also known as perchloroethylene), vinyl chloride (VC), 1,2-dichloroethane (1,2-DCA), 1,1-dichloroethene (1,1-DCE), 1,2-dichloroethene (cis and trans isomers, cDCE and tDCE respectively), 1,2 dichlorobenzene (1,2-DCB) and 1,4 dichlorobenzene (1,4-DCB).

Properties of the above compounds are included in Table 4.1.
Figure 4.7 presents data based upon 250 sites in Germany and 500 sites in the USA (Kerndorff et al., 1992) and indicates the prevalence of the above compounds in groundwater. A third (predominantly) organic chemical group of key concern in groundwater is pesticides.

![Graph of organic contaminants with frequency of detection (%)]

Figure 4.7. The 25 most frequently detected organic groundwater contaminants at hazardous waste sites in Germany (250 sites) and the USA (500 sites) (based on concentrations ≥ 1 µg/l) (adapted from Kerndorff et al., 1992)

Of the many organic chemicals that may potentially contaminate groundwater, these three groups have perhaps received the most attention from both the groundwater practitioner and research communities during the 1980s and 1990s. The following Sections 4.5.4, 4.5.5 and 4.6 are hence devoted to these three groups.

The focus upon the above three groups does not preclude the potential importance of other organic contaminants in groundwater. Although compounds may perhaps not occur frequently due to restricted use within specialized industries, some compounds may have low natural attenuation (NA) properties and potentially develop extensive plumes. Other chemical groups may, in contrast, have received widespread industrial use, but were perhaps thought (sometimes mistakenly) to pose a much lower risk to groundwater due to high NA properties. Examples of the latter may include PAHs and PCBs that are both briefly discussed below.
PAHs are a component of creosotes and coal tars frequently associated with former gasworks and coal carbonization (coking) works (Johansen et al., 1997). They are a diverse class of compounds of natural and anthropogenic origin, some of which show carcinogenic properties. WHO has derived a guideline value of 0.7 µg/l for benzo(a)pyrene because it may be released from coal tar coatings of drinking-water distribution pipes. Most PAHs have extremely low solubilities in water and have a high tendency to adsorb to the organic matrix of soils and sediments, particularly the higher molecular mass, higher-ring PAHs, e.g. the 5-ring benzo(a)pyrene. Thus, they are generally not found in water in notable concentrations, and human exposure is mostly through food prepared at high temperatures and air (particularly from open fires) (WHO, 2004a). Countering the processes that may serve to attenuate groundwater impacts, however, are: (i) creosote and coal tars may occur as a DNAPL (density is composition dependent, but may be around 1.05) and slowly migrate as a DNAPL deep into the subsurface potentially penetrating the water table; and (ii) higher molecular mass, higher ring-member PAHs are much more resistant to biodegradation and hence dissolved plumes, although slow to develop, may persist and grow over decades (King and Barker, 1999).

PCBs are a class of stable compounds, each containing a biphenyl nucleus (two linked benzene rings) with two or more substituent chlorine atoms. PCBs are produced industrially as complex mixtures that often contain between 40 and 60 different chlorinated biphenyls. Similar to PAHs, most PCBs are of low solubility in water and sorptive and hence dissolved-phase plumes in groundwater tend not to be large. However, PCB oils, historically used in electrical transformer facilities, are DNAPLs and may potentially penetrate deep into aquifer systems. Dissolved PCBs are generally slow to biodegrade and hence PCBs, like PAHs, may serve as long-term sources of groundwater contamination.

An emergent groundwater issue in the 1990s relating to hydrocarbon fuels has been the use of oxygenates, particularly methyl tertiary-butyl ether (MTBE) and methanol or ethanol within fuels (Squillace et al., 1996). Use of MTBE has been most significant in the USA with MTBE first used in gasoline at greater than 10 per cent by volume in 1992. MTBE has a strong taste and odour and is likely to impair drinking-water quality at concentrations in the 0.01-0.1 mg/l range. However, because of its low relevance to human health, MTBE is not further discussed in this chapter; see WHO (2005c) for further information on MTBE.

4.5.4 Aromatic hydrocarbons (BTEX)

Health aspects
Mononuclear (single-ring) aromatic hydrocarbons such as BTEX are amongst the most common groundwater contaminants (Figure 4.7) and the main aromatic faction of many hydrocarbon fuels. The key compound of health relevance within the BTEX group is benzene, a proven carcinogen in humans. The mechanism or metabolic form by which it exerts its action (haematological changes, including leukaemia) is not clear. WHO (2004a) has established a guideline value for benzene in drinking-water of 10 µg/l, corresponding to a lifespan risk of 10⁻⁵ to contract cancer by exposure to benzene via drinking-water. Alkylated benzenes are much less toxic than benzene, and correspondingly their WHO guideline values are 700 µg/l for toluene, 300 µg/L for
ethylbenzene and 500 µg/l for xylene (WHO, 2004a), whereas no health-based guideline values are given for trimethylbenzenes and butylbenzene. However, some of them may be perceived by odour and/or taste at only a few micrograms per litre.

Sources and occurrence
The aromatic hydrocarbons BTEX are the primary contaminants of concern associated with point-sources of fuels and fuel-related contamination originating from petroleum production, refining and wholesale and retail distribution (service stations) of petroleum products (Newell et al., 1995). They are also used as solvents and raw materials in chemical production. Spills and accidental releases of gasoline (petrol), kerosene and diesel are common sources of their occurrence in the environment. The German-USA groundwater survey data in Figure 4.7 indicate BTEX was relatively common, benzene being the most prominent.

