WATER-RELATED ENVIRONMENTAL FATE OF 129 PRIORITY POLLUTANTS

Volume I:

Introduction and Technical Background, Metals and Inorganics, Pesticides and PCBs

by

Michael A. Callahan, Michael W. Slimak,
Norman W. Gabel, Ira P. May, Charles F. Fowler, J. Randall Freed,
Patricia Jennings, Robert L. Durfee, Frank C. Whitmore, Bruno Maestri,
William R. Mabey, Buford R. Holt, and Constance Gould

EPA Contract No. 68-01-3852
EPA Contract No. 68-01-3867

Project Officer. Donald J. Ehreth
Monitoring and Data Support Division (WH-553)
Office of Water Planning and Standards
Washington, D.C. 20460

OFFICE OF WATER PLANNING AND STANDARDS
OFFICE OF WATER AND WASTE MANAGEMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

FOREWORD

Effective regulatory action for toxic chemicals requires an understanding of the human and environmental risks associated with the manufacture, use, and disposal of the chemical. The assessment of risk requires a scientific judgment about the probability of harm to the environment resulting from known or potential environmental concentrations. Environmental concentrations are a function of (1) the amount and form of the chemical released into the environment, (2) the geographic area, (3) prior accumulation, (4) time of measurement, and (5) the behavior of the chemical in the environment. The behavior, or fate and transport characteristics, of toxic pollutants in the environment depends on a variety of chemical, physical, and biological processes (e.g., photolysis, hydrolysis, volatilization, sorption, biodegradation, biotransformation). Evaluating these processes for specific compounds and placing each interaction into environmental perspective is the basic goal of this report.

This two-volume report is a comprehensive review of the water-related environmental fate and transport literature available for 129 chemical compounds and elements, sometimes referred to as the 129 priority pollutants.

Michael W. Slimak, Chief
Exposure Assessment Section
Water Quality Analysis Branch
Monitoring and Data Support Division (WH-553)
Office of Water Planning and Standards

DISCLAIMER

This report has been reviewed by the Office of Water Planning and Standards, U.S. EPA, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

TABLE OF CONTENTS AND LIST OF CHAPTERS

VOLUME I: INTRODUCTION AND TECHNICAL BACKGROUND, METALS AND INORGANICS, PESTICIDES, AND PCBs.

Preceding page blank

VOLUME II: HALOGENATED ALIPHATIC HYDROCARBONS, HALOGENATED ETHERS, MONOCYCLIC AROMATICS, PHTHALATE ESTERS, POLYCYCLIC AROMATIC HYDROCARBONS, NITROSAMINES, AND MISCELLANEOUS COMPOUNDS.

ACKNOWLEDGEMENTS

A number of people have actively participated in this study, which was begun in September of 1977. The assistance, support, and management guidance provided by Martin P. Halper, former Chief of the Water Quality Analysis Branch (1976-1978), and Donald J. Ehreth, present Chief of the Water Quality Analysis Branch, U.S. EPA, is gratefully acknowledged.

Michael A. Callahan, U.S. EPA, conceptualized and managed the Phase I tasks and was the principal technical editor of all fate chapters. In addition, he performed part of the literature search for the halogenated aliphatic hydrocarbons and participated in extensive rewrites of that section. Michael W. Slimak, U.S. EPA, managed the Phase II tasks, provided additional editorial assistance, and completed the final report. Acknowledgement is also given to the staff members of the Water Quality Analysis Branch. Specifically, our thanks to: Rod Frederick, Lynn Delpire, Charles Delos, Mark Segal, Charles Gentry, Chris Ehret, and Richard Seraydarian.

Most of the literature search and the writing of the report was done by two contractors, Versar, Inc. and SRI International. The following individuals participated as shown:

1. VERSAR INC. (EPA Contract No. 68-01-3852)

   Program Management: Robert L. Durfee, Donald H. Sargent, Gayaneh Contos, Bruno Maestri
   Technical Direction: Michael W. Slimak (1977-78), Norman W. Gabel (1978-80)
   Authors:

   - Metals and Inorganics: J. Randall Freed, Ira P. May
   - PCBs and Related Compounds: J. Randall Freed, Frank C. Whitmore, Charles F. Fowler
   - Halogenated Aliphatic Hydrocarbons: Patricia Jennings, Robert L. Durfee
   - Halogenated Ethers: Norman W. Gabel
   - Monocyclic Aromatics: Patricia Jennings, Norman W. Gabel, Robert L. Durfee, Charles F. Fowler
   - Monocyclic Aromatics - Phenols and Cresols: Norman W. Gabel
   - Phthalate Esters: Bruno Maestri, Charles F. Fowler
   - Polycyclic Aromatic Hydrocarbons: Michael W. Slimak, Charles F. Fowler
   - Nitrosamines and Miscellaneous Compounds: Norman W. Gabel

   Data Gathering and Automated Literature Searches: Theodore French, Michael Keller
   Editing: Norman W. Gabel, Robert L. Durfee, Bruno Maestri, Juliet Crumrine

VERSAR INC. (continued)

Typing: Laura Skiba, Shirley Harrison, Lorraine Douglas, Kathy Turnblom, Rebecca Brown, Nancy Downie, Neda Helmandollar
Graphics and Reproduction: Kenneth Ratkiewicz, Joseph Gillette, Carole Craddock, Michael Cairns.

2. SRI INTERNATIONAL (EPA Contract No. 68-01-3867)

Program Management: Stephen L. Brown, Oscar Johnson, William R. Mabey
Technical Direction: William R. Mabey
Authors:

- Pesticides: William R. Mabey, Buford Holt, Constance Gould

Automated Literature Searches: Shirley Radding, Jerie Etherton
Editing: Lee Work
Typing: Kathleen Williams, Maria Buyco.

The general assistance and guidance provided by personnel within EPA's Athens Environmental Research Laboratory, especially George Baughman and his staff, is also greatly appreciated.

Numerous individuals provided comments and suggestions on the draft report; their efforts are appreciated. A special note of gratitude is due those who carefully reviewed the draft report and provided timely and pertinent comments. These reviewers include:

G. Baughman, U.S. EPA-Athens
G. Zweig, U.S. EPA-Washington
J. Kariya, U.S. EPA-Washington
J. Cohen, U.S. EPA-Cincinnati
J. Gillette, U.S. EPA-Corvallis
M. Strier, U.S. EPA-Washington
J. Butler, Harvard University
R. Baker, U.S. Geological Survey
K. Irgolic, Texas A&M University
R. Bailey, Dow Chemical U.S.A.
W. Dilling, Dow Chemical U.S.A.

Special gratitude is due Bruno Maestri and Shirley Harrison, Versar Inc., for their efforts in completing the final document, especially their attention to detail.

SECTION I: INTRODUCTION AND TECHNICAL BACKGROUND

Chapters 1-4

1. INTRODUCTION

1.1 Background

The Office of Water Planning and Standards (Monitoring and Data Support Division) of the U.S. Environmental Protection Agency (EPA) is conducting a program to evaluate exposure and subsequent risk from the presence of toxic pollutants in our nation's environment. This program addresses the goals of the Clean Water Act of 1977.

The environmental fate processes discussed in this report are a key component in an exposure assessment. The goal of an exposure assessment is an exposure profile which identifies subpopulations (geographic, demographic, etc.) and associates how much, and what form, of a chemical comes in contact with each subpopulation. Ideally, this exposure profile can be synthesized by matching the location and habits of various subpopulations with the location and form of the chemical. If the characteristics of environmental release are well defined (location, amount released per unit time, form of chemical, etc.), environmental fate processes can be used to determine the ultimate location and form of the chemical. Therefore, environmental fate and environmental release data are a major part of an exposure assessment.

