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Filtration Materials for Groundwater

A Guide to Good Practice

Ivan Kozyatnyk



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Published by

IWA Publishing
Alliance House
12 Caxton Street
London SW1H 0QS, UK
Telephone: +44 (0)20 7654 5500
Fax: +44 (0)20 7654 5555
Email: publications@iwap.co.uk
Web: www.iwapublishing.com

First published 2016
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ISBN: 9781780406992 (Hardback)
ISBN: 9781780407005 (eBook)

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Chapter 1

Pollutants in groundwater

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1.1 INTRODUCTION

Groundwater contamination generically refers to modifications in biological, physical or chemical characteristics (e.g., salinity, temperature, etc.), the presence of undesirable solutes at significant concentrations, or radioactivity. It may be: (i) of natural origin, (ii) the result of human activity; or (iii) a combination of the previous two. Naturally occurring processes, such as decomposition of organic material in soils or leaching of mineral deposits, can result in increased concentrations of several substances such as manganese, sulphate, chloride, organic matter, fluoride, arsenic, nitrate, selenium, uranium, and radon. Sources of groundwater contamination due to human activities are widespread and include diffuse sources as well as point-sources of pollution, such as land application of animal manure containing contaminants (e.g., veterinary pharmaceuticals) and agrochemicals in agriculture, leakages from sewers or sanitation systems, from waste disposal sites, landfills, underground storage tanks and pipelines, and accidental spills in mining, industry, traffic, health care facilities and military sites. The exploitation of petroleum products and the development of the industrial chemistry have given rise to a large number of organic chemicals, many of which are found in the environment (Kurwadkar, 2014). Various studies have shown that anthropogenic chemicals such as pesticides (Arias-Estevez *et al.* 2008; Postigo & Barceló, 2015), pharmaceuticals and personal care products (Holm *et al.* 1995; Deo & Halden,

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2013; Postigo & Barceló, 2015), industrial chemicals (Diaz-Cruz & Barceló, 2008; Meffe & de Bustamante, 2014), and fuel additives (van Wezel *et al.* 2009) occur in groundwater. U.S. Geological Survey (USGS) investigations have assessed the occurrence, distribution, and benchmark exceedance of various contaminants in water from public-supply wells and domestic wells, including pesticides (Gilliom *et al.* 2006), volatile organic compounds (Squillace *et al.* 2002; Zogorski *et al.* 2006), pesticides and nitrate (Squillace *et al.* 2002; DeSimone, 2009). Chemical mixtures were frequently detected, often with concentrations of individual contaminants approaching human-health benchmarks. Chemical mixtures that most frequently occurred and had the greatest potential toxicity were composed of arsenic, strontium, uranium, radon, and nitrate (Toccalino *et al.* 2012).

Many organic chemicals are known to have potential human health impacts, and some of these may occur in groundwater at relevant concentrations. The list of those for which guideline values and national quality standards have been developed has been continually extended and revised. Among these: mono-aromatic hydrocarbons (benzene, toluene, ethylbenzene and xylenes – BTEX), volatile chlorinated hydrocarbons (tetrachloroethene – PCE, trichloroethene – TCE), and pesticides.

This chapter focuses on chemical substances that have reasonable potential to contaminate groundwater and have human health impacts. It provides information about: (i) the major sources of pollution (§ 1.2); (ii) inorganic contaminants (§ 1.3.1 to 1.3.3), (iii) organic contaminants (§ 1.3.4); and (iv) emerging issues (§ 1.3.5). Further information about the chemicals discussed in this chapter is available in the World Health Organization (WHO) Guidelines for Drinking-Water Quality, Volume 1 (WHO, 2004), as well as in the WHO's Water, Sanitation and Health website (http://www.who.int/water_sanitation_health/dwq/chemicals/en/index.html).

1.2 POLLUTION SOURCES

The occurrence of natural constituents in groundwater has large variability according to the nature of the aquifer. Saltwater intrusion or leaching from natural soil can bring solutes to groundwater and affect its quality for the intended uses, especially in case of drinking purposes.

