In the summer of 1996, nine individual cells were constructed within a contaminated NAPL zone of the shallow aquifer at the site (Bedient et al., 1999). The area at OU 1 is contaminated with a light nonaqueous phase mixture of chlorinated solvents and fuel hydrocarbons, which are present in residual and free phase across the site. Nine enhanced aquifer remediation technologies were demonstrated in side-by-side tests at the Hill AFB site. The demonstrations were performed inside 3 m x 5 m cells isolated from the surrounding shallow aquifer by steel sheet piling. The technologies demonstrated were designed to manipulate the solubility, mobility, and volatility of the contaminants in order to enhance the aquifer remediation over a standard "Pump-and-Treat" system. Over 80,000 samples of water and soil were collected as part of tracer tests, soil flushing demonstrations, and routine characterization efforts at OU 1.

Hill AFB's OU 1 site was chosen because all nine technologies could be demonstrated side-by-side, within a similar hydrogeology with similar contamination levels. To facilitate comparisons among the nine technologies being demonstrated, the cell instrumentation, characterization, and basic study methodology were standardized prior to the beginning of field work. Each of the studies was conducted in a test cell designed to separate the test area from the surrounding environment. The demonstrated technologies facilitated contaminant removal through dissolution, emulsification, or mobilization in ground water or through volatilization and enhanced bioremediation when air delivery systems were used. In some cases, this was the first time that remediation approach had been demonstrated in the field. More details and results from surfactant (Sabatini et al., 1999) and cosolvent (Rao et al., 1997) tests are described in the advanced remediation section of Chapter 13.

CLASSIFICATION OF ORGANIC COMPOUNDS

In the past 20 years, organic compounds in ground water have come to be recognized as one of the major threats to human health. This section will introduce some of the major classes and some of the most important compounds found in ground water. More detailed coverage on organic compounds in ground water can be found in Pankow and Cherry (1996), Manahan (1991), Sawyer et al. (1994), Schwarzenbach et al. (1993), and Fetter (1999).

Organic chemistry deals with the chemistry of carbon compounds; carbon is a unique element in that it forms four covalent bonds and is capable of bonding to other carbon atoms, with single, double, or triple bonds. It is this characteristic of carbon that gives rise to the possibility of great diversity in the physical and chemical properties of organic compounds. The simplest organic compounds are hydrocarbons consisting of carbon and hydrogen alone. The traditional approach to classifying organic compounds involves defining functional groups, which include a simple combination of two or more of the following atoms: C, H, O, S, N, P. Domenico and Schwartz (1998) present a condensed scheme of classification consisting of 16 major classes (Table 4.6) and is a useful approach for organizing organic contaminants in ground water. Elements such as O, N, S, P, H, and Cl can bond

TABLE 4.6 Classification of Organic Compounds

- 1. Miscellaneous Nonvolatile Compounds
- 2. Halogenated Hydrocarbons

Aliphatic

Trichloroethylene

Chlorobenzene

Aspartic acid

3. Amino Acids

Basic Structure

4. Phosphorous Compounds

Basic Structure

Malathion

5. Organometallic Compounds

Tetraethyllead

6. Carboxylic Acid

Basic Structure

Acetic acid

TABLE 4.6 Classification of Organic Compounds (continued)

7. Phenols

Basic Structure

OH

Cresol

8. Amines

Basic Structure

Aromatic NH₂

Aliphatic

CH₃
I

CH₃— N — H

Dimethylamine

9. Ketones

Basic Structure

0 || |R-C-R' Acetone

CH₃-C-CH₃

10. Aldehydes

Basic Structure

Formaldehyde O

O || R- C- H

11. Alcohols

Basic Structure

R-OH

Methanol CH₃ – OH

12. Esters

Basic Structure

O || |R-C-OR' Vinyl acetate

13. Ethers

Basic Structure

C-O-C

1,4-Dioxane

14. Polynuclear Aromatic Hydrocarbons

Phenanthrene

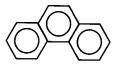


TABLE 4.6 Classification of Organic Compounds (continued)

15. Aromatic Hydrocarbons
Basic Structure
Toluene
CH

16. Alkane, Alkene, and Alkyne Hydrocarbons

R = aliphatic backbone

with carbon at any of four locations. Other groups such as OH and CH_3 can also bond with carbon to form many other compounds of interest. Hydrocarbons can be divided into aromatics, which contain a benzene ring, and aliphatics, which are compounds of C and H that are linked to a straight or branched carbon chain.

