6

Air Pollution Systems and Processes

I. CHEMICAL PROCESSES IN AIR POLLUTION

A. Chemical Characteristics

Air pollution processes are a function of both the chemical characteristics of the compartment (e.g. air) and those of the contaminant. The inherent properties of the air pollutant are influenced and changed by the extrinsic properties of the air and other media in which the pollutant resides in the environment. Thus, Table 6.1 describes both sets of properties.

B. Chemical Reactions in the Environment

Five categories of chemical reactions take place in the environment or in systems that ultimately lead to contamination (such as closed systems where toxic chemicals, like pesticides, are synthesized before being used and released into the ambient, environment, or thermal systems where precursor compounds form new contaminants, like dioxins and furans). The categories of chemical reactions are as follows:

1. Synthesis or combination:

$$A + B \rightarrow AB \tag{6.1}$$

In combination reactions, two or more substances react to form a single substance. Two types of combination reactions are important in environmental systems, i.e. formation and hydration.

TABLE 6.1

Physical, Chemical, and Biological Processes Important to the Fate and Transport of Contaminants in the Environment

Process	Description	Physical phases involved	Major mechanisms at work	Outcome of process	Factors included in process
Advection	Transport by turbulent flow; mass transfer	Aqueous, gas	Mechanical	Transport due to mass transfer	Concentration gradients, porosity, permeability, hydraulic conductivity, circuitousness or tortuosity of flow paths
Dispersion	Transport from source	Aqueous, gas	Mechanical	Concentration gradient and dilution driven	Concentration gradients, porosity, permeability, hydraulic conductivity, circuitousness or tortuosity of flow paths
Diffusion	Fick's law (concentration gradient)	Aqueous, gas, solid	Mechanical	Concentration gradient-driven transport	Concentration gradients
Liquid separation	Various fluids of different densities and viscosities are separated within a system	Aqueous	Mechanical	Recalcitrance due to formation of separate gas and liquid phases (e.g. gasoline in water separates among benzene, toluene, and xylene)	Polarity, solubility, K_d, K_{ow}, K_{oc}, coefficient of viscosity, density
Density stratification	Distinct layers of differing densities and viscosities	Aqueous	Physical/Chemical	Recalcitrance or increased mobility in transport of lighter fluids (e.g. light non-aqueous phase liquids, LNAPLs) that float at water table in groundwater, or at atmospheric pressure in surface water	Density (specific gravity)

(*continued*)

TABLE 6.1 (*Continued*)

Process	Description	Physical phases involved	Major mechanisms at work	Outcome of process	Factors included in process
Migration along flow paths	Faster through large holes and conduits, e.g. path between interstices of sorbant packing in air stripping towers	Aqueous, gas	Mechanical	Increased mobility through fractures	Porosity, flow path diameters
Sedimentation	Heavier compounds settle first	Solid	Chemical, physical, mechanical, varying amount of biological	Recalcitrance due to deposition of denser compounds	Mass, density, viscosity, fluid velocity, turbulence (R_N)
Filtration	Retention in mesh	Solid	Chemical, physical, mechanical, varying amount of biological	Recalcitrance due to sequestration, destruction, and mechanical trapping of particles	Surface charge, soil, particle size, sorption, polarity
Volatilization	Phase partitioning to vapor	Aqueous, gas	Physical	Increased mobility as vapor phase of contaminant migrates to soil gas phase and atmosphere	Vapor pressure (P^0), concentration of contaminant, solubility, temperature
Dissolution	Co-solvation, attraction of water molecule shell	Aqueous	Chemical	Various outcomes due to formation of hydrated compounds (with varying solubilities, depending on the species)	Solubility, pH, temperature, ionic strength, activity
Absorption	Retention on solid surface	Solid	Chemical, physical, varying amount of biological	Partitioning of lipophilic compounds into soil organic matter, and penetration into an aerosol	Polarity, surface charge, Van der Waals attraction, electrostatics, ion exchange, solubility, K_d, K_{ow}, K_{oc}, coefficient of viscosity, density

Adsorption	Retention on solid surface	Solid	Chemical, physical, varying amount of biological	Recalcitrance due to ion exchanges and charge separations on a particle's surface	Polarity, surface charge, Van der Waals attraction, electrostatics, ion exchange, solubility, K_d, K_{ow}, K_{oc}, coefficient of viscosity, density
Complexation	Reactions with matrix (e.g. soil compounds like humic acid) that form covalent bonds	Solid	Chemical, varying amount of biological	Recalcitrance and transformation due to reactions with soil organic compounds to form residues (bound complexes)	Available oxidants/ reductants, soil organic matter content, pH, chemical interfaces, available O_2, electrical interfaces, temperature
Oxidation/ Reduction	Electron loss and gain	All	Chemical, physical, varying amount of biological	Destruction or transformation due to mineralization of simple carbohydrates to CO_2 and water from respiration of organisms	Available oxidants/ reductants, soil organic matter content, pH, chemical interfaces, available O_2, electrical interfaces, temperature
Ionization	Complete co-solvation leading to separation of compound into cations and anions	Aqueous	Chemical	Dissolution of salts into ions	Solubility, pH, temperature, ionic strength, activity
Hydrolysis	Reaction of water molecules with contaminants	Aqueous	Chemical	Various outcomes due to formation of hydroxides (e.g. aluminum hydroxide) with varying solubilities, depending on the species)	Solubility, pH, temperature, ionic strength, activity
Photolysis	Reaction catalyzed by electromagnetic (EM) energy (sunlight)	Gas (major phase)	Chemical, physical	Photooxidation of compounds with hydroxyl radical upon release to the atmosphere	Free radical concentration, wavelength, and intensity of EM radiation

(*continued*)

TABLE 6.1 (*Continued*)

Process	Description	Physical phases involved	Major mechanisms at work	Outcome of process	Factors included in process
Biodegradation	Microbially mediated, enzymatically catalyzed reactions	Aqueous, solid	Chemical, biological	Various outcomes, including destruction and formation of daughter compounds (degradation products) intracellularly and extracellularly	Microbial population (count and diversity), pH, temperature, moisture, biofilm, acclimation potential of available microbes, nutrients, appropriate enzymes in microbes, available and correct electron acceptors (i.e. oxygen for aerobes, others for anaerobes)
Activation	Metabolic, detoxification process that renders a compound more toxic	Aqueous, gas, solid, tissue	Biochemical	Phase 1 or 2 metabolism, e.g. oxidation for epoxides on aromatics	Available detoxification and enzymatic processes in cells
Metal catalysis	Reactions sped up in the presence of certain metallic compounds (e.g. noble metal oxides in the degradation of nitric acid).	Aqueous, gas, solid, and biotic	Chemical (especially reduction and oxidation)	Same reaction, but faster	Species and oxidation state of metal

Formation reactions are those where elements combine to form a compound. Examples include the formation of ferric oxide and the formation of octane:

$$4\ Fe\ (s) + 3\ O_2\ (g) \rightarrow 2\ Fe_2O_3\ (s) \tag{6.2}$$

$$8\ C\ (s) + 9\ H_2\ (g) \rightarrow C_8H_{18}\ (l) \tag{6.3}$$

Hydration reactions involve the addition of water to synthesize a new compound, for example, when calcium oxide is hydrated to form calcium hydroxide, and when phosphate is hydrated to form phosphoric acid:

$$CaO\ (s) + H_2O\ (l) \rightarrow Ca\ (OH)_2\ (s) \tag{6.4}$$

$$P_2O_5\ (s) + 3\ H_2O\ (l) \rightarrow 2\ H_3PO_4\ (aq) \tag{6.5}$$

2. Decomposition (often referred to as "degradation" when discussing organic compounds in toxicology, environmental sciences, and engineering):

$$AB \rightarrow A + B \tag{6.6}$$

In decomposition, one substance breaks down into two or more new substances, such as in the decomposition of carbonates. For example, calcium carbonate breaks down into calcium oxide and carbon dioxide:

$$CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g) \tag{6.7}$$

3. Single replacement (or single displacement):

$$A + BC \rightarrow AC + B \tag{6.8}$$

This commonly occurs when one metal ion in a compound is replaced with another metal ion, such as when trivalent chromium replaces monovalent silver:

$$3\ AgNO_3\ (aq) + Cr\ (s) \rightarrow Cr(NO_3)_3\ (aq) + 3\ Ag\ (s) \tag{6.9}$$

4. Double replacement (also metathesis or double displacement):

$$AB + CD \rightarrow AD + CB \tag{6.10}$$

In metathetic reactions, metals are exchanged between the salts. These newly formed salts have different chemical and physical characteristics from those of the reagents and are commonly encountered in metal precipitation reactions, such as when lead is precipitated (indicated by the "(s)" following $PbCl_2$), as in the reaction of a lead salt with an acid like potassium chloride:

$$Pb(ClO_3)_2\ (aq) + 2\ KCl\ (aq) \rightarrow PbCl_2\ (s) + 2\ KClO_3\ (aq) \tag{6.11}$$

5. Complete or efficient combustion (thermal oxidation) occurs when an organic compound is oxidized in the presence of heat (indicated by Δ):

$$a(CH)_x + bO_2 \xrightarrow{\Delta} cCO_2 + dH_2O \tag{6.12}$$

Combustion is the combination of O_2 in the presence of heat (as in burning fuel), producing CO_2 and H_2O during complete combustion of organic compounds, such as the combustion of octane:

$$C_8H_{18}\ (l) + 17\ O_2\ (g) \xrightarrow{\Delta} 8\ CO_2\ (g) + 9\ H_2O\ (g) \tag{6.13}$$

Complete combustion may also result in the production of molecular nitrogen (N_2) when nitrogen-containing organics are burned, such as in the combustion of methylamine:

$$4CH_3NH_2\,(l) + 9\,O_2\,(g) \xrightarrow{\Delta} 4\,CO_2\,(g) + 10\,H_2O\,(g) + 2\,N_2\,(g) \qquad (6.14)$$

Incomplete combustion can produce a variety of compounds. Some are more toxic than the original compounds being oxidized, such as polycyclic aromatic hydrocarbons (PAHs), dioxins, furans, and CO. The alert reader will note at least two observations about these categories. First, all are kinetic, as denoted by the one-directional arrow ($\rightarrow$). Second, in the environment, many processes are incomplete, such as the common problem of incomplete combustion and the generation of new compounds in addition to carbon dioxide and water.

With respect to the first observation, indeed, many equilibrium reactions take place. However, as mentioned in previous discussions, getting to equilibrium requires a kinetic phase. So, upon reaching equilibrium, the kinetic reactions (one-way arrows) would be replaced by two-way arrows ($\leftrightarrow$). Changes in the environment or in the quantities of reactants and products can invoke a change back to kinetics.

Incomplete reactions are very important sources of environmental contaminants. For example, these reactions generate *products of incomplete combustion* (PICs), such as CO, PAHs, dioxins, furans, and hexachlorobenzene (HCB). However, even the products of complete combustion are not completely environmentally acceptable. Both carbon dioxide and water are a greenhouse gases. They are both essential to life on earth, but excessive amounts of CO_2 are strongly suspected of altering climate, especially increasing mean surface temperatures on earth. Thus, CO_2 is considered by many to be an "air pollutant."

II. AIR POLLUTION CHEMODYNAMICS

Environmental chemodynamics is concerned with how chemicals move and change in the environment. Up to this point we have discussed some of the fluid properties that have a great bearing on the movement and distribution of contaminants to, from, and within the atmosphere. However, we are now ready to consider three specific partitioning relationships that control the "leaving" and "gaining" of pollutants among compartments, especially air, particles, surfaces, and organic tissues. These concepts may be applied to estimating and modeling where a contaminant will go after it is released. These relationships are sorption, solubility, volatilization, and organic carbon–water partitioning, which are respectively expressed by coefficients of sorption (distribution coefficient, K_D, or solid–water partition coefficient, K_p), dissolution or solubility coefficients, air–water partitioning (and the Henry's Law, K_H, constant), and organic carbon–water (K_{oc}) partitioning.

In chemodynamics, the environment is subdivided into finite compartments. Thermodynamically, the mass of the contaminant entering and the mass leaving a control volume must be balanced by what remains within the control volume (ala the conservation laws). Likewise, within that control volume, each compartment may be a gainer or loser of the contaminant mass, but the overall mass must balance. The generally inclusive term for these compartmental changes is known as fugacity or the "fleeing potential" of a substance. It is the propensity of a chemical to escape from one type of environmental compartment to another. Combining the relationships between and among all of the partitioning terms is one means of modeling chemical transport in the environment.[1] This is accomplished by using thermodynamic principles and, hence, *fugacity* is a thermodynamic term.