Transport and attenuation
Most petroleum products are LNAPLs and hence the Figure 4.4 conceptual model applies. BTEX components typically comprise just a few per cent of the LNAPL fuel. BTEX concentrations dissolving in groundwater near fuel sources are reduced from their pure-phase solubility values (as individual component solubilized concentrations form NAPL mixtures depend upon the mass (strictly mole) faction of that component in the NAPL). BTEX-aromatics, being the most soluble hydrocarbons, are still the main risk driver for groundwater at hydrocarbon-contaminated sites, as solubilized concentrations and mobility of other alkane (branched and straight-chain) and PAH hydrocarbons are much lower. Since the early 1990s, it has been recognized that natural attenuation (NA) of BTEX is highly significant at most sites due to the high biodegradability of BTEX under a range of conditions. Monitored natural attenuation, i.e. monitoring of the growth, stability and eventual decline of dissolved-phase BTEX plumes, has indeed become a viable and cost-effective remediation option at many sites rather than active remedial measures such as pump-and-treat (McAllister and Chiang, 1994).

Studies that have examined dissolved-phase hydrocarbon plume lengths from over 600 hydrocarbon-release sites in the USA are particularly instructive on the potential for NA applicability (Newell and Connor, 1998; Wiedemeier et al., 1999 and references therein). Of the 604 plumes evaluated, 86 per cent were less than 300 feet (~100 m) long with only 2 per cent of plumes greater than 900 feet. One of the studies that examined 271 plumes indicated only 8 per cent of these plumes were still growing, 59 per cent of plumes were approximately stable as mass being dissolved from the source was balanced by mass being depleted by attenuation (biodegradation), and 33 per cent of plumes were shrinking as source mass inputs declined or biodegradation of contaminants perhaps became increasingly efficient with time. These studies hence provide a strong rationale for occurrence of NA across a variety of site conditions. Under the vast majority of circumstances the potential for impacts of hydrocarbon plumes is limited to distances of a few hundred meters from source zones. Thus although hydrocarbon sources can be numerous, hydrocarbon and BTEX impacts are likely to remain local to those source zones. However, although dissolved-phase plume may extend to relatively short distances from source areas, LNAPL source zones (i.e. pancake-like of hydrocarbon)
themselves can on occasion be very extensive, for example Albu et al. (2002) depict zones of LNAPL extending over 5 km around oil refinery sites near Ploiesti, Romania.

Much insight into the importance of biodegradation and associated controlling factors has been obtained in plume studies. A controlled injection of dissolved-phase benzene, toluene and xylene at the Borden site, Canada (Barker et al., 1987) showed complete benzene, toluene and xylene biodegradation by just over 400 days with only benzene persisting beyond 270 days. This study, and many real spill sites indicate BTEX are readily degraded when dissolved oxygen is present in groundwater. Under anaerobic conditions, rates of biodegradation of remaining hydrocarbon was governed by both the rate of oxygen re-entry across the contaminant plume fringe and rates of alternative anaerobic biodegradation pathways using less efficient electron acceptors such as nitrate, sulphate, and iron(III). Many other field sites have demonstrated the importance of anaerobic processes, primarily through changes in the groundwater geochemistry. For example, the Plattsburgh, Hill and Patrick Air Force Bases in the USA (Wiedemeier et al., 1999) indicate development of depleted dissolved oxygen, nitrate and sulphate coincident with the BTEX plumes as these electron acceptors are consumed in the oxidation of the BTEX. pH declines as well as production of Fe(II) and methane arising from methanogenic activity were also evident where the most reducing conditions prevailed.

A myriad of aerobic and anaerobic BTEX biodegradation rates are available from the literature, e.g. data and references within Wiedemeier et al. (1999) and Noble and Morgan (2002). Rates are typically expressed as a first order rate constant or an equivalent half-life. Table 4.2 summarizes half-life data provided in the review by Noble and Morgan (2002) for BTEX, naphthalene and some chlorinated hydrocarbons. These chemicals represent the most studied groundwater contaminants in relation to biodegradation. The table subdivides rate data between laboratory and field studies that are in turn subdivided to aerobic and anaerobic conditions. Although the work of Noble and Morgan is reasonably comprehensive and based upon many citations, it should be noted that Table 4.2 aims to be illustrative rather than comprehensive of all literature available on biodegradation rates for the chemicals listed; biodegradation is an active area of study worldwide and half-life data continue to be published.

Rates selected for risk assessment modelling at other sites (where field data are insufficient to determine rates) need to be used with care as modelling results, and hence plume attenuation predicted and any site risk-based remediation standards computed, are very sensitive to degradation mass-loss parameters selected. Rates may vary significantly for individual compounds that may be a reflection of rates being lab-based or field based and the particular aerobic-anaerobic site conditions. This is apparent from examination of Table 4.2. Also, field biodegradation rates may be derived from a localized point measurement, or more often a rate predicted from whole plume behaviour that will average varying rates and different biodegradation processes and aerobic/anaerobic conditions occurring throughout the plume.