4.11.1 Aliphatic Hydrocarbons

The aliphatic hydrocarbons with more than one carbon atom can be classified as alkanes (single bonds), alkenes (double bonds) or alkynes (triple bonds). Straight chain alkanes include methane (CH₄), ethane (H₃CCH₃), propane (H₃CCH₂CH₃), butane, pentane, and hexane. These compounds are known as saturated hydrocarbons or paraffins. Alkanes can also have branched chains creating isomers with the same formula but with different properties. They conform to the general formula C_nH_{2n+2} , where n is the number of carbon atoms. Cycloalkanes are characterized by a ring structure that contains single C-C bonds such as cyclopropane and cyclohexane.

4.11.2 Aromatic Hydrocarbons

Aromatic hydrocarbons are compounds with a molecular structure based on that of the benzene ring, C_6H_6 . These compounds are a major constituent of petroleum and related products. Typical benzene-related compounds are shown in Figure 4.13 where the benzene molecule consists of six carbon and six hydrogen atoms in a cyclical form. The ring in the center represents a delocalized cloud of electrons. The carbon atoms in benzene are also capable of bonding to functional groups, and isomerism is possible. Nomenclature includes numbering the ring from 1 to 6 starting at the top of the ring. More than one functional group may

Name	Structure	Molecular Weight	Solubility in Water	Soil-Water Partition Coefficient
Benzene		78.11	1780 mg/L	97
Toluene	CH ₃	92.1	500 mg/L	242
Xylene, ortho	CH ₃	106.17	170 mg/L	363
Xylene, meta	CH ₃	106.17	173 mg/L	182
Xylene, para	CH3	106.17	200 mg/L	331
Ethyl benzene	CH ₂ CH ₃	106.17	150 mg/L	622

Figure 4.13 Benzene related compounds.

result in *ortho-*, *meta-*, or *para-* isomers, as in the case of xylene, which contains two methyl groups (Figure 4.10).

When several of the benzene rings are joined together, polycyclic aromatic hydrocarbons (PAH), such as naphthalene (2 benzene rings), phenanthrene (3 benzene rings), and benzo-a-pyrene (5 benzene rings) are formed. Figure 4.14 shows several of the important PAH's in ground water. These compounds are found in petroleum products, asphalt, coal tar, creosote and result from the incomplete combustion of fossil fuels. If the benzene ring is joined to another group, it may be referred to as a functional group, phenyl, and in combination with chlorine these compounds are called polychlorinated biphenyls (PCBs). They are extremely resistant to chemical, thermal, or biological degradation and tend to persist in the

Name	Structure	Molecular Weight	Solubility in Water	Soil-Water Partition Coefficient
Naphthalene		128.16	31.7 mg/L	1300
Acenaphthene		154.21	7.4 mg/L	2580
Ancenaphthylene		152.2	3.93 mg/L	3814
Fluorene		166.2	1.98 mg/L	5835
Fluoranthene		202	0.275 mg/L	19000
Phenanthrene		178.23	1.29 mg/L	23000
Anthracene		178.23	0.073 mg/L	26000

Figure 4.14 Structure and properties of some polycyclic aromatic hydrocarbons (PAHs).

environment. Because of human health and environmental effects, the manufacture of PCBs was banned in the U.S. in 1977. PCBs associated with the energy industry comprise some of the most serious contaminants to soils and ground water.

