Chapter 13
Abiotic Contaminant Transformations in Subsurface Water

13.1 Abiotic Contaminant Transformations in Natural Subsurface Water

Natural subsurface water is considered here as the (bulk) body of water that completely or partially fills the porous matrix, from the soil surface to the groundwater zone. This water may be flowing or relatively static, having accumulated above an impermeable subsurface.

Abiotic transformation of contaminants in subsurface natural waters results mainly from hydrolysis or redox reactions and, to lesser extent, from photolysis reactions. Complexation with natural or anthropogenic ligands, as well as differential volatilization of organic compounds from multicomponent liquids or mixing with toxic electrolyte aqueous solutions, may also lead to changes in contaminant properties and their environmental effects. Before presenting an overview of the reactions involved in contaminant transformations, we discuss the main chemical and environmental factors that control these processes.

13.1.1 Factors Affecting Contaminant Transformations

The chemistry of subsurface water is a main factor to be considered when dealing with contaminant transformation processes. The acidity (pH) of subsurface aqueous solutions can vary over a wide range of values. For example, the pH of swamp water can be as low as 3.5, because of a high concentration of humic and fulvic acids in a eutrophic lake, but may reach a pH as high as 9.5 (Hutchinson 1957). In general, climatic conditions and properties of the surrounding porous media greatly affect the pH of subsurface water. For contaminants containing acid or basic functional groups, the pH of water controls species dissociation-association behavior and thus affects contaminant half-life (Bender and Silver 1963).

Variations in pH induce acid–base mediated hydrolysis. For base-catalyzed hydrolysis, for example, the rate equation for an organic contaminant is

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$$(-\mathrm{d}P/\mathrm{d}t) = k[\mathrm{OC}]\,[\mathrm{OH}^-] \tag{13.1}$$

where P is the product, k denotes a second-order rate constant, [OC] is the organic contaminant concentration and $[\mathrm{OH}^-]$ is the hydroxide ion concentration (see also Sect. 13.1.2). Subsurface waters contain organic and inorganic species (Table 13.1), which, as a function of their character, affect hydrolysis reactions in different ways. The presence of carbonate, fulvic acid, and silicate favor acid–base reactions in aerobic waters. In anaerobic interstitial waters, these reactions are induced by the presence of ammonia, carbonate, fulvic acid, phosphate, and sulfides. Both dissolved and suspended organic material can enhance or impede hydrolysis of selected organic contaminants. For example, dissolved fulvic acids accelerate atrazine hydrolysis, while humic acids retard alkaline hydrolysis of the hydrophobic n-octyl ester of 2, 4-D herbicide (Perdue and Wolfe 1983).

Metal ions in aerobic, natural waters, such as Cu^{2+}, Fe^{3+}, Mn^{2+}, Mg^{2+}, and Ca^{2+}, may catalyze hydrolysis of organic contaminants. Blanchet and St. George (1982), for example, showed that interaction of organophosphate esters with Cu^{2+} and Mn^{2+} led to the hydrolysis of pesticides. However, similar studies with Mg^{2+} and Ca^{2+} did not induce any transformation process.

The main environmental factors that control transformation processes are temperature and redox status. In the subsurface, water temperature may range from 0 °C to about 50 °C, as a function of climatic conditions and water depth. Generally speaking, contaminant transformations increase with increases in temperature. Wolfe et al. (1990) examined temperature dependence for pesticide transformation in water, for reactions with activation energy as low as 10 kcal/mol, in a temperature range of 0–50 °C. The results corresponded to a 12-fold difference in the half-life. For reactions with an activation energy of 30 kcal/mol, a similar temperature increase corresponded to a $\sim$2,500-fold difference in the half-life. The Arrhenius equation can be used to describe the temperature effect on the rate of contaminant transformation, k:

$$k = A\mathrm{e}^{-Ea/\mathrm{RT}}, \tag{13.2}$$

where Ea is the activation energy for the reaction, R is the gas constant, T is the absolute temperature, and A is a constant.

The redox potential in subsurface water varies with alterations from aerobic to anaerobic conditions. In and around anaerobic environments, conditions for reduction exist and contaminants are transformed accordingly. Under aerobic conditions, O_2 is the predominant oxidation agent (mainly through biological processes), because the transformation of contaminants is mainly through oxidative pathways. Aerobic and anaerobic states may occur both in surface waters and in deeper subsurface water.

Table 13.1 Concentration of selected organic and inorganic species in interstitial water, compared to river water and seawater (Wolfe et al. 1990)

Species	World average (mol/L)		
	Interstitial water	River	Seawater
Ammonia	2.00×10^{-4}		
Carbonate	9.09×10^{-3}	9.78×10^{-4}	2.33×10^{-3}
Fulvic acid	2.00×10^{-4}	1.00×10^{-4}	5.00×10^{-6}
Phosphate	1.80×10^{-5}		2.84×10^{-6}
Sulfide	3.96×10^{-7}		
Silicate		2.18×10^{-4}	1.03×10^{-4}
Borate			4.10×10^{-4}

13.1.2 Reactions in Natural Waters

Hydrolysis is a bond-making-bond-breaking process, which may be described by the equation

$$RX + H_2O \rightarrow ROH + H^+ + X \tag{13.3}$$

where R denotes an organic moiety. The general expression for the observed global rate constant K_{obs} is given by

$$K_{obs} = K_H[H^+] + K_{OH}[OH^-] + K_w + \sum_i (K_{HA}[HA] + K_A[A^-])_i, \tag{13.4}$$

where K_H and K_{OH} are specific acid-base catalyzed second-order rate constants; K_w is the neutral hydrolysis rate constant; K_{HA} and K_A are, in general, acid-base catalyzed rate constants; and the summation is over all components i. In Eq. (13.4), $[H^+]$ and $[OH^-]$ are the hydrogen and hydroxyl ion concentrations (activities), respectively, while [HA] and $[A^-]$ are, respectively, the concentrations (activities) of acid and bases in the reaction mixture. The term K_{obs} can include contributions from acid–or base-catalyzed hydrolysis, nucleophilic attack by water, or catalysis by buffers in the reaction medium.

Abiotic hydrolysis of pollutants in subsurface waters is pH dependent. The predominant pathways are acid-catalyzed, base-mediated, and neutral (pH-independent) hydrolysis. The acid-catalyzed hydrolysis reaction rate is dependent on proton concentration increases with a decrease in pH. This behavior occurs because the proton is not consumed in the reaction.

Increases in pH as a direct proportional augmentation of the hydroxyl ion activity leads to a base-mediated hydrolysis process. In this case, the hydroxyl behaves as a nucleophile and is consumed in the reaction. Neutral and alkaline hydrolysis are the most frequent reactions over the common environmental pH ranges. The relation between first-order hydrolysis rate constants and the pH often is presented as a pH rate profile (Wolfe et al. 1990).