The simplest chemodynamic approach addresses each compartment where a contaminant is found in discrete phases of air, water, soil, sediment, and biota. This can be seen graphically in Fig. 6.1. However, a complicating factor in environmental chemodynamics is that even within a single compartment, a contaminant may exist in various phases (e.g. dissolved in water and sorbed to a particle in the solid phase). The physical interactions of the contaminant at the interface between each compartment is a determining factor in the fate of the pollutant. Within a compartment, a contaminant may remain unchanged (at least during the designated study period), or it may move physically, or it may be transformed chemically into another substance. Actually, in many cases all three mechanisms will take place. A mass fraction will remain unmoved and unchanged. Another fraction remains unchanged but is transported to a different compartment. Another fraction becomes chemically transformed with all remaining products staying in the compartment where they were generated. And, a fraction of the original contaminant is transformed and then moved to another compartment. So, upon release from a source, the contaminant moves as a result of thermodynamics.

Fugacity requires that at least two phases must be in contact with the contaminant. For example, the K_{ow} value is an indication of a compound's likelihood to exist in the organic versus aqueous phase. This means that if a substance is dissolved in water and the water comes into contact with another substance, e.g. octanol, the substance will have a tendency to move from the water to the octanol. Its octanol–water partitioning coefficient reflects just how much of the substance will move until the aqueous and organic solvents (phases) will reach equilibrium. So, for example, in a spill of equal amounts of the polychlorinated biphenyl (PCB), decachlorobiphenyl

[1] Fugacity models are valuable in predicting the movement and fate of environmental contaminants within and among compartments. This discussion is based on work by one of the pioneers in this area, Don MacKay and his colleagues at the University of Toronto. See, for example, MacKay, D., and Paterson, S., Evaluating the fate of organic chemicals: a level III fugacity model. *Environ. Sci. Technol.* **25**, 427–436 (1991).

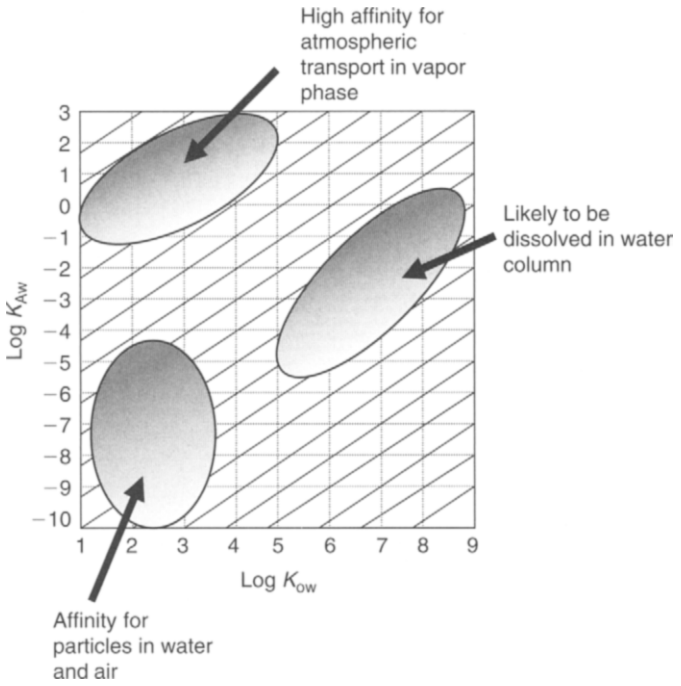

Fig. 6.1. Relationship between air–water partitioning and octanol–water partitioning and affinity of classes of contaminants for certain environmental compartments. A source of this information and format is: van de Meent, D., McKone, T., Parkerton, T., Matthies, M., Scheringer, M., Wania, F., Purdy, R., and Bennett, D., Persistence and transport potential of chemicals in a multimedia environment, in *Proceedings of the SETAC Pellston Workshop on Criteria for Persistence and Long-Range Transport of Chemicals in the Environment*, Fairmont Hot Springs, British Columbia, Canada, July 14–19, 1998. Society of Environmental Toxicology and Chemistry, Pensacola, FL, 1999.

(log K_{ow} of 8.23), and the pesticide chlordane (log K_{ow} of 2.78), the PCB has much greater affinity for the organic phases than does the chlordane (more than five orders of magnitude). This does not mean that a great amount of either of the compounds is likely to stay in the water column, since they are both hydrophobic, but it does mean that they will vary in the time and mass of each contaminant moving between phases. The rate (kinetics) is different, so the time it takes for the PCB and chlordane to reach equilibrium will be different. This can be visualized by plotting the concentration of each compound with time (see Fig. 6.2). When the concentrations plateau, the compounds are at equilibrium with their phase.

When phases contact one another, a contaminant will escape from one to another until the contaminant reaches equilibrium among the phases that are in contact with one another. Kinetics takes place until equilibrium is achieved.

We can now consider the key partitioning factors needed for a simple chemodynamic model.

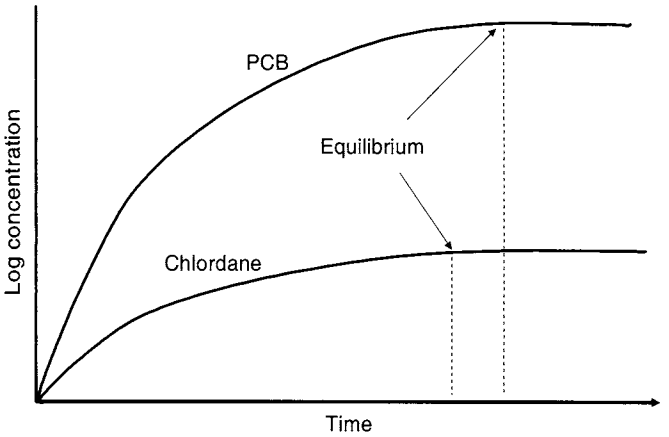

Fig. 6.2. Relative concentrations of a PCB and chlordane in octanol with time.

A. Partitioning to Solids: Sorption

Some experts spend a lot of time differentiating the various ways that a contaminant will attach to or permeate into surfaces of solid phase particles. Others, including many environmental engineers, lump these processes together into a general phenomenon called *sorption*, which is the process in which a contaminant or other solute becomes associated, physically or chemically, with a solid sorbent.

The physicochemical transfer[2] of a chemical, A, from liquid to solid phase is expressed as

$$A_{(solution)} + \text{solid} = \text{A-solid} \tag{6.15}$$

The interaction of the solute (i.e. the chemical being sorbed) with the surface of a solid surface can be complex and dependent on the properties of the chemical and the water. Other fluids are often of such small concentrations that they do not determine the ultimate solid–liquid partitioning. While, it is often acceptable to consider "net" sorption, let us consider briefly the four basic types or mechanisms of sorption:

1. *Adsorption* is the process wherein the chemical in solution attaches to a solid surface, which is a common sorption process in clay and organic constituents in soils. This simple adsorption mechanism can occur on clay particles where little carbon is available, such as in groundwater.
2. *Absorption* is the process that often occurs in porous materials so that the solute can diffuse into the particle and be sorbed onto the inside surfaces of the particle. This commonly results from short-range electrostatic interactions between the surface and the contaminant.

[2] Lyman, W., Transport and transformation processes, in *Fundamentals of Aquatic Toxicology: Effects, Environmental Fate, and Risk Assessment* (Rand, G., ed.), 2nd ed., Chapter 15. Taylor & Francis, Washington, DC, 1995.

3. *Chemisorption* is the process of integrating a chemical into porous materials surface via chemical reaction. In an airborne particle, this can be the result of a covalent reaction between a mineral surface and the contaminant.
4. *Ion exchange* is the process by which positively charged ions (cations) are attracted to negatively charged particle surfaces and negatively charged ions (anions) are attracted to positively charged particle surfaces, causing ions on the particle surfaces to be displaced. Particles undergoing ion exchange can include soils, sediment, airborne particulate matter, or even biota, such as pollen particles. Cation exchange has been characterized as being the second most important chemical process on earth, after photosynthesis. This is because the cation exchange capacity (CEC), and to a lesser degree anion exchange capacity (AEC) in tropical soils, is the means by which nutrients are made available to plant roots. Without this process, the atmospheric nutrients and the minerals in the soil would not come together to provide for the abundant plant life on planet earth.[3]

These four types of sorption are a mix of physics and chemistry. The first two are predominantly controlled by physical factors, and the second two are combinations of chemical reactions and physical processes. We will spend a bit more time covering these specific types of sorption when we consider the surface effects of soils. Generally, sorption reactions affect the following three processes[4] in aquatic systems:

1. The chemical contaminant's transport in water due to distributions between the aqueous phase and particles.
2. The aggregation and transport of the contaminant as a result of electrostatic properties of suspended solids.
3. Surface reactions such as dissociation, surface catalysis, and precipitation of the chemical contaminant.

Therefore, the difference between types of sorption is often important in air pollution control technologies. For example, collecting a contaminant on the surface of a sorbant depends solely on adsorption, while applying a control technology that traps the pollutant within the sorbant makes uses of absorption. Many technologies make use of both, as well as cation and anion exchange and chemisorption (see discussion below). Researchers attempt to parcel out which of the mechanisms are prominent in a given situation, since they vary according to the contaminant and the substrate.

When a contaminant enters the soil, some of the chemical remains in soil solution and some of the chemical is adsorbed onto the surfaces of the soil particles. Sometimes this sorption is strong due to cations adsorbing to the negatively charged soil particles. In other cases the attraction is weak. Sorption of

[3] Professor Daniel Richter of Duke University's Nicholas School of the Environment has waxed eloquently on this subject.

[4] See Westfall, J., Adsorption mechanisms in aquatic surface chemistry, in *Aquatic Surface Chemistry*. Wiley-Interscience, New York, NY, 1987.

chemicals on solid surfaces needs to be understood because they hold onto contaminants, not allowing them to move freely with the pore water or the soil solution. Therefore sorption slows that rate at which contaminants move downwardly through the soil profile.

Contaminants will eventually establish a balance between the mass on the solid surfaces and the mass that is in solution. Recall that molecules will migrate from one phase to another to maintain this balance. The properties of both the contaminant and the soil (or other matrix) will determine how and at what rates the molecules partition into the solid and liquid phases. These physicochemical relationships, known as *sorption isotherms*, are found experimentally. Figure 6.3 shows three isotherms for pyrene from experiments using different soils and sediments.

The x-axis shows the concentration of pyrene dissolved in water, and the y-axis shows the concentration in the solid phase. Each line represents the relationship between these concentrations for a single soil or sediment. A straight-line segment through the origin represents the data well for the range of concentrations shown. Not all portions of an isotherm are linear, particularly at high concentrations of the contaminant. Linear chemical partitioning can be expressed as

$$S = K_D C_W \tag{6.16}$$

where S is the concentration of contaminant in the solid phase (mass of solute per mass of soil or sediment); C_W is the concentration of contaminant in the liquid phase (mass of solute per volume of pore water); and K_D is the

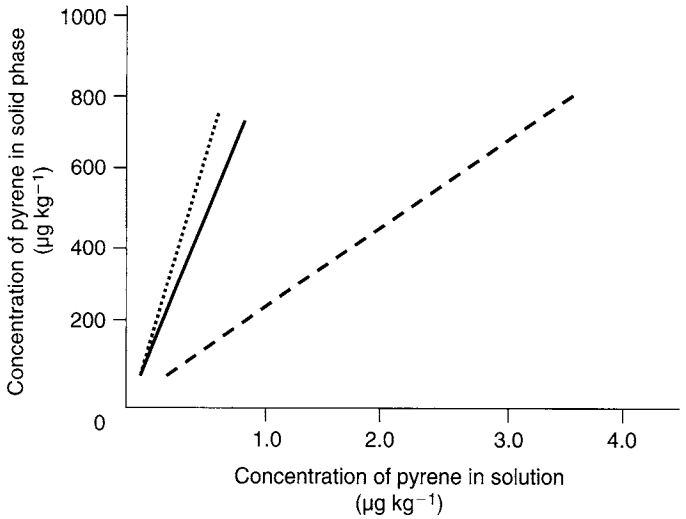

Fig. 6.3. Three experimentally determined sorption isotherms for the, polycyclic aromatic hydrocarbon, pyrene. *Source*: Hassett, J., and Banwart, W., 1989, The sorption of nonpolar organics by soils and sediments, in *Reactions and Movement of Organic Chemicals in Soils* (Sawhney, B., and Brown, K., eds.), p. 35. Soil Science Society of America. Special Publication 22.

partition coefficient (volume of pore water per mass of soil or sediment) for this contaminant in this soil or sediment.

For many soils and chemicals, the partition coefficient can be estimated using

$$K_D = K_{OC}\,OC \tag{6.17}$$

where K_{OC} is the organic carbon partition coefficient (volume of pore water per mass of organic carbon) and OC is the soil organic matter (mass of organic carbon per mass of soil).

