Chapter 5. Evaluating Environmental Fate: Approaches Based on Chemical Structure

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A new chemical is to be manufactured. Will its manufacture or use pose significant environmental or human health risks? If there are risks, what are the exposure pathways? Will the chemical degrade if it is released into the environment or will it persist? If the chemical degrades will the degradation products pose a risk to the environment?

The challenges involved in answering these questions are formidable. Over 9,000 chemicals are produced commercially and every year, a thousand or more new chemicals are developed. For any chemical, in use there are potential environmental risks to human health and the environment. In general, it will not be possible to rigorously and precisely evaluate all possible environmental impacts. Nevertheless, a preliminary screening of the potential environmental impacts of chemicals is necessary and is possible. Preliminary risk screenings allow businesses, government agencies and the public to identify problem chemicals and to identify potential risk reduction opportunities. The challenge is to perform these preliminary risk screenings with a limited amount of information.

This chapter presents qualitative and quantitative methods for estimating environmental risks when the only hazard information available is a chemical structure. Many of these methods have been developed by the US Environmental Protection Agency (US EPA) and its contractors. The methods are routiney used in evaluating premanufacture notices submitted under the Toxic Substances Control Act (TSCA). Under the provisions of TSCA, before a new chemical can be manufactured in the United States, a premanufacture notice (PMN) must be submitted to US EPA. The PMN specifies the chemical to be manufactured, the quantity to be manufactured and any known environmental impacts as well as potential releases from the manufacturing site. Based on these limited data, the US EPA must assess whether the manufacture or use of the proposed chemical may pose an unreasonable risk to human or ecological health. To accomplish that assessment, a set of tools has been developed that relate chemical structure to potential environmental risks.

Figure 5.1-1 provides a qualitative summary of the processes that determine environmental risks. Table 5.1-1 identifies the chemical and physical properties that will influence each of the processes that determine environmental exposure and hazard. The table makes clear that a wide range of properties need to be estimated to perform a screening level assessment of environmental risks.

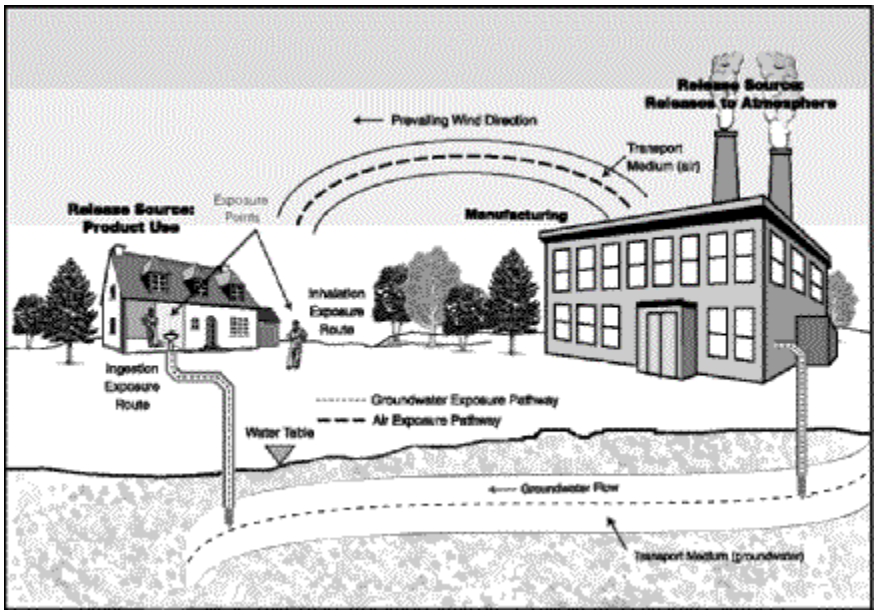

Figure 5.1-1 The chemical and physical properties that will influence each of the processes that determine environmental exposure and hazard.