Both inorganic (e.g., metals) and organic substances may be subject to a hydrolysis reaction in waters. Examples of several hydrolyzable functional groups are given in Table 13.2. Water is a weak acid and the acidity of the water molecules in the hydration shell of a metal ion usually is greater than that of the water. The acidity of aqueous metal ions is expected to increase with a decrease in the radius and an increase in the charge of the central ion. In the case of Fe(III), for example, hydrolysis can extend beyond the uncharged species $Fe(OH)_3(H_2O)_{3(s)}$, to form anions such as ferrate (FeO_4^{2-}). All hydrated ions, in principle, can donate a larger number of protons than that corresponding to their charge and can form anionic hydroxo-metal complexes (Stumm and Morgan 1996).

The rate of hydrolysis of an organic contaminant also may be affected by the pH, due to specific acid–base effects or changes in compound speciation. A change in the pH can shift the equilibrium in favor of the charged or uncharged species, which often have different hydrolysis rate constants. Under drastic reaction conditions (i.e., extremely low or high pH, high temperature), many of the major organic contaminants, such as pesticides, undergo hydrolysis. Functional groups of organic substances susceptible to hydrolysis include carboxylic acid esters, organophosphates, amides, anilides, carbamates, triazines, oximes, and nitriles. The role of hydrolysis in the overall transformation process, however, depends on the rate of other degradation processes that may occur simultaneously, such as photolysis, biolysis, or redox reactions. If, in the liquid phase, additional organic or inorganic chemicals of natural or anthropogenic origin are present, contaminant hydrolysis could be affected by the presence of other solutes. This is the case of dissolved metals or humic acids acting on the hydrolysis of organic toxic elements present in the same water phase. This effect, however, has only minor significance. Perdue and Wolfe (1983) considered the maximum predicted buffer-catalysis contribution to be $\leq 10\ \%$ of the uncatalyzed process.

Redox reactions in natural waters involve the transfer of electrons between chemical species or changes in the oxidation state of species involved in the reaction. Specifically, oxidation describes the loss of electrons by a molecule, atom, or ion, while reduction describes the gain of electrons by a molecule, atom, or ion. Therefore, *oxidation* is defined as an increase in oxidation number, while *reduction* is defined as a decrease in oxidation number. Differences in the oxidation states of natural waters generally exist between surface and ground waters, between locally inter aggregate stagnant and flowing waters, or in stagnant waters obstructed by biological or vegetative cover.

Reductants and *oxidants* are defined as electron donors and proton acceptors (Sect. 2.2.2). Because there are no free electrons, every oxidation is accompanied by a reduction and vice versa. In aqueous solutions, proton activities are defined by the pH:

$$pH = -\log[H^+]. \tag{13.5}$$

Similarly, we can define a convenient parameter for the redox intensity:

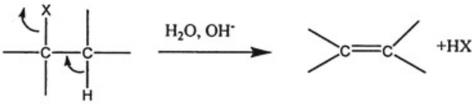
Table 13.2 Examples of hydrolyzable functional groups (Larson and Weber 1994)

1. Halogenated aliphatics

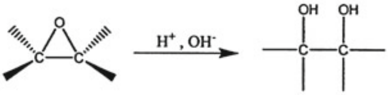
Nucleophilic substitution:

$$RCH_2X \xrightarrow{H_2O,\ OH^-} RCH_2OH + HX$$

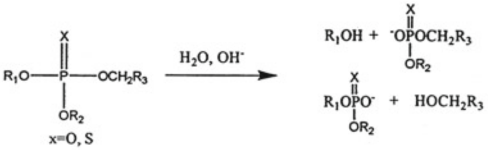
Elimination:



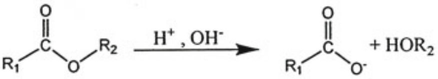
2. Epoxides:



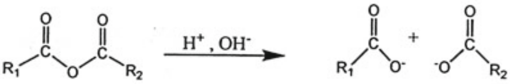
3. Organophosphorus esters:



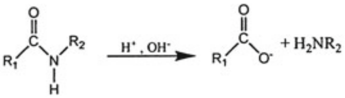
4. Carboxylic acid esters:



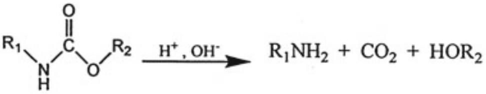
5. Anhydrides:



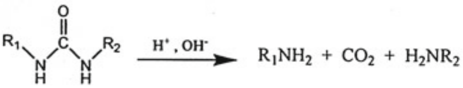
6. Amides:



7. Carbamates:



8. Ureas:



$$\mathrm{pE} = -\log[\mathrm{e}^-], \tag{13.6}$$

where pE gives the (hypothetical) electron (e^-) activity at equilibrium and measures the relative tendency of a solution to accept or transfer electrons.

Stumm and Morgan (1996) showed that C, N, O, S, Fe, and Mn are the main elements participating in aquatic redox processes. Table 13.3 presents equilibrium constants for several redox processes relevant to natural waters. The symbol pE°(W) expresses the redox situation in natural waters; that is, the values for pE°(W) apply to the electron activities for unit activities of oxidants and reductants in natural water at standard conditions (pH = 7.0 and 25 °C). Values for pE°(W) at 25 °C and pH = 7 can be determined according to

$$\mathrm{pE}^\circ(\mathrm{W}) = \mathrm{pE}^\circ + (n_H/2)\log\ K_w, \tag{13.7}$$

where n_H is the number of moles of protons exchanged per mole of electrons and K_w denotes the equilibrium constant for the redox reaction in natural water. A list of pE°(W) values is given in Table 13.3, showing the oxidizing intensity at standard conditions.

Reduction-or oxidation-induced transformations of contaminants occur in subsurface water as a function of environmental aerobic or anaerobic conditions. The presence or lack of O_2 is the determining factor in defining the transformation pathways. Redox reactions are driven by microbial activity and through abiotic processes. In both cases, though, the overall reactions may be very similar. Hence, most of the general redox reactions discussed here also are relevant for the biologically mediated processes considered later in this chapter and vice versa. We discuss reduction processes in a more detailed manner here; oxidation mechanisms are discussed later in Chap. 15, when considering biologically mediated transformations.

Reduction occurs when there is a transfer of electrons from an electron donor, or a reducing agent, to an electron acceptor, or oxidizing agent. Reducing environments are very common in the subsurface, being present in groundwater, bottom sediments, and anaerobic stagnant waters. Naturally occurring reducing agents constitute a complex array of species, ranging from chemical or “abiotic” reagents like sulfide minerals, reduced metals such as Fe and Mn, and natural organic matter, to biological systems such as microbial populations. In addition, extracellular biochemical substances may act as catalysts for reduction reactions, such as metalloporphyrins, corrinoids, and bacterial transition-metal coenzymes that abound in the subsurface. The relationship among these various reducing agents in the subsurface environment is quite complex. For example, chemical species, such as reduced metals and sulfide ions, may result directly from microbial metabolism (Larson and Weber 1994). A list of common reduction reactions is given in Table 13.4. Reduction of organic pesticides, for example, includes reactions such as dehalogenation of alkanes, nitroreduction to the corresponding amine, azo reduction to an hydrazo or amino group, quinine reduction

