ENVIRONMENTAL FATE SUMMARY

OVERVIEW: The environmental fate of chemicals describes the processes by which chemicals move and are transformed in the environment. Environmental fate processes that should be addressed include: persistence in air, water, and soil; reactivity and degradation; migration in groundwater; removal from effluents by standard waste water treatment methods; and bioaccumulation in aquatic or terrestrial organisms.

Note: *There is no single accepted methodology for evaluating the environmental behavior of chemicals; this is particularly true in the selection of mathematical models to predict environmental fate parameters. Thus it is important to document the approach and specific procedures used in the module. The approach presented below is one suggested by the types of information included in recent EPA Risk Management Reports.*

GOALS:

- Retrieve data or estimate key environmental fate parameters for each chemical in the use cluster.
- Prepare environmental fate and treatability summaries for each chemical.
- Provide data to the Human Health Hazards Summary, Environmental Hazards Summary, Exposure Assessment, and Control Technologies Assessment modules.

PEOPLE SKILLS: The following lists the types of skills or knowledge needed to complete this module.

- Knowledge of the physical, chemical, and biological reactions of chemicals in the environment.
- Knowledge of standard waste water treatment systems and unit processes.
- Experience with the use of mathematical models for predicting the fate and transformation of chemicals in the environment.

Note: *The analysis described in this module should only be undertaken by someone familiar with environmental fate calculations. Furthermore, peer-review of the completed environmental fate summary is recommended.*

DEFINITION OF TERMS: Several terms from the Chemical Properties module are also used in the Environmental Fate Summary module and are defined here as well.

Chemical Properties

Vapor Pressure (Pv): The pressure exerted by a chemical in the vapor phase in equilibrium with its solid or liquid form. It provides an indication of the relative tendency of a substance to volatilize from the pure state. Typical units are mm Hg, torr, or in. Hg.

Water Solubility (S): The maximum amount of a chemical that can be dissolved in a given amount of pure water at standard conditions of temperature and pressure. Typical units are mg/L, g/L, or lbs/gal.

Environmental Fate

Atmospheric Residence Time (τ): The ratio of the total mass of a chemical in an atmospheric compartment to either the total emission rate or the total removal rate, under steady-state conditions. Units are typically in hours or days.

Biochemical Oxygen Demand (BOD): The amount of oxygen consumed by microorganisms, over a specified time period, to metabolize a substance. Under certain environmental conditions, a high BOD may result in a reduction in oxygen levels in receiving waters to below critical levels for sustaining aquatic life.

Bioconcentration Factor (BCF): The equilibrium ratio of the concentration of a chemical in an exposed organism to the concentration of the chemical in the surrounding water.

Biodegradation: The transformation of chemical compounds by living organisms. Not confined to microorganisms (e.g., bacteria, fungi) but chiefly a microbial process in nature; typically expressed in terms of a rate constant and/or half-life.

Chemical Oxygen Demand (COD): The amount of oxygen consumed in the oxidation of a chemical substrate by a strong chemical oxidant (such as dichromate).

Half-life ($t_{½}$): The time required to reduce the concentration of a chemical to 50 percent of its initial concentration. Units are typically in hours or days.

Henry's Law Constant (H_c): The air/water partition coefficient, describing the relative concentrations of a chemical in air (the vapor phase) and the chemical dissolved in water, in a closed system at equilibrium. H_c can be measured directly or estimated as the ratio of Pv to S, and gives an indication of a chemical's tendency to volatilize from water to air or dissolve into water from air. H_c is typically expressed in units of atm-m^3/mole or in dimensionless terms.

Hydrolysis: A chemical transformation process in which a chemical reacts with water. In the process, a new carbon-oxygen bond is formed with oxygen derived from the water molecule, and a bond is cleaved within the chemical between carbon and some functional group.

Hydroxyl Radical Rate Constant ($K_{OH\cdot}$): The rate constant (in cm^3/mol/sec) for the reaction of photochemically produced hydroxyl radicals with organic compounds in the atmosphere.

Ionization or Acid Dissociation Constant (K_a, pK_a): An equilibrium ratio of the dissociation products and the parent compound in aqueous solutions. The degree of dissociation can alter the solubility and adsorption characteristics of the compound. The pK_a is the negative log of K_a.