This two-volume report is a comprehensive review of the water-related environmental fate and transport literature available for 129 chemical compounds and elements, sometimes referred to as the 129 priority pollutants. The pollutants (or in some cases classes of pollutants) are listed in Section 307(a)(1) of the 1977 Clean Water Act (33 U.S.C. 466 *et seq.*; Committee Print HR. 3199).

The objectives of this study were to:

1. Review and analyze the available information concerning significant environmental processes and associated kinetics for each of the 129 priority pollutants;

2. Identify the probable environmental pathways and fate of 129 priority pollutants when introduced into surface waters; and

3. Indicate the degree of confidence for the conclusions reached.

Volume I of this report contains an introduction, a description of fate and transport processes, conclusions and recommendations, and a brief discussion about the procedures used for collecting and reviewing the literature. Volume I also contains chapters describing the fate of metals and inorganic compounds, pesticides, and polychlorinated biphenyls. Volume II consists of a discussion of the fate of the halogenated aliphatic hydrocarbons, halogenated ethers, monocyclic aromatics, phthalate esters, polycyclic aromatic hydrocarbons, nitrosamines, and miscellaneous compounds.

1.2 Approach

The fate of chemicals in the environment depends on a variety of chemical, physical and biological processes. Evaluating these processes for a specific compound and placing each interaction into environmental perspective is the basic goal of this report. Transport and transformation processes have been studied for some time. The studies have ranged from laboratory experiments on individual processes to full scale field evaluations. Full-scale field experiments have been directed toward monitoring the distribution, concentration, and transformation products that result from releases of chemicals into the "real" environment. This approach is limited to those chemicals already present in the aquatic environment and is costly because of the large number of samples that must be collected and analyzed. Another approach has been to study the chemical in the laboratory in miniature ecosystems (microcosms) which are relatively inexpensive and more easily controlled. The results are potentially more applicable to different environmental conditions than are field monitoring studies alone. The microcosm approach has contributed to the knowledge of transport processes and is extensively used by Metcalf et al. (1976) and others (Isensee et al. 1973; Sanborn et al. 1976; Witherspoon et al. 1976, etc.) to indicate environmental behavior and to relate behavior to chemical properties. Both the full-scale field study and microcosm approaches are important for examining transformation pathways and the testing and validation of mathematical ecosystem models. They are, however, limited since they lack explicit rationale for direct extrapolation to other compounds or environments. Therefore, results from these studies are more indicative of what might occur under specific conditions than of what will probably occur over a wide variety of conditions in a specific natural environment. It is also important to note that results from microcosm studies cannot be used for directly predicting the actual environmental concentration of a specific chemical.

The approach taken in this study is directed toward the mathematical integration of independent transformation and transport processes, sometimes referred to as an environmental exposure analysis. This approach was developed, in part, by the U.S. EPA Environmental Research Laboratory in

Athens, Ga., and is described in a number of recent publications including the works of Wolfe et al. (1976), Paris et al. (1975), Hill et al. (1976), and Smith et al. (1977). The fundamental premises on which this approach is based are: (1) the overall rate of disappearance of a compound from the aquatic environment is controlled by the dominant transformation and transport processes; (2) these processes (e.g., photolysis, hydrolysis, volatilization, sorption, biotransformation/biodegradation) can be studied independently in the laboratory; and (3) the laboratory data can be integrated, using a model which simulates the environment, and extrapolated to environmental conditions to predict exposure levels or concentrations.

This two-volume report consists of a detailed review of the literature which describes the transport and transformation processes for each of 129 priority pollutants and indicates the most probable fate process of each compound. In certain cases, the data reviewed could not be analyzed in the context of the transport and transformation processes, and in many instances the studies reported in the literature were not conducted using typical environmental conditions. It should also be recognized that information and data available in the literature may not always be suitable for use in the context of an exposure model, and a critical review of experimental procedures described in the literature is required to obtain reliable data for exposure assessments.

1.3 Literature Cited

Hill, J., H.P. Kollig, D.F. Paris, N.L. Wolfe and R.G. Zepp. 1976. Dynamic behavior of vinyl chloride in aquatic ecosystems. U.S. Environ. Protection Agency, Athens, Ga. EPA-600/3-76-001.

Isensee, A.R., P.C. Kearney, E.A. Woolsen, G.E. Jones, and U.P. Williams. 1973. Distribution of alkyl arsenicals in model ecosystems. Environ. Sci. Technol. 7:841-845.

Metcalf, R.L., J.R. Sanborn, P.-Y. Lu and D. Nye. 1976. Laboratory model ecosystem studies of the degradation and fate of radiolabeled tri-, tetra-, and pentachlorobiphenyl compound with DDE. J. Environ. Qual. 5:482.

Paris, D.F., D.L. Lewis, J.T. Barnett, and G.L. Baughman. 1975. Microbial degradation and accumulation of pesticides in aquatic systems. U.S. Environ. Protection Agency, Athens, Ga. EPA-660/3-75-007.

Sanborn, J.R., R.L. Metcalf, W.N. Bruce, and P.-Y. Lu. 1976. The fate of chlordane and toxaphene in a terrestrial-aquatic model ecosystem. Environ. Entomol. 5:533.

Smith, J.H., W.R. Mabey, N. Bohonos, B.R. Holt, S. S. Lee, T.-W. Chou, D.C. Bomberger, and T. Mill. 1977. Environmental pathways of selected chemicals in freshwater systems; Part I: Background and experimental procedures. U.S. Environ. Protection Agency, Athens, Ga. EPA-600/7-77-113.

Witherspoon, J.P., E.A. Bondieth, S. Draggan, F. Taub, N. Pearson, and J.R. Trabokla. 1976. State-of-the-art and proposed testing for environmental transport of toxic substances. U.S. Environ. Protection Agency, Wash., D.C. EPA-560/5-76-001.

Wolfe, N.L., R.G. Zepp, G.L. Baughman, R.C. Fincher, and J.A. Gordon. 1976. Chemical and photochemical transformation of selected pesticides in aquatic systems. U.S. Environ. Protection Agency, Athens, Ga. EPA-600/3-76-067.

2. FATE AND TRANSPORT PROCESSES

2.1 Introduction

There are a number of physical, chemical and biological processes that may be important in affecting the concentration of a chemical in an aquatic system. These processes include photolysis, hydrolysis, volatilization, sorption, bioaccumulation, and biotransformation/biodegradation, and their relevance and mathematical expression are briefly described below. It must be noted, however, that much of the literature reviewed did not report data in the context of the theoretical discussions. Each author was responsible for carefully reviewing and evaluating the data and, where possible, presenting the data in a form or expression similar to the way data are presented for the processes discussed below. Often times this was not possible and qualitative judgments had to be made in order to interpret the results in light of these specific fate and transport processes.

2.2 Transport Processes

2.2.1 Volatilization

Volatilization of organic chemicals from water to the atmosphere can be an important pathway for chemicals with high vapor pressures or low solubilities. Early work reported in the literature often attributed losses of chemicals actually due to volatilization as being due to chemical or biological transformations. Recognition of the possible importance of volatilization in laboratory experiments and in the environment subsequently led to studies of, or at least consideration of, volatilization as a discrete process. Some papers refer to such losses as "co-distillation" with water, which is not technically correct since the loss of water and of the chemical are not interdependent (see Section 25.4.4). While the importance of the volatilization pathway has been reported for many chemicals, most of the reported data are difficult to apply to an environmental assessment because of incomplete information on the factors which influence the volatilization (e.g., turbulence, temperature, experimental design). Recent research has developed a better understanding of volatilization processes in the aquatic environment. The following discussion describes the current understanding of the fundamentals of the volatilization process, and discusses applications which have been employed in some exposure assessment models. This discussion is also useful for evaluating the deficiencies and limitations of the information reported in literature, which, in many instances, was never presented in the context of a theoretical treatment.