The laboratory half-lives in Table 4.2 are generally shorter than the equivalent field-based values, i.e. plumes are apparently more persistent in the field presumably as a reflection of field conditions, e.g. supply of electron acceptors being less optimal than can be achieved in a laboratory. In general, BTEX degradation rates will be lower under anaerobic conditions and plume may be persistent and indeed attain significant lengths...
where groundwater is naturally anaerobic, e.g. confined aquifer conditions. This is reasonably demonstrated by the Table 4.2 field data, but less so by the laboratory-based data; the latter is in part from the limited studies undertaken (at least reported) for some of the chemicals. A cautionary approach is warranted to the application to sites of the half-life data provided in Table 4.2 (and elsewhere); clearly the range in half-life values for a specific contaminant is large and for some contaminants and conditions insufficient data exist to yield a reliable average and range. Some Table 4.2 entries are based on a single study, in some cases no data are provided. The latter may be a reflection of a genuine lack of data or else biodegradation not being effective under the specific conditions (e.g. aerobic biodegradation of PCE).
### Table 4.2. Summary of biodegradation half-life data (at 10°C) for important organic groundwater contaminants (adapted from Noble and Morgan, 2002)

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Aerobic - laboratory data</th>
<th>Aerobic - field study data</th>
<th>Anaerobic - laboratory data</th>
<th>Anaerobic - field study data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No. of studies (n)</td>
<td>Mean half-life (days)</td>
<td>Range in half-life (days)</td>
<td>No. of studies (n)</td>
</tr>
<tr>
<td>Aromatic Hydrocarbons</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>5</td>
<td>120</td>
<td>5-320</td>
<td>3</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>No data provided</td>
<td></td>
<td></td>
<td>No data provided</td>
</tr>
<tr>
<td>Xylenes</td>
<td>1</td>
<td>11</td>
<td>11-11</td>
<td>3</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>11</td>
<td>138</td>
<td>10-400</td>
<td>No data provided</td>
</tr>
<tr>
<td>Chlorinated Hydrocarbons</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCE</td>
<td>No data provided</td>
<td></td>
<td>No data provided</td>
<td>6</td>
</tr>
<tr>
<td>TCE</td>
<td>No data provided</td>
<td></td>
<td>No data provided</td>
<td>8</td>
</tr>
<tr>
<td>DCE</td>
<td>5</td>
<td>2</td>
<td>0.5-3</td>
<td>3</td>
</tr>
<tr>
<td>VC</td>
<td>7</td>
<td>14</td>
<td>84</td>
<td>1</td>
</tr>
<tr>
<td>DCA</td>
<td>No data provided</td>
<td></td>
<td>No data provided</td>
<td>5</td>
</tr>
</tbody>
</table>
4.5.5 Chlorinated hydrocarbons

Health aspects
A number of aliphatic and aromatic chlorinated hydrocarbons are of health significance because of their toxicity and occurrence in drinking-water, particularly as in groundwater, their concentrations do not decrease rapidly through volatilisation, anaerobic degradation is slow, and in consequence contaminants may persist for some time.

WHO (2004) gives guideline values for dichloromethane (DCM), trihalomethanes chloromethane (e.g. chloroform which may be generated as by-products of disinfection), tetrachloromethane (also known as carbon tetrachloride, CTC), trichloroethene (TCE), tetrachloroethene (PCE, also known as perchloroethylene), vinyl chloride (VC), 1,2-dichloroethene (1,2-DCA), 1,1-dichloroethene (1,1-DCE), 1,2-dichloroethene (cis and trans isomers, cDCE and tDCE respectively), 1,2 dichlorobenzene (1,2-DCB) and 1,4 dichlorobenzene (1,4-DCB) (see Table 4.1 for selected physiochemical parameter values). Generally, among the saturated chlorinated compounds, the 1,1-halogenated ones (e.g. 1,1-dichloroethane) are of less health concern than the 1,2-halogenated ones (e.g. 1,2-DCA), since they are metabolized differently. This is also true for higher halogenated compounds (e.g. trichloroethenes).

Dichloromethane (DCM, also known as methylene chloride) is of low acute toxicity, and current evidence suggests that it is not a genotoxic carcinogen. The WHO drinking-water guideline value for DCM is 20 µg/l, based on hepatotoxic effects observed in rats (WHO, 2004a). Carbon tetrachloride (CTC) has a WHO guideline value of 4 µg/l based on its liver toxicity, and from carcinogenic effects observed in laboratory animals it is classified as possibly carcinogenic to humans. 1,2-dichloroethane (1,2-DCA) is potentially genotoxic and a proven carcinogen in experimental animals with a WHO guideline value of 30 µg/L (WHO, 2003d; 2004a).

Trichloroethene (TCE) and tetrachloroethene (PCE) may degrade to the more toxic vinyl chloride. The provisional WHO guideline value for TCE is 70 µg/l based on liver effects in mice (WHO, 2004a; 2005d). PCE causes nervous disorders at high dose, whereas at lower doses kidney and liver damage have been reported. It is classified as possible human carcinogen with overall evidence indicating that it is not genotoxic (WHO, 2003e), and its WHO guideline value for drinking-water is 40 µg/l (WHO, 2004a). Vinyl chloride (VC) is genotoxic and carcinogenic in experimental animals as well as in humans. Administered orally to experimental animals, it produced cancer at a variety of sites (WHO, 2004d). Its WHO drinking-water guideline value is 0.3 µg/l (WHO, 2004a).

1,1-Dichloroethene (1,1-DCE) is a weak in vitro-mutagen and not classifiable as to its carcinogenicity to humans. It is a central nervous system depressant and may cause liver and kidney toxicity. The WHO guideline value is 30 µg/l (WHO, 2004a; 2005e). Among the two isomers of 1,2-dichloroethene, the cis-form is detected more frequently and at higher concentrations than the trans-form as a water contaminant, since the former is the main anaerobic metabolite of TCE and PCE. As such it may indicate as well the presence of vinyl chloride, the next anaerobic breakdown product, which is not only much more toxic than all higher chlorinated ethenes but also a genotoxic human carcinogen (see above). In contrast, both 1,2-DEEs do not seem to be genotoxic and
there is no information on their carcinogenic potential. The WHO drinking-water
guideline value for each of the 2 isomers is 50 µg/l (WHO, 2003f; 2004a).

Dichlorobenzenes are the least toxic of this group of contaminants. Their health based
guideline values in drinking-water are 300 and 1000 µg/l for 1,2- and 1,4-DCB,
respectively. These exceed their odour threshold range of 0.3-30 µg/l by far (WHO,
2003g; 2004a).