Alkenes are unsaturated hydrocarbons and have a carbon-carbon double bond with the general formula C_nH_{2n} , and include such compounds as ethene and propene, also called ethyl-

ene and propylene. Alkenes are referred to as olefins or the ethylene series. If functional groups are present, their position is indicated by the carbon atom to which they are bonded, and structural isomers can exist. Many of the chlorinated solvents (such as trichlorothylene) are of great concern as ground water contaminants at industrial sites. The acetylene series (alkynes) have triple bonds between two adjacent carbon atoms.

Phenols are characterized by a benzene ring with one attached hydroxyl group. They originate in ground water mostly as contaminants from industrial wastes or biocides. Phenol is a common ground water contaminant due to its many industrial uses and can also occur naturally with decomposing organic matter. Cresols have a methyl group and OH attached to the benzene ring and are used for the coal tar refining and for wood preservation. For example, lysol is a mixture of cresols and is sold as a household disinfectant. Chlorophenols are used as wood and leather preservatives and as antimildew agents. Phenol, in general, has acute toxic effects on bacteria and has been used as a disinfectant and germacide. Pentachlorophenol has been found at a number of creosote wood preserving sites and represents a highly toxic and nonbiodegradable compound.

Benzene is a carcinogen and inhaled benzene is readily absorbed by blood and is strongly taken up by fatty tissues. Benzene can be converted to phenol by an oxidation reaction in the liver that is responsible for the unique toxicity of benzene, which involves damage to bone marrow, and is known to cause leukemia. Benzene is also a skin irritant and can affect the central nervous system. Toluene is classified as moderately toxic and is much less toxic than benzene because it is readily excreted from the body. (Manahan, 1991).

4.11.3 Alcohols

Alcohols have one or more OH groups, are miscible with water, and have the potential for significant mobility; however, they are readily biodegraded. Alcohols are considered the primary oxidation product of hydrocarbons. At many industrial sites, alcohols are discharged into ground water and can act as solvents for other organics. Common alcohols include methanol (CH₃OH), ethanol (C₂H₅OH), 1-propanol, and isopropyl (C₃H₇OH). Selected alcohols are being used experimentally as cosolvents to help solubilize NAPLs from the subsurface. Aldehydes are the oxidation products of primary alcohols, and ketones are the oxidation products of secondary alcohols.

4.11.4 Halogenated Hydrocarbons

Halogenated hydrocarbons are one of the largest and most important groups of contaminants found in ground water. This group consists of both aliphatic and aromatic subclasses and is characterized by the presence of one or more halogen atoms (Cl, Br, F). Included in the aliphatic group are solvents such as methylene chloride, chloroform, tetrachloroethylene (PCE), trichloroethylene (TCE), 1,2 dichloroethylene (1,2 DCE), and vinyl chloride. Many of the halogenated ethenes have been found in large quantities in ground water, associated with industrial sites where solvents, cleansers, and degreasers were used. Many of these compounds

in the halogenated group are biodegradation products from other chlorinated compounds in the production of plastics (Chapter 7 and Figure 4.15).

The aromatic group of chlorinated pesticides includes DDD, DDE, DDT, and 2,4-D and 2,4,5-T compounds. The latter two are herbicides and were used as defoliants in Vietnam. Dioxin (2,3,7,8-dioxin), an extremely toxic organic to humans, is a byproduct contaminant of 2,4,5-T production, and has been found at sites where chlorinated organics were burned. Organic phosphorus pesticides include malathion, which is toxic to insects but not to mammals.

The specific toxicity of halogenated hydrocarbons varies with the compound but most affect the central nervous system. Carbon tetrachloride, for example, is a systemic poison that affects the nervous system, the intestinal tract, liver and kidneys. Over the years the FDA compiled a grim record of toxic effects and eventually banned its household use in 1970. Vinyl chloride has been used widely in the production of PVC materials and exposure can affect the central nervous system, respiratory system, liver, blood and lymph systems. Most notably, vinyl chloride is a carcinogen. The dichlorobenzenes are irritants that affect the respiratory system, liver, skin and eyes, through inhalation or contact. Polychlorinated biphenyls (PCBs) have been widely used in the electrical industry as hydraulic fluids in transformers. They represent extremely persistent environmental pollutants with a strong tendency to undergo bioaccumulation in lipid tissue (Manahan, 1991).