A two-resistance theory, first proposed by Whitman (1923), can be used to describe the rate of volatilization of a chemical (Liss and Slater 1974; Mackay and Leinonen 1975). In general, the volatilization rate, R_V, is a first-order process and can be described by:

$$R_V = -\frac{d[C_W]}{dt} = k_V[C_W] \quad (1)$$

where,

$$k_V = \frac{1}{L}\left[\frac{1}{k_\ell} + \frac{RT}{H_C k_g}\right]^{-1} \quad (2)$$

and,

R_V = volatilization rate of a chemical, C (moles liter^{-1} hr^{-1});

C_W = concentration of C in water (mole liter^{-1} = M);

k_V = volatilization rate constant (hr^{-1});

L = depth (cm);

k_ℓ = liquid phase mass transport coefficient (cm hr^{-1});

H_C = Henry's law constant (torr M^{-1});

k_g = gas phase mass transport coefficient (cm hr^{-1});

R = gas constant (liter-atm. mole^{-1} deg^{-1}); and

T = temperature (deg. Kelvin).

In both the gas and liquid phase,

$$k_\ell = D_\ell / \delta_\ell \tag{3}$$

and,

$$k_g = D_g / \delta_g \tag{4}$$

where D is the diffusion coefficient and δ is the boundary layer thickness.

There are several approaches which can be used to estimate the mass transport coefficients for the chemical in the water body of interest. One convenient simplification is based on the observation that if $H_c >$ 3000 torr M^{-1}, R_v is determined by the value of k_ℓ and is limited by diffusion through the liquid phase boundary layer. For these highly volatile compounds, equation (5) should be useful over a wide range of environmental conditions:

$$(k_v^C)_{env} = (k_v^C / k_v^O)_{lab} (k_v^O)_{env} \tag{5}$$

where k_v^C is the volatilization rate constant for the chemical (hr^{-1}) and k_v^O is the oxygen reaeration rate constant (hr^{-1}) in the laboratory or the environment. The ratio k_v^C/k_v^O for benzene has been found to be independent of turbulence, salt concentration (seawater), temperature (4°-50°C), and the presence of a surface active compound (Smith et al. 1979).

Alternatively, if $H_c <$ 10 torr M^{-1}, only the second term in equation (2) is significant. Then

$$k_v = \frac{H_c k_g}{LRT} \tag{6}$$

and the volatilization rate is limited by diffusion through the gas phase boundary layer. If 3000 torr $M^{-1} > H_c >$ 10 torr M^{-1}, both terms in equation (2) are significant. In these cases, the mass transport coefficients of the chemical in the water body can be estimated from representative values of the mass transport coefficient for oxygen reaeration, which is liquid phase resistance controlled, and from the mass transport coefficient of water, which is gas phase resistance controlled.

2.2.2 Sorption

The sorption of chemicals to suspended sediments and bottom sediment can be an important process in aquatic environments. The term sorption is used in these reports since the other commonly used terms of adsorption and absorption have mechanistic connotations which cannot be identified in most experiments. In general, the more hydrophobic a chemical is the more likely it is to be sorbed to sediment.

Data for sorption of chemicals to particulates are frequently expressed in terms of the Freundlich isotherm equation,

$$C_s = K_p C_w^{1/n} \qquad (7)$$

where C_s and C_w are the concentrations of chemical in particulate and water phases, K_p is a partition coefficient for sorption, and 1/n is an exponential factor. At environmentally relevant concentrations of a chemical in solution which are low compared to the particulate sorption capacity, the 1/n term is usually equal to unity within experimental error. It should be realized also that the measurement of K_p must allow sufficient time for equilibrium between phases to be established; information in the literature indicate that times to reach equilibrium range from a few minutes to several days.

For neutral organic chemicals, the degree of sorption to suspended sediments is dominated by interaction with the organic content of the particulate; a partition coefficient corrected for organic carbon, K_{oc}, equal to K_p divided by the fraction of organic carbon, correlates well with water solubility and octanol/water partition coefficients (K_{ow}) (Kenaga and Goring 1978). This relationship between K_p and K_{oc} is useful for predicting K_p values for a number of sediments where the organic carbon content is known or chosen. It should be realized, however, that neutral compounds are also sorbed by materials with little or no organic content, such as sands and inorganic clays, and the K_p data for sorption on soils or sediments with very high sand or clay content do not fit the correlations for K_p data for soils/sediments where the organic content is greater than about 1 percent. Therefore, K_{oc} data should be used with appropriate limitations. Another important factor to be considered in the use of literature data is that concerning the units of K_p (or K_{oc}); although the units of C_s and C_w are usually the same so that K_p is unitless, some literature does not conform to this convention and requires K_p recalculation before use. Also, if the data were fit to a Fruendlich equation with the exponent, n, not equal to unity, the value of K_p with n = 1 at low concentrations of the chemical must be recalculated from the original data.

2.3 Chemical Processes

2.3.1 Photolysis

Photolyses of chemicals dissolved in aquatic systems occur at wavelengths greater than 290 nm since ozone in the stratosphere filters out light of shorter (higher energy) wavelengths. Photochemical transformations may occur by one or more processes depending on the chemical structure and substances in the environment. "Direct photolysis" processes take place if the chemical absorbs light and then undergoes a transformation reaction from an excited state by any one of several mechanisms (i.e., rearrangement, dissociation, oxidation, etc.). The rate of the reaction is dependent on the sunlight photon flux, the light adsorption coefficients of the chemical, and the reaction quantum yield; the last is the efficiency for conversion of the absorbed light into chemical reaction.

In contrast to direct photolysis, "indirect photolysis" takes place if substances naturally present in aquatic environments absorb sunlight to form excited chemical species or radicals which interact with the chemical to produce a reaction. One type of indirect photolysis is a photosensitized reaction, in which the light-absorbing substance transfers excited state energy to the chemical which then undergoes a reaction, which may or may not be similar to the reaction of those found in direct photolysis processes. Although the literature suggests that such photosensitized reactions may occur in natural waters, there is as yet no unambiguous evidence that this mechanism is actually important in the environment. Other types of photochemical reactions that may be considered in the indirect photolysis class are those in which photolyzed natural substances produce energetic intermediates that react with the ground state of the chemical; singlet oxygen and oxy radicals are examples of such intermediates which can result in transformations of chemicals. Since these intermediates result from photoreactions of naturally occurring substances and since the photochemistry of the chemical itself is not involved, it is not strictly correct to refer to such reactions as photolyses; rather they should be referred to as photooxygenation or photo-initiated free radical reactions (for singlet oxygen and oxy radicals, respectively). In most literature information, and frequently in laboratory studies, it is impossible to differentiate among the several types of photochemical mechanisms in natural waters, and therefore they are often necessarily grouped into discussions of photochemistry.