Sources and occurrence
Chlorinated hydrocarbons are employed in a variety of industrial activities, including
almost any facility where degreasing, e.g. of metals, circuit boards, textiles (dry cleaning)
and animal/leather hides, metal stripping, chemical manufacturing, pesticide production
or other activities where chlorinated solvents, cleaners, dry cleaning fluids, paint
removers are used (Chapter 11).

In many industrialized countries, chlorinated hydrocarbons are the most frequently
detected groundwater contaminants at hazardous waste sites (Kerndorff et al., 1992;
Plumb, 1992; NRC, 1994). This is highlighted by the German-USA survey data in
Figure 4.7. TCE and PCE together with their principal metabolites cDCE and VC have
been the most frequently detected chlorinated hydrocarbons at the investigated sites.
Point source release of chlorinated hydrocarbons to groundwater is anticipated to be the
main source of groundwater contamination. Complex mixtures of chlorinated
hydrocarbons may arise from leakages at hazardous waste disposal sites where many
solvent types may have been disposed. In contrast, spills at industrial
manufacturing/processing sites may well comprise liquid chlorinated hydrocarbon as a
DNAPL with a high proportion of a single chlorinated hydrocarbon component. A
multitude of point sources exist in many urban areas due to the diversity and frequency
of chlorinated hydrocarbon users.

Examples of regional chlorinated hydrocarbon contamination within aquifers
underlying urban towns and cities emerged during the 1980s. Many groundwater
supplies or monitoring wells were contaminated in some instances, particularly by TCE
and to a lesser extent PCE. Examples include Milan, Italy (Cavallero et al., 1985); the
New Jersey coastal plain aquifer, USA (Fusillo, 1985) and Birmingham, United
Kingdom (Rivett et al., 1990); the latter example is described in Box 4.2.

Transport and attenuation
Many of the chlorinated hydrocarbons will have entered the subsurface in the DNAPL
form and may reside to significant depths within aquifers (Pankow and Cherry, 1996).
They typically have low to medium water solubility (in the range of 0.2-20 g/l;
Table 4.1). Dissolution of DNAPL sources is expected to be slow taking years to
decades, particularly from long lengths of residual DNAPL pools that have invaded or
diffused into low-permeability strata. Dissolved-phase plumes of chlorinated
hydrocarbons can be very extensive, for example Mackay and Cherry (1989) depict
several plumes in the km-scale and Jackson (1998) several plumes in the alluvial aquifers
of the southwestern USA that are around 10 km in length. Some plumes have lead to
high profile court cases and set legal precedents on apportioning liability for historic
contamination events, e.g. the near 2-km PCE plume that caused contamination of the
Sawston public water supply borehole in Cambridgeshire, United Kingdom (Ashley, 1998).

**Box 4.2.** Chlorinated-hydrocarbon contamination of groundwater in Birmingham, United Kingdom (based on Rivett *et al.*, 1990; Rivett *et al.*, 2005)

Birmingham is the second largest city in the United Kingdom and has a long history of manufacturing, particularly in metal-related industries. Groundwater samples were taken during the late 1980s from 59 abstraction boreholes typically screened over 100 m in the Triassic Sandstone aquifer underlying the city. Chlorinated solvents were found to be widespread, particularly TCE detected in 78 per cent of abstraction boreholes with over 40 per cent of the sampled boreholes showing concentrations over 30 µg/l to a maximum of 5500 µg/l. The majority of highly contaminated abstractions were located in solvent-user sites, predominantly metals-related industry. The predominance of TCE was ascribed to its main United Kingdom use within metal cleaning applications since the 1930s. PCE was less evident as it has generally only been used for dry cleaning in the United Kingdom since 1950s. Lower TCA occurrence was ascribed to its much later introduction in the United Kingdom starting about 1965 as a less toxic replacement to TCE. Greatest groundwater contamination occurred in the Tame valley area that was hydrogeologically vulnerable due to low depths to groundwater and limited aquifer protection by low permeability drift. Moderate contamination was present in other less vulnerable areas of the unconfined aquifer with least contamination evident in the Mercia Mudstone confined aquifer.

The aquifer was re-visited a decade later during the late 1990s. Declines in industrial use of groundwater meant only 36 abstractions were active and available for sampling, of these 26 were from the 1980s survey. Overall contamination detected was less and attributed to most of the new boreholes being located in industry areas where solvent use appeared limited. Also, many of the former highly contaminated abstractions had ceased operation due to industry closure. The latter was of some concern as contamination previously inadvertently captured by such abstractions was now able to more freely migrate into the wider aquifer. Comparison of the 26 abstractions common to both surveys indicated contamination at individual boreholes was at similar or greater concentrations in the more recent survey compared to the decade-earlier survey. These levels are unlikely to be due to major ongoing contamination, rather, it is reasonably assumed that incidences of new contamination will have declined over the decade as industry has become much more environmentally aware. The sustained level of contamination was hence ascribed to persistent sources of chlorinated solvents, likely DNAPL sources at depth. These will have remained unaffected by remedial works implemented at many sites to date because under a land redevelopment focused agenda these predominantly focused upon shallow soil and groundwater problems.
Under aerobic conditions, biodegradation of solvents such as TCE and PCE can be limited to non-existent and may account for the extensive plume examples noted above. Sorption is often limited too, particularly for the less hydrophobic compounds where compound solubility exceeds 1g/l (Table 4.1). A controlled emplacement of a DNAPL chlorinated solvent source in the Borden aquifer research site, Canada, resulted in TCM and TCE plumes exhibiting near conservative behaviour with retardation factors in the range of 1.0-1.2 and no evidence of biodegradation for these solvents and also PCE that was more retarded at about 1.6 (Rivett et al., 2001; Rivett and Allen-King, 2003). Dispersion of these plumes, although moderate in this relatively homogeneous sand aquifer, nevertheless produced leading plume contours at concentrations in the range of drinking-water standards that had travelled toward 100 per cent further than the mean advection (groundwater) velocity.