Table 1.1 summarizes the most frequent contaminants of natural origin. Arsenic and fluoride are examples of relevant naturally occurring groundwater constituents on worldwide basis. Further natural constituents of potential interest include selenium, radon and uranium. In some settings, also nitrate occur naturally at relevant concentrations, though it usually has anthropogenic origin.

Despite natural pollution sources can exist, groundwater becomes polluted primarily because of human activities. Table 1.2 summarizes pollution sources potentially affecting groundwater quality, which are roughly classifiable as industrial, municipal-residential, and agricultural sources.

Table 1.1 Most frequent contaminants of natural origin.

| Contaminant | Origin | Possible Effects |
|--------------------|--|--|
| Iron | Mineral dissolution in acidic and reducing environment | Affects water potability |
| Manganese | Mineral dissolution in acidic and reducing environment | Affects water potability |
| Arsenic | Dissolution from sediments and rocks under some chemical circumstances | Human health effects |
| Boron | Marine sediments and volcanic rocks | Human health effects, detrimental to plants |
| Fluoride | Volcanic acidic rocks and ash | Human bone and teeth damages |
| Selenium | Sedimentary rocks of marine origin | Wildlife damages |
| Radon | Uranium minerals | Human health effects caused by radioactivity |
| Uranium | Trace elements in most rocks and soils, formed by radioactive decay | Human health effects caused by radioactivity |

Table 1.2 List of the Potential Groundwater Contamination.

| Industrial Sources | Municipal Residential Sources | Agricultural Sources |
|----------------------------|---------------------------------------|---|
| Chemicals storage & spills | Municipal waste land-spreading | Chemical spills |
| Fuels storage & spills | Salt for de-icing streets | Fertilizers and pesticides application |
| Mine tailing piles | Streets & parking lots | Livestock waste storage facilities & land-spreading |
| Pipelines | Cleaners | Underground storage tanks |
| Underground storage tanks | Landfills | Wells poorly constructed or abandoned |
| | Leaky sewer lines | |
| | Septic systems | |
| | Wells poorly constructed or abandoned | |

Sources: <http://www.lennotech.com/groundwater/pollution-sources.htm#ixzz3frbGDNc7>.

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Many industrial facilities handle substances potentially causing groundwater contamination, such as metals, petroleum products, paints and coatings, rubber and plastics, electrical components, pharmaceuticals, pesticides, non-chlorinated and chlorinated solvents, paper, inks and dyes, fabrics, adhesives, fertilizers, wood preservatives, cleaning solvents and explosives.

Municipal wastewater systems can be a source of many categories of contaminants, such as nitrates and pollutants of emerging concern, such as ingredients of personal care products, drugs, detergents and disinfectants.

Agricultural activities have significant impact on water resources as they use herbicides, fertilizers and pesticides in direct contact with soil. Moreover land spreading of animal manures can cause nitrate pollution.

Instead of being released from industrial facilities, some substances are rather formed for natural degradation phenomena once the release of a parent chemical has occurred (Mattes *et al.* 2010; Chambon *et al.* 2013). For example, in rare instances 1,2-dichloroethene (1,2-DCE) or vinyl chloride (VC) may be released directly into groundwater but, more commonly, they are detected as breakdown products of the anaerobic biodegradation of tetrachloroethene (PCE) or trichloroethene (TCE). Similar changes can occur in the sequential reductive dehalogenation of polychlorinated biphenyls (PCBs), resulting in the formation of lower chlorinated homologues from the parent PCBs.

Pollution sources are usually classified also in term of extent, as point or diffuse pollution sources. Point-source pollution refers to contaminant inputs in relatively small areas, such as waste disposal sites and accidental spills. It results in a groundwater plume that has the highest pollutant concentrations nearest the source and diminishing concentrations farther away from the source. Diffuse pollution (or non-point pollution) refers to pollution inputs throughout a large territory. This kind of contamination may be caused by agriculture and extensive animal farming, which involve agrochemicals, nutrients, water and soil quality amendments, pesticides, and herbicides.