Mobility: The tendency for a chemical to move in the environment (i.e., through soil with the percolation of water).

Octanol-Water Partition Coefficient (K_{ow}): The equilibrium ratio of a chemical's concentration in the octanol phase to its concentration in the aqueous phase of a two-phase octanol/water system, typically expressed in log units (log K_{ow}). K_{ow} provides an indication of a chemical's S, fat solubility (lipophilicity), its tendency to bioconcentrate in aquatic organisms, and to sorb to soil or sediment.

Organic Carbon Partition Coefficient (K_{oc}): The proportion of a chemical sorbed to the solid phase, at equilibrium in a two-phase, water/soil or water/sediment system expressed on an organic carbon basis. Chemicals with higher K_{oc} values are more strongly sorbed and, therefore, tend to be less mobile in the environment.

Oxidation: In general, a reaction in which electrons are transferred from a chemical to an oxidizing agent, or where a chemical gains oxygen from an oxidizing agent. (Also see Redox and Reduction.)

Percent Removal: The amount of the chemical that can be removed from sewage by standard waste water treatment processes, expressed in terms of the percent of the initial amount removed from the influent (liquid) waste stream. The chief processes that may contribute to removal from a liquid waste stream are degradation (biotic or abiotic), sorption, and volatization (also known as air stripping).

Persistence: The ability of a chemical substance to remain in a particular environment in an unchanged form.

Photolysis: The transformation of a chemical by light energy.

Plant Uptake: The uptake of a chemical into plants is expressed in terms of a bioconcentration factor for vegetation (B_v), which is the ratio of the concentration in the plant tissue to the concentration in soil.

Redox: Reduction-oxidation reactions. Oxidation and reduction occur simultaneously; in general, the oxidizing agent gains electrons in the process (and is reduced) while the reducing agent donates electrons (and is oxidized).

Reduction: In general, a reaction in which electrons are transferred to a chemical from a reducing agent, or where oxygen is removed from a chemical. (Also see Oxidation and Redox.)

Soil or Sediment Sorption Coefficient (K_d): The equilibrium ratio between a chemical sorbed to the solid phase and in solution in a two-phase, soil/water or sediment/water system.

Smog-Forming Potential: The chemical reaction of hydrocarbons to produce atmospheric photochemical oxidants such as ozone and other by-products contributing to the formation of smog.

Transport: The movement of a chemical through the environment, within a single phase or from one phase to another.

Treatability: The amenability of a chemical substance or waste stream to removal during waste water treatment, without adversely affecting the normal operation of the treatment plant.

Ultraviolet (UV): That part of the electromagnetic spectrum at a frequency higher than visible light (corresponding to wavelengths of 3000-4000 Å).

Volatilization: The transport process by which a chemical substance enters the atmosphere by evaporation from soil or water.

ADDITIONAL TERMS: The following additional terms are not used in this module discussion *per se*, but are likely to be found in the literature pertaining to chemical fate parameters.

Acclimation: The process in which continuous exposure of a microbial population to a chemical results in a more rapid transformation (biodegradation) of the chemical than initially observed.

Activated Sludge: The flocculated mixture of microorganisms and inert organic and inorganic material normally produced by aeration of sewage. Constitutes the biological treatment process most frequently employed for purification of domestic sewage.

BOD/COD Ratio: The ratio of the BOD to the COD for a chemical mixture.

Direct Aqueous Photolysis Rate Constant (k_d): The rate constant (in day^{-1} or $year^{-1}$) for the direct photolytic transformation of an organic compound in water.

Ozone Rate Constant(k_{O3}): The rate constant ($cm^3/mol/sec$) for the reaction of ozone with an organic compound.

Photooxidation: A process in which solar radiation generates an oxidizing agent, such as the hydroxyl radical, which reacts with (and transforms) a chemical.

Wet Deposition: The process by which a chemical that is dissolved in water in the atmosphere reaches land or a water body via precipitation (synonym: atmospheric washout).

APPROACH/METHODOLOGY: The following outlines the technical approach or methodology for preparing an environmental fate summary. Further methodology details for Steps 3 and 4 follow this section.

Step 1: Obtain CAS RNs and synonyms, information on chemical structure, and physical and chemical properties of the chemicals in the use cluster from the Chemical Properties module.

Step 2: Obtain measured or estimated environmental fate and treatability data for each chemical from primary and secondary sources (see Table 5-7: Sources of Environmental Fate Data).