In contrast, other sites have shown significant natural attenuation of chlorinated hydrocarbons due to biodegradation activity. The most well known biodegradation pathways are those involving the sequential reductive dechlorination of chlorinated hydrocarbons where lesser chlorinated organics, chloride and ultimately hydrocarbons such as ethane or ethane, are formed (Vogel et al., 1987), e.g. PCE is transformed to TCE to cDCE (usually the predominant isomer) to VC to ethene. On average chlorinated hydrocarbon plumes are significantly longer than the aforementioned BTEX plumes. For example, Newell et al. (1990) reported a median length of 1000 feet (about 300 m) for chlorinated ethene (PCE, TCE, DCE, VC) plumes (88 sites sampled).

Biodegradation of chlorinated hydrocarbons has proven to be relatively complicated with five possible degradation processes (Wiedemeier et al., 1999). Most chlorinated compounds have been observed to biodegrade by three or four of these processes, only DCE and VC may biodegrade via all five processes. Under anaerobic or low oxygen conditions degradation processes include (i) dehalorespiration, in which the chlorinated hydrocarbon is used as the electron acceptor and effectively respired, (ii) direct anaerobic oxidation and (iii) anaerobic co-metabolism. Under aerobic conditions, further processes are (iv) direct aerobic oxidation and (v) aerobic co-metabolism. Direct processes involve the chlorinated hydrocarbon being used as the primary growth substrate. Dehalorespiration and co-metabolism both require an alternative primary growth substrate to be present. That primary substrate is normally a relatively biodegradable substrate and may include anthropogenic carbon such as BTEX contamination. Alternatively, anaerobic conditions may be driven by high levels of naturally occurring carbon acting as the substrate, a primary example being wetland sediments and sub riverbed deposits, e.g. Lorah and Olsen (1999) observed TCE and 1,1,2,2-PCE dechlorinations in the former.

Due to the complexity of degradation processes outlined, there is a wide divergence in reported biodegradation rates of chlorinated hydrocarbons (Wiedemeier et al., 1999; Noble and Morgan, 2002; Table 4.2). This is clearly illustrated by the Table 4.2 half-life data for the more common chlorinated hydrocarbon groundwater contaminants, e.g. DCE field-based half life data vary from just 42 days to nearly 17 000 days. Also, Table 4.2 indicates laboratory half-life data are generally much shorter (by 1-2 orders of magnitude) than equivalent field data, e.g. TCE data under anaerobic conditions indicate a laboratory half life mean of 43 days compared to a field mean of
1460 days. This is perhaps ascribed to the fact that optimal anaerobic reducing conditions can be achieved in the laboratory for the whole sample, whereas in the field such anaerobic conditions may in fact only occur in localized portions of a plume. Table 4.2 emphasizes the sensitivity of half life to aerobic and anaerobic conditions and that much longer half life values may occur for chlorinated hydrocarbons relative to the aromatics. The above strongly endorses the need to recognize that literature half-life data have very significant uncertainty when applied in a predictive manner to sites elsewhere. The unfortunate reality is that most sites require individual case-by-case assessment to allow effective prediction of natural attenuation rates.

4.6 PESTICIDES

Pesticides represent a wide range of compounds used mostly as insecticides, herbicides, and fungicides. Formerly a small number of classes of chemicals included most pesticides, i.e. organochlorines, organophosphates, carbamates, phenoxyacetic acids and triazine herbicides. However, modern pesticides include other types of chemicals, and therefore such a classification is of more limited use for descriptive purposes. Many of the historically used pesticides, such as the organochlorines, are however environmentally persistent and may pose a long-term groundwater problem.

Health aspects

In general, health effects associated with pesticides are specific for each chemical. This is reflected in their different WHO guideline values for drinking-water quality (see WHO, 2004a) and in the wide range of acceptable daily intake values derived by the Food and Agricultural Organization (FAO) for exposure through food (resulting from pesticide uses on crops; FAO, 2004). Most health effect studies are conducted using single compounds, little is known about effects associated with pesticide mixtures. Health effects from acute (short-term and high level) or chronic (long-term and low-level) exposure include liver and kidney damage, major interference with nervous, immune and reproductive system functions, birth defects and cancer. In most cases the risk from food contaminated by unduly high levels of pesticides is likely to be more significant than that posed by pesticide levels in drinking-water.

Chronic exposure associated with pesticides has declined in Europe and North America as many of the more persistent herbicides (such as chlordane, DDT, dieldrin, endrin, heptachlor, γ-HCH and toxaphene) have been restricted or phased out (Barnard et al., 1997). They have been replaced with less persistent and more species-specific toxicants. While acute toxicities have often increased, some important new biologically-derived insecticides have very low mammalian toxicity.

Sources and occurrence

Pesticides are intentionally applied to protect crops in agriculture (Chapter 9) as well as to control pests and unwanted vegetation in gardens, buildings, railway tracks, forests and roadsides (Chapter 13). They may be accidentally released from production sites (Chapter 11) or, more often, transported away from their site of application in water, air or dust. Pesticides can reach groundwater after accidental spills or excessive application
in geologically sensitive settings, from contamination of poorly sealed wells by surface runoff after intensive rains following field application and from storage or production sites. Though some organochlorine insecticides have been banned or are subject to severe restrictions in many countries, in several developing countries production and use of, for example, DDT has continued because of its relatively inexpensive production and its high efficacy against mosquitoes in malaria control. Generally the dilemma of the low cost and high efficacy of persistent pesticides versus their long term health and environmental effects remains a contentious global issue which has been addressed by a global convention (see Box 9.5).