The use and disposal of chlorinated solvents by industries involved in electronics manufacturing, metal degreasing, engine repair, paint stripping, and plastics have created a number of serious chlorinated organics plumes, especially in the western U.S. The Hughes Plant 44 Superfund site in Arizona is an example of a site seriously contaminated with halogenated hydrocarbons (see Chapter 10).

4.11.5 Other Organic Compounds

Table 4.6 indicates other classes of organic compounds. Esters are the result of the combination of an alcohol with a carboxylic acid. Esters are used as flavorings, perfumes, solvents and paints. One important class of esters is the phthalates, which are used to improve the flexibility of various plastics. Ethers have an oxygen atom strongly bonded between two carbon atoms and thus have relatively low toxicities.

Organic compounds that contain nitrogen are common in industry and are used for the manufacturing of explosives. Aniline and diphenylamine are aromatic compounds that contain nitrogen in aromatic rings. Trinitrotoluene (2,4,6-TNT) is the main ingredient of military explosives, and has been reported as a soil contaminant in areas where munitions are manufactured.

Name	Structure	Uses and Other Sources
Trichloromethane (chloroform)	CI CI	Liquid used in manufacture of anesthetics, pharmaceuticals, fluorocarbon refrigerants and plasics. Used as solvent and insecticide. Formed from methane when chlorinating drinking water.
Vinyl chloride (chloroethene)	H C=C H	Gas used in the manufacture of polyvinyl chloride. End product of microbial degradation of chlorinated ethenes.
Chloroethane	H H H-C-C-CI H H	Liquid used to manufacture tetraethyl lead. Degradation product of chlorinated ethanes.
1,2-Dichloroethane	H H H H	Liquid used to manufacture vinyl chloride. Degradation product of trichloroethane.
Trichloroethene (Trichloroethylene)	CI H	Solvent used in dry cleaning and metal degreasing. Organic synthesis. Degradation product of tetrachloroethene.
Tetrachloroethene (perchloroethene) (perchloroethylene)	CI CI	Solvent used in dry cleaning and metal degreasing. Used to remove soot from industrial boilers. Used in manufacture of paint removers and printing inks.
1,2-Dibromo-3-chloropropane (DBCP)	Br Br Cl 	Soil fumigant to kill nematodes. Intermediate in organic synthesis.
o-Dichlorobenzene (1,2-dichlorobenzene)	CI	Chemical intermediate. Solvent. Fumigant and insecticide. Used for industrial odor control. Found in sewage form odor control chemicals used in toilets.

Figure 4.15 Chlorinated organics found in hazardous waste.

The above review of organic compounds has been very brief and is not designed to address details contained in texts on organic or environmental chemistry. More details on organic compounds, their degradation, and reactions in ground water can be found in Sawyer, McCarty, and Parkin (1994), Pankow and Cherry (1996), Fetter (1999), and Manahan (1991). Chapter 7 presents important chemical reactions, adsorption processes, and biodegradation mechanisms that affect organic contaminants in the subsurface.

4.12 INORGANIC COMPOUNDS IN GROUND WATER

The quality of water is a direct result of the reactions that occur between sources of contamination and other compounds that it may contact. In ground water, chemistry and chemical processes are important primarily because ground water is in contact with soil and rocks that contain a variety of minerals. In addition, the carbon and the nitrogen cycles contribute greatly to the quality of ground water. For instance, rainfall may come in contact with high levels of carbon dioxide in the atmosphere and become acidic. There is potential for this acidic water to infiltrate to ground water and dissolve minerals as it encounters them. Because of the processes that affect it, ground water naturally contains dissolved inorganic ions. A list of major and minor inorganic constituents and trace metals of ground water is presented in Table 4.7.