Step 3: If environmental fate and treatability data are not available, estimate parameters using regression equations and mathematical models (see Details: Step 3, below).

Step 4: Prepare environmental fate and treatability summaries for each chemical, focussing on water, air, soil and waste water treatment environments as appropriate. Fate summaries should focus on the fate processes that are most important for that particular chemical. (See Details: Step 4, below.)

Step 5: Provide environmental fate summaries and environmental fate parameter values, and identify any products of chemical degradation (if applicable) to the Human Health Hazards Summary, Environmental Hazards Summary, and Exposure Assessment modules; and provide treatability parameters (e.g., percent removal), environmental fate, and treatability summaries to the Control Technologies Assessment module.

METHODOLOGY DETAILS: This section presents methodology details for completing Steps 3 and 4, and examples of environmental fate and treatability summaries. If necessary, additional information on these and other steps can be found in the previously published guidance.

Details: Step 3, Estimating Environmental Fate Parameters

Numerous mathematical models, such as regression equations, have been developed for estimating environmental parameters for chemicals. Only a few examples will be presented here; many others exist, and the ones most appropriate for a given chemical will depend on the circumstances. Published guidance should be consulted for selecting specific methods and equations.

The K_{oc} of a chemical can be estimated from K_{ow}, from S or from BCF, for example:

$$\log K_{oc} = 0.544 \log K_{ow} + 1.377$$

$$\log K_{oc} = -0.55 \log S + 3.64$$

$$\log K_{oc} = 0.681 \log BCF + 1.963$$

The τ for a chemical can be estimated from the rate at which the chemical reacts with hydroxyl radicals, for example:

$$\tau_{OH\cdot} = 1/\{K_{OH}\,[OH\cdot]\}$$

where:

K_{OH} is in liters/mole/sec and $[OH\cdot]$ is in units of moles/liter

The bioconcentration of a chemical in aquatic species can be estimated from the chemical's octanol-water partition coefficient (K_{ow}), for example:

$$\log BCF = 0.76 \log K_{ow} - 0.23$$

Details: Step 4, Preparing Environmental Fate and Treatability Summaries

Examples of environmental fate and treatability summaries (from the Screen Printing CTSA) for acetone and dichloromethane are shown below:

Environmental Fate Summary for Acetone

If released on soil, acetone will volatilize into the air or leach into the ground where it will probably biodegrade. Photolysis will be important on terrestrial surfaces and in surface waters exposed to sunlight. If released to water, acetone may also be lost due to volatilization (estimated $t_{½}$ is 20 hours from a model river) and biodegradation. Bioconcentration in aquatic organisms and adsorption to sediment should not be important transport processes in water. In the atmosphere, acetone will be lost by photolysis and reaction with photochemically produced hydroxyl radicals. Half-life estimates from these combined processes average 22 days and are shorter in summer and longer in winter. In air, acetone may also be washed out by rain. A rapid and a moderate biodegradation rate for acetone used in the Sewage Treatment Plant (STP) fugacity model results in 97 and 84 percent predicted total removal from waste water treatment plants, respectively.

Environmental Fate Summary for Dichloromethane

If released to soil, dichloromethane is expected to display high mobility. It may rapidly volatilize from both moist and dry soil to the atmosphere. Aerobic biodegradation may be important for dichloromethane in acclimated soils. If released to water, volatization to the atmosphere is expected to be a rapid process. Neither bioconcentration in fish and aquatic organisms, nor adsorption to sediment and suspended organic matter are expected to be significant. Dichloromethane has been found to slowly biodegrade under aerobic conditions. It is also expected to slowly biodegrade under anaerobic conditions in sediment and groundwater. If released to the atmosphere, dichloromethane is expected to persist for long periods of time. The estimated $t_{½}$ for the gas-phase reaction of dichloromethane with hydroxyl radicals is approximately 88 days. Direct photolytic degradation is not expected to occur. Dichloromethane may undergo atmospheric removal by wet deposition processes, although any removed by this process is expected to rapidly re-volatilize to the atmosphere. Using a slow biodegradation rate for dichloromethane in the STP fugacity model, 64 percent total removal can be predicted from waste water treatment plants.