As sampling has become more extensive and monitoring programmes developed, increasing numbers of pesticide compounds are being detected in groundwater. A major study, the National Pesticide Survey, conducted by the US EPA in the late 1980s detected 46 pesticides in groundwater in 26 states originating from normal agricultural practice (Williams et al., 1988) but with low frequency and usually below health-based standards. Pesticides detected in more than five states were alachlor, aldicarb, atrazine, cyanazine, metolachlor and simazine. More recently, extensive sampling within the USGS National Water Quality Assessment programme has confirmed the widespread occurrence of pesticides in both surface water resources and groundwater, but generally at concentrations below their respective allowable maximum contaminant levels (Kolpin et al., 2000). The newer work has, however, shown that pesticides, especially insecticides, are also reaching water resources in urban and suburban areas, including residential sources. This work has also demonstrated widespread detection of pesticide metabolites, often at concentrations exceeding the parent compound, and for which there may not be adequate toxicity data to establish their health significance.

This picture is largely confirmed by monitoring efforts in Europe. Herbicides which are widely used in cereal cultivation, such as MCPP and isoproturon are detected in the countries of northern Europe (Spliid and Køppen, 1998) with carbamates perhaps more common further south. Most detected groundwater pesticide concentrations were in the range 0.1 to 10 µg/l. Concentrations significantly above this range can probably be attributed to local point source contamination from poor disposal practices, or from non-agricultural usage such as on railways.

Because of high analysis costs, much less monitoring has been undertaken in low-income countries and data from tropical regions are scarce. However, atrazine residues from its use in sugar cane cultivation were widely observed in groundwater in Barbados and carbofuran was detected in shallow groundwater beneath irrigated vegetable cultivation in Sri Lanka (Chilton et al., 1998). Elsewhere, presence of organochlorines in groundwater reflects their highly persistent nature and perhaps continuing usage even when banned (Matin et al., 1996).

**Transport and attenuation**
The mobility and persistence of pesticides in the environment are well understood because admission of a new pesticide for the market requires a series of standardized laboratory and field experiments.

The overall likelihood of a pesticide to be a groundwater pollutant is dependent both on its persistence and its soil sorption. Table 4.3 lists pesticides used in agriculture for
which WHO has derived health-based drinking-water guideline values. It provides a classification of their leaching and runoff potential based on their physical-chemical characteristics, i.e. their persistence (characterized by soil half-lives) and soil organic carbon sorption (KOC). Other pesticides used for public health purposes (e.g. DDT, chlorpyrifos and pyriproxyfen in malaria control) and wood conservation (e.g. pentachlorophenol or PCP) are not listed in Table 4.3.

As for the organic contaminants discussed in Sections 4.1.2 and 4.5.2, soil organic matter content, clay content and permeability all affect the potential for pesticides to leach through soils. In general, soils with moderate-to-high organic matter and clay content will absorb pesticides onto soil particles, making them less available for leaching, and moderate or low permeability soils allow less water infiltration.

A wide range of pesticide soil sorption Kd values (as defined earlier in Section 4.5.2) exist. DDT, for example, has a Kd value roughly 20 000 times as high as that for aldicarb and 1500 times as high as that for atrazine. This explains why aldicarb and atrazine have been found in groundwater in agricultural areas while DDT has not.

There are several processes by which pesticide may be degraded. Exposure to sunlight may cause photolysis before they leach into soils. Hydrolysis, the degradation of a chemical in reaction with water that may occur at surface, in the soil zone and underlying groundwater; the longer the hydrolysis half-life the more probable it will enter groundwater. Biodegradation, i.e. enzymatic reactions driven by microorganisms, will occur at greatest rates in microbially active soil. Chlorinated pesticides and triazine herbicides are the most resistant to biodegradation and may persist for years following application. Although the mobility of some organochlorine insecticides is limited by their high hydrophobicity (Table 4.3), their persistence is mirrored in the accumulation in fatty tissues in animals, including fish and humans, mostly from pesticides in surface-water food chains. Organic phosphorus pesticides tend to hydrolyse rather quickly at pH values above neutral, thus losing their toxic properties. However, under dry conditions some have been observed to persist for many months (Graham-Bryce, 1981). Carbamates are noted for their high susceptibility to degradation (Williams et al., 1988).

Higher water solubility does not necessarily correlate with a lower degree of persistence, but highly sorbed pesticides tend to be more persistent. The biodegradability of pesticides depends on their molecular structure and soil half-lives can vary between a couple of days to years (Table 4.3). Quite long half lives can occur once pesticides leave the soil and reach the less biologically active zones of aquifers (Lavo et al., 1996; Chilton et al., 2000). It should be noted that although many pesticide half-lives, have been determined for soils (Table 4.3); use of such half-lives to predict aquifer behaviour may cause misleadingly optimistic attenuation estimates.

Several other pesticide concerns remain. Little is known about the fate of pesticides in tropical environments, most published data are from registration trials in temperate regions. For all pesticides there is potential for incomplete transformation of the parent compound into metabolites which may also be more or less toxic (Sawyer et al., 1994) and may themselves be persistent enough to be detected in groundwater. When pesticides do get into groundwater, cleanup of the contamination is usually prohibitively costly and often may not be practically feasible. The contamination can last many years...
and spread over a large area before dilution and degradation eventually reduce the pesticide concentrations.