1.3 RELEVANT CLASSES OF CONTAMINANTS

1.3.1 Inorganic species

1.3.1.1 Arsenic

Arsenic is a metalloid, having properties of both metal and nonmetal. It can occur in several oxidation states (−3, 0, +3 and +5). It is ubiquitous in the environment and is naturally present in soil, water, air, plants, and animals (Tamaki & Frankenberger, 1989).

Naturally occurring arsenic is commonly found in a variety of solid phases: as a component of volcanic rocks (in sulfide minerals, principally arsenopyrite), adsorbed to and co-precipitated with metal oxides (especially iron oxides), adsorbed to surfaces of clays, and associated with sulfide minerals and organic

carbon. The average arsenic concentration in the earth's crust has been estimated to be approximately 2 parts per million (Hem, 1989; Yan-Chu, 1994).

Background concentrations of arsenic in groundwater in most countries are $<10 \mu\text{g/l}$. However, surveys performed in arsenic-rich areas showed a very large range of values, from <0.5 to $5000 \mu\text{g/l}$ (Smedley & Kinniburgh, 2001). Investigations performed in Bangladesh indicate that 20 per cent of 25000 boreholes tested in that country have arsenic concentrations exceeding $50 \mu\text{g/l}$ (Alaerts *et al.* 2001). Arsenic concentration in German groundwater downstream of abandoned waste disposal sites was found to have an average concentration of $61 \mu\text{g/l}$ (253 sites), due to arsenic leaching from domestic coal ashes contained in the household waste. In contrast, the mean arsenic concentration in uncontaminated aquifers was $0.5 \mu\text{g/l}$ (472 sites) (Kerndorff *et al.* 1992). Naturally occurring arsenic can be mobilized and subsequently migrate into groundwater at landfills and other sites where contaminants, such as petroleum products, can cause anaerobic conditions (Welch *et al.* 2000).

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 can interact at some extent by reactions on mineral surface (Smedley & Kinniburgh, 2001).

In natural waters arsenic is mostly found as inorganic oxyanion forms (trivalent arsenite or pentavalent arsenate). Redox potential (Eh) and pH are the most important factors controlling its speciation (Smedley & Kinniburgh, 2001). Arsenic shows high sensitivity to mobilization at the pH values typically found in groundwater (6.5–8.5) and under either oxidizing or reducing conditions. Under oxidizing conditions, H_2AsO_4^- is dominant at low pH (<6.9), while at higher pH, HAsO_4^{2-} becomes dominant (H_3AsO_4 and AsO_4^{3-} may be present in extremely acidic and alkaline conditions, respectively). Under reducing conditions at pH <9.2 , the uncharged As(III) species H_3AsO_3 will predominate.

Transport is largely controlled by the aquifer conditions, particularly by adsorption on ferric oxohydroxides, humic substances and clays. There is no process in the subsurface that alters arsenic species beside precipitation and adsorption. Arsenic adsorption is most likely to be non-linear, with the rate of adsorption disproportionately decreasing with increasing concentrations in groundwater. This leads to reduced retardation at high concentrations. The different arsenic species exhibit different retardation behaviors. This was demonstrated by Gulens *et al.* (in Smedley & Kinniburgh, 2001) by soil column experiments with different 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 faster than under the conditions (i), but it 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 As(III) and As(V) was greatly reduced.

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1.3.1.2 Fluoride

Fluoride (F^-) is an inorganic anion of fluorine.

It naturally occurs in rocks in many geological environments. High concentrations occur in some metamorphic and sedimentary rocks that contain significant amounts of fluoride-bearing minerals such as fluorite and apatite (Hem, 1989; Vithanage & Bhattacharya, 2015).