This relationship is a very useful tool for estimating K_D from the known K_{OC} of the contaminant and the organic carbon content of the soil horizon of interest. The actual derivation of K_D is

$$K_D = C_S\,(C_W)^{-1} \tag{6.18}$$

where C_S is the equilibrium concentration of the solute in the solid phase and C_W is the equilibrium concentration of the solute in the water.

Therefore, K_D is a direct expression of the partitioning between the aqueous and solid (e.g. particle) phases. A strongly sorbed chemical like a dioxin or the banned pesticide dichlorodiphenyltrichloroethane (DDT) can have a K_D value exceeding 10^6. Conversely, a highly hydrophilic, miscible substance like ethanol, acetone, or vinyl chloride, will have K_D values less than 1. This relationship between the two phases demonstrated by Eq. (6.18) and Fig. 6.4 is roughly what environmental scientists call the Freundlich sorption isotherm:

$$C_{sorb} = K_F C^n \tag{6.19}$$

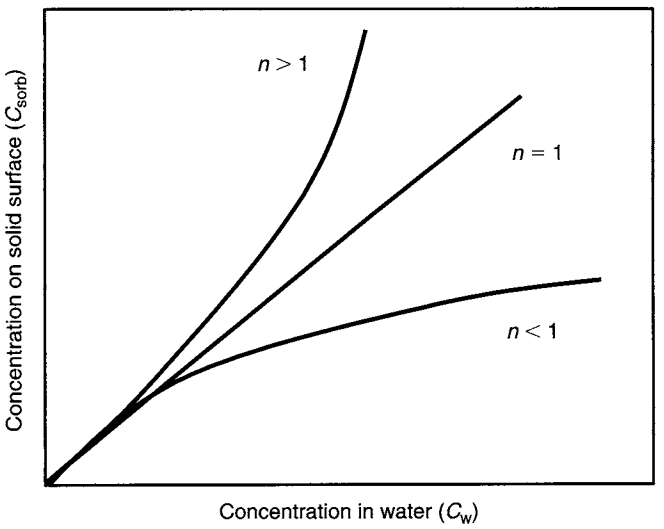

Fig. 6.4. Hypothetical Freundlich isotherms with exponents (n) less than, equal to, and greater than 1, as applied to the equation $C_{sorb} = K_F C^n$. *Sources*: Schwarzenbach, R., Gschwend, P., and Imboden, D., *Environmental Organic Chemistry*. John Wiley & Sons Inc., New York, NY, 1993; and Hemond, H. F., and Fechner-Levy, E. J., *Chemical Fate and Transport in the Environment*. Academic Press, San Diego, CA, 2000.

where C_{sorb} is the concentration of the sorbed contaminant, i.e. the mass sorbed at equilibrium per mass of sorbent, and K_F is the Freundlich isotherm constant. The exponent determines the linearity or order of the reaction. Thus, if $n = 1$, then the isotherm is linear; meaning the more of the contaminant in solution, the more would be expected to be sorbed to surfaces. For values of $n < 1$, the amount of sorption is in smaller proportion to the amount of solution and, conversely, for values of $n > 1$, a greater proportion of sorption occurs with less contaminant in solution. These three isotherms are shown in Fig. 6.4. Also note that if $n = 1$, then Eq. (6.20) and the Freundlich sorption isotherm are identical.

Research has shown that when organic matter content is elevated in the particle, the amount of a contaminant that is sorbed is directly proportional to the particle's organic matter content. This allows us to convert the K_D values from those that depend on specific soil or sediment conditions to those that are substrate-independent sorption constants, K_{OC}:

$$K_{OC} = K_D (f_{OC})^{-1} \tag{6.20}$$

where f_{OC} is the dimensionless weight fraction of organic carbon in the particle. K_{OC} and K_D have units of mass per volume. Table 6.2 provides the $\log K_{OC}$ values that are calculated from chemical structure and those measured empirically for several organic compounds, and compares them to the respective K_{ow} values.

B. Partitioning to the Liquid Phase: Dissolution

Unless otherwise stated, one can usually assume that when a compound is described as insoluble, such a statement means that the compound is *hydrophobic*. However, in environmental matters, it can be dangerous to make such assumptions, since such as wide range of scientific and engineering disciplines are involved. A good resource for contaminant solubilities for water, dimethylsulfoxide (DMSO), ethanol, acetone, methanol, and toluene is the National Toxicology Program's *Chemical Solubility Compendium*[5] and the program's Health and Safety reports.[6] The latter are updated frequently and provide useful data on properties of toxic chemicals.

Most characterizations of contaminants will describe solubility in water and provide values for aqueous solubility, as well as a substance's solubility in other organic solvents, such as methanol or acetone.

[5] Keith, L., and Walters, D., *National Toxicology Program's Chemical Solubility Compendium*. Lewis Publishers Inc., Chelsea, MI, 1992.

[6] http://ntp-db.niehs.nih.gov/htdocs/Chem_Hs_Index.html

TABLE 6.2

Calculated and Experimental Organic Carbon Coefficients (K_{oc}) for Selected Contaminants Found at Hazardous Waste Sites Compared to Octanol-Water Coefficients (K_{ow})

		Calculated		Measured	
Chemical	$\log K_{ow}$	$\log K_{oc}$	K_{oc}	$\log K_{oc}$	K_{oc} (geomean)
Benzene	2.13	1.77	59	1.79	61.7
Bromoform	2.35	1.94	87	2.10	126
Carbon tetrachloride	2.73	2.24	174	2.18	152
Chlorobenzene	2.86	2.34	219	2.35	224
Chloroform	1.92	1.60	40	1.72	52.5
Dichlorobenzene, 1,2- (*o*)	3.43	2.79	617	2.58	379
Dichlorobenzene, 1,4- (*p*)	3.42	2.79	617	2.79	616
Dichloroethane, 1,1-	1.79	1.50	32	1.73	53.4
Dichloroethane, 1,2-	1.47	1.24	17	1.58	38.0
Dichloroethylene, 1,1-	2.13	1.77	59	1.81	65
Dichloroethylene, *trans*-1,2-	2.07	1.72	52	1.58	38
Dichloropropane, 1,2-	1.97	1.64	44	1.67	47.0
Dieldrin	5.37	4.33	21 380	4.41	25 546
Endosulfan	4.10	3.33	2138	3.31	2040
Endrin	5.06	4.09	12 303	4.03	10 811
Ethylbenzene	3.14	2.56	363	2.31	204
Hexachlorobenzene	5.89	4.74	54 954	4.90	80 000
Methyl bromide	1.19	1.02	10	0.95	9.0
Methyl chloride	0.91	0.80	6	0.78	6.0
Methylene chloride	1.25	1.07	12	1.00	10
Pentachlorobenzene	5.26	4.24	17 378	4.51	32 148
Tetrachloroethane, 1,1,2,2-	2.39	1.97	93	1.90	79.0
Tetrachloroethylene	2.67	2.19	155	2.42	265
Toluene	2.75	2.26	182	2.15	140
Trichlorobenzene, 1,2,4-	4.01	3.25	1778	3.22	1659
Trichloroethane, 1,1,1-	2.48	2.04	110	2.13	135
Trichloroethane, 1,1,2-	2.05	1.70	50	1.88	75.0
Trichloroethylene	2.71	2.22	166	1.97	94.3
Xylene, *o*-	3.13	2.56	363	2.38	241
Xylene, *m*-	3.20	2.61	407	2.29	196
Xylene, *p*-	3.17	2.59	389	2.49	311

Source: US Environmental Protection Agency, 1996, Soil Screening Program.

The process of *co-solvation* is a very important mechanism by which a highly lipophilic and hydrophobic compound enters water. If a compound is hydrophobic and nonpolar, but is easily dissolved in acetone or methanol, it may well end up in the water because these organic solvents are highly miscible in water. The organic solvent and water mix easily, and a hydrophobic compound will remain in the water column because it is dissolved in the

organic solvent, which in turn has mixed with the water. Compounds like PCBs and dioxins may be transported as co-solutes in water by this means. So, the combination of hydrophobic compounds being sorbed to suspended materials and co-solvated in organic co-solvents that are miscible in water can mean that they are able to move in water and receptors can be exposed through the water pathways.

Solubility is determined from saturation studies. In other words, in the laboratory at a certain temperature, as much of the solute is added to a solvent until the solvent can no longer dissolve the substance being added. So, if compound A has a published solubility of $10\,mg\,L^{-1}$ in water at 20°C, this means that the 1 L of water could only dissolve 10 mg of that substance. If, under identical conditions, compound B has a published aqueous solubility of $20\,mg\,L^{-1}$, this means that 1 L of water could dissolve 20 mg of compound B, and that compound B has twice the aqueous solubility of compound A.

Actually, solutions are in "dynamic equilibrium" because the solute is leaving and entering the solution at all times, but the average amount of solute in solution is the same. The functional groups on a molecule determine whether it will be more or less polar. So, compounds with hydroxyl groups are more likely to form H-bonds with water. Thus, methane is less soluble in water than methanol. Also, since water interacts strongly with ions, salts are usually quite hydrophilic. The less the charge of the ion, the greater the solubility in water.

C. Partitioning to the Gas Phase: Volatilization

In its simplest connotation, volatilization is a function of the concentration of a contaminant in solution and the contaminant's partial pressure.

Henry's law states that the concentration of a dissolved gas is directly proportional to the partial pressure of that gas above the solution:

$$p_a = K_H[c] \tag{6.21}$$

where, K_H is the Henry's law constant; p_a is the partial pressure of the gas; and $[c]$ is the molar concentration of the gas

or,

$$p_a = K_H C_W \tag{6.22}$$

where C_W is the concentration of gas in water.

So, for any chemical contaminant we can establish a proportionality between the solubility and vapor pressure. Henry's law is an expression of

this proportionality between the concentration of a dissolved contaminant and its partial pressure in the headspace (including the open atmosphere) at equilibrium. A dimensionless version of the partitioning is similar to that of sorption, except that instead of the partitioning between solid and water phases, it is between the air and water phases (K_{AW}):

$$K_{AW} = \frac{C_A}{C_W} \tag{6.23}$$

where C_A is the concentration of gas A in the air.

The relationship between the air/water partition coefficient and Henry's law constant for a substance is:

$$K_{AW} = \frac{K_H}{RT} \tag{6.24}$$

where R is the gas constant (8.21×10^{-2} L atm mol^{-1}K^{-1}) and T is the temperature (°K).

Henry's law relationships work well for most environmental conditions. It represents a limiting factor for systems where a substance's partial pressure is approaching zero. At very high partial pressures (e.g. 30 Pa) or at very high contaminant concentrations (e.g. >1000 ppm), Henry's law assumptions cannot be met. Such vapor pressures and concentrations are seldom seen in ambient environmental situations, but may be seen in industrial and other source situations. Thus, in modeling and estimating the tendency for a substance's release in vapor form, Henry's law is a good metric and is often used in compartmental transport models to indicate the fugacity from the water to the atmosphere.

HENRY'S LAW EXAMPLE

At 25°C, the log Henry's Law constant ($\log K_H$) for 1,2-dimethylbenzene (C_8H_{10}) is 0.71 L atm mol^{-1} and the log octanol–water coefficient ($\log K_{ow}$) is 3.12. The $\log K_H$ for the pesticide parathion ($C_{10}H_{14}NO_5PS$) is -3.42 L atm mol^{-1}, but its $\log K_{ow}$ is 3.81. Explain how these substances can have similar values for octanol–water partitioning yet so different Henry's law constants. What principle physicochemical properties account for much of this difference?

Answer

Both dimethylbenzene and parathion have an affinity for the organic phase compared to the aqueous phase. Since Henry's law constants are a function of both vapor pressure (P^0) and water solubility, and both compounds have similar octanol–water coefficients, the difference in the Henry's law characteristics must be mainly attributable to the compounds' respective water solubilities, their vapor pressures, or both.

Parathion is considered "semivolatile" because its vapor pressure at 20°C is only 1.3×10^{-3} kPa. Parathion's solubility[7] in water is 12.4 mg L^{-1} at 25°C.

1,2-Dimethylbenzene is also known as *ortho*-xylene (*o*-xylene). The xylenes are simply benzenes with more two methyl groups. The xylenes have very high vapor pressures of 4.5×10^2 kPa, and water solubilities[8] of about 200 mg L^{-1} at 25°C.

Thus, since both the solubilities are relatively low, it appears that the difference in vapor pressures is responsible for the large difference in the Henry' law constants, i.e. the much larger tendency of the xylene to leave the water and enter the atmosphere. Some of this tendency may result from the higher molecular weight of the parathion, but is also attributable to the additional functional groups on the parathion benzene than the two methyl groups on the xylene (see Fig. 6.5).