The rate of loss of chemical ($-\frac{dC}{dt}$) by either direct or indirect photochemical processes may be expressed by simple first order kinetic expressions. The equation for direct photolysis is

$$-\frac{dC}{dt} = k_p [C] = k_a \phi [C] \tag{8}$$

or,

$$k_p = k_a \phi \tag{9}$$

where k_p is a first order rate constant, ϕ is the reaction quantum yield, and k_a is a rate constant for absorption of light by the chemical; the last is a function of the photon flux, the distribution of light and the light absorption coefficient of the chemical (Zepp and Cline 1977; Mabey et al. 1979). The rate equation for indirect photolysis by any mechanism may be expressed by

$$-\frac{dC}{dt} = k_2 [C][X] = k_p' [C] \tag{10}$$

where k_2 is a second order rate constant for reaction of chemical C with the reactive intermediate X; for a photosensitized reaction the k_p' rate constant would be a combined term for concentration of excited state species and quantum yields (or efficiencies) of energy transfer to and subsequent reaction of the chemical. In any estimation of k_p' or k_p, values of k_a or [X] will either be for instantaneous rates (or concentrations), or for those averaged over a specific time interval, because the first order rate constants will be dependent on the sunlight intensity which varies with time of day, season, and latitude.

2.3.2 Oxidation

As discussed in the photolysis section, oxidation may occur as a result of oxidants formed during photochemical processes in natural waters. The complex chemistry of free radical reactions in natural waters has recently been reviewed by Mill et al. (1979), along with the production and reaction of singlet oxygen in these systems. Based on limited experimental work, the average effective concentrations of the two oxidant species, alkylperoxyl radicals and singlet oxygen, were estimated to be 10^{-9} M and 10^{-12} M, respectively.

Other oxidation processes have also been investigated in connection with water treatment processes using chemical oxidants such as chlorine, ozone, or permanganate. While this information may be relevant to water treatment processes, it obviously has little quantitative relevance to aquatic environments except for providing a qualitative measure of susceptibility to oxidation; a chemical which is inert to those oxidants will probably be stable to oxidation in aquatic systems.

The kinetic expression for the rate of loss of a chemical by reaction with an oxidant [Ox] is given by

$$-\frac{dC}{dt} = k_{OX}[Ox][C] \qquad (11)$$

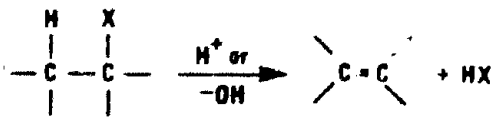
where k_{OX} is a second order rate constant for reaction of the oxidant with chemical C, and [Ox] and [C] are the concentrations of oxidant and chemical, respectively. Data for k_{OX} and the use of such information in estimating oxidation half-lives has recently been reviewed by Mill (1979) and Mill et al. (1979). As for sunlight variations in photolysis rates, the value of [Ox] must be defined in terms of an average effective oxidant concentration over a time period. Since most literature information has not identified oxidants responsible for loss of a chemical nor separated out the component photolysis mechanisms that may have contributed to the loss of a chemical, use of such information must usually be considered particular to defined experimental conditions, and therefore not applicable to more general evaluations of oxidation.

2.3.3 Hydrolysis

Hydrolysis of organic compounds usually results with the introduction of a hydroxyl group (-OH) into a chemical structure, commonly with the loss of a leaving group (-X):

$$RX + H_2O \rightarrow ROH + HX \text{ (or } H^+, X^-). \qquad (12)$$

The rate of the reaction may be promoted by acid (hydronium ion, H_3O^+) and/or base (hydroxyl ion, OH^-). Some chemicals will also show a pH dependent elimination reaction:



Both processes are included in the scope of hydrolysis studies, where the rate of hydrolysis is given by the equation,

$$-\frac{dC}{dt} = k_h[C] = k_A[H^+][C] + k_B[OH^-][C] + k_N[C] \qquad (13)$$

where k_h is the first order rate constant at a specific pH; k_A and k_B are second order rate constants for the acid and base promoted processes, respectively; and k_N is the first order constant for the pH independent reaction of a chemical with water.

Mabey and Mill (1978) have recently reviewed data for hydrolysis of a variety of organic chemicals for use in prediction of half-lives in aquatic systems. Some chemicals such as alkyl halides have hydrolysis rates which are independent of pH over the environmental pH range 4-9, while others such as carboxylic acid esters are acid and base promoted with a minimum hydrolysis rate at pH 4-5. Rate constants k_A, k_B and k_N for a large number of hydrolyzable structures can be estimated with reasonable accuracy from published data (Mabey and Mill 1978) or from structure reactivity correlations for these processes (Mill 1979).

2.4 Biological Processes

2.4.1 Bioaccumulation

Bioaccumulation of chemicals in various living species has been shown to result in significant ecological effects, and is especially important for hydrophobic chemicals which can be partitioned into fat and lipid tissues. Bioaccumulation also occurs with inorganic chemicals being partitioned into bone marrow, etc. Although bioaccumulation has been the subject of much valuable research, interpretation and subsequent use of bioaccumulation data must be performed with careful attention to the experimental procedures employed. The bioconcentration factor (BCF) is usually defined as the concentration of a chemical in tissue (on a dry-weight basis) divided by the concentration in water; some literature data, however, reported the concentration in tissue on a wet-weight basis, and therefore the BCF is lower than when reported on a dry-weight basis. It should be noted that BCFs frequently may be low as a result of insufficient time being allowed for the true partitioning equilibrium to be attained in the system. The use of bioconcentration data is also complicated by the fact that concentrations of a chemical will usually be higher in fatty tissues of the species than in leaner tissues. The rate of uptake and time for attainment of equilibrium in various organs (and species) will also

depend on the route of uptake (i.e., dietary, skin absorption, etc.); for obvious reasons, most bioconcentration data for aquatic systems are from fish studies.

In spite of these problems, bioconcentration/bioaccumulation data are an important parameter for evaluating the impact of chemicals in an aquatic environment; it is significant to note that most of the above problems will lead to estimates of bioconcentration values that are lower than the actual values. Kenaga and Goring (1978) have also provided a useful correlation between BCF and octanol/water partition coefficients and water solubility data. The correlation is useful in assessing a chemical's potential for bioaccumulation; therefore, the log P octanol/water partition coefficient is included in the physical properties section of each chapter.

2.4.2 Biotransformation and Biodegradation

Biodegradation results from the enzyme-catalyzed transformation of chemicals. Organisms require energy, carbon, and other fundamental inputs from the environment for their growth and maintenance. In the process, they manufacture enzymes to transform many chemicals introduced into the environment. Because biodegradation processes in aquatic and soil environments are carried out primarily by microbes, the effects of macrobiota are usually considered insignificant in studying biotransformation and biodegradation.

The biodegradation rate is the function of a microbial biomass and a chemical's concentration under given environmental conditions. When microorganisms utilize chemical substrates, there are increases in biomass, and biodegradation rates will then be a function of cell growth rate. When an organic compound is utilized by microorganisms as a sole carbon source, the specific growth rate of organisms is a function of chemical concentration. The widely used Monod kinetic equation, describing the relation between growth-limiting substrate concentration (C) and the specific growth rate in a well mixed system is expressed as

$$\mu = \frac{dX/dt}{X} = \frac{\mu_m C}{K_s + C} \qquad (14)$$

where μ is the specific growth rate, X is the biomass per unit volume, μ_m is the maximum specific growth rate, and K_s is the concentration of substrate supporting half-maximum specific growth rate (0.5 μm).

The rate of substrate utilization is then

$$-\frac{dC}{dt} = \frac{\mu X}{Y} = \left(\frac{\mu_m}{Y}\right) \cdot \left(\frac{CX}{K_s + C}\right) = \left(k_b\right) \cdot \left(\frac{CX}{K_s + C}\right) \qquad (15)$$

where k_b is the substrate utilization constant or biodegradation constant, equal to μ_m/Y, and Y is the biomass produced from a unit amount of substrate consumed. The constants μ_m, K_s and Y are dependent on the characteristics of microbes, pH, temperature, other nutrients, etc.

