Volume I
Large Production and Priority Pollutants

Handbook of Environmental

FATE and EXPOSURE DATA

For Organic Chemicals

Philip H. Howard

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The following individuals from the Syracuse Research Corporation's Chemical Hazard Assessment Division either were authors of the individual chemical records prepared for the Hazardous Substances Data Bank or edited the expanded and updated chemical chapters in this volume. The order of names, which will vary in each volume, is by the number of chemicals for which the individual was responsible.

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Preface

Many articles and books have been written on how to review the environmental fate and exposure of organic chemicals (e.g., [11] and [19]). Although these articles and books often give examples of the fate and exposure of several chemicals, rarely do they attempt to review large numbers of chemicals. These "how to" guides provide considerable insight into ways of estimating and using physical/chemical properties as well as mechanisms of environmental transport and transformation. However, when it comes to reviewing the fate and exposure of individual chemicals, there are discretionary factors that significantly affect the overall fate assessment. For example, is it reasonable to use regression equations for estimating soil or sediment adsorption for aromatic amine compounds? Is chemical oxidation likely to be important for phenols in surface waters? These discretionary factors are dependent upon the available data on the individual chemical or, when data are lacking, on chemicals of related structures.

This series of books outlines in detail how individual chemicals are released, transported, and degraded in the environment and how they are exposed to humans and environmental organisms. It is devoted to the review and evaluation of the available data on physical/chemical properties, commercial use and possible sources of environmental contamination, environmental fate, and monitoring data of individual chemicals. Each review of a chemical provides most of the data necessary for either a qualitative or quantitative exposure assessment.

Chemicals were selected from a large number of chemicals prepared by Syracuse Research Corporation (SRC) for inclusion in the National Library of Medicine's (NLM) Hazardous Substances Data Bank (HSDB). Chemicals selected for the first two volumes were picked from lists of high volume commercial chemicals, priority pollutants, and solvents. The chemicals in the first two volumes include most of the non-pesticidal priority pollutants and many of the chemicals on priority lists for a variety of environmental regulations (e.g., RCRA and CERCLA Reportable Quantities, Superfund, SARA). Pesticides, polycyclic aromatic hydrocarbons, and other groups of chemicals will be included in later volumes.

The chemicals are listed in strict alphabetical order by the name considered to be the most easily recognized. Prefixes commonly used in organic chemistry which are not normally considered part of the name, such as ortho-, meta-, para-, alpha-, beta-, gamma-, n-, sec-, tert-, cis-, trans-, N-, as well as all numbers, have no been considered for alphabetical order. Other prefixes which normally are considered part of the name, such as iso-, di-, tri-, tetra-, and cyclo-, are used for alphabetical positioning. For example, 2,4-Dinitrotoluene is under D and tert-Butyl alcohol is under B. In addition, cumulative indices are provided at the end of each volume to allow the reader to find a given chemical by chemical name synonym, Chemical Abstracts Services (CAS) number, and chemical formula.

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Explanation of Data

In the following outline, each field covered for the individual chemicals is reviewed with such information as the importance of the data, the type of data included in each field, how data are usually handled, and data sources. For each chemical, the physical properties as well as the environmental fate and monitoring data were identified by conducting searches of the Environmental Fate Data Bases of Syracuse Research Corporation (SRC) [12].

SUBSTANCE IDENTIFICATION

Synonyms: Only synonym names used fairly frequently were included.

Structure: Chemical structure.

CAS Registry Number: This number is assigned by the American Chemical Society's Chemical Abstracts Services as a unique identifier.

Molecular Formula: The formula is in Hill notation, which is given as the number of carbons followed by the number of hydrogens followed by any other elements in alphabetic order.

Wiswesser Line Notation: This is a chemical structure representation that can be used for substructure searching. It was designed back when computer notations had to fit into 80 characters and, therefore, is very abbreviated (e.g., Q is used for a benzene ring).

CHEMICAL AND PHYSICAL PROPERTIES

The Hazardous Substances Data Bank (HSDB) of the National Library of Medicine was used as a source of boiling points, melting points, and molecular weights. The dissociation constant, octanol/water partition coefficient, water solubility, vapor pressure, and Henry's Law constant were judiciously selected from the many values that were identified in SRC's DATALOG file. All values selected were referenced to the primary literature source when possible.

Boiling Point: The boiling point or boiling point range is given along with the pressure. When the pressure is not given it should be assumed that the value is at 760 mm Hg.