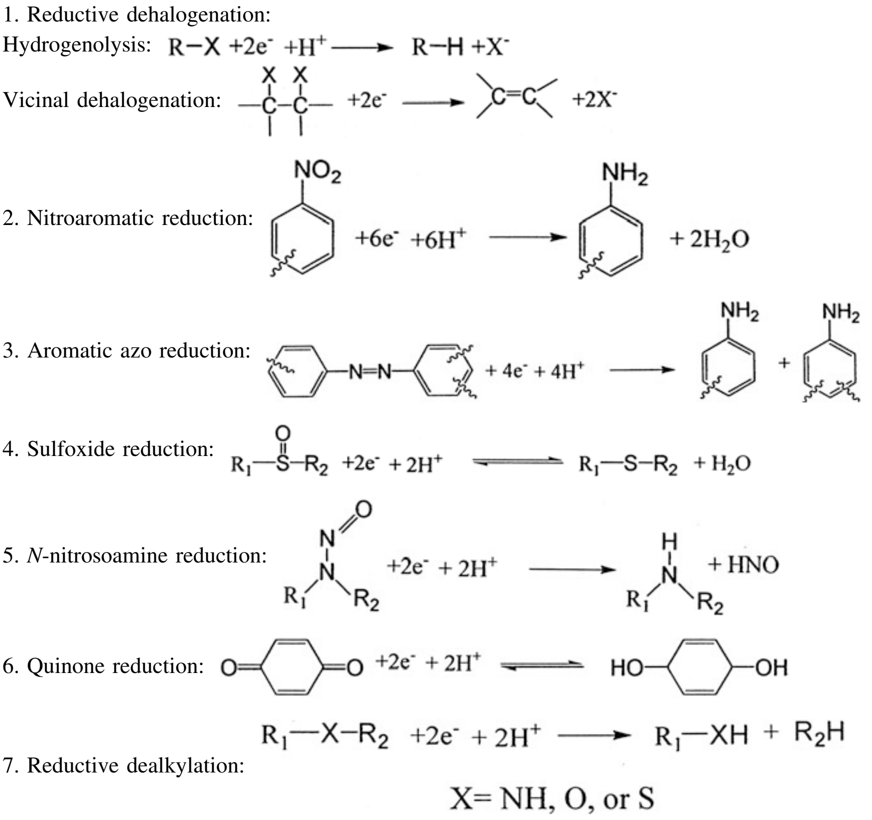
Table 13.3 Examples of equilibrium constants of redox processes pertinent in aquatic conditions (25 °C) (Stumm and Morgan 1996)

Reaction	pE° (≡log K)	pE° (W)
$\frac{1}{4}O_2(g) + H^4 + e = \frac{1}{2}H_2O$	+20.75	+13.75
$\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e = \frac{1}{10}N_2(g) + \frac{3}{5}H_2O$	+21.05	+12.65
$\frac{1}{8}NO_3^- + \frac{5}{4}H^+ + e = \frac{1}{8}NH_4^+ + \frac{3}{8}H_2O$	+14.90	+6.15
$\frac{1}{6}NO_2^- + \frac{4}{3}H^+ + e = \frac{1}{6}NH_4^+ + \frac{1}{3}H_2O$	+15.14	+5.82
$\frac{1}{2}CH_3OH + H^+ + e = \frac{1}{2}CH_4(g) + \frac{1}{2}H_2O$	+9.88	+2.88
$\frac{1}{4}CH_2O + H^+ + e = \frac{1}{4}CH_4(g) + \frac{1}{4}H_2O$	+6.94	−0.06
$\frac{1}{2}CH_2O + H^+ + e = \frac{1}{4}CH_3OH$	+3.99	−3.01
$\frac{1}{8}SO_4^{2-} + \frac{5}{4}H^+ + e = \frac{1}{8}H_2S(g) + \frac{1}{2}H_2O$	+5.25	−3.50
$\frac{1}{8}SO_4^{2-} + \frac{9}{8}H^+ + e = \frac{1}{8}HS^- + \frac{1}{2}H_2O$	+4.25	−3.75
$\frac{1}{8}S(s) + H^+ + e = \frac{1}{2}H_2S(g)$	+2.89	−4.11
$\frac{1}{8}CO_2(g) + H^+ + e = \frac{1}{8}CH_4(g) + \frac{1}{4}H_2O$	+2.87	−4.13
$\frac{1}{6}N_2(g) + \frac{4}{3}H^* + e = \frac{1}{3}NH_4^+$	+4.68	−4.68
$\frac{1}{2}(NADP^+) + \frac{1}{2}H^+ + e = \frac{1}{2}(NADPH)$	−2.0	−5.5
$H^+ + e = \frac{1}{2}H_2(g)$	0.0	−7.00
Oxidized ferredoxin + e = reduced ferredoxin	−7.1	−7.1
$\frac{1}{4}CO_2(g) + H^+ + e = \frac{1}{24}(glucose) + \frac{1}{4}H_2O$	−0.20	−7.20
$\frac{1}{2}HCOO^- + \frac{3}{2}H^+ + e = \frac{1}{2}CH_2O + \frac{1}{2}H_2O$	+2.82	−7.68
$\frac{1}{2}CO_2(g) + \frac{1}{2}H^+ + e = \frac{1}{24}HCOO^-$	−4.83	−8.33

to semiquinones or hydroquinones, and sulfone reduction to sulfoxide or sulfide (Macalady et al. 1986).

Reductive Dehalogention Reductive dehalogenation is a general phenomenon in many subsurface environments (e.g., anaerobic sediments, soils, groundwater, aquifers). For many substances containing one or more halogenated functional groups, reduction is the pathway of choice for degradation. Note that some metabolites of halogenated compounds may be as toxic (or even more toxic) than the parent compound. Reductive dehalogenation of halo-aliphatic substances generally is initiated by formation of carbon radicals through electron transfer, which can then (1) abstract an H atom from a suitable donor (hydrogenolysis) (2) form a C=C double bond (dehydrogenation) (3) induce radical coupling (dimerization), or (4) form a C=C double bond through elimination of vicinal halides (vicinal dehalogenation). The reduction of halo-aromatic compounds occurs mainly through hydrogenolysis. It usually is a slower process than aliphatic dehalogenation, and in many cases, occurs through microbially mediated reactions.

Table 13.4 Reductive transformation known to occur in natural reducing environments (Larson and Weber 1994)



1. Reductive dehalogenation:

Hydrogenolysis: $R-X + 2e^- + H^+ \rightarrow R-H + X^-$

Vicinal dehalogenation: $+2e^- \rightarrow$ $+2X^-$

2. Nitroaromatic reduction: $+6e^- + 6H^+ \rightarrow$ $+ 2H_2O$

3. Aromatic azo reduction: $+ 4e^- + 4H^+ \rightarrow$

4. Sulfoxide reduction: $R_1-S(=O)-R_2 + 2e^- + 2H^+ \rightleftharpoons R_1-S-R_2 + H_2O$

5. *N*-nitrosoamine reduction: $+2e^- + 2H^+ \rightarrow$ $+ HNO$

6. Quinone reduction: $+2e^- + 2H^+ \rightleftharpoons$

7. Reductive dealkylation: $R_1-X-R_2 + 2e^- + 2H^+ \rightarrow R_1-XH + R_2H$

X= NH, O, or S

Nitroaromatic Reduction Nitroaromatics constitute an important class of potential environmental contaminants, because of their wide use in agrochemicals, textile dyes, munitions, and other classes of industrial chemicals. Reduction of nitroaromatics produces amines, through a series of electron transfer reactions with nitroso and hydroxylamines as intermediates (Fig. 13.1). Compared to the parent nitroaromatic compound, all intermediates typically reduce readily (Larson and Weber 1994).