Levels in water are normally below 1.5 mg/l, but groundwater has been found to contain values >50 mg/l in some areas rich in fluoride-containing minerals. Fluoride concentrations in groundwater are particularly high in groundwater flowing through acid volcanic rocks, e.g. in Sudan, Ethiopia, Uganda, Kenya and Tanzania. In Kenya, 61% of groundwater samples collected nationally from drinking water wells exceeded 1 mg/l (WHO, 2006).

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. The concentration of F^- in groundwater is driven by calcium ions and the solubility product of fluorite (CaF_2). At equilibrium conditions, a calcium concentration of 40 mg/l equates to a fluoride concentration of 3.2 mg/l. In groundwater with high concentrations of calcium ions, fluoride concentrations rarely exceed 1 mg/l. High fluoride concentrations in groundwater are usually caused by a lack of calcium. During high percolation rate experiments, 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 high pH (>8), dominated by sodium ions and carbonate species, fluoride concentrations commonly exceed 1 mg/l (Vithanage & Bhattacharya, 2015). Concentrations >50 mg/l have been recorded in groundwater in South Africa and in Arizona (Hem, 1989).

Fluoride ions form strong complexes with aluminum, beryllium and iron (III).

1.3.1.3 Nitrogen species

Nitrogen is present in human and animal waste under organic forms, which may be mineralized to inorganic forms. Ammonia (ionized as NH_4^+ , non-ionized as NH_3) mainly results from animal feed lots and the use of manures in agriculture, or from on-site sanitation or leaking sewers. 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 concentrations can be greatly elevated due to agricultural activities and sanitation practices. 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.

Natural levels of ammonia in groundwater are usually <0.2 mg/l. Nitrate concentration is normally low, and typically in the range 0–18 mg/l as NO_3^- . High

concentrations of nitrate in groundwater are mostly caused by agricultural activity or sanitation practices. However, natural nitrate concentrations can also exceed 100 mg/l as NO_3^- in some arid parts of the world, such as Sahel and North Africa and the arid zones of Australia (WHO, 2006).

NH_4^+ shows high tendency for adsorption on 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 typically very 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. When moving with water into a geologic medium that lacks oxygen, nitrate undergoes denitrification, whereby some of it can be converted into gas and released to the atmosphere (US EPA, 2007).

1.3.1.4 Metals

This paragraph focuses on metals related to human activities with physical, chemical and toxicological properties that make them potential contaminants for groundwater, i.e. cadmium (Cd), lead (Pb), nickel (Ni), chromium (Cr), and copper (Cu).

These metals are natural constituents in groundwater, having their origin in weathering and solution of numerous minerals. However, natural concentrations in groundwater are generally low. Typical values are <10 $\mu\text{g/l}$ (copper, nickel), <5 $\mu\text{g/l}$ (lead) or <1 $\mu\text{g/l}$ (cadmium, chromium). The concentrations can locally increase naturally in aquifers containing high amounts of heavy metal bearing minerals, up to levels that are of toxicological relevance and exceeding drinking-water guidelines.

Metal concentrations in groundwater may be of particular concern where it is directly affected by activities such as mining, manufacturing industries, metal finishing, wastewater and waste disposal, agriculture. As an example Table 1.3 reports ranges of typical background concentrations compared to ranges at metal mining sites or in oilfield groundwater for Cd, Ni and Pb. Corrosion of copper pipes can cause high copper levels in drinking-water (Araya *et al.* 2003). Another anthropogenic cause of elevated metal concentrations in groundwater 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, due to higher deposition rates of the acidifying anions sulfur and nitrate from the atmosphere in forests due to the large surface of needles and leaves and low neutralization capacity against acids of forest soils typically poor in nutrients (WHO, 2006).

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

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cations is severely limited by precipitation as an oxide, hydroxide, carbonate or phosphate minerals, or more likely by strong adsorption onto 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 chemical degradation.