Another way to look at the chemical structures is to see them as the result of adding increasing complex functional groups, i.e., moving from the unsubstituted benzene to the single methylated benzene (toluene) to *o*-xylene to parathion. The substitutions result in respective progressively decreasing vapor pressures:

Benzene's P^0 at 20°C = 12.7 kPa

Toluene's P^0 at 20°C = 3.7 kPa

o-Xylene's P^0 at 20°C = 0.9 kPa

Parathion's P^0 at 20°C = 1.3×10^{-3} kPa

The effect of these functional group additions on vapor pressure is even more obvious when seen graphically (Fig. 6.6)

[7] Meister, R. (ed.), *Farm Chemicals Handbook '92*. Meister Publishing Company, Willoughby, OH, 1992.

[8] National Park Service, US Department of the Interior, Environmental Contaminants Encyclopedia, 1997. *O*-Xylene Entry: http://www.nature.nps.gov/toxic/xylene_o.pdf

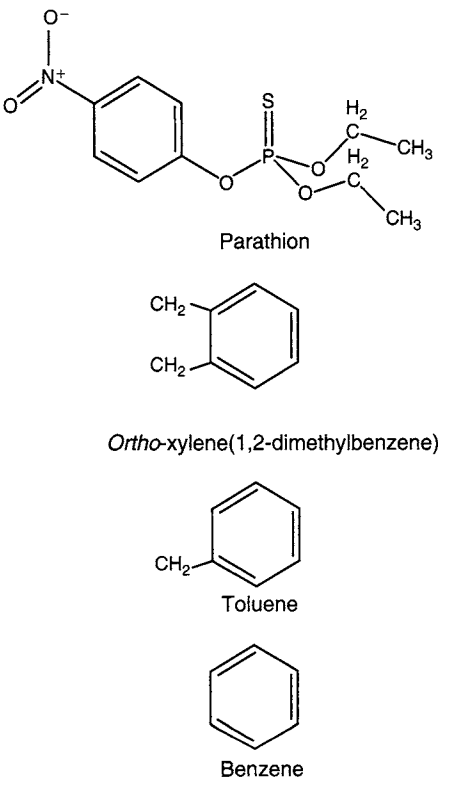

Fig. 6.5. Molecular structure of the pesticide parathion and the solvents *ortho*-xylene, toluene, and benzene.

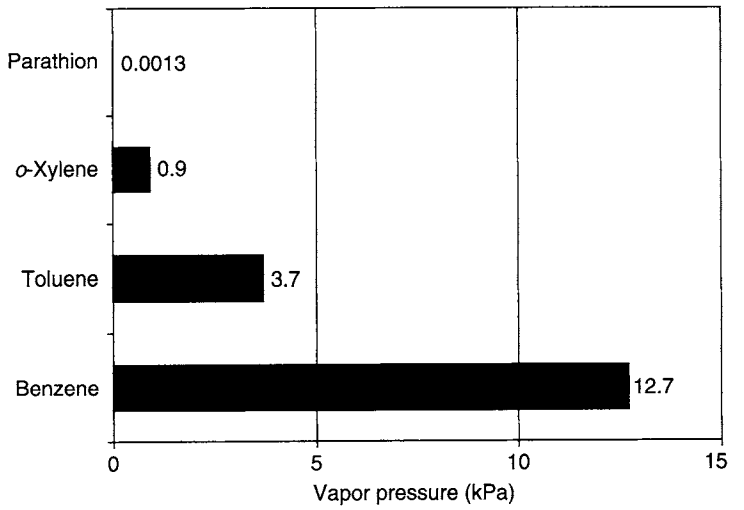

Fig. 6.6. Effect of functional group substitutions on vapor pressure of four organic aromatic compounds.

It is important to keep in mind that Henry's law constants are highly dependent on temperature, since both vapor pressure and solubility are also temperature dependent. So, when using published K_H values, one must compare them isothermically. Also, when combining different partitioning coefficients in a model or study, it is important to either use only values derived at the same temperature (e.g. sorption, solubility, and volatilization all at 20°C), or to adjust them accordingly. A general adjustment is an increase of a factor of 2 in K_H for each 8°C temperature increase.

Also, any sorbed or otherwise bound fraction of the contaminant will not exert a partial pressure, so this fraction should not be included in calculations of partitioning from water to air. For example, it is important to differentiate between the mass of the contaminant in solution (available for the K_{AW} calculation) and that in the suspended solids (unavailable for K_{AW} calculation). This is crucial for many hydrophobic organic contaminants, where they are most likely not to be dissolved in the water column (except as co-solutes), with the largest mass fraction in the water column being sorbed to particles.

The relationship between K_H and K_{ow} is also important. It is often used to estimate the *environmental persistence*, as reflected in the chemical *half-life* ($T_{1/2}$) of a contaminant. However, many other variables determine the actual persistence of a compound after its release. Note in the table, for example, that benzene and chloroform have nearly identical values of K_H and K_{ow}, yet benzene is far less persistent in the environment. We will consider these other factors in the next chapters, when we discuss abiotic chemical destruction and biodegradation.

With these caveats in mind, however, relative affinity for a substance to reside in air and water can be used to estimate the potential for the substance to partition not only between water and air, but more generally between the atmosphere and biosphere, especially when considering the long-range transport of contaminants (e.g. across continents and oceans).[9] Such long-range transport estimates make use of both atmospheric $T_{1/2}$ and K_H. The relationship between octanol–water and air–water coefficients can also be an important part of predicting a contaminant's transport. For example, Fig. 6.1 provides some general classifications according to various substances' K_H and K_{ow} relationships. In general, chemicals in the upper left-hand group have a great affinity for the atmosphere, so unless there are contravening factors, this is where to look for them. Conversely, substances with relatively low K_H and K_{ow} values are less likely to be transported long distance in the air.

Partitioning to Organic Tissue: Relatively hydrophobic substances frequently have a strong affinity for fatty tissues (i.e. those containing high K_{ow} compounds). Therefore, such contaminants can be sequestered and

[9] See Mackay, D., and Wania, F., Transport of contaminants to the arctic: partitioning, processes and models. *Sci. Total Environ.* **160/161**, 26–38, 1995.

can accumulate in organisms. In other words, certain chemicals are very *bioavailable* to organisms that may readily take them up from the other compartments. Bioavailability is an expression of the fraction of the total mass of a compound present in a compartment that has the potential of being absorbed by the organism. *Bioaccumulation* is the process of uptake into an organism from the abiotic compartments. *Bioconcentration* is the concentration of the pollutant within an organism above levels found in the compartment in which the organism lives. So, for a fish to bioaccumulate DDT, the levels found in the total fish or in certain organs (e.g. the liver) will be elevated above the levels measured in the ambient environment. In fact, DDT is known to bioconcentrate many orders of magnitude in fish. A surface water DDT concentration of 100 ppt in water has been associated with 10 ppm in certain fish species (a concentration of 10 000 times!). Thus the straightforward equation for the *bioconcentration factor* (BCF) is the quotient of the concentration of the contaminant in the organism and the concentration of the contaminant in the host compartment. So, for a fish living in water, the BCF is

$$\text{BCF} = \frac{C_{\text{organism}}}{C_{\text{w}}} \tag{6.25}$$

The BCF is applied to an individual organism that represents a genus or some other taxonomical group. However, considering the whole food chain and trophic transfer processes, in which a compound builds up as a result of predator/prey relationships, the term *biomagnification* is used. Some compounds that may not appreciably bioconcentrate within lower trophic state organisms may still become highly concentrated. For example, even though plankton have a small BCF (e.g. 10), if subsequently higher-order organisms sequester the contaminant at a higher rate, by the time top predators (e.g. alligators, sharks, panthers, and humans) may suffer from the continuum of biomagnification, with levels many orders of magnitude higher than what is found in the abiotic compartments.

For a substance to bioaccumulate, bioconcentrate, and biomagnify, it must be at least somewhat persistent. If an organism's metabolic and detoxification processes are able to degrade the compound readily, it will not be present (at least in high concentrations) in the organism's tissues. However, if an organism's endogenous processes degrade a compound into a chemical species that is itself persistent, the metabolite or degradation product will bioaccumulate, and may bioconcentrate, and biomagnify. Finally, cleansing or *depuration* will occur if the organism that has accumulated a contaminant enters an abiotic environment that no longer contains the contaminant. However, some tissues have such strong affinities for certain contaminants that the persistence within the organism will remain long after the source of the contaminant is removed. For example, the piscivorous birds, such as the Common Loon (*Gavia immer*), decrease the concentrations of the metal mercury (Hg) in their bodies by translocating the metal to feathers and eggs.

So, every time the birds molt or lay eggs they undergo Hg depuration. Unfortunately, when the birds continue to ingest mercury that has bioaccumulated in their prey (fish), they often have a net increase in tissue Hg concentrations because the bioaccumulation rate exceeds the depuration rate.[10]

Bioconcentration can vary considerably in the environment. The degree to which a contaminant builds up in an ecosystem, especially in biota and sediments, is related to the compound's persistence. For example, a highly persistent compound often possesses chemical structures that are also conducive to sequestration by fauna. Such compounds are generally quite often lipophilic, have high K_{ow} values, and usually low vapor pressures. This means that they may bind to the organic molecules in living tissues and may resist elimination and metabolic process, so that they build up over time. However, the bioaccumulation and bioconcentration can vary considerably, both among biota and within the same species of biota. For example, the pesticide mirex has been shown to exhibit BCFs of 2600 and 51 400 in pink shrimp and fathead minnows, respectively. The pesticide endrin has shown an even larger interspecies variability in BCF values, with factors ranging from 14 to 18 000 recorded in fish after continuous exposure. Intraspecies BCF ranges may also be high, e.g., oysters exposed to very low concentrations of the organometallic compound, tributyl tin, exhibit BCF values ranging from 1000 to 6000.[11]

Even the same compound in a single medium, e.g. a lake's water column or sediment, will show large BCF variability among species of fauna in that compartment. An example is the so-called "dirty dozen" compounds. This is a group of *persistent organic pollutants* (POPs) that have been largely banned, some for decades, but that are still found in environmental samples throughout the world. As might be expected from their partitioning coefficients, they have concentrated in sediment and biota.

The worst combination of factors is when a compound is persistent in the environment, builds up in organic tissues, and is toxic. Such compounds are referred to as *persistent bioaccumulating toxic* substances (PBTs). Recently, the United Nations Environmental Program (UNEP) reported on the concentrations of the persistent and toxic compounds. Each region of the world was evaluated for the presence of these compounds. For example, the North American report[12] includes scientific assessments of the nature and scale of environmental threats posed by persistent toxic compounds. The results of these assessments are summarized in Tables 6.3 (organic compounds) and 6.4 (organometallic compounds). In the US, mining and mineral extraction

[10] Schoch, N., and Evers, D., Monitoring Mercury in Common Loons: New York Field Report, 1998–2000. Report BRI 2001-01 submitted to US Fish Wildlife Service and New York State Department of Environmental Conservation, BioDiversity Research Institute, Falmouth, ME, 2002.

[11] United Nations Environmental Program, Chemicals: North American Regional Report, Regionally Based Assessment of Persistent Toxic Substances, Global Environment Facility, 2002.

[12] United Nations Environmental Program, 2002.