Aromatic Azo Compounds Reduction of aromatic azo compounds involves a four-electron process that proceeds through a short-lived intermediate, hydrazobenzene, and ends with complete reductive cleavage of the azo linkage and formation of aromatic amines.

Sulfoxide Reduction Sulfoxide reduction is a two-electron-transfer reversible reaction resulting in thioethers. Organic sulfoxides are used mainly as agrochemicals, and their reduction (abiotic and microbially mediated) has been found in anaerobic soils, sediments, and groundwater (Larson and Weber 1994).

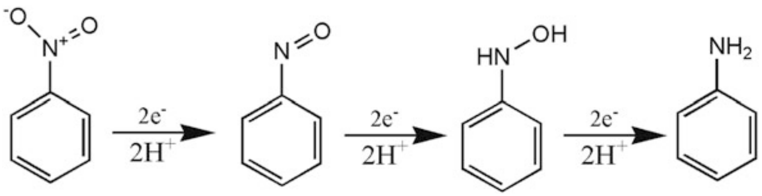


Fig. 13.1 Reduction of nitrobenzene to aniline

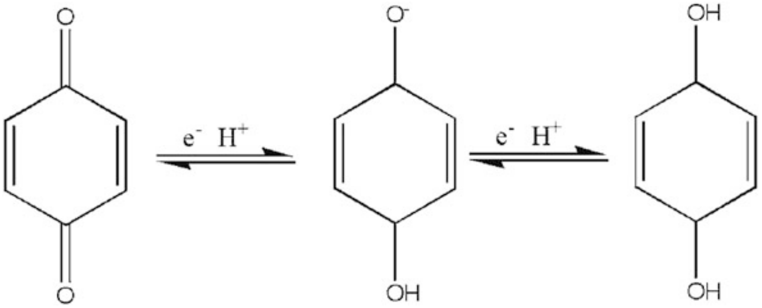


Fig. 13.2 Reduction of quinone to semiquinone and hydroquinone through two one-electron transfer steps (Larson and Weber 1994)

***N*-nitosoamine Reduction** The reduction of *N*-nitrosoamines can occur across either the N–N bond or the N–O bond. Both reactions ultimately result in the formation of the parent amine and ammonia.

Quinone Reduction This is a reversible, one-electron transfer reaction to the semiquinone radical, followed by a second, reversible electron transfer that results in the formation of hydroquinone, as shown in Fig. 13.2.

Reductive Dealkylation Reductive dealkylation involves replacement of an alkyl group on a heteroatom by hydrogen. The reaction is considered to be mainly biologically mediated and usually is important in the subsurface for transformation of agrochemicals.

Photolysis Abiotic oxidation occurring in surface water is often light mediated. Both direct oxidative photolysis and indirect light-induced oxidation via a photolytic mechanism may introduce reactive species able to enhance the redox process in the system. These species include singlet molecular O_2, hydroxyl-free radicals, super oxide radical anions, and hydrogen peroxide. In addition to the photolytic pathway, induced oxidation may include direct oxidation by ozone (Spencer et al. 1980) autooxidation enhanced by metals (Stone and Morgan 1987) and peroxides (Mill et al. 1980).

Photolysis is an environmental process in which a substrate in a natural aqueous solution is subjected to ultraviolet (UV) or visible light, causing its transformation. Sunlight at the surface of the earth consists of direct and scattered light entering a

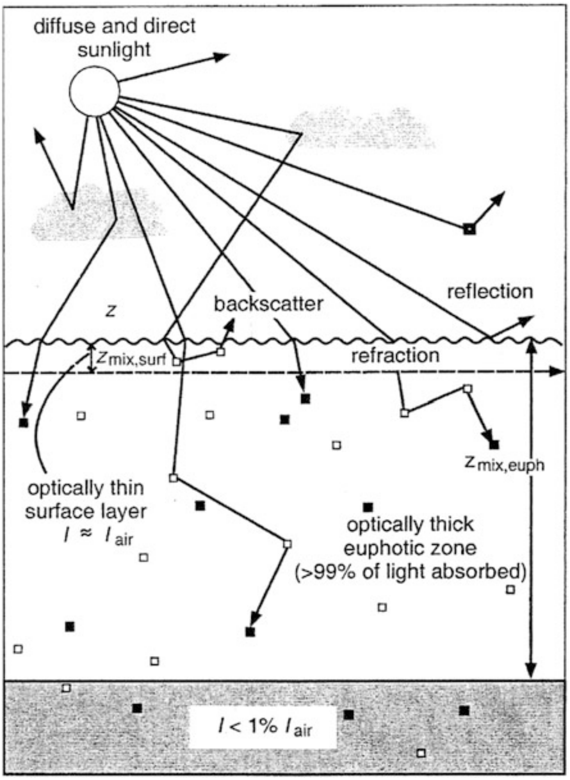


Fig. 13.3 Fate of photons in a natural water body. *Open Square* reflective particles; *Filled Square* absorptive particles or molecules (Schwarzenbach et al. 2003)

water body at various angles. From Fig. 13.3, the distribution of photons in a natural water body may be seen. The rate of transformation may be enhanced in the presence of additional reactants of natural or anthropogenic origin. Contaminant photolysis in water has been studied extensively over the last three decades (e.g., Zepp 1980; Miller and Crosby 1983; Zafiriou 1984; Leifer 1988; Acher and Saltzman 1989; and Schwarzenbach et al. 2003).

The solar spectrum at a particular location depends on a large range of factors, including season of the year, time of day, weather conditions, and atmospheric pollution. The intensity of solar irradiance depends on the optical thickness of the atmosphere, which together with ozone absorption and molecular scattering, are strongly wavelength dependent. Direct and indirect photoreactions can be distinguished.

Direct photolysis processes involve the direct adsorption of light by the substrate

$$\mathrm{P} + \text{light} \rightarrow \mathrm{P}^* \rightarrow \text{products} \tag{13.8}$$

where P is a photoreactive substance and P* is the excited state that reacts to form products. The photolysis rate is related directly to the adsorption spectrum of contaminants having the spectral distribution of sunlight. Because radiation at wavelengths below 290 nm is adsorbed by atmospheric ozone, organo or organometallic contaminants that do not absorb radiation above this wavelength do not undergo direct photolysis.

The rate of any type of photoreaction depends also on the rate of light absorption by the photoactive species. The light transmission characteristics of an aqueous system must be determined to account for the degree to which system components other than the contaminant itself attenuate radiation in the water column. Summing over all wavelengths absorbed by all contaminants and natural organic compounds in the water body gives the total rate constant of light absorption.

Indirect photolysis occurs when a species other than the organic or organometallic toxic compound absorbs sunlight and initiates reactions leading to contaminant transformation. Natural products present in natural waters, such as humic substances, clay colloids, and transition metals, absorb the radiation required for subsequent reactions and act as natural sensitizers. Electrically excited molecules are capable of greatly accelerating the process and determine a number of light-induced transformations of toxic organic chemicals.