TABLE 4.7 Dissolved Constituents in Ground Water Classified According to Relative Abundance.

Major Constituents (greater than 5 mg/L)
Bicarbonate Calcium	Magnesium Silicon
Carbonic Acid	Sodium
Chloride	Sulfate
Minor Constituents (0.1–5.0 mg/L)
Boron	Nitrate
Carbonate	Potassium
Fluoride	Strontium
ron	
race Constituents (I	ess than 0.1 mg/L)
Aluminum	Lithium
Antimony	Lithium Manganese
Antimony Arsenic	Manganese Molybdenum
Antimony Arsenic Barium	Manganese Molybdenum Nickel
Aluminum Antimony Arsenic Barium Beryllium	Manganese Molybdenum Nickel Phosphate
Antimony Arsenic Barium Beryllium Bromide	Manganese Molybdenum Nickel Phosphate Radium
Antimony Arsenic Barium Beryllium Bromide Cadmium	Manganese Molybdenum Nickel Phosphate Radium Selenium
Antimony Arsenic Barium Beryllium Bromide Cadmium Cesium	Manganese Molybdenum Nickel Phosphate Radium Selenium Silver
Antimony Arsenic Barium Beryllium Bromide Cadmium Cesium Chromium	Manganese Molybdenum Nickel Phosphate Radium Selenium Silver Tin
Antimony Arsenic Barium	Manganese Molybdenum Nickel Phosphate Radium Selenium Silver

Chemical parameters of particular importance to ground water constituents and contaminants include solubility product, pH, and oxidation-reduction reactions (Chapter 7). More detailed information may be found in Freeze and Cherry (1979), Domenico and Schwartz (1998), and Fetter (1999), or in Environmental Chemistry texts such as Manahan (1991) or Sawyer, McCarty, and Parkin (1994).

Of the inorganic contaminants in ground water, those of greatest concern are nitrates, ammonia, and trace metals. Nitrates in ground water originate from nitrate sources on land and are associated with fertilizers and the disposal of sewage waste, especially associated with faulty septic tanks. Feedlots are also a major source of nitrate in ground water, especially in rural areas. Nitrate concentrations are not limited by solubility constraints, resulting in high mobility of nitrates in ground water. It has been known since 1940 that ground waters containing high nitrate levels could cause methemoglobinemia in infants, and based on data from the mid-western U.S., EPA set the limit for nitrate—N not to exceed 10 mg/L in public water supplies.

Arsenic, cadmium, chromium, lead, zinc, and mercury are metal pollutants of major concern in ground water. Most of them arise from industrial practices and discharges from mining, metal plating, plumbing, coal, gasoline, and pesticide related industries. Many of these metals are very toxic to humans, especially cadmium, lead, and mercury. Cadmium and zinc are common water and sediment pollutants in areas associated with industrial installations. A major source of lead comes from leaded gasoline and lead piping. Mercury is associated with discarded batteries, laboratory products, and lawn fungicides. Arsenic is produced through phosphate mining and is a by-product of copper, gold, and lead refining.

These metals are of concern in ground water due to their unique acid-base and solubility characteristics in aerobic systems. Metals occur as cations in ground water of low pH and have a greater mobility in acidic waters. Mobility tends to decrease as the solid phase is approached. Mobility of metals is also increased by complexation of ions, and nearly all the trace metals in ground water are influenced by redox conditions, especially when complexation occurs. Heavy metals are particularly toxic in their chemically combined forms and some, notably mercury, are toxic in the elemental form.

Chromium is perhaps the most mobile of all metals in ground water, and contaminant plumes have been identified and sampled at a number of industrial facilities where metal plating was a predominant activity. A classic plume on Long Island, New York, was reported and modeled by Wilson and Miller (1978). More recently the U.S. Air Force Hughes Plant 44 Site in Tucson, Arizona had a major chromium plume migrating more than 150 ft below the surface in a sand and gravel aquifer, but most of it was remediated via a pump and treat system.