Melting Point: The melting point or melting point range is given.

Molecular Weight: The molecular weight to two decimal points is given.

Dissociation Constants: The acid dissociation constant as the negative log (pKa) is given for chemicals that are likely to dissociate at environmental pH's (between 5 and 9). Chemical classes where dissociation is important include, for example, phenols, carboxylic acids, and aliphatic and aromatic amines. Once the pKa is known, the percent in the dissociated and undissociated form can be determined. For example, for an acid with a pKa of 4.75, the following is true at different pH's:

1% dissociated at pH 2.75
10% dissociated at pH 3.75
50% dissociated at pH 4.75
90% dissociated at pH 5.75
99% dissociated at pH 6.75

The degree of dissociation affects such processes as photolysis (absorption spectra of chemicals that dissociate can be considerably affected by the pH), evaporation from water (ions do not evaporate), soil or sediment adsorption, and bioconcentration. Values from evaluated sources such as Perrin [21] and Serjeant and Dempsey [23] were used when available.

Log Octanol/Water Partition Coefficient: The octanol/water partition coefficient is the ratio of the chemical concentration in octanol divided by the concentration in water. The most reliable source of values is from the Medchem project at Pomona College [8]. When experimental values are unavailable, estimated values have been provided using a fragment constant estimation method, CLOGP3, from Medchem. Occasionally chemical octanol/water partition coefficients were not calculated because a necessary fragment constant for the chemical was not available. The octanol/water partition coefficient has been shown to correlate well with bioconcentration factors in aquatic organisms [26] and adsorption to soil or sediment [13], and recommended regression equations have been reviewed [15].

Water Solubility: The water solubility of a chemical provides considerable insight into the fate and transport of a chemical in the environment. High water soluble chemicals, which have a tendency to remain dissolved in the water column and not partition to soil or sediment or bioconcentrate in aquatic organisms, are less likely to volatilize from water (depending upon the vapor pressure - see Henry's Law constant) and are generally more likely to biodegrade. Low water soluble chemicals are just the opposite; they partition to soil or sediments and bioconcentrate in aquatic organisms, volatilize more readily from water, and are less likely to be biodegradable. Other fate processes that are, or can be, affected by water solubility include photolysis, hydrolysis, oxidation, and washout from the atmosphere by rain or fog. Water solubility values were taken from either the Arizona Data Base [27] or from SRC's DATALOG or CHEMFATE files. The values were reported in ppm at a temperature at or as close as possible to 25 °C. Occasionally when no values were available, the value was estimated from the octanol/water partition coefficient using recommended regression equations [15].

Vapor Pressure: The vapor pressure of a chemical provides considerable insight into the transport of a chemical in the environment. The volatility of the pure chemical is dependent upon the vapor pressure, and volatilization from water is dependent upon the vapor pressure and water solubility (see Henry's Law constant). The form in which a chemical will be found in the atmosphere is dependent upon the vapor pressure; chemicals with a vapor pressure less than 10^{-6} mm Hg will be mostly found associated with particulate matter [7]. When available, sources such as Boublik et al [3], Riddick et al [22], and Daubert and Danner [5] were used, since the data in these sources were evaluated and some of them provided recommended values. Vapor pressure was reported in mm Hg at or as close as possible to 25 °C. In many cases, the vapor pressure was calculated from a vapor pressure/temperature equation.

Henry's Law Constant: The Henry's Law constant, H, is really the air/water partition coefficient, and therefore a nondimensional H relates the chemical concentration in the gas phase to its concentration in the water phase. The dimensional H can be determined by dividing the vapor pressure in atm by the water solubility in mole/cu m to give H in atm-cu m/mole. H provides an indication of the partition between air and water at equilibrium and also is used to calculate the rate of evaporation from water (see discussion under Evaporation from Water/Soil). Henry's Law constants can be directly measured, calculated from the water solubility and vapor pressure, or estimated from structure using the method of Hine and Mookerjee [9], and this same order was used in selecting values. Some critical review data on Henry's Law constants are available (e.g., [16]).

ENVIRONMENTAL FATE/EXPOSURE POTENTIAL

Data for the following sections were identified with SRC's Environmental Fate Data Bases. Biodegradation data were selected from the DATALOG, BIOLOG, and BIODEG files. Abiotic degradation data were identified in the Hydrolysis, Photolysis, and Oxidation fields in DATALOG and CHEMFATE. Transport processes such as Bioconcentration, Soil Adsorption/Mobility, and Volatilization as well as the monitoring data were also identified in the DATALOG and CHEMFATE files.