Singlet oxygen is a selective oxidant that reacts at appreciable rates with electron-rich groups. Singlet oxygen is formed when an excited sensitizer transfers its energy to ground-state (triplet) oxygen. In natural waters, the sensitizers are generally related to dissolved humic substances. In addition, any substance dissolved in water, on adsorbing sunlight, crosses to a triplet state and potentially produces singlet oxygen; such substances include hydrogen peroxide, superoxide, alkyl peroxy radicals, and hydroxyl radicals.

In natural water, singlet oxygen originating from humic substances has been shown, for example, to oxidize thioether pesticide contaminants such as disulfoton (Zepp et al. 1981). Irradiation of dilute hydrogen peroxide in the presence of various non-sunlight-absorbing herbicides results in enhanced oxidation of these substances (Draper and Crosby 1981).

Coordinative interactions in natural waters change as a result of a variation in coordinative species or coordination number, which in turn leads to a transformation of contaminant properties. Any combination of cations with molecules or anions containing free pairs of electrons (bases) is called *coordination* (or *complex formation*). The coordination can be electrostatic, covalent, or a mixture of both. The metal cation is called the *central atom,* and the anion or molecule with which it forms a coordinative compound is referred to as a *ligand.*

The actual form in which a contaminant molecule or ion is present in natural water, as result of a change in the coordinative relationship, emphasizes a specific *chemical speciation.* A *chemical species* is defined by IUPAC "as the isotopic composition, electronic or oxidation state, and/or complex or molecular structure," and the *speciation of an elemen*t as "the distribution of an element amongst defined chemical species in a system" (Templeton et al. 2000).

Speciation is important for understanding the behavior of toxic heavy metals, because different chemical species may behave differently in the subsurface environment (including subsurface water). Subsurface water contains a broad spectrum of dissolved and colloidally dispersed natural products, so it is possible that the same molecule exists in one or more species. For example, in evaluating the presence of heavy metals in subsurface water, one should recognize that the subsurface environment has a direct influence on heavy metal speciation and, thus, on the environmental impact. By complexation with the various components of water, the initial properties of a contaminant can be changed. A free metal ion in an aqueous solution is more biologically active than an ion adsorbed on suspended particles or complexed to other species.

Natural inorganic ligands of heavy metals in subsurface water, which are present in a concentration of about 1 mM, include nitrite, sulfate, chloride, carbonate, and bicarbonate. These potential ligands generally are efficient only under special conditions. For example, in an alkaline environment, carbonate and bicarbonate can be significant complexors of transition metals like Cu^{2+} or the uranyl ion, UO_2^{2+}, and cadmium may be complexed with Cl^- or SO_4^{2-} to form $CdCl^+$ or $CdSO_4$. Additional inorganic ligands, at a micromolecular level, include phosphate and fluoride, which have high affinities for Fe^{3+} and Al^{3+} (Sauve and Parker 2005).

Dissolved organic chemicals acting as potential ligands may be found in the subsurface (including the root zone). This group is very diverse and comprises many compounds like sugars, organic acids, phenols, and lipids. Not all natural organic acids found in subsurface water are able to function as ligands for heavy metals. The common amino acids, such as a root exhudate, are too weak to enhance metal complexation. Low-molecular-weight organic acids (e.g., citric acid), however, exhibit affinity for metals due to their carboxylic functionality. While the aliphatic organic acids are very active in the speciation of metals, in most environmental situations, the ability of phenolic acids to form ligands is of minor significance. On the other hand, the presence of high-molecular-weight compounds in natural waters, such as fulvic or humic acids, leads to significant heavy metal speciation; this is an effect explained by the affinity of carboxyl groups.

By complexation with various components of the natural subsurface solution, the initial properties of a toxic molecule can be changed. These transformations involve adsorption on the subsurface solid phase, transport into the saturated or partially saturated zone, and contaminant half-life in the subsurface environment.

It is operationally difficult to distinguish between dissolved and colloidally dispersed substances. For example, colloidal metal-ion precipitates occasionally have particle sizes smaller than 100 A, sufficiently small to pass through a membrane filter, and organic substances can exist as a stable colloidal suspension. Information on the types of species encountered under different chemical conditions (type of complexes, their stabilities, rate of formation) is a prerequisite to better understanding of the transformation in properties of toxic chemicals in a water body.

Liquid Mixture Transformation Changes in the composition and concentration of volatile fractions of a *volatile organic liquid mixture* (VOLM) contaminating a subsurface water occur when the (immiscible with water) liquid is volatilized into the gaseous phase of the porous medium and subsequently transported into the atmosphere. Fine and Yaron (1993) showed that the volatilization of each hydrocarbon from kerosene (containing more than 100 hydrocarbons), added to a subsurface, occurred at different rates. The mass transfer of spilled VOLM from natural water bodies into the subsurface and near surface atmosphere and the effect of this process on their distribution between the gaseous, liquid and solid phases have been the subject of a series of studies (e.g., Mackay and Yeun 1983; Burris and Macintyre 1986; Nye et al. 1994; Yaron et al. 1998; Dror 2005). The rate of volatilization is controlled by the vapor pressure of the components and environmental conditions. The less-volatile components of a VOLM are transported as liquid into the porous medium. During their transport, differential dissolution of the component mixture into the subsurface water or adsorption on the subsurface solid phase occurs simultaneously with the transport of the volatile fraction in the gaseous phase. Adsorption leads to retardation of volatilization but not to cessation of the process. A change in the VOLM composition occurs as result of this process.

Adapting the approach of Nye et al. (1994) to subsurface conditions, the following stages in contaminant transformations of VOLMs can be identified:

1. A volatilization-induced VOLM depletion stage of the components, characterized by a high vapor pressure.
2. A VOLM depletion stage caused by dissolution in the liquid and adsorption on solid phases of the components, characterized by aqueous solubility.
3. A VOLM enrichment stage caused by desorption of the previously adsorbed fraction on the solid phase.
4. A liquid depletion stage of the gas molecules sorbed on solids or dissolved in water phases.

In stages 2 and 3, the components accumulate or deplete according to their aqueous solubility, volatility, diffusivity, and cosolvent presence. The transformation rate of VOLMs occurs accordingly. In this system, two distinct liquid phases can be recognized: the first is a VOLM, insoluble in water and having chemical properties different from the original VOLM; the second is a mixed aqueous solution of partially miscible organic compounds dissolved in water from the original VOLM.

The *chemodynamic properties* of a multiphase liquid are transformed with respect to the initial state of their components. In the case of VOLMs, both chemical and physical properties of the initial liquid are changed. A second type of liquid transformation is that of water with a given quality, when it mixes with water of different chemical composition. For example, consider the case of a mixture of two aqueous solutions having a similar total salt content and different electrolyte composition, with one having a high Na content and low Ca concentration (SAR = 2.5) and the other having a low Na and high Ca content

(SAR = 2.5). The result is an aqueous solution with a sodium adsorption ratio (SAR) between the volumes of water mixed together. In both cases, with organic and inorganic contaminants, the chemodynamic properties and the quality of the resulting water change.