When substrate concentration is high and $C >> K_s$, then the above expression becomes.

$$-\frac{dC}{dt} = k_b X \quad . \tag{16}$$

The degradation rate is first order with respect to all biomass concentrations and zero order with respect to chemical concentration.

For many pollutants in the environment, substrate concentrations are very low, such that $C << K_s$. Equation (15) then becomes

$$-\frac{dC}{dt} = \left(k_b\right)\left(\frac{CX}{K_s}\right) = k_{b2}\,[C]\,[X] \tag{17}$$

where k_{b2} is a second order rate constant. The degradation rate is then first order early in cell concentration and in chemical concentration.

In the environment, where the cell concentration X is relatively large and pollutant concentration is low, microbial populations will not change significantly when the chemical is consumed. The degradation rate under these conditions is pseudo first order and can be described by the equation

$$-\frac{dC}{dt} = k_b' C \tag{18}$$

where k_p' is a pseudo first order rate constant. The factor k_p' is dependent on cell concentration (X_o), therefore

$$\frac{k_b'}{X_o} = k_{b2} \tag{19}$$

and k_{b2} is the second order rate constant. The half-life of the chemical ($t_{1/2}$) at a given X_o will be

$$t_{1/2} = \frac{\ln 2}{k_{b2} X_o} = \frac{0.693}{k_{b2} X_o} \quad . \tag{20}$$

The degradation rate constants shown above are to be used under those conditions where microorganisms are acclimated to the chemical and can actively utilize the chemical. However, when a pollutant is initially introduced into the environment, there is often a lag period between the exposure of the chemical to the organisms and the initiation of biodegradation for some chemicals. A lag or acclimation period is required to induce the organisms to produce necessary enzyme(s) or to develop biodegradation organisms by mutation. A lag period may also result when there are too few degrading microbes initially present in the system. Under these conditions, no significant substrate consumption is usually detected until bacterial cells reach a substantial level. This acclimation period may also be caused by diauxic utilization of substrates where other readily metabolizable organic compounds are present.

Monod kinetics is applicable if the lag period is caused by too low an initial microbial level; mathematical treatment is difficult if acclimation is caused by physiological adjustment of the microbial community. In most cases, it is possible to assume that the environment has already been exposed to the chemical and that acclimated organisms are already present; the biodegradation rate constant is then used for such a calculation with a given level of microorganisms. When a chemical is newly released into an uncontaminated place, the lag period cannot be ignored and the time required to reduce 50 percent of the original concentration ($T_{1/2}$) is the sum of time required to reach acclimation (t_o) and the half-life of transformation ($t_{1/2}$)

$$T_{½} = t_o + t_{½} . \qquad (21)$$

Natural aquatic environments contain a number of organic compounds of natural and anthropogenic origin. Some pollutants may be biotransformed only when another organic compound is present to serve as a carbon and energy source; this phenomenon is known as cometabolism. Methods to evaluate the biodegradation of chemicals as a sole carbon source may then often underestimate the rate of the biodegradation in the natural environment. Mathematical treatment of cometabolic transformation of chemicals is not currently available, but cometabolism should be considered in any environmental fate assessment.

2.5 Other Reactions

The foregoing processes are those which have been the subject of some research and have been described in a quantitative manner suitable for estimating half-lives or for use in various modelling efforts. Other

processes have also been infrequently reported as being possible important pathways for some chemicals in aquatic systems, but have not been quantitatively expressed in ways that are useful for inclusion in modelling efforts. Two of these processes are described below.

2.5.1 Reduction

In anaerobic environments, reduction of chemicals by both biological and non-biological processes can occur. Most frequently reported for these reactions are organochlorine chemicals, where a chlorine atom is replaced by a hydrogen atom (see chapters on DDT, toxaphene.) It is expected that further work in this subject will provide knowledge of specific reducing agents in aquatic environments and kinetic expressions for the use of this information in environmental assessments.

2.5.2 Hydration

Another process that may be important in aquatic systems for some chemicals is hydration. Carbonyl compounds are known to form hydrates, which will have different properties than the parent chemicals. Therefore both the transport and transformation pathways of the chemical in the aquatic environment will be affected. The existance of hydrated species must be considered in using experimental kinetic and equilibrium data for environmental assessments. Thus, since the hydration reaction is reversible,

$$\text{unhydrated} + H_2O \rightleftharpoons \text{hydrated},$$

the kinetic expression for loss of the chemical may then include a kinetic loss term and the hydration equilibrium term.

2.6 Evaluation of Processes

2.6.1 Kinetics (Half-lives)

The transport and transformation processes, discussed above, were reviewed and evaluated for each of the 129 priority pollutants to determine a chemical's most probable aquatic fate by identifying the processes with relatively short half-lives. A half-life is an estimate of the environmental persistence of a chemical or the time required for removal of one-half of the initial concentration of the chemical. The principal experimental approach to the derivation of chemical "half-lives" is to measure the rate constants with which a reaction proceeds and the dependence

of the reaction rate constant on the concentration of the reacting species and physical parameters (e.g., temperature). The rates of chemical reactions range from those that are completed almost instantaneously to those that proceed so slowly that the reaction is essentially imperceptible. Techniques of measurement typically involve the determination of the change in concentration of a reactant or product as a function of time.

For example, at constant volume, and for a unimolecular reaction such as

$$A \longrightarrow \text{Products} \qquad \text{or} \qquad A \longrightarrow B + C,$$

the rate of disappearance of A can be expressed as:

$$-\frac{dC_A}{dt} = k_j C_A \tag{22}$$

where C_A = concentration of A, in moles per liter;
t = time, appropriate units;
k_j = reaction rate constant for process j, units of inverse time; and
$\frac{dC_A}{dt}$ = rate of change of C_A with respect to time.

Integrating the above between the limits of t_o (initial time) and t produces:

$$k_j = \frac{1}{(t-t_o)} \ln\left(\frac{C_{A_o}}{C_A}\right) \tag{23}$$

where C_{A_o} = initial concentration of A.

The above is a first order reaction, in which the rate of reaction of a species depends upon the first power of the chemical concentration. Other reactions may be of higher order, for example the nominal second order reaction:

$$A + B \longrightarrow C + D$$

for which

$$-\frac{dC_A}{dt} = k_j C_A C_B \tag{24}$$

Although some reactions of this form can be treated as first order with some assumptions (many hydrolysis reactions of pollutants in water, at fixed pH, for example), this cannot be assumed until experimental data are available which indicate first order kinetics.

An estimate of environmental persistence for a process is given in the form of a "half-life". For first-order decomposition reactions when $C_A=0.5C_{A_0}$, the half-life takes the form,

$$t_{1/2} = \frac{1}{k_j} \ln \left(\frac{2C_{A_0}}{C_{A_0}} \right) \tag{25}$$

or,

$$t_{1/2} = 0.693 \left(\frac{1}{k_j} \right) . \tag{26}$$

Other equations for half-life must be used if the order of the reaction is other than first order. Obviously, knowledge of the rate constant is required for half-life calculations based on first-order reactions; knowledge of concentration levels are required in addition to rate constants if the order is higher than first order.

If all the transformation and transport processes have been expressed as first or pseudo first order rate expressions, it is possible to calculate an overall or net half-life for the chemical by the equation,

$$t_{1/2} = \frac{\ln 2}{\sum_j k_j} . \tag{27}$$

2.6.2 Microcosm Studies, Field Studies and Modelling

Field studies and, on a more controllable scale, microcosm studies, are considered by some researchers as direct approaches to environmental fate assessments of chemicals. The modelling approach, on the other hand, is a way of synthesizing information on the fate of a chemical

using data on component processes. Each approach has its merits and disadvantages for use in the determination of the fate and pathways of chemicals in aquatic environments. When available, information on such studies has been included in this literature review. The discussion is presented by individual process, such as biotransformation or bioaccumulation, when that process is clearly dominant over others.