Table 1.3 A few element concentrations ($\mu\text{g/l}$) from oilfield and metal mining sites compared to groundwater background values (adapted from WHO 2006).

| Element | Oilfield Groundwater | Metal Mining Groundwater | Background Values |
|---------|----------------------|--------------------------|-------------------|
| Cd | 1–100 | 1–400 | 1–5 |
| Ni | 1–500 | 1–100,000 | 1–170 |
| Pb | 1–30 | 10–1500 | <1–10 |

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 can be found in the environment in two valence states, Cr(III) and Cr(VI). The former predominates in soils, whereas the latter occurs exclusively as chromate (CrO_4^{2-}) from anthropogenic sources. 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. In most aquifers chromium is not very mobile because of precipitation of hydrous Cr(III) oxide. (Smedley & Kinniburgh, 2001).

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. 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 changed in groundwater by naturally occurring complexing agents like fulvic acids, which is especially true for copper (Schnitzer & Khan, 1972).

1.3.2 Organic pollutants

Human activity has released and release to the environment a vast range of anthropogenic organic chemicals, commonly termed 'micro-pollutants', that may detrimentally impact groundwater quality. Here the focus is on commercially and industrially derived class of chemicals which have been observed to occur frequently as groundwater contaminants, due to widespread use and associated release potential and physical and chemical properties facilitating their occurrence in groundwater. Of the many organic chemicals that potentially contaminate groundwater, the major chemical groups include:

- aromatic hydrocarbons: benzene, toluene, ethylbenzene and xylenes (BTEX);
- chlorinated hydrocarbons (aliphatic and aromatic): dichloromethane, trichloromethane (also known as chloroform), tetrachloromethane (also known as carbon tetrachloride), vinyl chloride, 1,1-dichloroethene, 1,2-dichloroethene *cis*- and *trans*- isomers, trichloroethene, tetrachloroethene (also known as perchloroethene), 1,2-dichloroethane, 1,2-dichlorobenzene, and 1,4-dichlorobenzene.

Other chemical groups may have received widespread industrial use, but are thought to pose a much lower risk to groundwater. Examples of the latter may include Polycyclic Aromatic Hydrocarbons (PAHs) and Polychlorinated Biphenyls (PCBs).

1.3.2.1 Aromatic hydrocarbons (BTEX)

Mononuclear (single-ring) aromatic hydrocarbons, such as BTEX, are amongst the most common groundwater contaminants and the major aromatic fraction of many fuels. Thus this class of compounds is typically associated with fuel and fuel-related contamination point-sources, originating from petroleum production, refining and wholesale and retail distribution (service stations) of petroleum products. They are also used as solvents and raw materials in chemical production (Newell *et al.* 1995).

A German-USA groundwater survey performed in the past (Kerndorff *et al.* 1992) showed that BTEX were quite diffused, benzene being the most frequently detected.

Natural attenuation processes (volatilization, dispersion and biodegradation) of BTEX are very significant mechanisms reducing the pollutant concentrations and plume extension in groundwater. Usually the BTEX plume is limited to distances of a few hundred meters from source zones. In Newell and Connor (1998) and Wiedemeier *et al.* (1999), 86% of the 604 plumes evaluated in the USA were less than 100 m long, with only 2% of plumes longer than about 300 m. One of the studies indicated 8% of 271 plumes as still growing, 59% of plumes as approximately stable, and 33% of plumes as shrinking. Thus although hydrocarbon sources can be numerous, BTEX impacts are likely to remain local to the sources zones.

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Among the natural attenuation processes, biodegradation is usually the most affecting mechanism BTEX removal, due to their high biodegradability under a wide range of conditions. BTEX are readily degraded when dissolved oxygen is present in groundwater while, in general, their degradation rate is lower under anaerobic conditions. Rates may vary significantly for individual compounds (Barker *et al.* 1987; Wiedemeier *et al.* 1999; Noble & Morgan, 2002).