Also, Appendix H presents an example of an Initial Review Exposure Report for dichloromethane. This form shows the environmental fate data that are typically reported along with some additional chemical property and toxicity information.

Relevant Environmental Fate Properties by Environmental Medium

For each type of environment, the types of fate and property data that are likely to be most relevant are listed below.

For water, the following are likely to be the most important properties and processes which should be considered in developing an environmental fate summary:

- S.
- Volatilization (H_c, $t_{½}$).
- Adsorption to sediments and suspended particulate matter (K_{oc}, K_d).
- Photolysis ($t_{½}$).
- Hydrolysis (rate constant and $t_{½}$).
- BCF.
- Biodegradation.

For soil, the following are likely to be the most important properties and processes which should be considered in developing an environmental fate summary:

- S.
- Volatilization (H_c).
- Adsorption to organic matter (K_{oc} and K_d).
- Adsorption to inorganic matter.
- Potential for groundwater contamination.
- Potential for uptake by plants.
- Biodegradation.
- Hydrolysis.
- Photolysis on soil surfaces.

For air, the following are likely to be the most important properties and processes which should be considered in developing an environmental fate summary:

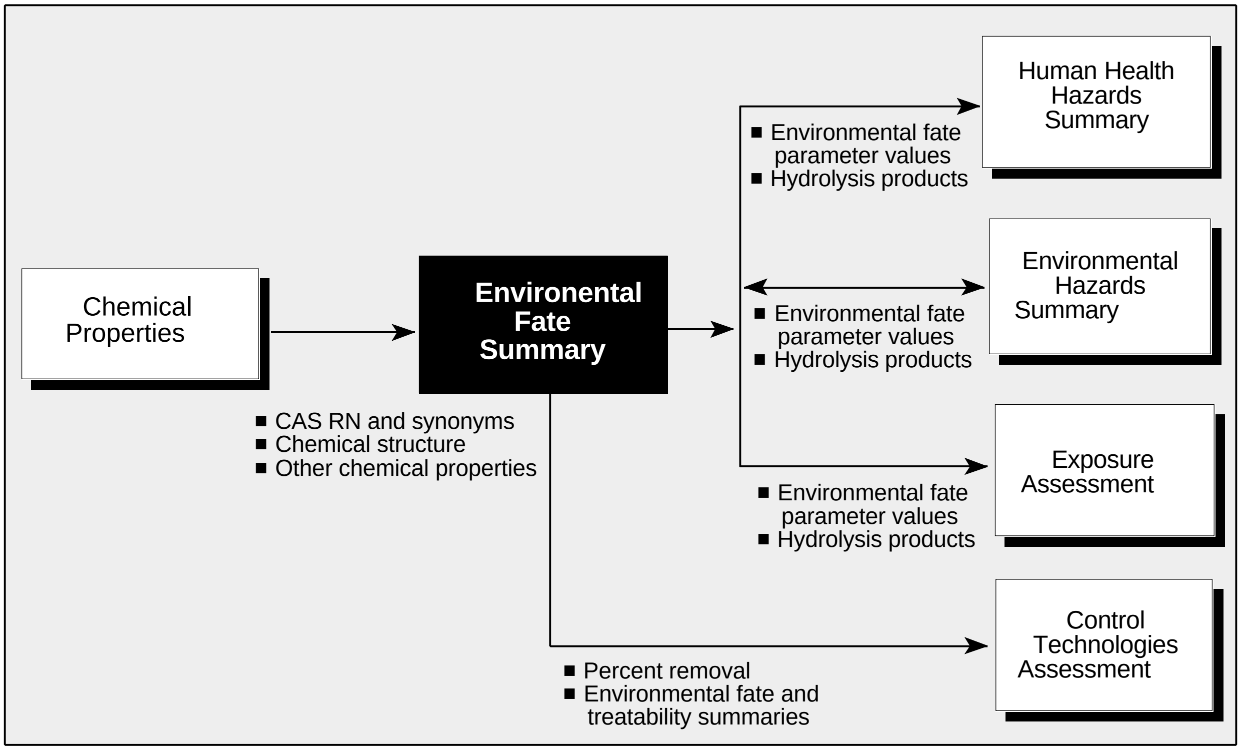
- Volatility (Pv, H_c).
- τ.
- Photolysis ($t_{1/2}$).
- Reactivity with hydroxyl radicals, ozone (k_{O_3}), and other oxidants.
- UV absorption.
- Smog-forming potential.
- Ozone depleting potential.
- Wet deposition.