Field studies and microcosm experiments use real or physically similar environmental situations to evaluate the rate of disappearance of a chemical. Such studies readily measure the bioaccumulation or movement to sediment of a chemical, but generally do not provide information on the relative importance of some component loss processes (e.g., photolysis, volatilization, biotransformation) which may be subsequently applied to evaluations of other aquatic environments. While microcosms provide more control and knowledge of the factors influencing the experiments, they often must also depart from reality in scale and in other factors such as wind speed, sunlight variations and sediment scouring. In summary, field studies, and to an extent microcosms, are holistic approaches to predicting the fate of chemicals in aquatic systems, but suffer from their specificity and unknown interactions which limit the application of results to other aquatic systems.

The modelling approach to environmental fate assessments combines kinetic and equilibrium data on component processes to predict the transport, transformation, and concentration of chemicals in the environment. Provided that suitable data for a chemical are available by measurement or estimation methods, the model may be designed with any degree of sophistication. An important advantage of such models is that the fate of a chemical can be predicted for any environmental situation; one such scenario may be designed to estimate a conservative half-life or concentration for general environmental assessment purposes, whereas a specific field study may fortuitously provide an unrealistically rapid rate of loss of the chemical due to dominance of a uniquely rapid process. The model may also allow for prediction of only transport and dilution in an environment where transformation data are unreliable, which could also be used for a conservative risk assessment. A major disadvantage of the modelling approach with the present state of knowledge is that no chemical degradation and transport model has been verified by comparison to actual environmental experience, although work is underway in this area. It is likely that the verification of an aquatic fate model will eventually require a series of field studies or microcosm experiments, with the model being used to design the sampling strategy. It is also important to realize that the model must be verified on several chemicals, each with different dominant fate processes, before a widely applicable model can be established.

2.7 Literature Cited

Kenega, E.E. and C.A.I. Goring. 1978. Relationship between water solubility, soil-sorption, octanol-water partitioning, and bioconcentration of chemicals in biota. Amer. Soc. Test. Mat. Third Aquatic Tox. Symp., New Orleans, La. 63 pp.

Liss, P.S. and P.G. Slater. 1974. Flux of gases across the air sea interface. Nature. 247:181-184.

Mabey, W.R., T. Mill, and D.G. Hendry. 1979. Test protocols for environmental processes: Photolysis in water. EPA Draft Report. EPA Contract 68-03-2227.

Mabey, W.R. and T. Mill. 1978. Critical review of hydrolysis of organic compounds in water under environmental conditions. J. Phys. Chem. Ref. Data 7:383.

Mackay, D. and P. J. Leinonen. 1975. Rate of evaporation of low solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 9:1178-1180.

Mill, T., W.R. Mabey, and D.G. Hendry. 1979. Test protocols for environmental processes: Oxidation in water. EPA Draft Report. EPA Contract 68-03-2227.

Mill, T. 1979. Structure reactivity conditions for environmental reactions. EPA Report - EPA 560/11-79-012.

Smith, J.H., D.C. Bomberger, and D.M. Haynes. 1979. Prediction of the volatilization rates of high volatility chemicals for natural water bodies. Paper submitted for publication. Study supported by NSF Grant No. PFR78-10691.

Whitman, W.G. 1923. Preliminary experimental confirmation of the 2-film theory of gas absorption. Chem. Metall. Eng. 29:146-148.

Zepp, R.G. and D.M. Cline. 1977. Rates of direct photolysis in aquatic environments. Environ. Sci. Technol. 11:359-366.

3. DETERMINATION OF WATER-RELATED ENVIRONMENTAL FATE: PROCEDURES, METHODS, AND REPORT FORMAT

3.1 Identification and Collection of Data

3.1.1 Automated Data Searches

Computerized databases were used as one of the intitial steps in collecting data on priority pollutants and fate-related processes. The bulk of the automated data activity was conducted between December 1977 and March 1978. The following databases were searched for all priority pollutants:

AGRICOLA
APTIC
ASFA
BIOSIS
CHEM ABSTRACTS
COMPENDEX
DISSERTATION ABSTRACTS
ENERGYLINE
ENVIROLINE
EPB
NTIS
OCEANIC ABSTRACTS
POLLUTION ABSTRACTS
SCISEARCH
SSIE CURRENT RESEARCH

For all databases except CHEM ABSTRACTS, every citation containing the priority pollutant's name or synonym was selected and combined into a single data set using the Boolean operator "or." From this data set, specific citations were further evaluated using such keywords as "volatility, photolysis, adsorption, etc.," and compiled into a second data set. The Boolean operator "and" was used to combine the two data sets and yield the final data set with one or more chemical names and one or more keyword identifiers.

The CHEM ABSTRACTS database was searched using the combination of registry numbers and chemical area (e.g., photolytic reaction mechanisms) to create a data set. In the case of some chemical groups (such as polycyclic aromatic hydrocarbons) all data were retrieved without qualification.

3.1.2 Manual Data Search

The automated data search was followed by a comprehensive manual search of the literature. The scope and depth of the search varied for each chemical. Both published and unpublished data were collected, reviewed and filed for use in developing the individual fate chapters. References within reviewed papers were also used to identify literature not found by computer searching methods. Journal articles published up to January 1979 were included.

3.2 Estimation of Physical and Chemical Parameters

For many of the priority pollutants, basic data on physicochemical properties were not available. Since information on vapor pressure, octanol/water partitioning, and solubility in water was necessary to evaluate fate and transport processes, these parameters were estimated when no literature values were found. The methods used to estimate these parameters are discussed below.

3.2.1 Vapor Pressure

Vapor pressure at 25°C was estimated by using one of four methods, in descending order of preference:

1. Where constants were available in handbooks, vapor pressure was calculated.

2. Where data for vapor pressure at temperatures bracketing 25°C (e.g., 20°C and 30°C) was available from the literature, an interpolation was used.

3. Tables compiled by Driesbach (1952) were consulted. These tables relate pressure, volume, and temperature for major "Cox Chart" chemical families.

4. The Clausius-Clapeyron equation was employed.

The above methods are summarized below.

Calculation/interpolation. Vapor pressures of many compounds were reported for temperatures above and below 25°C, but not specifically for 25°C. For these compounds, the vapor pressure at 25°C was calculated using the following formula (Weast 1974):

$$\log_{10} P = (-0.2185\ A/K) + B \qquad (1)$$

where P is the vapor pressure expressed in torr, A is the molar heat of vaporization, K is the temperature in degrees Kelvin, and B is a constant. For a given compound, A and B are unique and can be assumed constant over a moderate temperature range. Values for A and B are tabulated in Weast (1974) for several of the priority pollutants and can be used to calculate vapor pressures directly.

Where two or more values of vapor pressure were given in the literature for two or more temperatures bracketing 25°C, and the constants A and B were not reported, a linear interpolation method was employed. Since Equation (1) has the general linear form of $y = mx + b$, where two sets of ordered pairs (K_1, P_1) and (K_2, P_2) were known, A and B could be calculated. These constants were then substituted into Equation (1) to calculate P at K = 298° (=25°C).

Tabular Values for Chemical Families. If equation (1) could not be employed because of insufficient data, tables in Driesbach (1952) were consulted. These tables were developed for the "Cox Chart" chemical families (e.g., naphthalenes, halo-benzenes with saturated side chains, phenols), using Antoine's equation, a variant of equation (1). To estimate vapor pressure at 25°C, it is necessary to know the boiling point at 760 torr and the chemical family to which a compound belongs. The appropriate table is then referenced for an estimated vapor pressure.