TABLE 6.3

Summary of Persistent and Toxic Organic Compounds in North America, Identified by the United Nations as Highest Priorities for Regional Actions

Compound	Properties	Persistence/Fate	Toxicity*
Aldrin 1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo,exo-5,8-dimethanonaphthalene ($C_{12}H_8Cl_6$).	Solubility in water: 27 $\mu g\,L^{-1}$ at 25°C; Vapor pressure: 2.31 × 10^{-5} mmHg at 20°C; log K_{ow}: 5.17–7.4.	Readily metabolized to dieldrin by both plants and animals. Biodegradation is expected to be slow and it binds strongly to soil particles, and is resistant to leaching into groundwater. Classified as moderately persistent with $T_{1/2}$ in soil ranging from 20–100 days.	Toxic to humans. Lethal dose for an adult estimated to be about 80 $mg\,kg^{-1}$ body weight. Acute oral LD_{50} in laboratory animals is in the range of 33 $mg\,kg^{-1}$ body weight for guinea pigs to 320 $mg\,kg^{-1}$ body weight for hamsters. The toxicity of aldrin to aquatic organisms is quite variable, with aquatic insects being the most sensitive group of invertebrates. The 96-h LC_{50} values range from 1–200 $\mu g\,L^{-1}$ for insects, and from 2.2–53 $\mu g\,L^{-1}$ for fish. The maximum residue limits in food recommended by the World Health Organization (WHO) varies from 0.006 $mg\,kg^{-1}$ milk fat to 0.2 $mg\,kg^{-1}$ meat fat. Water quality criteria between 0.1 and 180 $\mu g\,L^{-1}$ have been published.
Dieldrin 1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydroexo-1,4-endo-5,8-dimethanonaphthalene ($C_{12}H_8Cl_6O$).	Solubility in water: 140 $\mu g\,L^{-1}$ at 20°C; vapor pressure: 1.78 × 10^{-7} mmHg at 20°C; log K_{ow}: 3.69–6.2.	Highly persistent in soils, with a $T_{1/2}$ of 3–4 years in temperate climates, and bioconcentrates in organisms.	Acute toxicity for fish is high (LC_{50} between 1.1 and 41 $mg\,L^{-1}$) and moderate for mammals (LD_{50} in mouse and rat ranging from 40 to 70 $mg\,kg^{-1}$ body weight). Aldrin and dieldrin mainly affect the central nervous system but there is no direct evidence that they cause cancer in humans. The maximum residue limits in food recommended by WHO varies from 0.006 $mg\,kg^{-1}$ milk fat and 0.2 $mg\,kg^{-1}$

			poultry fat. Water quality criteria between 0.1 and 18 $\mu g\,L^{-1}$ have been published.
Endrin 3,4,5,6,9,9-Hexachloro-1a,2,2a,3,6,6a,7,7a-octahydro-2,7:3,6-dimethanonaphth[2,3-b] oxirene ($C_{12}H_8Cl_6O$).	Solubility in water: 220–260 $\mu g\,L^{-1}$ at 25°C; vapor pressure: 7×10^{-7} mmHg at 25°C; log K_{ow}: 3.21–5.34.	Highly persistent in soils ($T_{1/2}$ of up to 12 years have been reported in some cases). BCFs of 14 to 18 000 have been recorded in fish, after continuous exposure.	Very toxic to fish, aquatic invertebrates, and phytoplankton; the LC_{50} values are mostly less than 1 $\mu g\,L^{-1}$. The acute toxicity is high in laboratory animals, with LD_{50} values of 3–43 $mg\,kg^{-1}$, and a dermal LD_{50} of 6–20 $mg\,kg^{-1}$ in rats. Long-term toxicity in the rat has been studied over 2 years and a NOEL of 0.05 $mg\,kg^{-1}$bw day^{-1} was found.
Chlordane 1,2,4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene ($C_{10}H_6Cl_8$).	Solubility in water: 180 $\mu g\,L^{-1}$ at 25°C; vapor pressure: 0.3×10^{-5} mmHg at 20°C; log K_{ow}: 4.4–5.5.	Metabolized in soils, plants, and animals to heptachlor epoxide, which is more stable in biological systems and is carcinogenic. The $T_{1/2}$ of heptachlor in soil is in temperateregions 0.75–2 years. Its high partition coefficient provides the necessary conditions for bioconcentrating in organisms.	Acute toxicity to mammals is moderate (LD_{50} values between 40 and 119 $mg\,kg^{-1}$ have been published). The toxicity to aquatic organisms is higher and LC_{50} values down to 0.11 $\mu g\,L^{-1}$ have been found for pink shrimp. Limited information is available on the effects in humans and studies are inconclusive regarding heptachlor and cancer. The maximum residue levels recommended by FAO/WHO are between 0.006 $mg\,kg^{-1}$ milk fat and 0.2 $mg\,kg^{-1}$ meat or poultry fat.
Dichlorodiphenyltrichloroethane (DDT) 1,1,1-Trichloro-2,2-bis-(4-chlorophenyl)-ethane ($C_{14}H_9Cl_5$).	Solubility in water: 1.2–5.5 $\mu g\,L^{-1}$ at 25°C; vapor pressure: 0.02×10^{-5} mmHg at 20°C; log K_{ow}: 6.19 for pp-DDT, 5.5 for pp-DDD and 5.7 for pp-DDE.	Highly persistent in soils with a $T_{1/2}$ of about 1.1–3.4 years. It also exhibits high BCFs (in the order of 50 000 for fish and 500 000 for bivalves). In the environment, the parent DDT is metabolized mainly to DDD and DDE.	Lowest dietary concentration of DDT reported to cause egg shell thinning was 0.6 $mg\,kg^{-1}$ for the black duck. LC_{50} of 1.5 $mg\,L^{-1}$ for largemouth bass and 56 $mg\,L^{-1}$ for guppy have been reported. The acute toxicity of DDT for mammals is moderate with an LD_{50} in rat of 113–118 $mg\,kg^{-1}$ body weight. DDT has been shown to have an estrogen-like

(*continued*)

TABLE 6.3 (*Continued*)

Compound	Properties	Persistence/Fate	Toxicity*
			activity and possible carcinogenic activity in humans. The maximum residue level in food recommended by WHO/FAO, ranges from 0.02 mg kg^{-1} milk fat to 5 mg kg^{-1} meat fat. Maximum permissible DDT residue levels in drinking water (WHO) is 1.0 μg L^{-1}.
Toxaphene Polychlorinated bornanes and camphenes ($C_{10}H_{10}Cl_8$).	Solubility in water: 550 μg L^{-1} at 20°C; vapor pressure: 0.2–0.4 mmHg at 25°C; log K_{ow}: 3.23–5.50.	Half-life in soil from 100 days up to 12 years. It has been shown to bioconcentrate in aquatic organisms (BCF of 4247 in mosquito fish and 76 000 in brook trout).	Highly toxic in fish, with 96-h LC_{50} values in the range of 1.8 μg L^{-1} in rainbow trout to 22 μg L^{-1} in bluegill. Long-term exposure to 0.5 μg L^{-1} reduced egg viability to zero. The acute oral toxicity is in the range of 49 mg kg^{-1} body weight in dogs to 365 mg kg^{-1} in guinea pigs. In long-term studies NOEL in rats was 0.35 mg kg^{-1} bw day^{-1}, LD_{50} ranging from 60 to 293 mg kg^{-1} bw. For toxaphene, there exists strong evidence of the potential for endocrine disruption. Toxaphene is carcinogenic in mice and rats and is of carcinogenic risk to humans, with a cancer potency factor of 1.1 mg kg^{-1} day^{-1} for oral exposure.
Mirex 1,1a,2,2,3,3a,4,5,5a,5b,6-Dodecachloroacta-hydro-1,3,4-metheno-1H-cyclobuta[cd] pentalene ($C_{10}Cl_{12}$).	Solubility in water: 0.07 μg L^{-1} at 25°C; vapor pressure: 3×10^{-7} mmHg at 25°C; log K_{ow}: 5.28.	Among the most stable and persistent pesticides, with a $T_{1/2}$ in soils of up to 10 years. BCFs of 2600 and 51 400 have been observed in pink shrimp and fathead minnows, respectively.	Acute toxicity for mammals is moderate with an LD_{50} in rat of 235 mg kg^{-1} and dermal toxicity in rabbits of 80 mg kg^{-1}. Mirex is also toxic to fish and can affect their behavior (LC_{50} (96 h) from 0.2 to 30 mg L^{-1} for rainbow trout and bluegill,

		Capable of undergoing long-range transport due to its relativevolatility (VPL = 4.76 Pa; $H = 52\,Pa\,m^3\,mol^{-1}$).	respectively). Delayed mortality of crustaceans occurred at $1\,\mu g\,L^{-1}$ exposure levels. There is evidence of its potential for endocrine disruption and possibly carcinogenic risk to humans.
Hexachlorobenzene (HCB) (C_6H_6).	Solubility in water: $50\,\mu g\,L^{-1}$ at 20°C; vapor pressure: 1.09×10^{-5} mmHg at 20°C; log K_{ow}: 3.93–6.42.	Estimated "field half-life" of 2.7–5.7 years. HCB has a relatively high bioaccumulation potential and long $T_{1/2}$ in biota.	LC_{50} for fish varies between 50 and $200\,\mu g\,L^{-1}$. The acute toxicity of HCB is low with LD_{50} values of $3.5\,mg\,g^{-1}$ for rats. Mild effects of the [rat] liver have been observed at a daily dose of 0.25 mg HCB kg^{-1} bw. HCB is known to cause liver disease in humans (porphyria cutanea tarda) and has been classified as a possible carcinogen to humans by IARC.
Polychlorinated biphenyls (PCBs) ($C_{12}H_{(10-n)}Cl_n$, where n is within the range of 1–10).	Water solubility decreases with increasing chlorination: 0.01–0.0001 $\mu g\,L^{-1}$ at 25°C; vapor pressure: $1.6–0.003 \times 10^{-6}$ mmHg at 20°C; log K_{ow} : 4.3–8.26.	Most PCB congeners, particularly those lacking adjacent unsubstituted positions on the biphenyl rings (e.g. 2,4,6-, 2,3,6- or 2,3,6-substituted on both rings) are extremely persistent in the environment. They are estimated to have $T_{1/2}$ ranging from 3 weeks to 2 years in air and, with the exception of mono- and dichlorodiphenyl, more than6 years in aerobic soils and sediments. PCBs also have extremely long $T_{1/2}$ in adult fish,for example, an 8-year study of eels found that the $T_{1/2}$ of CB153 was more than 10 years.	LC_{50} for the larval stages of rainbow trout is $0.32\,\mu g\,L^{-1}$ with a NOEL of $0.01\,\mu g\,L^{-1}$. The acute toxicity of PCB in mammals is generally low and LD_{50} values in rat of $1\,g\,kg^{-1}$ bw. IARC has concluded that PCBs are carcinogenic to laboratory animals and probably also for humans. They have also been classified as substances for which there is evidence of endocrine disruption in an intact organism.

(*continued*)

TABLE 6.3 (*Continued*)

Compound	Properties	Persistence/Fate	Toxicity*
Polychlorinated dibenzo-p-dioxins (PCDDs) and *Polychlorinated dibenzofurans (PCDFs)* ($C_{12}H_{(8-n)}Cl_nO_2$) and PCDFs ($C_{12}H_{(8-n)}Cl_nO$) may contain between 1 and 8 chlorine atoms. Dioxins and furans have 75 and 135 possible positional isomers, respectively.	Solubility in water: in the range 550–0.07 ng L^{-1} at 25°C; vapor pressure: 2–0.007 × 10^{-6} mmHg at 20°C; log K_{ow}: in the range 6.60–8.20 for tetra- to octa-substituted congeners.	PCDD/Fs are characterized by their lipophilicity, semivolatility, and resistance to degradation ($T_{1/2}$ of TCDD in soil of 10–12 years) and to long-range transport. They are also known for their ability to bioconcentrate and biomagnify under typical environmental conditions.	Toxicological effects reported refers to the 2,3,7,8-substituted compounds (17 congeners) that are agonist for the AhR. All the 2,3,7,8-substituted PCDDs and PCDFs plus dioxin-like PCBs (DLPCBs) (with no chlorine substitution at the ortho positions) show the same type of biological and toxic response. Possible effects include dermal toxicity, immunotoxicity, reproductive effects and teratogenicity, endocrine disruption, and carcinogenicity. At the present time, the only persistent effect associated with dioxin exposure in humans is chloracne. The most sensitive groups are fetus and neonatal infants. Effects on the immune systems in the mouse have been found at doses of 10 ng kg^{-1} bw day^{-1}, while reproductive effects were seen in rhesus monkeys at 1–2 ng kg^{-1} bw day^{-1}. Biochemical effects have been seen in rats down to 0.1 ng kg^{-1} bw day^{-1}. In a re-evaluation of the TDI for dioxins, furans (and planar PCB), the WHO decided to recommend a range of 1–4 TEQ pg kg^{-1} bw, although more recently the acceptable intake value has been set monthly at 1–70 TEQ pg kg^{-1} bw.

