Appendix 1

Physicochemical Properties Important in Hazard Identification of Chemical Compounds

Property of substance or environment	Chemical importance	Physical importance
Molecular weight (MW)	Contaminants with MW > 600 may not be bioavailable because they are too large to pass through membranes (known as *steric hindrance*). Larger molecules tend initially to be attacked and degraded at more vulnerable functional groups (e.g., microbial degradation often first removes certain functional groups).	The heavier the molecule, the lower the vapor pressures. For example, the more carbon atoms in an organic compound, the less likely that it will exist in the gas phase under common environmental conditions. Heavier molecules are more likely to remain sorbed to soil and sediment particles.
Chemical bonding	Chemical bonds determine the resistance to degradation. Ring structures are generally more stable than chains. Double and triple bonds add persistence to molecules compared to single-bonded molecules.	Large aromatic compounds have affinity for lipids in soil and sediment. Solubility in water is enhanced by the presence of polar groups in structure. Sorption is affected by the presence of functional groups and ionization potential.
Stereochemistry	Stereochemistry is the spatial configuration or shape of a molecule. Neutral molecules with cross-sectional dimensions > 9.5 Å have been considered to be sterically hindered in their ability to penetrate the polar surfaces of the cell membranes. A number of persistence, bioaccumulation, and toxicity properties of chemicals are determined, at least in part, by a molecule's stereochemistry.	Lipophilicity (i.e., solubility in fats) of neutral molecules generally increases with molecular mass, volume, or surface area. Solubility and transport across biological membranes are affected by a molecule's size and shape. Molecules that are planar, such as polycyclic aromatic hydrocarbons, dioxins, or certain forms of polychlorinated biphenyls, are generally more lipophilic than are globular molecules of similar molecular weight. However, the restricted rate of bioaccumulation of octachlorodibenzo-*p*-dioxin (9.8 Å) and decabromobiphenyl (9.6 Å) has been associated with these compounds' steric hindrance.

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Solubility	Lipophilic compounds may be very difficult to remove from particles and may require highly destructive (e.g., combustion) remediation techniques. Insoluble forms (e.g., valence states) may precipitate out of the water column or be sorbed to particles.	Hydrophilic compounds are more likely to exist in surface water and in solution in the interstices of pore water of soil, vadose zone, and aquifers underground. Lipophilic compounds are more likely to exist in organic matter of soil and sediment.
Co-solvation	If a compound is hydrophobic and nonpolar but is easily dissolved in acetone or methanol, it can still be found in 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.	Important mechanism for getting a highly lipophilic and hydrophobic compound into water, where the compound can then move by advection, dispersion, and diffusion. Like PCBs and dioxins, PBTs may be transported as co-solutes in water by this means.
Vapor pressure or volatility	Volatile organic compounds (VOCs) exist almost entirely in the gas phase since their vapor pressures in the environment are usually greater than 10^{-2} kilopascal, whereas semivolatile organic compounds (SVOCs) have vapor pressures between 10^{-2} and 10^{-5} kPa, and nonvolatile organic compounds (NVOCs) have vapor pressures $<10^{-5}$ kPa.	Volatility is a major factor in where a compound is likely to be found in the environment. Higher vapor pressures mean larger fluxes from the soil and water to the atmosphere. Lower vapor pressures, conversely, cause chemicals to have a greater affinity for the aerosol phase.
Fugacity	Often expressed as Henry's law constant (K_H; i.e., the vapor pressure of the chemical divided by its solubility of water). Thus, high-fugacity compounds are likely candidates for remediation using the air (e.g., pump and treat, air stripping).	Compounds with high fugacity have a greater affinity for the gas phase and are more likely to be transported in the atmosphere than are those with low fugacity. Care must be taken not to allow these compounds to escape prior to treatment.
Octanol–water coefficient (K_{ow})	Substances with high K_{ow} values are more likely to be found in the organic phase of soil and sediment complexes than in the aqueous phase. They may also be more likely to accumulate in organic tissue.	Transport of substances with higher K_{ow} values is more likely to be on particles (aerosols in the atmosphere and sorbed to fugitive soil and sediment particles in water) rather than in water solutions.