Summary: This section is an abbreviated summary of all the data presented in the following sections and is not referenced; to find the citations the reader should refer to appropriate sections that follow. In general, this summary discusses how a chemical is used and released to the environment, how the chemical will behave in soil, water, and air, and how exposure to humans and environmental organisms is likely to occur.

Natural Sources: This section reviews any evidence that the chemical may have any natural sources of pollution, such as forest fires and volcanos, or may be a natural product that would lead to its detection in various media (e.g., methyl iodide is found in marine algae and is the major source of contamination in the ocean).

Artificial Sources: This section is a general review of any evidence that the chemical has anthropogenic sources of pollution. Quantitative data are reviewed in detail in Effluent Concentrations; this section provides a qualitative review of various sources based upon how the chemical is manufactured and used as well as the physical/chemical properties. For example, it is reasonable to assume that a highly volatile chemical which is used mostly as a solvent will be released to the atmosphere as well as the air of occupational settings even if no monitoring data are available. Information on production volume and uses was obtained from a variety of chemical marketing sources including the Kirk-Othmer Encyclopedia of Chemical Technology, SRI International's Chemical Economics Handbook, and the Chemical Profiles of the Chemical Marketing Reporter.

Terrestrial Fate: This section reviews how a chemical will behave if released to soil or groundwater. Field studies or terrestrial model ecosystems studies are used here when they provide insight into the overall behavior in soil. Studies which determine an individual process (e.g., biodegradation, hydrolysis, soil adsorption) in soil are reviewed in the appropriate sections that follow. Quite often, except with pesticides, field or terrestrial ecosystem studies either are not available or do not give enough data to make conclusions on the terrestrial fate of a chemical. In these cases, data from the sections on Biodegradation, Abiotic Degradation, Soil Adsorption/Mobility, Volatilization from Water/Soil, and any appropriate monitoring data will be used to synthesize how a chemical is likely to behave if released to soil.

Aquatic Fate: This section reviews how a chemical will behave if released to fresh, marine, or estuarine surface waters. Field studies or aquatic model ecosystems are used here when they provide insight into the overall behavior in water. Studies which determine an individual process (e.g., biodegradation, hydrolysis, photolysis, sediment adsorption, and bioconcentration in aquatic organisms) in water are reviewed in the appropriate sections that follow. When field or aquatic ecosystems studies are not available or do not give enough data to make conclusions on the aquatic fate of the chemical, data from the appropriate degradation, transport, or monitoring sections will be used to synthesize how a chemical is likely to behave if released to water.

Atmospheric Fate: This section reviews how a chemical will behave if released to the atmosphere. The vapor pressure will be used to determine if the chemical is likely to be in the vapor phase or adsorbed to particulate matter [7]. The water solubility will be used to assess the likelihood of washout with rain. Smog chamber studies or other studies where the mechanism of degradation is not determined will be reviewed in this section; studies of the rate of reaction with hydroxyl radical or ozone or direct photolysis will be reviewed in Abiotic Degradation and integrated into this section.

Biodegradation: The principles outlined by Howard and Banerjee [10] are used in this section to review the relevant biodegradation data pertinent to biodegradation in soil, water, or wastewater treatment. In general, the studies have been separated into screening studies (inoculum in defined nutrient media), biological treatment simulations, and grab samples (soil or water sample with chemical added and loss of concentration followed). Pure culture studies are only used to indicate potential metabolites, since the artificial nutrient conditions under which the pure cultures are isolated provide little assurance that these same organisms will be present in any quantity or that their enzymes will be functioning in various soil or water environments. Anaerobic biodegradation studies, which are pertinent to whether a chemical will biodegrade in biological treatment digestors, sediment, and some groundwaters, are discussed separately.