Atrazine 2-Chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine ($C_{10}H_6Cl_8$).	Solubility in water: 28 mg L^{-1} at 20°C; vapor pressure: 3.0 × 10^{-7} mmHg at 20°C; log K_{ow}: 2.34.	Does not adsorb strongly to soil particles and has a lengthy $T_{1/2}$ (60 to > 100 days). Atrazine has a high potential for groundwatercontamination despite its moderate solubility in water.	Oral LD_{50} is 3090 mg kg^{-1} in rats, 1750 mg kg^{-1} in mice, 750 mg kg^{-1} in rabbits, and 1000 mg kg^{-1} in hamsters. The dermal LD_{50} in rabbits is 7500 mg kg^{-1} and greater than 3000 mg kg^{-1} in rats. Atrazine is practically nontoxic to birds. The LD_{50} is greater than 2000 mg kg^{-1} in mallard ducks. Atrazine is slightly toxic to fish and other aquatic life. Atrazine has a low level of bioaccumulation in fish. Available data regarding atrazine's carcinogenic potential are inconclusive.
Hexachlorocyclohexane (HCH) 1,2,3,4,5,6-hexachlorocyclohexane (mixed isomers) ($C_6H_6Cl_6$).	γ-HCH (lindane): solubility in water: 7 mg L^{-1} at 20°C; vapor pressure: 3.3 × 10^{-5} mmHg at 20°C; log K_{ow}: 3.8.	Lindane and other HCH isomers are relatively persistent in soils and water, with half-lives generally greater than 1 and 2 years, respectively. HCHs are much less bioaccumulative than other organochlorines of concern because of their relatively low lipophilicity. On the contrary, their relatively high vapor pressures, particularly of the α-HCH isomer, determine their long-range transport in the atmosphere.	Lindane is moderately toxic for invertebrates and fish, with LC_{50} values of 20–90 μg L^{-1}. The acute toxicity for mice and rats is moderate with LD_{50} values in the range of 60–250 mg kg^{-1}. Lindane resulted to have no mutagenic potential in a number of studies but an endocrine disrupting activity.
Chlorinated paraffins (CPs) Polychlorinated alkanes ($C_xH_{(2x-y+2)}Cl_y$). Manufactured by chlorination of liquid *n*-alkanes or paraffin wax and contain from 30% to 70%	Properties largely dependent on the chlorine content. Solubility in water: 1.7–236 μg L^{-1} at 25°C; vapor pressure: very low, highest for short chains – those with	May be released into the environment from improperly disposed metal-working fluids or polymers containing CPs. Loss of CPs by leaching from paints and coatings may also	Acute toxicity of CPs in mammals is low with reported oral LD_{50} values ranging from 4 to 50 g kg^{-1} bw, although in repeated dose experiments, effects on the liver have been seen at doses of 10–100 mg kg^{-1} bw day^{-1}. Short-chain

(*continued*)

TABLE 6.3 (*Continued*)

Compound	Properties	Persistence/Fate	Toxicity*
chlorine. The products are often divided into three groups depending on chain length: short chain (C10–C13), medium (C14–C17), and long (C18–C30) chain lengths.	50% chlorine: 1.6×10^2 mmHg at 40°C; log K_{ow} in the range from 5.06 to 8.12.	paints and coatings may also contribute to environmental contamination. Short-chain CPs with less than 50% chlorine content seem to be degraded under aerobic conditions. The medium-and long-chain products are degraded more slowly. CPs are bioaccumulated and both uptake and elimination are faster for thesubstances with low chlorine content.	and mid-chain grades have been shown, in laboratory tests, to show toxic effects on fish and other forms of aquatic life after long-term exposure. The NOEL appears to be in the range of 2–5 $\mu g\,L^{-1}$ for the most sensitive aquatic species tested.
Chlordecone or Kepone Chemical name: 1,2,3,4,5,5,6,7,9,10,10-dodecachlorooctahydro-1,3,4-metheno-2H-cyclobuta(cd) pentalen-2-one ($C_{10}Cl_{10}O$).	Solubility in water: 7.6 mg L^{-1} at 25°C; vapor pressure: less than 3×10^{-5} mmHg at 25°C; log K_{ow}: 4.50	Estimated $T_{1/2}$ in soils is between 1 and 2 years, whereas in air is much higher, up to 50 years. Not expected to hydrolyze, biodegrade in the environment. Also direct photodegradation and vaporization from what not significant. General population exposure to chlordecone mainly through the consumption of contaminated fish and seafood.	Workers exposed to high levels of chlordecone over a long period (more than 1 year) have displayed harmful effects on the nervous system, skin, liver, and male reproductive system (likely through dermal exposure to chlordecone, although they may have inhaled or ingested some as well). Animal studies with chlordecone have shown effects similar to those seen in people, as well as harmful kidney effects, developmental effects, and effects on the ability of females to reproduce. There are no studies available on whether chlordecone is carcinogenic in people. However, studies in mice and rats have shown that ingesting chlordecone can cause liver, adrenal gland, and kidney tumors. Very highly toxic for

			some species such as Atlantic menhaden, sheepshead minnow, or Donaldson trout with LC_{50} between 21.4 and 56.9 mg L^{-1}.
Endosulfan 6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide ($C_9H_6Cl_6O_3S$).	Solubility in water: 320 μg L^{-1} at 25°C; vapor pressure: 0.17 × 10^{-4} mmHg at 25°C; log K_{ow}: 2.23–3.62.	Moderately persistent in soil, with a reported average field $T_{1/2}$ of 50 days. The two isomers have different degradation times in soil ($T_{1/2}$ of 35 and 150 days for α- and β-isomers, respectively, in neutral conditions). It has a moderate capacity to adsorb to soils and it is not likely to leach to groundwater. In plants, endosulfan is rapidly broken down to the corresponding sulfate, on most fruits and vegetables, 50% of the parent residue is lost within 3–7 days.	Highly to moderately toxic to bird species (Mallards: oral LD_{50} 31–243 mg kg^{-1}) and it is very toxic to aquatic organisms (96-h LC_{50} rainbow trout 1.5 μg L^{-1}). It has also shown high toxicity in rats (oral LD_{50}: 18–160 mg kg^{-1}, and dermal: 78–359 mg kg^{-1}). Female rats appear to be 4–5 times more sensitive to the lethal effects of technical-grade endosulfan than male rats. The α-isomer is considered to be more toxic than the β-isomer. There is a strong evidence of its potential for endocrine disruption.
Pentachlorophenol (PCP) (C_6Cl_5OH).	Solubility in water: 14 mg L^{-1} at 20°C; vapor pressure: 16 × 10^{-5} mmHg at 20°C; log K_{ow}: 3.32–5.86.	Photodecomposition rate increases with pH ($T_{1/2}$ 100 h at pH 3.3 and 3.5 h at pH 7.3). Complete decomposition in soil suspensions takes > 72 days, other authors report $T_{1/2}$ in soils of about 45 days. Although enriched through the food chain, it is rapidly eliminated after discontinuing the exposure ($T_{1/2}$ 10–24 h for fish).	Acutely toxic to aquatic organisms. Certain effects on human health. 24 h LC_{50} values for trout were reported as 0.2 mg L^{-1}, and chronic toxicity effects were observed at concentrations down to 3.2 μg L^{-1}. Mammalian acute toxicity of PCP is moderate–high. LD_{50} oral in rat ranging from 50 to 210 mg kg^{-1} bw have been reported. LC_{50} ranged from 0.093 mg L^{-1} in rainbow trout (48 h) to 0.77–0.97 mg L^{-1} for guppy (96 h) and 0.47 mg L^{-1} for fathead minnow (48 h).

(*continued*)

TABLE 6.3 (*Continued*)

Compound	Properties	Persistence/Fate	Toxicity*
Hexabromobiphenyl (HxBB) ($C_{12}H_4Br_6$). A congener of the class polybrominated biphenyls (PBBs)	Solubility in water: 11 $\mu g\,L^{-1}$ at 25°C; vapor pressure: mmHg at 20°C; log K_{ow}: 6.39.	Strongly adsorbed to soil and sediments and usually persist in the environment. Resists chemical and biological degradation. Found in sediment samples from the estuaries of large rivers and has been identified in edible fish.	Few toxicity data are available from short-term tests on aquatic organisms. The LD_{50} values of commercial mixtures show a relatively low order of acute toxicity (LD_{50} range from > 1 to 21.5 $g\,kg^{-1}$ body weight in laboratory rodents). Oral exposure of laboratory animals to PBBs produced body weight loss, skin disorders, and nervous system effects, and birth defects. Humans exposed through contaminated food developed skin disorders, such as acne and hair loss. PBBs exhibit endocrine disrupting activity and possible carcinogenicity to humans.
Polybrominated diphenyl ethers (PBDEs) ($C_{12}H_{(10-n)}Br_nO$, where $n = 1-10$). As in the case of PCBs the total number of congeners is 209, with a predominance in commercial mixtures of the tetra-, penta- and octa-substituted isomers.	Solubility in water: mg L^{-1} at 25°C; vapor pressure: 3.85 up to 13.3 × 10^{-3} mmHg at 20–25°C; log K_{ow}: 4.28–9.9.	Biodegradation does not seem to be an important degradation pathway, but that photodegradation may play a significant role. Have been found in high concentrations in marine birds and mammals from remote areas. The half-lives of PBDE components in rat adipose tissue vary between 19 and 119 days, the higher values being for the more highly brominated congeners.	Lower (tetra- to hexa-) PBDE congeners likely to be carcinogens, endocrine disruptors, and/or neurodevelopmental toxicants. Studies in rats with commercial penta BDE indicate a low acute toxicity via oral and dermal routes of exposure, with LD_{50} values > 2000 mg kg^{-1} bw. In a 30-day study with rats, effects on the liver could be seen at a dose of 2 mg kg^{-1} bw day^{-1}, with a NOEL at 1 mg kg^{-1} bw day^{-1}. The toxicity to Daphnia magna has also been investigated and LC_{50} was found to be 14 $\mu g\,L^{-1}$ with a NOEC of 4.9 $\mu g\,L^{-1}$. Although data on toxicology is limited, they have potential endocrine disrupting properties, and there are concerns over the health effects of exposure.

Polycyclic aromatic hydrocarbons (PAHs) A group of compounds consisting of two or more fused aromatic rings.	Solubility in water: 0.000 14–2.1 mg L^{-1} at 25°C; vapor pressure: ranges from relatively volatile (e.g. naphthalene, 9×10^{-2} mmHg at 20°C) to semivolatile (e.g. benzo(a)pyrene, 5×10^{-9} mmHg at 25°C) to nearly nonvolatile (e.g. Indeno(1,2,3-cd)pyrene, 1×10^{-10} mmHg at 25°; log K_{ow}: 4.79–8.20	Persistence of the PAHs varies with their molecular weight. The low molecular weight PAHs are most easily degraded. The reported $T_{1/2}$ of naphthalene, anthracene, and benzo(e)pyrene in sediment are 9, 43, and 83 h, respectively, whereas for higher molecular weight PAHs' $T_{1/2}$ are up to several years in soils and sediments. The BCFs in aquatic organisms frequently range between 100 and 2000, and it increases with increasing molecular size. Due to their wide distribution, the environmental pollution by PAHs has aroused global concern.	Acute toxicity of low PAHs is moderate with an LD_{50} of naphthalene and anthracene in rat of 490 and 18 000 mg kg^{-1} body weight respectively, whereas the higher PAHs exhibit higher toxicity and LD_{50} of benzo(a)anthracene in mice is 10 mg kg^{-1} body weight. In Daphnia pulex, LC_{50} for naphthalene is 1.0 mg L^{-1}, for phenanthrene 0.1 mg L^{-1} and for benzo(a)pyrene is 0.005 mg L^{-1}. The critical effect of many PAHs in mammals is their carcinogenic potential. The metabolic actions of these substances produce intermediates that bind covalently with cellular DNA. IARC has classified benz[a]anthracene, benzo[a]pyrene, and dibenzo[a, h]anthracene as probable carcinogenic to humans. Benzo[b]fluoranthene and indeno[1,2,3-c,d]pyrene were classified as possible carcinogens to humans.
Phthalates Includes a wide family of compounds. Among the most common contaminants are: dimethylphthalate (DMP), diethylphthalate (DEP), dibutylphthalate (DBP), benzylbutylphthalate (BBP), di(2-ethylhexyl)phthalate (DEHP)($C_{24}H_{38}O_4$) and dioctylphthalate (DOP).	Properties of phthalic acid esters vary greatly depending on the alcohol moieties. log K_{ow} 1.5–7.1.	Ubiquitous pollutants, in marine, estuarine and freshwater sediments, sewage sludges, soils,and food. Degradation ($T_{1/2}$) values generally range from 1 to 30 days in freshwaters.	Acute toxicity of phthalates is usually low: the oral LD_{50} for DEHP is about 26–34 g kg^{-1}, depending on the species; for DBP reported LD_{50} values following oral administration to rats range from 8 to 20 g kg^{-1} body weight; in mice, values are approximately 5–16 g kg^{-1} body weight. In general, DEHP is not toxic for aquatic communities at the low levels usually present. In animals, high levels of DEHP damaged the liver and

(*continued*)

TABLE 6.3 (*Continued*)

Compound	Properties	Persistence/Fate	Toxicity*
			kidney and affected the ability to reproduce. There is no evidence that DEHP causes cancer in humans but they have been reported as endocrine disrupting chemicals. The Environmental Protection Agency (EPA) proposed a maximum admissible concentration (MAC) of $6\,\mu g\,L^{-1}$ of DEHP in drinking water.
Nonyl- and octyl-phenols NP: $C_{15}H_{24}O$; OP: $C_{14}H_{22}O$.	$\log K_{ow}$: 4.5 (NP) and 5.92 (OP).	NP and OP are the end degradation products of APEs under both aerobic and anaerobic conditions. Therefore, the major part is released to water and concentrated in sewage sludges. NPs and *t*-OP are persistent in the environment with $T_{1/2}$ of 30–60 years in marine sediments, 1–3 weeks in estuarine waters and 10–48 h in the atmosphere. Due to their persistence they can bioaccumulate to a significant extent in aquatic species. However, excretion and metabolism are rapid.	Acute toxicity values for fish, invertebrates, and algae range from 17–$3000\,\mu g\,L^{-1}$. In chronic toxicity tests the lowest NOEC are $6\,\mu g\,L^{-1}$ in fish and $3.7\,\mu g\,L^{-1}$ in invertebrates. The threshold for vitellogenin induction in fish is $10\,\mu g\,L^{-1}$ for NP and $3\,\mu g\,L^{-1}$ for OP (similar to the lowest NOEC). Alkylphenols are endocrine disrupting chemicals also in mammals.