13.2 Selected Contaminant Transformations in Sediments and Groundwater

Special consideration should be given to the transformation of contaminants in sediments and groundwater. Under saturated conditions, the solid phase may function as a sink, reservoir, and reactor for contaminants. Contaminant presence, persistence, and transformation in the water phase is controlled by the chemistry of the water body, the surface properties of the materials forming the solid phase (sediments or suspended particles), and environmental conditions (temperature and aerobic or anaerobic status).

Pore waters of confining beds in an aquifer (e.g., Black Creek) may contain relatively high concentrations (~100 μM) of dissolved organic acid anions, such as acetate and formate, whereas aquifer water contains relatively low concentrations of organic acid anions (~1 μM). In addition, confining bed pore waters also may contain sulfate in higher concentrations, that is, ~100 μM, while sulfate concentrations in aquifers are only about ~5 μM (McMahon and Chapelle 1991; McMahon et al. 1992). Discussing these findings for the Black Creek aquifer, Chapelle (2005) assumed that diffusion of DIC (dissolved inorganic carbon), together with DOC (dissolved organic carbon), sulfate, and cations (Mg and Ca) from confining bed pore waters, provide an electron donor (organic carbon) and an electron acceptor (sulfate) for microbial metabolism. Additional inorganic carbon enhances magnesium-calcite dissolution-precipitation, as driven by microbially produced carbon dioxide. Under these conditions, microbial processes occurring in the aquifer (sulfate reduction), as well as microbial processes in confining beds (organic matter fermentation), have an important impact on contaminant transformation in sediments and groundwater.

13.2.1 pH and Hydrolysis Reactions

The pH in ponds and rivers generally is within one pH unit of that of the underlying water. Wolfe et al. (1990) explain these differences by noting that pH values measured in sediments are a composite of the pH of the interstitial water and the pH in the vicinity of the charged surface. Because most solids in sediment systems exhibit a negative charge, the pH near the surface becomes lower than in the bulk water phase. Partially saturated conditions in sediments favor biological activity, leading to carbonate formation and a rise in pH.

In addition to the environmental pH and type of hydrolysis, contaminant hydrolysis in sediments is controlled by the properties of the contaminant molecule and the sediment constituents. In natural sediment, it is difficult to determine if hydrolysis is a biologically mediated or an abiotic reaction. A simple test consists of measuring the contaminant disappearance rate in the sediment and in distilled water, with a pH adjusted to that of the sediment. If the two disappearance rates are similar, the process can be assumed to be abiotic, while if the rate is greater in the sediment system, the hydrolysis is biologically mediated.

In a sediment system, the hydrolysis rate constant of an organic contaminant is affected by its retention and release with the solid phase. Wolfe (1989) proposed the hydrolysis mechanism shown in Fig. 13.4, where P is the organic compound, S is the sediment, P:S is the compound in the sorbed phase, k^1 and k^{-1} are the sorption and desorption rate constants, respectively, and k_w and k_s are the hydrolysis rate constants. In this proposed model, sorption of the compound to the sediment organic carbon is by a hydrophobic mechanism, described by a partition coefficient. The organic matrix can be a reactive or nonreactive sink, as a function of the hydrolytic process. Laboratory studies of kinetics (e.g., Macalady and Wolfe 1983, 1985; Burkhard and Guth 1981), using different organic compounds, show that hydrolysis is retarded in the solid-associated phase, while alkaline and neutral hydrolysis is unaffected and acid hydrolysis is accelerated.

Based on these results and on additional publications (e.g., Konrad and Chester 1969; Armstrong and Konrad 1974), Wolfe et al. (1990) suggested that the tendency of an organic contaminant to hydrolyze in sediments is influenced by the proximity of the molecule to the solid surface in the interstitial water and the direct effect of solid particles on the susceptibility of adsorbed toxic organic molecules to hydrolyze. Because abiotic hydrolysis of organic contaminants in the sediment liquid phase, in many cases, exhibits the same degradation products as those in clear water, it might be suggested that the solid phase in a sediment system alters only the rate of hydrolysis, not the reaction pattern. Some constituents of the sediment solid phase, however, may enhance hydrolysis of organic contaminants adsorbed on their surfaces. For example, in heterogeneous hydrolysis of nonionic pesticides, significant participation by acid groups belonging to solid phase organic matter was observed.

13.2.2 Redox State and Reactions

Redox activity in sediments may be defined by an equilibrium approach, considering that the Eh of an aqueous system is bound in the upper boundary by the oxidation of water and in the lower boundary by reduction of water. The term Eh is defined as the redox potential relative to the standard hydrogen half-cell (see Sect. 2.2.2). Measurements of Eh in sediments of ponds and rivers show that the Eh stabilizes at a depth of about 1 cm and remains stable to a depth of 5–6 cm (Wolfe et al. 1986). Sediments are strongly electron buffered, which is shown by titration

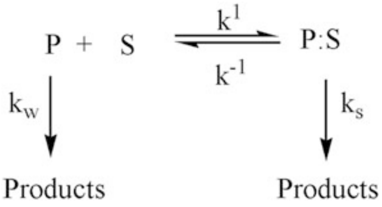


Fig. 13.4 Proposed two-step hydrolysis mechanism (Wolfe 1989)

with chemical oxidants. Although molecular O_2 oxidizes sediments, which affects their reduction capacity, this reaction occurs slowly (Macalady et al. 1986).

The redox state also is defined by a kinetic approach, when the electron acceptors are used predominantly by microorganisms found in the system. It is difficult to define the terminal electron-accepting processes. Chapelle (2005) considers that microbially mediated redox processes tend to become segregated into discrete zones. At the sediment-water interface, oxic metabolism predominates. This oxic zone may comprise zones dominated by nitrate, manganese, or ferric iron reduction. The redox zonation is a result of the ecology of aquatic sediments. The reduction rate of sediment oxidation is explained by intrinsically slow reaction rates of O_2 with reducing moieties in the sediment or by slow diffusion of O_2 into the sediment. In anoxic sediments, oxidation of organics is carried out in the food chain; fermentative microorganisms partially oxidize organic matter with the production of fermentation products, such as acetate and hydrogen. These fermentation products then are consumed by terminal electron-accepting microorganisms such as Fe(III) or sulfate reducers.

Wolfe (1989) suggested a model to describe abiotic reduction in sediments, where a nonreactive sorptive site and an independent reactive sorptive site are considered. The nonreactive sorptive sink is consistent with partitioning of the contaminant to the organic carbon matrix of the solids. The model is described by Fig. 13.5 where P:S′ is the compound at the reactive sorbed site; P is the compound in the aqueous phase; S and S′ are the sediments, P:S is the compound in the non-reactive sink; k^2, k^{-2}, k^1, and k^{-1} are the sorption–desorption rate constants, and k_c, k_w, and k_s are the respective reaction rate constants. If the reaction constants k_w and k_s are neglected, two rate-limiting situations are observed: transport to the reactive site and reduction at the reactive site. The available kinetic data, however, do not allow one to distinguish between the two mechanisms.

An example of a redox transformation in natural water (oxidation) and sediments (reduction) of an organ chlorinated contaminant (aldicarb insecticide) is given in Fig. 13.6.