Abiotic Degradation: Non-biological degradation processes in air, water, or soil are reviewed in this section. For most chemicals in the vapor phase in the atmosphere, reaction with photochemically generated hydroxyl radicals is the most important degradation process. Occasionally reaction in the atmosphere with ozone (for olefins), nitrate radicals at night, and direct photolysis (direct sunlight absorption resulting in photochemical alteration) are significant for some chemicals [2]. For many chemicals, experimental reaction rate constants for hydroxyl radical are available (e.g., [1]) and are used to calculate an estimated half-life by assuming an average hydroxyl radical concentration of 5 x 10^{+5} molecules/cu cm in non-smog conditions (e.g., [2]). If experimental rate constants are not available, they have been estimated using the fragment constant method of Atkinson [1] and then a half-life estimated using the assumed radical concentration. The reaction rate for ozone reaction with olefins may be experimentally available or can be estimated using the Fate of Atmospheric Pollutants (FAP) from the Graphic Exposure and Modelling System (GEMS) (available from the Exposure Evaluation Division, Office of Toxic Substances, U.S. Environmental Protection Agency). Using either the experimental or estimated rate constant and an assumed concentration of 6.0 x 10^{+11} molecules/cu cm (FAP) or 7.2

x 10^{+11} molecules/cu m [2], an estimated half-life for reaction with ozone can be calculated. Nitrate radicals are significant only with certain classes of chemicals such as higher alkenes, dimethyl sulfide and lower thiols, furan and pyrrole, and hydroxy-substituted aromatics [2].

The possibility of direct photolysis in air or water can be partially assessed by examining the ultraviolet spectrum of the chemical. If the chemical does not absorb light at wavelengths provided by sunlight (>290 nm), the chemical cannot directly photolyze. If it does absorb sunlight, it may or may not photodegrade depending upon the efficiency (quantum yield) of the photochemical process, and unfortunately such data are rarely available. Indirect photolysis processes may be important for some chemicals in water [17]. For example, some chemicals can undergo sensitized photolysis by absorbing triplet state energy from the excited triplet state of chemicals commonly found in water, such as humic acids. Transient oxidants found in water, such as peroxy radicals, singlet oxygen, and hydroxyl radicals, may also contribute to abiotic degradation in water for some chemicals. For example, phenols and aromatic amines have half-lives of less than a day for reaction with peroxy radicals; substituted and unsubstituted olefins have half-lives of 7 to 8 days with singlet oxygen; and dialkyl sulfides have half-lives of 27 hours with singlet oxygen [17].

Chemical hydrolysis at pH's that are normally found in the environment (pH's 5 to 9) can be important for a variety of chemicals that have functional groups that are potentially hydrolyzable, such as alkyl halides, amides, carbamates, carboxylic acid esters, epoxides and lactones, phosphate esters, and sulfonic acid esters [18]. Half-lives at various pH's are usually reported in order to provide an indication of the influence of pH.

Bioconcentration: Certain chemicals, due to their hydrophobic nature, have a tendency to partition from the water column and bioconcentrate in aquatic organisms. This concentration of chemicals in aquatic organisms is of concern because it can lead to toxic concentrations being reached when the organism is consumed by higher organisms such as wildlife and humans. Such bioconcentrations are usually reported as the bioconcentration factor (BCF), which is the concentration of the chemical in the organism at equilibrium divided by the concentration of the chemical in water. This unitless BCF value can be determined experimentally by dosing water containing the organism and dividing the concentration in the organism by the concentration in the water once equilibrium is reached, or if equilibration is slow, the rate of uptake can be used to calculate the BCF at equilibrium. The BCF value can also be estimated by using recommended regression equations that have been shown to correlate well with physical properties such as the octanol/water partition coefficient and water solubility [15]; however, these estimation equations assume that little metabolism of the chemical occurs in the aquatic organism, which is not always correct. Therefore, when available, experimental values are preferred.

Soil Adsorption/Mobility: For many chemicals (especially pesticides), experimental soil or sediment partition coefficients are available. These values are measured by determining the concentration in both the solution (water) and solid (soil or sediment) phases after shaking for about 24 to 48 hours and using different initial concentrations. The data are then fit to a Freundlich equation to determine the adsorption coefficient, Kd. These Kd values for individual soils or sediments are normalized to the organic carbon content of the soil or sediment by dividing by the organic content (Koc), since of the numerous soil properties that affect sorption (organic carbon content, particle size, clay mineral composition, pH, cation-exchange capacity) [14], organic carbon is the most important for undissociated organic chemicals. Occasionally the experimental adsorption coefficients are reported on a soil-organic matter basis (Kom) and these are converted to Koc by multiplying by 1.724 [15]. When experimental values are unavailable, estimated Koc values are calculated using either the water solubility or octanol/water partition coefficient and some recommended regression equations [15]. The measured or estimated adsorption values are used to determine the likelihood of leaching through soil or adsorbing to sediments using the criteria of Swann" et al [24]. Occasionally experimental soil thin-layer chromatography studies are also available and can be used to assess the potential for leaching.