Perfluorooctane sulfonate (PFOS) ($C_8F_{17}SO_3$)	Solubility in water: 550 mg L^{-1} in pure water at 24–25°C; the potassium salt of PFOS has a low vapor pressure, 3.31×10^{-4} Pa at 20°C. Due to the surface-active properties of PFOS, the log K_{ow} cannot be measured.	Does not hydrolyze, photolyze, or biodegrade under environmental conditions. It is persistent in the environment and has been shown to bioconcentrate in fish. It has been detected in a number of species of wildlife, including marine mammals. Animal studies show that PFOS is well absorbed orally and distributes mainly in the serum and the liver. The half-life in serum is 7.5 days in adult rats and 200 days in cynomolgus monkeys. The half-life in humans is, on average, 8.67 years (range 2.29–21.3 years, SD = 6.12).	Moderate acute toxicity to aquatic organisms, the lowest LC_{50} for fish is a 96-h LC_{50} of 4.7 mg L^{-1} to the fathead minnow (*Pimephales promelas*) for the lithium salt. For aquatic invertebrates, the lowest EC_{50} for freshwater species is a 48-h EC_{50} of 27 mg L^{-1} for *Daphnia magna* and for saltwater species, a 96-h LC_{50} value of 3.6 mg L^{-1} for the Mysid shrimp (*Mysidopsis bahia*). Both tests were conducted on the potassium salt. The toxicity profile of PFOS is similar among rats and monkeys. Repeated exposure results in hepatotoxicity and mortality; the dose–response curve is very steep for mortality. PFOS has shown moderate acute toxicity by the oral route with a rat LD_{50} of 251 mg kg^{-1}. Developmental effects were also reported in prenatal developmental toxicity studies in the rat and rabbit, although at slightly higher dose levels. Signs of developmental toxicity in the offspring were evident at doses of 5 mg kg^{-1} day^{-1} and above in rats administered PFOS during gestation. Significant decreases in fetal body weight and significant increases in external and visceral anomalies, delayed ossification, and skeletal variations were observed.

(*continued*)

TABLE 6.3 (*Continued*)

Compound	Properties	Persistence/Fate	Toxicity*
			An NOAEL of 1 mg kg^{-1} day^{-1} and an LOAEL of 5 mg kg^{-1} day^{-1} for developmental toxicity were indicated. Studies on employees conducted at PFOS manufacturing plants in the US and Belgium showed an increase in mortality resulting from bladder cancer and an increased risk of neoplasms of the male reproductive system, the overall category of cancers and benign growths, and neoplasms of the gastrointestinal tract.

$T_{1/2}$: chemical half-life; LD_{50}: lethal dose to 50% of tested organism; LC_{50}: lethal concentration to 50% of tested organism; BCF: bioconcentration factor; NOEL: no observable effect level; NOEC: no observable effect concentration; DDD: 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane; DDE: 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene; VPL: vapor pressure lowering; IARC: International Agency for Research on Cancer; TCDD: tetrachlorodibenzo-*p*-dioxin; AhR: aryl hydrocarbon receptor; TDI: tolerable daily intake; TEQ: toxic equivalent; APEs: alkylphenol ethoxylates; NOAEL: no observed adverse effect level; LOAEL: lowest observed adverse effect level.

Source: United Nations Environmental Program, 2002, Chemicals: North American Regional Report, Regionally Based Assessment of Persistent Toxic Substances, Global Environment Facility.

TABLE 6.4

Summary of Persistent and Metallic Compounds in North America, Identified by the United Nations as Highest Priorities for Regional Actions

Compound	Properties	Persistence/Fate	Toxicity*
Compounds of tin (Sn) Organ tin compounds comprise mono-,di-, tri-, and tetra-butyl and triphenylene tin compounds. They conform to the following general formula $(n\text{-}C_4H_9)_nSn-X$and $(C_6H_5)3Sn-X$, where X is an anion or a group linked covalently through a heteroatom.	$\log K_{ow}$: 3.19–3.84. In sea water and under normal conditions, tributyl tin exists as three species (hydroxide, chloride, and carbonate).	Under aerobic conditions, tributyl tin takes 30–90 days to degrade, but in anaerobic soils may persist for more than 2 years Due to low water solubility it binds strongly to suspended material and sediments. Tributyl tin is lipophilic and accumulates in aquatic organisms. Oysters exposed to very low concentrations exhibit BCF values ranging from 1000 to 6000.	Tributyl tin is moderately toxic and all breakdown products are even less toxic. Its impact on the environment was discovered in the early 1980s in France with harmful effects in aquatic organisms, such as shell malformations of oysters, imposex in marine snails, and reduced resistance to infection (e.g. in flounder). Gastropods react adversely to very low levels of tributyl tin ($0.06–2.3\,\mu g\,L^{-1}$). Lobster larvae show a nearly complete cessation of growth at just $1.0\,\mu g\,L^{-1}$ tributyl tin. In laboratory tests, reproduction was inhibited when female snails exposed to $0.06–0.003\,\mu g\,L^{-1}$ tributyl tin developed male characteristics. Large doses of tributyl tin have been shown to damage the reproductive and central nervous systems, bone structure, and the liver bile duct of mammals.
Compounds of mercury (Hg) The main compound of concern is methyl mercury ($HgCH_3$).		Mercury released into the environment can either stay close to its source for long periods, or be widely dispersed on a regionalor even worldwide basis. Not only are methylated mercury compounds toxic, but highly bioaccumulative as well.	Long-term exposure to either inorganic or organic mercury can permanently damage the brain, kidneys, and developing fetus. The most sensitive target of low-level exposure to metallic and organic mercury from short- or long-term exposures is likely the nervous system.

(*continued*)

TABLE 6.4 (*Continued*)

Compound	Properties	Persistence/Fate	Toxicity*
		The increase in mercury as it rises in the aquatic food chain results in relatively high levels of mercury in fish consumed by humans. Ingested elemental mercury is only 0.01% absorbed, but methyl mercury is nearly 100% absorbed from the gastrointestinal tract. The biological $T_{1/2}$ of Hg is 60 days.	
Compounds of lead (Pb) Alkyl lead compounds may be confined to tetramethyl lead (TML, $Pb(CH_3)_4$) and tetraethyl lead (TEL, $Pb(C_2H_5)_4$).	Solubility in water: 17.9 mg L^{-1} (TML) and 0.29 mg L^{-1} (TEL) at 25°C; vapor pressure: 22.5 and 0.15 mmHg at 20°C for TML and TEL, respectively.	Under environmental conditions, dealkylation produces less alkylated forms and finally inorganic Pb. However, there is limited evidence that under some circumstances, natural methylation of Pb salts may occur. Minimal bioaccumulations have been observed for TEL in shrimps (650), mussels (120), and plaice (130) and for TML in shrimps (20), mussels (170), and plaice (60).	Exposure to Pb and its compounds have been associated with cancer in the respiratory and digestive systems of workers in lead battery and smelter plants. However, tetra-alkyl lead compounds have not been sufficiently tested for the evidence of carcinogenicity. Acute toxicity of TEL and TML are moderate in mammals and high for aquatic biota. LD_{50} (rat, oral) for TEL is 35 mg Pb kg^{-1} and 108 mg Pb kg^{-1} for TML. LC_{50} (fish, 96 h) for TEL is 0.02 mg kg^{-1} and for TML is 0.11 mg kg^{-1}.

$T_{1/2}$: Chemical half-life; LD_{50}: Lethal dose to 50% of tested organism; LC_{50}: Lethal concentration to 50% of tested organism; BCF: Bioconcentration factor; NOEL: No observable effect level; NOEC: No observable effect concentration.

Source: United Nations Environmental Program, 2002, Chemicals: North American Regional Report, Regionally Based Assessment of Persistent Toxic Substances, Global Environment Facility.

activities contribute the large quantity of PBTs, with energy production the second largest source category (see Fig. 6.7). Organometallic compounds, especially lead and its compounds comprise the lion's share of PBTs in the US. And, the second largest quantity is represented by another metal, mercury and its compounds (see Fig. 6.8).

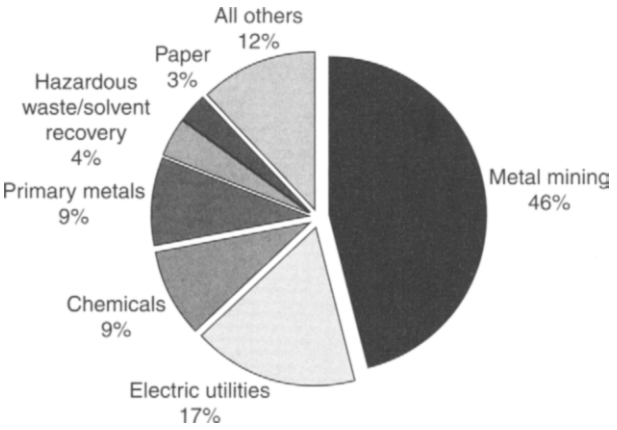

Fig. 6.7. Total US releases of contaminants in 2001, as reported to the Toxic Release Inventory. Total releases = 2.8 billion kg. *Note*: Off-site releases include metals and metal compounds transferred off-site for solidification/stabilization and for wastewater treatment, including publicly owned treatment works. Off-site releases do not include transfers to disposal sent to other TRI facilities that reported the amount as an on-site release. *Source*: US Environmental Protection Agency.

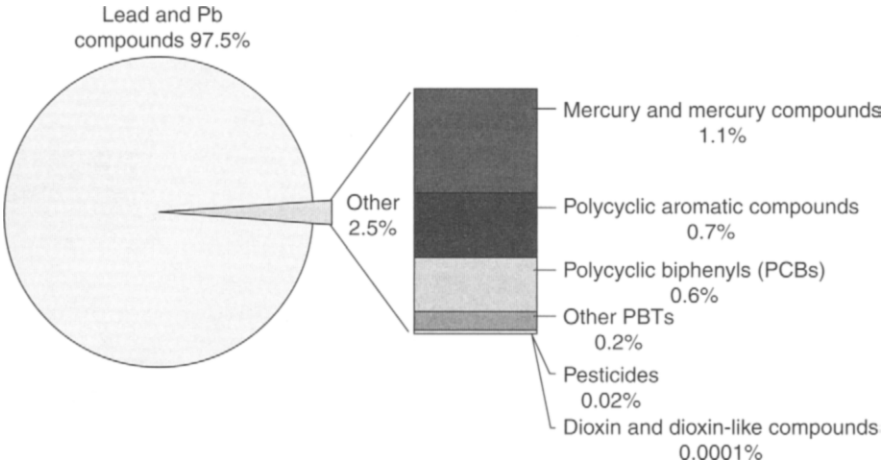

Fig. 6.8. Total US releases of PBTs in 2001, as reported in the Toxic Release Inventory (TRI). Total releases = 206 million kg. *Note*: Off-site releases include metals and metal compounds transferred off-site for solidification/stabilization and for wastewater treatment, including publicly owned treatment works. Off-site releases do not include transfers to disposal sent to other TRI facilities that reported the amount as an on-site release. *Source*: US Environmental Protection Agency.

The sources of PBTs are widely varied. Many are intentionally manufactured to serve some public need, such as the control of pests that destroy food and spread disease. Other PBTs are generated as unintended byproducts, such as the PICs. In either case, there are often measures and engineering controls available that can prevent PBT releases, rather than having to deal with them after they have found their way into the various environmental compartments.