Because hydrocarbon mixtures originating from petrogenic or pyrogenic residues are a major group of groundwater contaminants, which originate mainly from human activity, these compounds are considered to illustrate transformation of organic molecules in the subsurface environment. These hydrocarbon mixtures generally contain a diverse group of compounds, whose behaviors, persistence, and transformation in the subsurface and in groundwater are dissimilar. In the partially saturated subsurface, a range of selective processes, such as solid phase

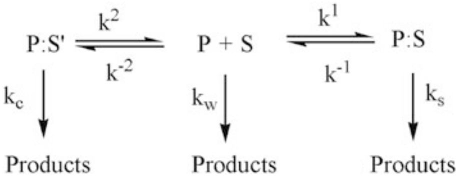


Fig. 13.5 Proposed model for abiotic reduction in a sorbing sediment system (Wolfe 1989)

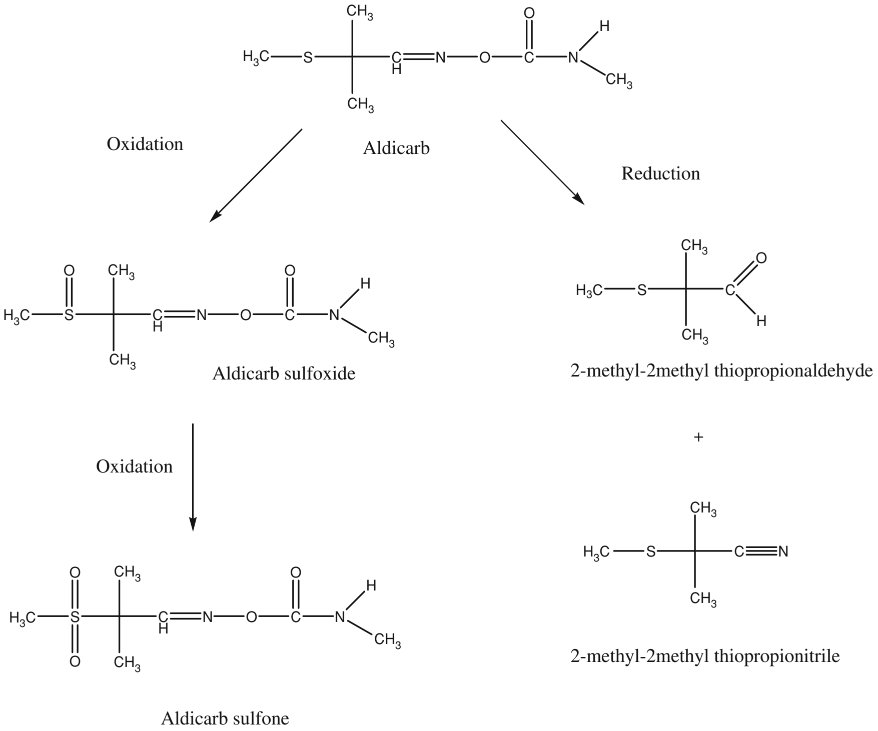


Fig. 13.6 Redox transformation pathways of aldicarb (Macalady et al. 1986; Wolfe et al. 1986)

retention, volatilization, dissolution, photolysis and surface-, chemically, and biologically induced degradation can affect hydrocarbons in groundwater. Biodegradation is a major transformation process of petroleum hydrocarbons.

Both aerobic and anaerobic biological degradation control the persistence of hydrocarbons in groundwater, such as the n-alkane group. A generalized biodegradation pathway is presented in Fig. 13.7. The aerobic pathway shows conversion of an alkane chain to fatty acids, fatty alcohols, and aldehyde and carboxylic acids, which are then channeled into the central metabolism for subsequent *β*-oxidation.

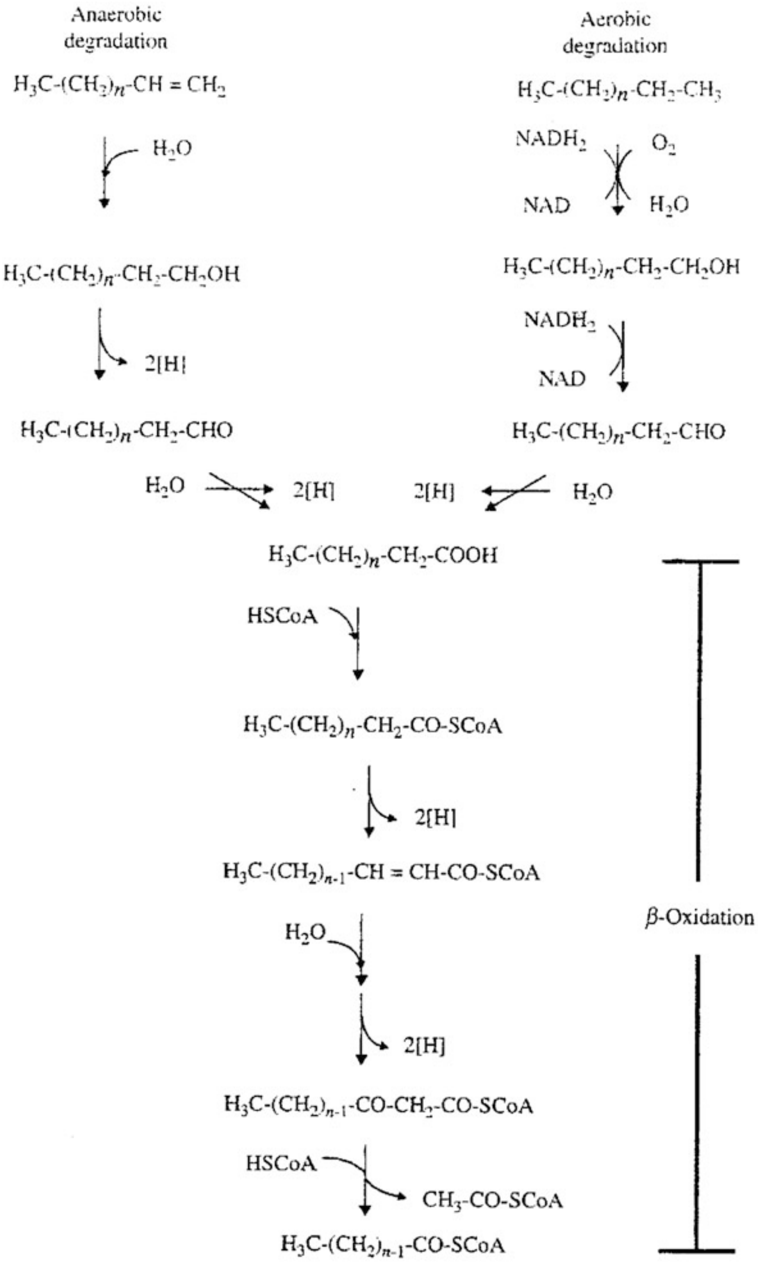


Fig. 13.7 Generalized aerobic and anaerobic biodegradation pathways for *n*-alkanes. Reprinted from Abrajano et al. (2005). Copyright 2005 with permission of Elsevier

The degradation pathway involves independent oxidation to fatty acids, followed by β-oxidation.