Table 4.3. Classification of leaching potential for agricultural pesticides for which WHO has derived guideline values (data from the US Department of Agriculture Natural Resources Conservation Service and Agricultural Research Service)

<table>
<thead>
<tr>
<th>Common name</th>
<th>CAS-No.</th>
<th>WHO GV (mg/l)</th>
<th>Water solubility at 20-25 °C (mg/l)</th>
<th>Soil half-life (days)</th>
<th>Leaching potential</th>
<th>Solution runoff potential</th>
<th>Adsorbed runoff potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alachlor</td>
<td>15972-60-8</td>
<td>20</td>
<td>240</td>
<td>15</td>
<td>Medium</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Aldicarb</td>
<td>116-06-3</td>
<td>10</td>
<td>6000</td>
<td>170</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Aldrin</td>
<td>309-00-2</td>
<td>0.03</td>
<td>0.027</td>
<td>365</td>
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<td>High</td>
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<td>Dieldrin</td>
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<td>0.03</td>
<td>0.20</td>
<td>1000*</td>
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<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td>Atrazine</td>
<td>1912-24-9</td>
<td>2</td>
<td>33</td>
<td>60</td>
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<td>High</td>
<td>Medium</td>
</tr>
<tr>
<td>Carbofuran</td>
<td>1563-66-2</td>
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<td>351</td>
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<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Chloranate</td>
<td>57-74-9</td>
<td>0.2</td>
<td>0.060</td>
<td>350*</td>
<td>Very low</td>
<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td>Chlorotoluene</td>
<td>15545-48-9</td>
<td>30</td>
<td>74</td>
<td>35</td>
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<td>High</td>
<td>Low</td>
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<td>Cyanazine</td>
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<td>0.6</td>
<td>170</td>
<td>14</td>
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<td>Medium</td>
<td>High</td>
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<tr>
<td>2,4-D</td>
<td>94-75-7</td>
<td>30</td>
<td>890</td>
<td>10</td>
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<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>2,4-DB</td>
<td>94-82-6</td>
<td>90</td>
<td>46</td>
<td>5</td>
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<td>Low</td>
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<tr>
<td>1,2-Dibromo-3-chloropropane</td>
<td>96-12-8</td>
<td>1</td>
<td>1000</td>
<td>190</td>
<td>Medium</td>
<td>High</td>
<td>Medium</td>
</tr>
<tr>
<td>1,2-Dibromoethane (ethylene dibromide)</td>
<td>106-93-4</td>
<td>0.4 (P)</td>
<td>4300</td>
<td>100*</td>
<td>High</td>
<td>High</td>
<td>Medium</td>
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<tr>
<td>1,2-Dichloropropane</td>
<td>78-87-5</td>
<td>40 (P)</td>
<td>2700</td>
<td>700*</td>
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<td>High</td>
<td>Medium</td>
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<td>1,3-Dichloropropene</td>
<td>542-75-6</td>
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<td>2250</td>
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<td>39800</td>
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<td>Endrin</td>
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</tr>
<tr>
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<td>93-72-1</td>
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<td>140</td>
<td>21</td>
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<tr>
<td>HCB</td>
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<td>0.005</td>
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<td>Medium</td>
<td>High</td>
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<td>Isoproturon</td>
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<td>700</td>
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<td>Medium</td>
<td>Low</td>
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<tr>
<td>γ-HCH</td>
<td>58-89-9</td>
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<td>400</td>
<td>Medium</td>
<td>Medium</td>
<td>High</td>
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<tr>
<td>MCPA</td>
<td>2039-46-5</td>
<td>2</td>
<td>866000*</td>
<td>25</td>
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<td>Medium</td>
<td>Low</td>
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<tr>
<td>MCPP</td>
<td>708-51-90</td>
<td>None²</td>
<td>660000*</td>
<td>21</td>
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<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Methoxychloride</td>
<td>72-43-5</td>
<td>20</td>
<td>0.100</td>
<td>120</td>
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<tr>
<td>Metolachlor</td>
<td>51218-45-2</td>
<td>10</td>
<td>530</td>
<td>90</td>
<td>High</td>
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<td>Medium</td>
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<tr>
<td>Molinate</td>
<td>2212-67-1</td>
<td>6</td>
<td>970</td>
<td>21</td>
<td>Medium</td>
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<tr>
<td>Pendimethalin</td>
<td>40487-42-1</td>
<td>20</td>
<td>0.275</td>
<td>90</td>
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<tr>
<td>Simazine</td>
<td>122-34-9</td>
<td>2</td>
<td>6</td>
<td>60</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>2,4,5-T</td>
<td>93-76-5</td>
<td>9</td>
<td>278</td>
<td>30</td>
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<td>Medium</td>
<td>Low</td>
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<tr>
<td>Terbutylazine</td>
<td>5915-41-3</td>
<td>7</td>
<td>9</td>
<td>45</td>
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<tr>
<td>Trifluralin</td>
<td>1582-09-8</td>
<td>20</td>
<td>0.300</td>
<td>60</td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
</tr>
</tbody>
</table>

* Estimated value; ¹ occurs in drinking-water at concentrations well below those causing toxic effects; ² unlikely to occur in drinking-water
4.7 EMERGING ISSUES

4.7.1 Pharmaceuticals
There is increasing concern about micropollutants originating from pharmaceuticals and active ingredients in personal care products excreted by people as complex mixtures into wastewater systems (Kümmerer, 2004). There are a number of routes through which pharmaceuticals can impact groundwater, but primarily the sources are both untreated and treated sewage. There is also evidence that substances of pharmaceutical origin are not completely eliminated during wastewater treatment or biodegraded in the environment (Daughton and Ternes, 1999; Drewes and Shore, 2001).