D. Concentration-Based and Fugacity-Based Transport Models

Let us now combine these phase and compartmental distributions into a simple fugacity-based, chemodynamic transport model. Such models are classified into three types:

- *Level 1 model*: This model is based on an equilibrium distribution of fixed quantities of contaminants in a closed environment (i.e. conservation of contaminant mass). No chemical or biological degradation, advection (discussed in detail later), and no transport among compartments (such as sediment loading or atmospheric deposition to surface waters).
  A Level 1 calculation describes how a given quantity of a contaminant will partition among the water, air, soil, sediment, suspended particles, and fauna, but does not take into account chemical reactions. Early Level 1 models considered an area of 1 km^2 with 70% of the area covered in surface water. Larger areas are now being modeled (e.g. about the size of the state of Ohio).
- *Level 2 model*: This model relaxes the conservation restrictions of Level 1 by introducing direct inputs (e.g. emissions) and advective sources from air and water. It assumes that a contaminant is being continuously loaded at a constant rate into the control volume, allowing the contaminant loading to reach steady state and equilibrium between contaminant input and output rates. Degradation and bulk movement of contaminants (advection) is treated as a loss term. Exchanges between and among media are not quantified.

  Since the Level 2 approach is a simulation of a contaminant being continuously discharged into numerous compartments and which achieves a steady-state equilibrium, the challenge is to deduce the losses of the contaminant due to chemical reactions and advective (non-diffusive) mechanisms.

  Reaction rates are unique to each compound and are published according to reactivity class (e.g. fast, moderate, or slow reactions), which allows modelers to select a class of reactivity for the respective contaminant to insert into transport models. The reactions are often assumed to be first order, so the model will employ a first-order rate constant for each compartment in the environmental system (e.g. x mol h^{-1} in water, y mol h^{-1} in air, z mol h^{-1} in soil). Much uncertainty is associated with the reactivity class and rate constants, so it is best to use

rates published in the literature based on experimental and empirical studies, wherever possible.

Advection flow rates in Level 2 models are usually reflected by residence times in the compartments. These residence times are commonly set to 1 h in each medium, so the advection rate (G_i) is volume of the compartment divided by the residence time (t):

$$G_i = V\,t^{-1} \tag{6.26}$$

- *Level 3 model*: Same as Level 2, but does not assume equilibrium between compartments, so each compartment has its own fugacity. Mass balance applies to whole system and each compartment within the system. It includes mass transfer coefficients, rates of deposition and re-suspension of contaminant, rates of diffusion (discussed later), soil runoff, and area covered. All of these factors are aggregated into an intermedia transport term (D) for each compartment.

  The assumption of equilibrium in Level 1 and 2 models is a simplification, and often a gross oversimplification of what actually occurs in environmental systems. When, the simplification is not acceptable, kinetics must be included in the model. Numerous diffusive and non-diffusive transport mechanisms are included in Level 3 modeling. For example, values for the various compartments' unique intermedia transport velocity parameters (in length per time dimensions) are applied to all contaminants being modeled (these are used to calculate the *D values* mentioned above).

E. Kinetics Versus Equilibrium

Since, Level 3 models do not assume equilibrium conditions, a word about chemical kinetics is in order at this point. Chemical kinetics is the description of the rate of a chemical reaction.[13] This is the rate at which the reactants are transformed into products. This may take place by abiotic or by biological systems, such as microbial metabolism. Since a rate is a change in quantity that occurs with time, the change we are most concerned with is the change in the concentration of our contaminants into new chemical compounds:

$$\text{Reaction rate} = \frac{\text{change in product concentration}}{\text{corresponding change in time}} \tag{6.27}$$

[13] Although "kinetics" in the physical sense and the chemical sense arguably can be shown to share many common attributes, for the purposes of this discussion, it is probably best to treat them as two separate entities. Physical kinetics, as discussed in Chapter 4, is concerned with the dynamics of material bodies and the energy in a body owing to its motions. Chemical kinetics address rates of chemical reactions. The former is more concerned with mechanical dynamics, the latter with thermodynamics.

and

$$\text{Reaction rate} = \frac{\text{change in reactant concentration}}{\text{corresponding change in time}} \tag{6.28}$$

In environmental degradation, the change in product concentration will be decreasing proportionately with the reactant concentration, so, for contaminant X, the kinetics looks like

$$\text{Rate} = -\frac{\Delta(X)}{\Delta t} \tag{6.29}$$

The negative sign denotes that the reactant concentration (the parent contaminant) is decreasing. It stands to reason then that the degradation product Y resulting from the concentration will be increasing in proportion to the decreasing concentration of the contaminant X, and the reaction rate for Y is

$$\text{Rate} = \frac{\Delta(Y)}{\Delta t} \tag{6.30}$$

By convention, the concentration of the chemical is shown in parentheses to indicate that the system is not at equilibrium. $\Delta(X)$ is calculated as the difference between an initial concentration and a final concentration:

$$\Delta(X) = \Delta(X)_{\text{final}} - \Delta(X)_{\text{initial}} \tag{6.31}$$

So, if we were to observe the chemical transformation[14] of one isomer of the compound butane to different isomer over time, this would indicate the kinetics of the system, in this case the homogeneous gas phase reaction of *cis*-2-butene to *trans*-2-butene (see Fig. 6.9 for the isomeric structures). The transformation is shown in Fig. 6.10. The rate of reaction at any time is the negative of the slope of the tangent to the concentration curve at that specific time (see Fig. 6.11).

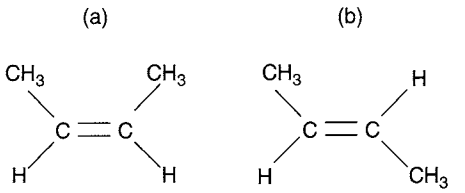

Fig. 6.9. Two isomers of butane: (a) *cis*-2-butene and (b) *trans*-2-butene.

[14] This example was taken from Spencer, J., Bodner, G., and Rickard, L., *Chemistry: Structure and Dynamics*, 2nd ed. John Wiley & Sons, New York, NY, 2003.

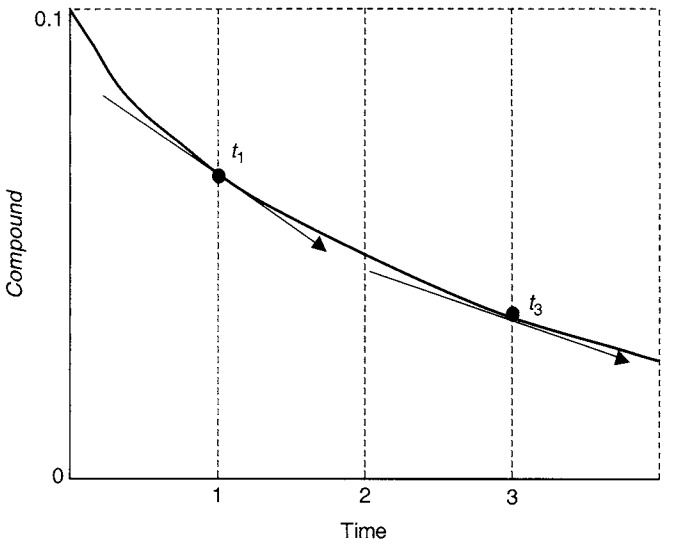

Fig. 6.10. The kinetics of the transformation of a compound. The rate of reaction at any time is the negative of the slope of the tangent to the concentration curve at that time. The rate is higher at t_1 than at t_3. This rate is concentration dependent (first order).

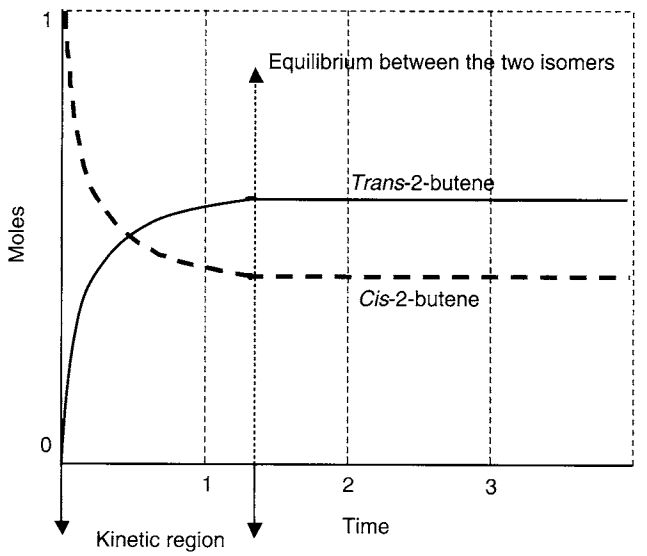

Fig. 6.11. Change in respective moles of two butene isomers. Equilibrium is reached at about 1.3 time units. The concentrations of the isomers depend on the initial concentration of the reactant (*cis*-2-butene). The actual time that equilibrium is reached depends on environmental conditions, such as temperature and other compounds present; however, at a given temperature and conditions, the ratio of the equilibrium concentrations will be the same, no matter the amount of the reactant at the start.

For a reaction to occur, the molecules of the reactants must meet (collide). So, high concentrations of a contaminant are more likely to collide than low concentrations. Thus, the reaction rate must be a function of the concentrations of the reacting substances. The mathematical expression of this function is known as the "rate law." The rate law can be determined experimentally for any contaminant. Varying the concentration of each reactant independently and then measuring the result will give a concentration curve. Each reactant has a unique rate law (this is one of a contaminant's physicochemical properties). So, let us consider the reaction of reactants A and B which yield product C (i.e., $A + B \rightarrow C$), where the reaction rate increases in accord with the increasing concentration of either A or B. This means that if we triple the amount of A, the rate of this whole reaction triples. Thus, the rate law for such a reaction is

$$\text{Rate} = k[A][B] \tag{6.32}$$

However, let us consider another reaction $X + Y \rightarrow Z$, in which the rate is only increased if the concentration of X is increased (changing the Y concentration has no effect on the rate law). In this reaction, the rate law must be

$$\text{Rate} = k[X] \tag{6.33}$$

Thus, the concentrations in the rate law are the concentrations of reacting chemical species at any specific point in time during the reaction. The rate is the velocity of the reaction at that time. The constant k in the equations above is the *rate constant*, which is unique for every chemical reaction and is a fundamental physical constant for a reaction, as defined by environmental conditions (e.g. pH, temperature, pressure, type of solvent). The rate constant is defined as the rate of the reaction when all reactants are present in a 1 molar (M) concentration, so the rate constant k is the rate of reaction under conditions standardized by a unit concentration.

We can demonstrate the rate law by drawing a concentration curve for a contaminant that consists of an infinite number of points at each instant of time, so an instantaneous rate can be calculated along the concentration curve. At each point on the curve the rate of reaction is directly proportional to the concentration of the compound at that moment in time. This is a physical demonstration of *kinetic order*. The overall kinetic order is the sum of the exponents (powers) of all the concentrations in the rate law. So for the rate $k[A][B]$, the overall kinetic order is 2. Such a rate describes a second-order reaction because the rate depends on the concentration of the reactant raised to the second power. Other decomposition rates are like $k[X]$, and are first-order reactions because the rate depends on the concentration of the reactant raised to the first power.

The kinetic order of each reactant is the power that its concentration is raised in the rate law. So, $k[A][B]$ is first order for each reactant and $k[X]$ is

first order for X and zero order for Y. In a zero-order reaction, compounds degrade at a constant rate and are independent of reactant concentration.

Further, if we plot the change in the number of moles with respect to time, we would see the point at which kinetics ends and equilibrium begins. This simple example applies to any chemical kinetics process, but the kinetics is complicated in the "real world" by the ever changing conditions of the atmosphere, industrial processes, ecosystems, tissues, and human beings.

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References 1–11 are generally resources used by the author and, as such, are not cross-referenced in the text.

SUGGESTED READING

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QUESTIONS

1. What are the advantages of using Henry's law constants versus vapor pressure to estimate the likelihood of a contaminant moving to the atmosphere?
2. Look up the physicochemical characteristics of benzo(a)pyrene. Where do you believe it will fall on Fig. 6.1? What will be some of the likely routes it will take to reach the atmosphere?
3. What types of chemical reactions would you expect to occur in a copper smelter? What types of reactions would you expect in the atmosphere immediately downwind from the stack of the smelter? What reactions would you expect on the particles that are deposited 10 m from the stack? ... 1000 m from the stack?
4. Consider three products of incomplete combustion. What practices can a facility take to improve (i.e. lower) emissions of these compounds?
5. Consider the products of complete combustion. What practices can a facility take to improve (i.e. lower) emissions of these compounds?
6. Explain what might account for some of the differences between calculated and measured coefficients in Table 6.2. What, if any, relationship can you draw between K_{ow} and K_{oc}?
7. What might be some differences between a soil particle and an airborne aerosol? What are some similarities? How might these differences affect the chemodynamics of the two particle types?