1.3.2.2 Chlorinated hydrocarbons

Chlorinated hydrocarbons are used in a variety of industrial activities (e.g., metal stripping, chemical manufacturing, pesticide production, etc.), including almost any facility where solvents, cleaners or paint removers are used on metals, textiles and leathers. 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 hydrocarbons with a high proportion of a single component. A multitude of point sources exist in many urban areas, due to the diversity and frequency of chlorinated hydrocarbon users.

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). Trichloroethene (TCE) and tetrachloroethene (PCE), 1,2-dichloroethene *cis* (1,2-DCE *cis*) and vinyl chloride (VC) have been the most frequently detected chlorinated hydrocarbons. Many groundwater supplies or monitoring wells were contaminated particularly by TCE and to a lesser extent by PCE (Cavallero *et al.* 1985; Fusillo, 1985; Rivett *et al.* 1990).

Many chlorinated hydrocarbons enter the subsurface in the Dense Non Aqueous Phase Liquid (DNAPL) form and may travel down to significant depths within the aquifers (Pankow & Cherry, 1996). Dissolution of DNAPL sources is expected to be slow, taking years to decades, particularly from residual DNAPL pools that have diffused into low-permeability strata.

On average chlorinated hydrocarbon plumes are significantly longer than BTEX plumes. Newell *et al.* (1990) reported a median length of about 300 m for chlorinated ethenes (PCE, TCE, DCE, VC) plumes (88 sites), while Mackay and Cherry (1989) and Jackson (1998) mentioned dissolved-phase plumes in the 1–10 km-scale. This is partially due to limited sorption, particularly for the less hydrophobic compounds (Rivett *et al.* 2001; Rivett & Allen-King, 2003).

Under aerobic conditions, biodegradation of solvents such as TCE and PCE can be limited to non-existent. Under reducing conditions biodegradation pathways exist, the most known being those involving the sequential reductive dechlorination of chlorinated hydrocarbons where lesser chlorinated organics (TCE, 1,2-DCE *cis*, VC) and ultimately hydrocarbons, such as ethane or ethene, are formed (Vogel *et al.* 1987). Biodegradation of chlorinated hydrocarbons has proven to be relatively complicated with five possible degradation processes

(Wiedemeier *et al.* 1999). Under anaerobic or low oxygen conditions, degradation processes include: (i) dehalorespiration, where chlorinated hydrocarbons are 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 (Lorah & Olsen, 1999). Due to the complexity of biodegradation processes, there is a wide divergence in reported biodegradation rates of chlorinated hydrocarbons (Wiedemeier *et al.* 1999; Noble & Morgan, 2002). Much longer half-life values may occur for chlorinated hydrocarbons compared to BTEX.

1.3.2.3 Pesticides

Pesticides represent a wide range of compounds used mostly as insecticides, herbicides, and fungicides. Pesticides are intentionally applied to protect crops in agriculture as well as to control pests and unwanted vegetation in gardens, buildings, railway tracks, forests and roadsides. They may be accidentally released from production sites 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.

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). 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 program has confirmed the widespread occurrence of pesticides (Kolpin *et al.* 2000). The newer work has 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. This picture is largely confirmed by monitoring efforts in Europe. Herbicides, which are widely used in cereal cultivation, such as methylchlorophenoxypropionic acid and isoproturon are detected in the countries of northern Europe (Spliid & Køppen, 1998). 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 nonagricultural usage such as on railways. Because

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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).

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. 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.

There are several processes by which pesticide may be degraded. Organic phosphorus pesticides tend to hydrolyze rather quickly at pH values above neutral (Graham-Bryce, 1981). The biodegradability of pesticides depends on their molecular structure and soil half-lives can vary between a couple of days to years (Lavy *et al.* 1996; Chilton *et al.* 2000). Carbamates are noted for their high susceptibility to degradation (Williams *et al.* 1988). Chlorinated pesticides and triazine herbicides are the most resistant to biodegradation and may persist for years following application. 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.