The above discussion applies generally to undissociated chemicals, but there are some exceptions. For example, aromatic amines have been shown to covalently bond to humic material [20] and this slow but non-reversible process can lead to aromatic amines being tightly bound to the humic material in soils. Methods to estimate the soil or sediment adsorption coefficient for dissociated chemicals which form anions are not yet available, so it is particularly important to know the pKa value for chemicals that can dissociate so that a determination of the relative amounts of the dissociated and undissociated forms can be determined at various pH conditions. Chemicals that form cations at ambient pH conditions are generally thought to sorb strongly to clay material, similar to what occurs with paraquat and diquat (pyridine cations).

Volatilization from Water/Soil: For many chemicals, volatilization can be an extremely important removal process, with half-lives as low as several hours. The Henry's Law constant can give qualitative indications of the importance of volatilization; for chemicals with values less than 10^{-7} atm-cu m/mole, the chemical is less volatile than water and as water evaporates the concentration will increase; for chemicals around 10^{-3} atm-cu m/mole, volatilization will be rapid. The volatilization process is dependent upon physical properties of the chemical (Henry's Law constant, diffusivity coefficient), the presence of modifying materials (adsorbents, organic films, electrolytes, emulsions), and the physical and chemical properties of the environment (water depth, flow rate, the presence of waves, sediment content, soil moisture, and organic content) [15]. Since the overall volatilization rate cannot be estimated for all the various environments to which a chemical may be released, common models have been used in order to give an indication of the relative importance of volatilization. For most chemicals that have a Henry's Law constant greater than 10^{-7} atm-cu m/mole, the simple volatilization model outlined in Lyman et al [15] was used; this model assumes a 20 °C river 1 meter deep flowing at 1 m/sec with a wind velocity of 3 m/sec and requires only the Henry's Law constant and the molecular weight of the chemical for input. This model gives relatively rapid volatilization rates for this model river and values for ponds, lakes, or deeper rivers will be considerably slower. Occasionally a chemical's measured reaeration coefficient ratio relative to oxygen is available, and this can be used with typical oxygen reaeration rates in ponds, rivers, and streams to give volatilization rates for these types of bodies of water. For chemicals that have extremely high Koc values, the EXAMS-II model has been used to estimate volatilization both with and without sediment adsorption (extreme differences are noted for these high Koc chemicals). Soil volatilization models are less validated and only qualitative statements are given of the importance of volatilization from moist (about 2% or greater water content) or dry soil, based upon the Henry's Law constant or vapor pressure, respectively. This assumes that once the soil is saturated with a molecular layer of water, the volatilization rate will be mostly determined by the value of the Henry's Law constant, except for chemicals with high Koc values.

Water Concentrations: Ambient water concentrations of the chemical are reviewed in this section, with subcategories for surface water, drinking water, and groundwater when data are available. In general, the number of samples, the percent positive, the range of concentrations, and the average concentration are reported when the data are available.

Effluents Concentration: Air emissions and wastewater effluents are reviewed in this section. In general, the number of samples, the percent positive, the range of concentrations, and the average concentration are reported when the data are available.

Sediment/Soil Concentrations: Sediment and soil concentrations are reviewed in this section. In general, the number of samples, the percent positive, the range of concentrations, and the average concentration are reported when the data are available.

Atmospheric Concentrations: Ambient atmospheric concentrations are reviewed in this section, with subcategories for rural/remote and urban/suburban when data are available in such sources as Brodzinsky and Singh [4]. In general, the number of samples, the percent positive, the range of concentrations, and the average concentration are reported when the data are available.

Food Survey Values: Market basket survey data such as found in Duggan et al [6] and individual studies of analysis of the chemical in processed food are reported in this section. In general, the number of samples, the percent positive, the range of concentrations, and the average concentration are reported when the data are available.

Plant Concentrations: Concentrations of the chemical in plants are reviewed in this section. If the plant has been processed for food, it is reported in Food Survey Values.

Fish/Seafood Concentrations: Concentrations in fish, seafood, shellfish, etc. are reviewed in this section. If the fish or seafood have been processed for food, the data are reported in Food Survey Values.