Anaerobic degradation proceeds with nitrate, Fe^{3+}, or sulfate as the terminal electron acceptor, without any intermediate, such as alcohols. Sulfate reducers apparently show specificity toward utilization of short chain alkanes. Susceptibility to *n*-alkane degradation is an inverse function of chain length. Branched alkanes are less susceptible than straight-chain *n*-alkanes, and the most resilient saturated components are the pristine and phytane isoprenoids (Wang et al. 1998).

As with aliphatic hydrocarbons, oxidative biodegradation of aromatic compounds requires insertion of oxygen into the molecule to form catechol. The susceptibility to biodegradation increases with decreasing molecular weight and degree of alkylation. The most easily degradable polyaromatic hydrocarbons mentioned are the alkyl homologues of dibenzothiophene, fluorine, phenanthrene, and chrysene (Wang et al. 1998).

Microbially induced degradation is recognized as the major mechanism in the transformation of PAHs in the aquatic environment (NRC 2000). In general, PAH degradation rates are a factor of 2–5 slower than degradation rates of monoaromatic hydrocarbons and of similar magnitude as for high-molecular-weight *n*-alkanes (C_{15}–C_{36}). Under similar aerobic conditions, the most rapid biodegradation of PAHs occurs at the water-sediment interface. Prokaryotic microorganisms metabolize PAHs primarily by an initial dioxygenase attack to yield cis-dihydrodiols and finally catechol. General aerobic biodegradation pathways for aromatic hydrocarbons are shown in Fig. 13.8.

Higher-molecular-weight PAHs, such as pyrene, benzo(a)pyrene, and benzo(e)pyrene, exhibit a high resistance to biodegradation. PAHs with three or more condensed rings tend not to act as a sole substrate for microbial growth and require cometabolic transformations. Neilson and Allard (1998) report a cometabolic reaction of pyrene, 1,2-benzanthracene, 3,4-benzopyrene, and phenanthrene in the presence of either naphthalene or phenanthrene. However, the co metabolic reactions are very slow in natural ecosystems.

Natural attenuation processes occurring in groundwater, which include dilution, sorption, volatilization, and biodegradation, may affect the downward migration of hydrocarbon plumes over time. Cozzarelli et al. (1999) report such behavior in the configuration of a petroleum hydrocarbon plume in groundwater, due to rupture of an oil pipeline that occurred in Minnesota in 1979. The oil spill induced formation of an oil lens floating on the water table. The behavior of this lens was studied between 1980 and 1990. In 1980, the dissolved hydrocarbon plume was composed mainly of soluble benzene, toluene, ethylbenzene, and xylene (BTEX), and developed a downward gradient. From groundwater samples collected in 1985, it was observed that the BTEX plume stopped spreading. The dynamic steady state of the plume reflected a balance between the rate at which soluble hydrocarbons spread into the groundwater and the rate at which the hydrocarbons were

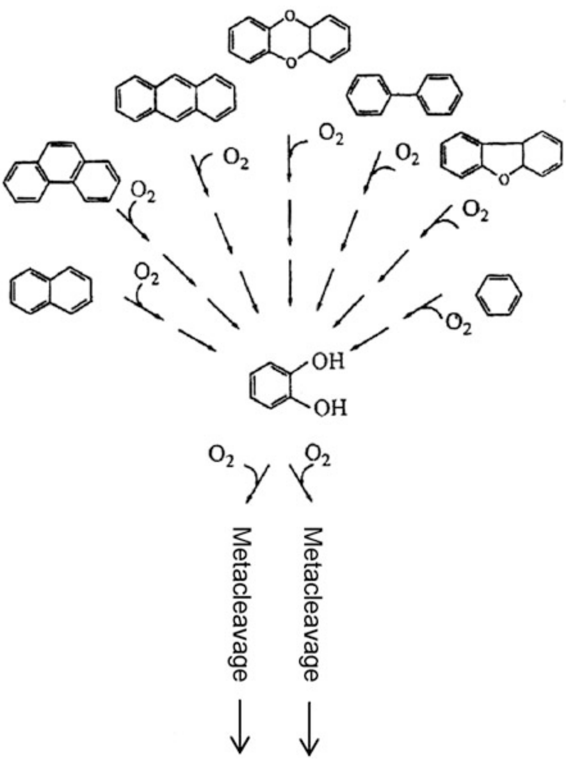


Fig. 13.8 Generalized aerobic biodegradation pathways for aromatic hydrocarbons. Reprinted from Abrajano et al. (2005). Copyright 2005 with permission of Elsevier

consumed by microorganisms or affected by additional processes causing natural attenuation (Baedecker et al. 1993).

Persistence and degradation of chlorinated solvent contaminants in groundwater systems have been the object of a large number of investigations over the last 20 years. In flowing groundwater systems, chlorinated solvents, such as trichloroethylene (TCE) and perchloroethylene (PCE), act as persistent contaminants. The degradation of TCE and PCE, and their transformation into more lightly chlorinated ethenes such as cis-dichloro ethene (DCE) and vinyl chloride (VC), are depicted in Fig. 13.9. Chlorinated ethenes may be subject to microbial degradation processes, including reductive dechlorination and aerobic and anaerobic oxidation. In many natural environments, the initial reductive dechlorination drives the transformation of PCE and TCE to DCE and VC, respectively. The combined effects of methane-oxidizing cometabolism and anaerobic oxidation lead to the transformation of DCE and VC into carbon dioxide, chloride, and water. Because these biodegradation processes are all redox processes, the efficiency of biodegradation is very sensitive to reduction-oxidation conditions (Chapelle 1996).

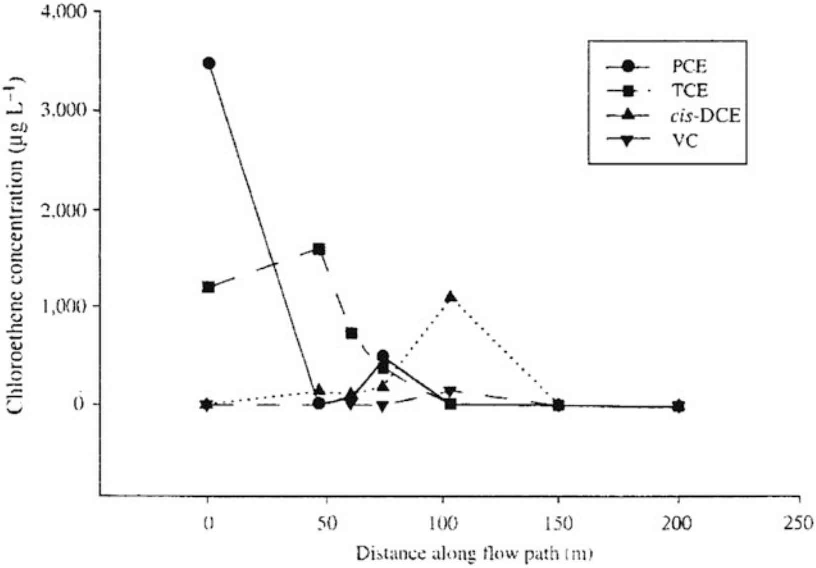


Fig. 13.9 Observed transformations of chlorinated ethenes in groundwater system. (Chapelle and Bradley 1998)

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