Health aspects
Current knowledge on the health effects of pharmaceutically active compounds at concentration levels found in groundwater samples, which are several orders of magnitude lower than concentrations which would be therapeutically active, indicates that there are no effects on human health reasonably to be expected from this source of exposure (Ternes, 2001). However, there is an ongoing debate on how comprehensive health effect data from short-term high dose exposure during diagnosis and treatment should be extrapolated to long-term low dose exposure during drinking-water consumption. Moreover, the problem of correctly assessing the risk from unexpected environmental (underground) and technical metabolites (from oxidative drinking-water treatment) is not resolved. Investigation on the fate of pharmaceutically active substances in drinking-water unit operations and processes is in progress in numerous research studies e.g. in Europe, Australia, Japan, and North America. Additionally, proposals for risk assessment procedures have been suggested (Montforts, 2001).

Transport and attenuation
A lack of knowledge still persists regarding the fate of pharmaceuticals during travel through the subsurface. Findings of recent studies indicate that travel through the subsurface can substantially attenuate the majority of pharmaceutically active compounds where surface water or domestic wastewater is used for groundwater recharge. However, where groundwater is influenced by surface water, such as artificial recharge, polar pharmaceutically active compounds such as clofibric acid (blood-lipid regulating agent), carbamazepine and primidone (antiepileptic drugs) and iodinated X-ray contrast agent can migrate through the subsurface and have been detected in groundwater samples in Germany and the USA (Heberer et al., 1998; Kuehn and Mueller, 2000; Drewes et al., 2001).

4.7.2 Endocrine disrupting compounds
There has been increasing public concern about various environmental contaminants which mimic estrogens and other sex-hormones and hence interfere with endogenous endocrine systems, with potential adverse effects on human health. A global assessment of the state of knowledge on endocrine disrupters was published by the International Programme on Chemical Safety (Damstra et al., 2002).
More than 70,000 chemicals are discussed with respect to endocrine disruptive potential (Bradley and Zacharewski, 1998). These compounds represent both synthetic chemicals produced industrially (such as cleaners, pesticides, food additives, birth control pills, cosmetics) and naturally occurring compounds (such as steroidal hormones, plant-produced estrogens, herbal supplements and metals). Whilst endocrine disrupting compounds (EDCs) are largely organic compounds, it should be noted that some inorganic substances such as metals are also suspected of endocrine disrupting effects. Although their potential occurrence in drinking-water has been the subject of public attention and discussion in some countries, it is important to note that human exposure is chiefly through food.

The steroidal sex hormones estradiol, estrone and testosterone are a class of hormonally active agents of particular interest because they are naturally excreted into the environment from human and animal sources as well as extensively used as pharmaceuticals (e.g. birth control pills). Of the numerous synthetic chemicals that have been implicated as endocrine disrupters, many are no longer used in commerce in many countries, such as some organochlorine pesticides (e.g. DDT, endosulphan, dieldrin, and toxaphene), and PCBs. Other hormonally active compounds, such as various phenolics and phthalates, continue to be used in a variety of industrial applications worldwide (NRC, 1999). Alkylphenol is a biological metabolite of alkylphenol polyethoxylates commonly used in a variety of industrial, agricultural and household applications as non-ionic surfactants. Alkylphenol and compounds are both believed to be endocrine disrupters (Lye et al., 1999). Another synthetic chemical that has measurable hormonal activity is Bisphenol A used as a chemical intermediate for numerous industrial products including polymers, resins, dyes and flame retardants.

Health effects of hormonally active compounds are based on binding of these compounds on steroid hormone receptors which control fundamental mechanisms of gene regulation. The disruption of this process can result mainly in reproductive changes. Developmental defects, neurobehavioral abnormalities, immunological deficits, carcinogenesis and ecologic effects can also be induced (NRC, 1999).

Determining the risk of EDCs to humans is difficult because exposure to these agents has not been routinely monitored, and effects that might be attributed to background concentrations could be complicated by endogenous hormones, pharmacological estrogens (e.g. hormonal contraceptives), and naturally occurring hormonally active agents (e.g. phytoestrogens) that are ubiquitous in the environment (NRC, 1999). Although it is clear that exposures to EDCs at high concentrations can affect human health, the extent of harm caused by exposure to these compounds in concentrations that are commonly found in groundwater is debated (NRC, 1999). Generally, natural and synthetic steroidal hormones are several thousand times more potent than industrial chemicals, pesticides and metals (Khan and Ongerth, 2000).

The WHO has not yet specifically proposed any guidelines for the occurrence of EDCs in drinking-water. However, some of the organochlorine compounds are regulated as pesticides.

The relevance to human health of EDCs occurring in water is currently uncertain. Their occurrence in groundwater is linked to the release of sewage, manure, or spill of specific synthetic chemicals into the environment. The specific processes used in
wastewater treatment facilities play a key role in the introduction of EDCs into surface water and groundwater (Drewes and Shore, 2001). The transport of EDCs to groundwater depends on their hydrophobicity and degradability. The majority of highly potent compounds such as steroids are hydrophobic and degradable. Degradation rates of EDC compounds depend on temperature, soil characteristics and their molecular weights (IUPAC, 2003).

The potential risk related to an uptake of individual EDCs present in wastewater affected groundwater by humans does not appear to be very significant. The small data set about the fate of EDCs (such as natural and synthetic hormones, surfactants and pesticides) during percolation through the soil and aquifer and the lack of toxicity data on long-term exposure of low concentrations makes it at present impossible to finally assess the impact of EDCs in groundwater on human health. However, contaminated groundwater may be impacted by a mix of different compounds, which could additively impose endocrine disrupting effects.

4.8 REFERENCES