13 A TYPICAL INDUSTRIAL WASTE SITE

A typical abandoned industrial site, which has source areas that are leaking organic contaminants, is shown in Figure 4.16. Possible source areas consist of a process area for chemicals

and wastes, drum storage areas, an old drum burial area, an unlined landfill for solid and liquid wastes, surface pits, an injection well for liquid wastes and brines, and leaking industrial sewer lines. A great deal of effort was expended in the 1980s searching aerial photographs, state permit records, and ground water quality records to find active and abandoned industrial waste sites. Many of the older or abandoned sites that were eventually put on the Superfund list resembled the site shown in Figure 4.16. The presence of surface pits or impoundments, drums stored above ground, distressed vegetation from contaminated runoff, and fish kills in surface streams were all indicators of a serious problem at the site.

4.13 A TYPICAL INDUSTRIAL WASTE SITE

Source areas often leaked out organic and hazardous contaminants into shallow subsurface aquifers. Because of the slow rate of velocity in ground water compared to surface water (ft/day vs. ft/sec), it can take years or decades for contaminant plumes to migrate from a source area to a receptor off-site where contamination is first observed.

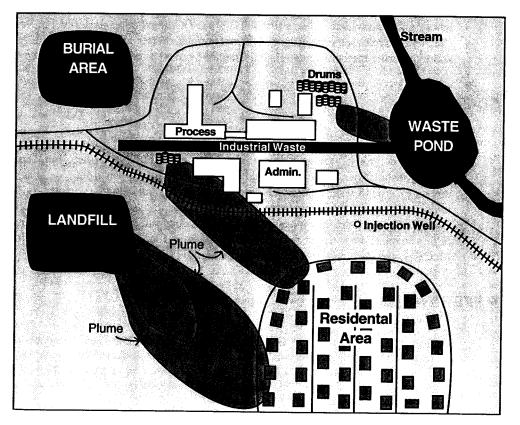


Figure 4.16 Typical contaminated industrial site.

Plumes of contamination are often associated with leaking drums, landfills, burial areas, ponds, and leaking pipe systems. Oftentimes, these plumes can extend for hundreds or thousands of feet from the source area, and impact neighborhoods, commercial areas, or receiving streams. Note the ground water plumes emanating from the process area, the landfill, and the drum storage areas. In the 1980s, these plumes became the subject of intense investigation and remedial activity, designed to cleanup shallow aquifers that had been contaminated with organics. Many of the hazardous waste sites were discovered when contaminant plumes finally arrived at receptor wells or impacted surface streams.

Mechanisms of transport in the subsurface include vertical migration through the unsaturated zone, advection and dispersion in the saturated zone, adsorption to soils, and possibly biodegradation under the right chemical conditions (see Chapters 6, 7 and 8). The most commonly found organic contaminants in ground water from industrial sites include the most mobile and soluble of the compounds listed in Table 4.3 and Table 7.1 in Chapter 7. These primarily include the fuel aromatics (benzene, toluene, ethyl benzene, and the xylenes), and chlorinated solvents (PCE, TCE, 1,2-DCE, and others described in Section 4.11). Chapter 5 addresses the investigation of contaminated sites and describes drilling, sampling, and monitoring methods in detail, and Chapter 6 covers transport mechanisms in detail.

UMMARY

Chapter 4 has reviewed the main sources and types of ground water contamination. In particular, underground storage tanks, septic tanks, agricultural activities, municipal landfills, military installations, nuclear sites, and abandoned hazardous waste sites are considered major threats to ground water. These are described in some detail in the chapter, with examples indicated for each of the major source categories. The nomenclature and characteristics of the most common organic and inorganic compounds found in ground water are addressed briefly in this chapter; other major references on organic and inorganic compounds include Sawyer, McCarty, and Parkin (1994), Pankow and Cherry (1996), and Fetter (1999).

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