For treatability, the following are likely to be the most important properties and processes which should be considered in developing an environmental fate summary:

- Biodegradability.
- Sorption potential (K_{oc}).
- Volatilization (H_c).
- Hydrolysis.

FLOW OF INFORMATION: In a CTSA, the Environmental Fate Summary module receives information from the Chemical Properties module and transfers information to the Human Health Hazards Summary, Environmental Hazards Summary, Exposure Assessment, and Control Technologies Assessment modules. Example information flows are shown in Figure 5-4.

FIGURE 5-4: ENVIRONMENTAL FATE SUMMARY MODULE: EXAMPLE INFORMATION FLOWS



ANALYTICAL MODELS: Environmental fate and transport modeling is performed as part of the Exposure Assessment module. Models for estimating environmental fate parameters are included in Table 5-6, below.

PUBLISHED GUIDANCE: EPA has not published comprehensive guidance on the development of environmental fate summaries. Individual program offices may utilize different approaches. Table 5-6 lists references in which methods for estimating chemical properties and environmental fate parameters are discussed.

TABLE 5-6: REFERENCES FOR ESTIMATING ENVIRONMENTAL FATE PARAMETERS

Reference	Type of Guidance
BioByte, Inc. CLOGP for Windows, Version 1.0. 1996. MACLOGP (for Macintosh computers), Version 2.0. 1996. CLOGP VAX/VMS, Version 2.10. 1996.	Mathematical models used to estimate K_{ow}. Three versions currently available (as of June, 1996).
Boethling, R.S. 1993. "Structure Activity Relationships for Evaluation of Biodegradability in the EPA's Office of Pollution Prevention and Toxics."	Describes the development, validation, and application of SARs in EPA OPPT.
Briggs, G.C. 1981. "Theoretical and Experimental Relationships between Soil Adsorption, Octanol-Water Partition Coefficients, Water Solubilities, Bioconcentration Factors, and the Parachor."	BCFs are estimated for neutral compounds from K_{ow}.
Hamrick, K.J., et. al. 1992. "Computerized Extrapolation of Hydrolysis Rate Data."	Provides estimates of hydrolysis rate constants at specific temperatures.
Hassett, J.J. 1981. "Correlation of Compound Properties with Sorption Characteristics of Nonpolar Compounds by Soils and Sediments: Concepts and Limitations."	Sorption constants for nonpolar organic compounds are correlated with S, K_{ow}, or with organic carbon content of soil or sediment.
Kollig, H.P. 1993. *Environmental Fate Constants for Organic Chemicals under Consideration for EPA's Hazardous Waste Identification Projects*.	Literature-derived data as well as model computations are used to estimate hydrolysis, adsorption, and oxidation-reduction parameters.

TABLE 5-6: REFERENCES FOR ESTIMATING ENVIRONMENTAL FATE PARAMETERS	
Reference	**Type of Guidance**
Lyman, W.J., et. al. 1990. *Handbook of Chemical Property Estimation Methods*.	Describes methods for estimating residence time, K_{ow}, K_{oc}, BCF, acid dissociation constants, hydrolysis, aqueous photolysis, biodegradation, and volatilization rates, and other chemical properties.
Mackay, D., et. al. 1992. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals*.	Provides physical-chemical data and fugacity calculations for organic compounds.
Meylan, W., et. al. 1992. "Molecular Topology/Fragment Contribution Method for Predicting Soil Sorption Coefficients."	Program for estimating K_{oc} based on molecular connectivity indices and structure-based correction factors.
Syracuse Research Corporation (SRC). Continually Updated. Estimation Programs Interface (EPI©).	Series of models to estimate log K_{ow}, volatilization $t_{½}$ for water, soil-sediment sorption coefficient, H_c, biodegradation, atmospheric oxidation rates, rate of hydrolysis, rate of removal in waste water treatment plants, and other chemical properties.

Note: References are listed in shortened format, with complete references given in the reference list following Chapter 10.

DATA SOURCES: Table 5-7 lists major sources of environmental fate data.