Clausius - Clapeyron Equation. If neither of the aforementioned methods could be used, vapor pressure was calculated using the Clausius-Clapeyron Equation:

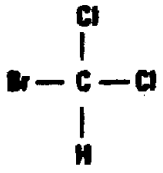
$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_v}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \qquad (2)$$

where P is vapor pressure in torr, ΔH_v is the molar heat of vaporization, T is temperature in degrees Kelvin, R is the gas law constant (1.99 cal./mole °K), and the subscripts 1 and 2 represent two different temperatures. To solve this equation for vapor pressure at 25°C, the boiling point and heat of vaporization must be known. Although the vapor pressure calculated by this formula is generally not as accurate as the estimates derived from the other methods, the Clausius-Clapeyron equation is useful for providing a rough estimate.

3.2.2 Octanol/Water Partition Coefficient

Several investigators, notably Hansch et al. (1974), Leo et al. (1971), and Tute (1971), have demonstrated that log P (log of the octanol/-

water partition coefficient) can be estimated based on the functional groups in organic molecules. The basic approach used in this method is to consider a molecule as the sum of its functional groups. These functional groups can be assumed to cause a certain proportion of the partitioning between octanol and water. An index value called the "π" value has been estimated for many of the common functional groups; this value can be positive or negative. Estimated π values for various functional groups are listed in Tute (1971). These values are summed to give an approximation of log P. An example of this calculation is given for dichlorobromomethane:



This molecule can be divided into the following components with corresponding π values:

	CH	0.50
2 x	Cl	2 x 0.39 = 0.78
	Br	0.60
		Σ = 1.88

The estimated log P for dichlorobromomethane is thus 1.88. For further information on estimation of log P values, the reader is referred to Tute (1971) and Leo et al. (1971).

3.2.3 Aqueous Solubility

Although aqueous solubility is readily available for most of the priority pollutants, there were several cases where an estimate had to be made. A number of different techniques are documented in the literature, but the one chosen for this study was that of Moriguchi (1975). This technique is based on factoring water solubility into two intrinsic components: free molecular volume and hydrophilic effect of polar groups.

Moriguchi (1975) tested six different additive parameters relating to molecular volume and concluded that Quayle's parachor (Quayle 1953) was most satisfactory for predictive purposes. Like the techniques used for estimating octanol/water partitioning, Quayle's parachor is calculated by considering a molecule as the sum of its functional groups. Each group is assigned a certain value, based on interpretation of empirical data (Quayle 1953). Quayle's parachor, and other parachors, were developed as physical parameters which can be readily correlated with the structure of organic compounds to estimate molecular volumes.

The second component in Moriguchi's (1975) technique, hydrophilic effect of polar groups, accounts for solute-solvent and solute-solute interactions. By examining empirical data, a "hydrophilic group effect" factor was calculated for various functional groups; factors are listed in Moriguchi (1975).

Finally, after calculating the Quayle's parachor for a molecule and referencing the appropriate hydrophilic group factor, aqueous solubility can be estimated via the following formula:

$$\log_{10}\left(\frac{1}{S}\right) = \left(1.50\right)\bullet\left(P_r\right)\bullet\left(10^{-2}\right) - \left(1.51\right)\bullet\left(E_w\right) - 1.01 \qquad (3)$$

where S is the water solubility in molal concentration, P_r is Quayle's parachor, and E_w is the hydrophilic group factor. This formula appears to be fairly reliable: when known aqueous solubilities for 156 compounds were tested against estimated solubility, the correlation coefficient was r = 0.962 (Moriguchi 1975).

For more information on this method of estimating solubility, the reader is referred to Moriguchi (1975) and Quayle (1953).

3.3 Review and Assessment of Data

3.3.1 Evaluation of Data

The literature was searched, using both automated and manual methods, by individuals who were assigned specific chemicals or chemical groups. There was substantial interchange of information among the individuals assigned to the project (including individuals in EPA and both contractors), and periodic meetings were held to discuss common problems and share various interpretations of the fate literature. The basic Phase I evaluation lasted for approximately 5 months, with an interim draft submitted at the end of the period. There were insufficient data to determine many of the compounds' most probable aquatic fate. For others, data were sufficient to adequately describe the dominant transport and transportation processes. The data collected after 5 months were evaluated and used to prepare the interim draft report.

3.3.2 Preparation of Interim Draft

Each individual assigned a compound or group of compounds was responsible for writing an interim draft report summarizing the data evaluated at the end of 5 months. These reports were carefully reviewed by the Contractor's task manager and, whenever necessary, meetings were held

among staff members to review the literature and help ascertain the predominant transport and transportation process. In addition to summarizing the data reviewed, the interim draft reports highlighted data gaps and areas where information was insufficient for drawing conclusions. As a result, the interim draft reports focused on additional data needs for each chemical, and provided the direction for additional data analysis.

3.3.3 The Peer Review Process

Additional literature was collected during months 7,8, and 9 of the program and a considerable amount of effort was put into evaluating the collected literature. In many cases, original authors were actually contacted by telephone to clarify their results, and in most cases, literature was traced back to its primary source or author; secondary references were used only when no alternatives existed. As a result of this thorough literature review and comprehensive evaluation, a more complete picture of the aquatic fate of many of the compounds was obtained. Still, for some compounds, there was not enough information to adequately determine the aquatic fate and more work was necessary.

To satisfy the EPA's standards for the technical accuracy of each fate chapter and to make each chapter read as if it were written by the same author, an elaborate internal peer review process (EPA and the contractors) was used. Each scientist prepared a detailed oral presentation covering his or her chemicals which was presented at a meeting attended by senior scientists and project staff within the organization and the EPA task manager and staff members. During this presentation, data were summarized, their weaknesses and strengths discussed, and conclusions reviewed as a group, with general concurrence attained for each chemical. This internal peer review process brought about a stimulating exchange of information and ideas. Conclusions reached were based on the group's consensus rather than the assessment of one individual.

3.3.4 Preparation of Final Draft

The final draft report (a separate fate chapter for each chemical) was prepared on the basis of the conclusions reached during the internal peer review. This report was substantially more comprehensive than the interim draft because it covered more data and was much more carefully reviewed and evaluated by other individuals in addition to the principal author. The report format was agreed upon for the final draft and a common expression of data confidence or reliability was followed by all authors. A uniform method of citing literature was adopted, and all chapters conformed to this method.

The chapters were typed using computerized word processing equipment which eventually facilitated final changes. The final draft report was distributed to approximately 75 individuals and/or organizations for review and comment; about half of this number were EPA personnel in other program offices and research laboratories who were not participants in the internal peer review. The remaining half consisted of industrial or academic personnel and individuals with special knowledge and expertise about specific chemical groups. The distribution of the final draft for external peer review (March to September 1979) completed the first phase of the program.

3.3.5 Preparation of the Final Report

The final fate chapters, as they appear in this two-volume report, were based on the draft final report but included the incorporation of current literature (since September of 1977) and those comments (that were considered appropriate) which were submitted by the external reviewers. In some cases individual compounds were combined into one chapter (e.g., phthalate esters, polychlorinated biphenyls) and some chapters were completely revised requiring an extensive technical rewrite. Examples of the latter were the chapters on metals; the draft final did not adequately consider how polluted environments affect the behavior of the metals, especially with regard to metal-organic interactions.

Each author prepared a brief technical letter to EPA describing the changes that were to be made in the final report based on the external reviewers' comments. This provided a mechanism for EPA's continued participation in the peer review process. In addition to the final fate chapters, an introductory section and a description of the transport and transformation processes were prepared and are included in this final report.