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Sorption	Adsorption (onto surfaces) dominates in soils and sediments low in organic carbon (solutes precipitate onto soil surface). Absorption (three-dimensional sorption) is important in soils and sediments high in organic carbon (partitioning into organic phase/aqueous phase matrix surrounding mineral particles), so the organic partitioning coefficient (K_{oc}) is often a good indicator of the sorption potential of a PBT.	Partitioning determines which environmental media will dominate. Strong sorption constants indicate that soil and sediment may need to be treated in place. Phase distributions favoring the gas phase indicate that contaminants may be offgassed and treated in their vapor phase. This is particularly important for ‘‘semivolatile’’ PBTs, which under typical environmental conditions exist in both the gas and solid phases.
Substitution, addition, and elimination	These processes are important for treatment and remediation of PBT contamination. For example, dehalogenation (e.g., removal of chlorine atoms) of organic compounds by anaerobic treatment processes often renders them much less toxic. Adding or substituting a functional group can make the compound more or less toxic. Hydrolysis is an important substitution mechanism where a water molecule or hydroxide ion substitutes for an atom or group on molecule. Phase 1 metabolism by organisms also uses hydrolysis and redox reactions (discussed below) to breakdown complex molecules at the cellular level.	These processes can change the physical phase of a compound (e.g., dechlorination can change an organic compound from a liquid to a gas) and can change their affinity to or from one medium (e.g., air, soil, and water) to another. That is, properties such as fugacity, solubility, and sorption will change and may allow for more efficient treatment and disposal. New species produced by hydrolysis are more polar and thus more hydrophilic than their parent compounds, so they are more likely to be found in the water column.
Dissociation	Molecules break down by a number of types of dissociation, including hydrolysis, acid–base reactions, photolysis, dissociation of complexes, and nucleophilic substitution [i.e., a nucleophile (‘‘nucleus lover’’) is attracted to a positive charge in a chemical reaction and donates electrons to the other compound (i.e., an electrophile) to form a chemical bond].	Hydrolysis involves the dissociation of compounds via acid–base equilibria among hydroxyl ions and protons and weak and strong acids and bases. Dissociation may also occur by photolysis ‘‘directly’’ by the molecules absorbing light energy, and ‘‘indirectly’’ by energy or electrons transferred from another molecule that has been broken down photolytically.

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Reduction–oxidation (redox)	*Reduction* is the chemical process where at least one electron is transferred to another compound. *Oxidation* is the companion reaction where an electron is transferred from a molecule. These reactions are important in hazardous waste remediation. Often, toxic organic compounds can be broken down ultimately to CO_2 and H_2O by oxidation processes, including the reagents ozone, hydrogen peroxide, and molecular oxygen (i.e., aeration). Reduction is also used in treatment processes. For example, hexavalent chromium is reduced to the less toxic trivalent form in the presence of ferrous sulfate: $2CrO_3 + 6FeSO_4 \rightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 6H_2O$ The trivalent form is removed by the addition of lime, where it precipitates as $Cr(OH)_3$.	Reductions and oxidations are paired into *redox reactions.* Such reactions occur in the environment, leading to chemical speciation of parent compounds into more or less mobile species. For example, elemental or divalent mercury is reduced to the toxic species, mono- and dimethyl mercury, in sediment and soil low in free oxygen. The methylated metal species have greater affinity than the inorganic species for animal tissue.
Diffusion	Diffusion is the mass flux of a chemical species across a unit surface area. It is a function of the concentration gradient of the substance. A compound may move by diffusion from one compartment to another (e.g., from the water to the soil particle).	The concentration gradients within soil, underground water, and air determine to some degree the direction and rate that the contaminant will move. This is a very slow process in most environmental systems. However, in rather quiescent systems[a] ($<2.5 \times 10^{-4}$ cm s^{-1}), such as aquifers and deep sediments, the process can be very important.