TABLE 5-7: SOURCES OF ENVIRONMENTAL FATE DATA	
Reference	**Type of Data**
Bedar, R.G. 1976. *Biodegradability of Organic Compounds*.	Biodegradability values for various organic compounds.
Callahan, M.A., et. al. 1979. *Water-related Environmental Fate of 129 Priority Pollutants*.	Information on environmental fate of priority pollutants in aqueous systems.
Darnall, K.R. 1986. "Reactivity Scale for Atmospheric Hydrocarbons Based on Reaction with Hydroxyl Radicals."	A classification of atmospheric chemical reactivity and potential for smog formation based on hydroxyl radical rate constants.
Farley, F. 1977. *Photochemical Reactivity Classification of Hydrocarbons and Other Organic Compounds*.	Classification for photochemical reactivity of organic compounds.
Hansch, C. and A. Leo. 1987. *The Log P Data Base*.	List of K_{ow} values.

TABLE 5-7: SOURCES OF ENVIRONMENTAL FATE DATA

Reference	Type of Data
Helfgott, T.B., et. al. 1977. *An Index of Refractory Organics*.	Biodegradability values for various organic compounds.
Hendry D.G. and R.A. Kenley. 1979. *Atmospheric Reaction Products of Organic Compounds.*	Rate constants (K_{OH}) for the reaction of organic compounds with hydroxyl radical.
Howard, P.H., et. al. 1991. *Handbook of Environmental Degradation Rates.*	Provides environmental degradation $t_{½}$ data for chemicals in soil, air, surface water and groundwater, and aerobic and anaerobic aqueous biodegradation.
HSDB®. Hazardous Substances Data Bank (HSDB). Updated Periodically.	On-line data base including measured and estimated chemical property and environmental fate parameters.
Kollig, H.P. 1993. *Environmental Fate Constants for Organic Chemicals Under Consideration for EPA's Hazardous Waste Identification Projects.*	Literature-derived data as well as model computations to estimate hydrolysis, adsorption, and oxidation-reduction parameters.
Lyman, W.J., et. al. 1974. *Survey Study to Select a Limited Number of Hazardous Materials to Define Amelioration Requirements*.	List of BOD_5/COD ratios for various organic compounds.
Mabey, W. and T. Mill. 1978. "Critical Review of Hydrolysis of Organic Compounds in Water Under Environmental Conditions."	Data on hydrolysis rate constants of organic compounds.
Mackay, D., et. al. 1992. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals*.	Provides physical-chemical data and fugacity calculations for organic compounds.
Pitter, P. 1976. "Determination of Biological Degradability of Organic Substances."	List of removal efficiencies and average rate of biodegradation for various organic compounds.
Reinbold, K.A., et. al. 1979. *Adsorption of Energy-Related Organic Pollutants: A Literature Review*.	Adsorption data extracted from the literature.
State of California Air Resources Board. 1986. *Adoption of a System for the Classification of Organic Compounds According to Photochemical Reactivity*.	Relative atmospheric reactivity scale.
Syracuse Research Corporation (SRC). 1994. Environmental Fate Data Bases (EFDB©).	Comprehensive on-line and personal computer-based data base containing quantitative data on environmental fate parameters.

TABLE 5-7: SOURCES OF ENVIRONMENTAL FATE DATA

Reference	Type of Data
Trapp, S. 1993. "Modelling the Uptake of Organic Compounds into Plants."	Describes estimating plant-soil BCFs using a fugacity model based on the ratio of K_{ow}:K_{oc}, the lipid fraction of plants, the organic carbon and water content of the soil, and transfer and metabolism kinetics.
U.S. Environmental Protection Agency. 1974. *Proceedings of the Solvent Reactivity Conference*.	Classification of chemical reactivity for compounds associated with mobile source emissions.
U.S. Environmental Protection Agency. 1991a. *The Environmental Fate Constants Information System Database (FATE).*	Provides data on H_c, K_{ow}, K_{oc}, K_d, k_{OH}, pK_a, and oxidation-reduction reactions of organic compounds.
U.S. Environmental Protection Agency. 1994d. *Treatability Database. Version 5.0.*	Personal computer-based collection of data including H_c, K_{ow}, treatability of organic compounds, and other chemical properties.
Verschueren, K. 1983. *Handbook of Environmental Data on Organic Chemicals.*	Information derived from primary literature on environmental parameters, including treatability.

Note: References are listed in shortened format, with complete references given in the reference list following Chapter 10.