Table 5.1-1 Chemical Properties Needed to Perform Environmental Risk Screenings

Environmental Process	Relevant Properties
Dispersion and fate	Volatility, density, melting point, water solubility, effectiveness of wastewater treatment
Persistence in the environment	Atmospheric oxidation rate, aqueous hydrolysis rate, photolysis rate, rate of microbial degradation, and adsorption
Uptake by organism	Volatility, lipophilicity, molecular size, degradation rate in organism
Human uptake	Transport across dermal layers, transport rates across lung membrane, degradation rates within the human body
Toxicity and other health effects	Dose-response relationships

The first group of properties that must be estimated in an assessment of environmental risk are the basic physical and chemical properties that describe a chemical's partitioning between solid, liquid and gas phases. These include melting point, boiling point, vapor pressure and water solubility. Additional molecular properties, related to phase partitioning, that are frequently used in assessing the environmental fate of chemicals include octanol-water partition coefficient, soil sorption coefficients, Henry's law constants and bioconcentration factors. (Each of these properties is defined in Section 5.2). Once the basic physical and chemical properties are defined, series of properties that influence the fate of chemicals in the environment are estimated. These include estimates of the rates at which chemicals will react in the atmosphere, the rates of reaction in aqueous environments and the rate at which the compounds will be metabolized by organisms. If environmental concentrations can be estimated based on release rates and

environmental fate properties, then human exposures to the chemicals can be estimated. Finally, if exposures and hazards are known, then risks to humans and the environment can be estimated.

The remainder of this chapter describes estimation tools for the properties outlined above. Section 5.2 describes estimation tools for physical and chemical properties. Section 5.3 describes how properties that influence environmental fate are estimated. Methods for estimating hazards to ecosystems are discussed in Section 5.4, and Section 5.5 presents simple models that can be used to characterize the environmental partitioning of chemicals. Finally, Section 5.6 describes how chemical property data can be used to classify the risks associated with chemicals.

Chapter 5 Example Problem

Example 5.2-3

Estimate the vapor pressure at 298 K for toluene (a liquid) and naphthalene (a solid).

Solution

Toluene has the molecular structure $CH_3-C_6H_5$ and in Example 5.2-1, it's boiling point was estimated to be 399 K. The experimental value for the boiling point is 384 K. We will estimate the vapor pressure using both the predicted and the experimental value for boiling point. Using the predicted value of 399 K:

$$C = -18 + 0.19\ T_b = 57.8$$

$$A = K_F\ (8.75 + R\ \ln T_b) = 1.0(8.75 + 1.987 * \ln(399)) = 20.6$$

$$\ln P_{vp} = \frac{[A(T_b - C)^2]}{[0.97\ R\ T_b]}\ [1/(T_b - C) - 1/(T - C)] = \frac{[20.6*(399-57.8)^2]}{[0.97*1.987*399]}\ [1/341 - 1/240]$$

$$\ln P_{vp} = -3.83; \quad P_{vp} = 0.021\ \text{atm} = 16\ \text{mm Hg}$$

Repeating the calculation for the predicted boiling point leads to a vapor pressure estimate of 19 mm Hg.

Naphthalene has the formula $C_{10}H_8$ and is a solid with a melting point of 81 °C. The boiling point can be estimated from the methods described earlier in this section. The uncorrected group contribution estimate is:

$$T_b = 198.2 + 2(45.46) + 8(28.53) = 517 \text{ K}$$

The corrected value is: $T_b = 505$ K

Applying Equation 5-10:

$$\ln P = -(4.4 + \ln T_b)[1.803\,(T_b/T - 1) - 0.803\,\ln(T_b/T)] - 6.8\,(T_m/T - 1)$$

$$\ln P = -(4.4 + \ln 505)[1.803\,(505/298 - 1) - 0.803\,\ln(505/298)] - 6.8\,(354/298 - 1)$$

$$P = 4.4 * 10^{-5} \text{ atm} = 0.03 \text{ mm Hg}$$

Chapter 5 Sample Homework Problem

1. Estimate the properties listed in the table given below.

Property	*ethanol*	*1-propanol*	*1-hexanol*	*n-propane*	*n-hexane*
Boiling point (T_b)					
Vapor pressure (P_{vp})					
Henry's Law constant (H)					
Octanol-water partition coefficient (K_{ow})					
Water solubility (S)					
Soil sorption coefficient (K_{oc})					
Atmospheric half life					
Biodegradability					