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Isomerization	A *congener* is any chemical compound that is a member of a chemical family, the members of which have different molecular weights and various substitutions (e.g., there are 75 congeners of chlorinated dibenzo-*p*-dioxins). *Isomers* are chemical species with identical molecular formulas but which differ in atomic connectivity (including bond multiplicity) or spatial arrangement. An *enantiomer* is one of a pair of molecular species that are nonsuperimposable mirror images of each other.	The fate and transport of chemicals can vary significantly depending on the isomeric form. For example, the rates of degradation of left-handed chiral compounds (mirror images) are often more rapid than for right-handed compounds (possibly because left-handed chirals are more commonly found in nature, and microbes have acclimated their metabolic processes to break them down). Isomeric forms also vary in their fate.
Biotransformation	Many of the processes discussed in this table can occur in or be catalyzed by microbes; these are ‘‘biologically mediated’’ processes. Reactions that may require long periods of time to occur can be sped up by biological catalysts (i.e., enzymes). Many fungi and bacteria reduce compounds to simpler species to obtain energy. Biodegradation is possible for almost any organic compound, although it is more difficult in very large molecules, insoluble species, and completely halogenated compounds.	Microbial processes will transform parent compounds into species that have their own transport properties. Under aerobic conditions, the compounds can become more water soluble and are transported more readily than their parent compounds in surface and ground water. The fungicide example given later in this chapter is an example of how biological processes change the flux from soil to the atmosphere.
Availability of free oxygen	Complete microbial processing degrades hydrocarbons by oxidation to CO_2 and H_2O when free O_2 is available (aerobic digestion). In the absence of free O_2, microbes completely degrade organic compounds to CH_4 and H_2O (anaerobic digestion).	Aerobic and anaerobic processes may need to be used in a series for persistent compounds. For example, aerobic processes can cleave the aromatic ring of PCBs that have up to three chlorines. PCBs with four or more chlorines may first need to be treated anaerobically to remove the excess chlorines before the rings can be cleaved.

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Potential to bioaccumulate	Bioaccumulation is the process by which an organism takes up and stores chemicals from its environment through all environmental media. This includes *bioconcentration* (i.e., the direct uptake of chemicals from an environmental medium alone) and is distinguished from *biomagnification* (i.e., the increase in chemical residues in organisms that have been taken up through two or more levels of a food chain).	Numerous physical, biological, and chemical factors affect the rates of bioaccumulation needed to conduct environmental risk assessment. For chemicals to bioaccumulate, they must be sufficiently stable, conservative, and resistant to chemical degradation. Elements, especially metals, are inherently conservative, and are taken up by organisms either as ions in solution or via organometallic complexes such as chelates. Complexation of metals may facilitate bioaccumulation by taking forms of higher bioavailability, such as methylated forms. The organisms will metabolize by hydrolysis, which allows the free metal ion to bond ionically or covalently with functional groups in the cell, such as sulfhydryl, amino, purine, and other reactive groups. Organic compounds with structures that shield them from enzymatic actions or from nonenzymatic hydrolysis have a propensity to bioaccumulate. However, readily hydrolyzed and eliminated compounds are less likely to bioaccumulate (e.g., phosphate ester pesticides such as parathion and malathion). Substitution of hydrogen atoms by electron-withdrawing groups tends to stabilize organic compounds such as the polycyclic aromatic hydrocarbons (PAHs). For example, the chlorine atoms are large and highly electronegative, so chlorine substitution shields the PAH molecule against chemical attack. Highly chlorinated organic compounds, such as the PCBs, bioaccumulate to high levels since they possess properties that allow them to be taken up easily but do not allow easy metabolic breakdown and elimination.

Source: Adapted from D. A. Vallero, *Environmental Contaminants: Assessment and Control,* Elsevier Academic Press, Burlington, MA, 2004.

[a] W. Tucker and L. Nelken, Diffusion Coefficients in Air and Water, *Handbook of Chemical Property Estimation Methods,* McGraw-Hill, New York, 1982.