1.3.2.4 Polycyclic aromatic hydrocarbons

PAHs are a diverse class of compounds of natural and anthropogenic origin. They are a component of creosotes and coal tars frequently associated with former gasworks and coal carbonization (coking) works (Johansen *et al.* 1997).

PAHs are generally not found in water in notable concentrations. Most of them, in fact, have extremely low solubility in water and have a high tendency to adsorb to the organic matrix of soils, particularly the higher molecular mass (higher-ring PAHs, such as the 5-ring benzo(a)pyrene). However: (i) creosote and coal tars may occur as a DNAPL and slowly migrate deep into the subsurface, and (ii) 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 & Barker, 1999).

1.3.2.5 Polychlorinated biphenyls

PCBs are a class of stable compounds, each containing a biphenyl nucleus (two linked benzene rings) with two or more substituent chlorine atoms. PCBs were produced industrially as complex mixtures that often contained between 40 and 60 different chlorinated biphenyls. PCB oils, historically used in electrical transformer facilities, were DNAPLs.

Most PCBs are of low solubility in water and sorptive and hence dissolved-phase plumes in groundwater tend not to be large. Dissolved PCBs are generally slow to biodegrade and hence may serve as long-term sources of groundwater contamination.

1.3.3 Chemicals of emerging concern

Recently an increasing concern is posed by: (i) micropollutants originating from pharmaceuticals, and (ii) endocrine disrupting compounds, i.e. various environmental contaminants which mimic estrogens and other sex-hormones and hence interfere with endogenous endocrine systems, with potential adverse effects on human health.

1.3.3.1 *Pharmaceuticals*

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 & Ternes, 1999; Drewes & Shore, 2001).

A lack of knowledge still persists regarding the fate of pharmaceuticals during travel through the subsurface. However, pharmaceutically active compounds such as clofibric acid (blood-lipid regulating agent), carbamazepine and primidone (antiepileptic drugs) and iodinated X ray contrast agent have been detected in groundwater samples in Germany and the USA (Heberer *et al.* 1998; Kuehn & Mueller, 2000; Drewes *et al.* 2001).

1.3.3.2 *Endocrine disrupting compounds (EDCs)*

More than 70000 chemicals are discussed with respect to endocrine disruptive potential (Bradley & 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). 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). Other hormonally active compounds, such as various phenolics and phthalates, are 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 nonionic 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

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intermediate for numerous industrial products including polymers, resins, dyes and flame retardants. Of the numerous synthetic chemicals that have been implicated as endocrine disruptors, many are no longer used in commerce in many countries, such as some organochlorine pesticides (e.g., DDT, endosulphan, dieldrin, and toxaphene), and PCBs. Whilst endocrine disrupting compounds are largely organic compounds, it should be noted that some inorganic substances such as metals are also suspected of endocrine disrupting effects.

The occurrence of EDCs 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 & 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).

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Filtration Materials for Groundwater

A Guide to Good Practice

Ivan Kozyatnyk

Groundwater is a source for drinking and industrial water supply and pollution created by active industrial sites which often cause social, health, and environmental problems. This groundwater eventually drains into adjacent water sources.

Filtration Materials for Groundwater: A Guide to Good Practice presents the up-to-date technology of purification of polluted ground water, its treatment for industrial and human needs and the remediation of polluted sites.

The book examines:

- Types of pollutants in ground water including the main inorganic and organic pollutants and their behaviour
- Filtration materials for water treatment and principles of their choice. How to choose suitable filtration materials according to targeted compounds and estimate its efficiency
- Technologies for ground water treatment.
- Cost and risks estimation of treatment facilities. Lifetime, risks and cost estimation of technology
- Examples of modern ongoing facilities for ground water treatment and polluted sites remediation.

This book is of interest to scientists and engineers who deal with the problem of purification of groundwater for different purposes and the remediation of polluted sites.



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ISBN: 9781780406992 (Paperback)

ISBN: 9781780407005 (eBook)