In summary, this report represents over two years of careful data collection and review. It is the product of an extensive exchange of information and ideas which underwent a thorough peer review. The result, we believe, is a document that meets the objectives of the program.

3.3.6 Confidence of Data

One of the basic objectives of the study was to indicate the degree of confidence for the conclusions reached. Each fate chapter in this document contains a table which summarizes the aquatic fate information. The last column in the table describes the confidence of the summary statement made from the data reviewed. Three somewhat subjective levels of confidence were used -- Low, Medium, and High. A brief description of these levels follows.

High Confidence. This usually required that the data reviewed be quantitative; rate constants and rates were either explicitly described or could be calculated from the results. In addition, experiments were considered relevant if done at typical ambient environmental conditions of temperature, pH, etc. Normally, corroborating evidence from an unrelated associate or experiment (i.e., "a second opinion") was also required to place data in the "high" category. In many instances, the chemical structure itself and its inertness to certain processes (e.g., no hydrolyzable groups for hydrolysis) was sufficient to place a summary statement in the "high" category.

Medium Confidence. Qualitative data about a particular chemical (i.e., no rate data or information from which rates could be derived) were typically given a "medium" confidence ranking. In some cases, the data were collected at somewhat irrelevent conditions (e.g., temperature, pH) for the purpose of this study or in such a way that only a qualitative judgment could be made about the results. Some quantitative data were placed in this category if there were no other data to corroborate the results. Quantitative data reported for a different but structurally related compound were sometimes given a "medium" ranking if the different compound was thought to react analogously to the actual compound being studied.

Low Confidence. Summary statements made speculatively, or based on theoretical estimates or calculations, were given a "low" ranking of confidence. In many cases, the reviewers believed a particular process to be important, based on theory; however, a "low" confidence was assigned to the statement when there were no actual investigations performed on the particular chemical. If the quantitative data were characterized by controversy over rates and mechanisms, then usually the confidence was given a "low" ranking.

3.4 Report Format

The first four chapters of this report serve as introductory and explanatory material for the individual fate chapters that follow. Chapters 5 through 105 are reports for each chemical or group of chemicals comprising the 129 priority pollutants.

The fate chapters for each organic priority pollutant (chapters 20 through 105) generally follow a uniform format. For several chemicals (some well-studied pesticides, for example), however, there are slight deviations from the format presented below. For an organic chemical in a typical chapter "X", the following sections are included:

X.1 Statement of Probable Fate

This section summarizes the entire chapter. A statement on the probable transport and aquatic fate mechanisms is given. Other processes thought to be possibly important are identified.

X.2 Identification

This section includes the chemical structure, alternate chemical names, the Chemical Abstract Service Registry Number (CAS), and the Toxic Substances List (TSL) number (as found in the 1977 NIOSH Registry of Toxic Effects of Chemical Substances).

X.3 Physical Properties

This includes literature or calculated values for: molecular weight, melting point, boiling point, vapor pressure, water solubility, and octanol/water partition coefficient.

X.4 Summary of Fate Data

X.4.1 Photolysis

Statements are made on direct photolysis in aquatic systems and, if volatile, in the atmosphere. A discussion of available spectral data is also included, where relevant.

X.4.2 Oxidation

Reactions which involve oxidation processes are described.

X.4.3 Hydrolysis

Data on expected hydrolysis under natural conditions (temp. 0°C - 30°C, pH 6-9) are presented.

X.4.4 Volatilization

Experimental data or information are presented when available; if not, inferences are drawn based on vapor pressure and solubility data.

X.4.5 Sorption

Specific experimental evidence (e.g., % adsorption on clay) is presented. Without these data, inferences are drawn based on partitioning values and other data.

X.4.6 Bioaccumulation

Same as for sorption.

X.4.7 Biotransformation and Biodegradation

A summary of data on *in vivo* and *in vitro* degradation is presented.

X.4.8 Other Reactions (Optional, depending on the chemical)

All data on processes that cannot be specifically characterized in the previous sections (X.4.1 through X.4.7) are presented here.

X.4.9 Microcosm Studies, Field Studies, and Modelling (Optional, depending on the chemical)

Pertinent data from microcosm studies, field studies, and modelling evaluations are presented in detail in this section.

X.5 Data Summary

A summary matrix is presented with an identification of the most probable fate process(es) included. Also, all literature or calculated rate constants or half-lives are summarized.

X.6 Literature Cited

All literature cited in the "X" chapter are presented using the American Institute of Biological Sciences standard format (AIBS, 3rd Edition).

The format for the metals chapters (chapters 5-19) is slightly different from that shown above. For metals, the identification section of the report includes a discussion on the geochemistry of the substance. Also, the oxidation/reduction and hydrolysis sections were combined and expanded into a section entitled "chemical speciation," which deals with the environmental chemistry of each metal. The data summary matrix was simplified because, barring radioactive decay, there are no possible half-lives for metals.

3.5 Literature Cited

Dreisbach, R.R. 1952. Pressure-volume-temperature relationship of organic compounds. Handbook Publishers, Sandusky, Ohio. p.3-260.

Hansch, C., A. Vittoria, C. Silipo, and P.Y.C. Jow. 1974. Partition coefficients and the structure-activity relationship of the anesthetic gases. J. Med. Chem. 18(6):546-548.

Leo, A., C. Hansch, and D. Elkins. 1971. Partition coefficients and their uses. Chem. Rev. 71(6):525-565.

Moriguchi, I. 1975. Quantitative structure-activity studies. I. Parameters relating to hydrophobicity. Chem. Pharm. Bull. 23(2):247-257.

Quayle, O.R. 1953. The parachors of organic compounds. Chem. Reviews 53:439-585.

Tute, M.S. 1971. Principles and practice of Hansch analysis: a guide to structure-activity correlation for the medicinal chemist. Adv. Drug Res. 6:1-77.

Weast, R.C. (ed.). 1974. CRC Handbook of chemistry and physics, 54th edition. CRC Press, Cleveland, Ohio. p.D-162 to D-188.

4. CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

The literature search in support of these efforts, comprising both automated and manual searches in addition to direct contacts with current workers in the field and chemical manufacturers, was thorough. This conclusion has been corroborated by technical reviewers from industry, universities, and the U.S. Environmental Protection Agency.

In general, the behavior of most of the metals but only a few of the organics has been extensively studied in natural surface water systems. The well-studied organics include PCBs, DDT, chloroethene (vinyl chloride), pentachlorophenol, and bis(2-ethylhexyl) phthalate. Despite the relatively large amount of effort expended on these compounds, quantitative models of their environmental transport and fate are, at present, somewhat inconclusive. For the rest of the organic pollutants discussed in these chapters, data sufficient to quantitatively define the principal transport and fate processes were not available, with the exception of a few specialized cases. The information obtained for most pollutants, however, was sufficient to qualitatively identify the importance of the discrete processes considered.

Conclusions regarding aspects of environmental behavior of pollutant groups are listed below:

1. Metals. Transport and fate of metals are, in general, controlled by sorption processes in the sediments. The metal-organic relationships, both in the sediments and in the water column, increase in importance as the organic content increases and strongly affect metal transport in polluted areas, for example, industrialized urban areas. These metal-organic relationships have not been thoroughly studied.

2. Chlorinated Pesticides. The fate of most chlorinated pesticides in the aquatic environment will be determined by sorption, volatilization, and biotransformation. Very little reliable quantitative data are available for assessing the half-lives of these processes, however. Except for the rapid hydrolysis of heptachlor, there is insufficient and sometimes contradictory information to support a conclusion that chemical transformation processes will be important in aquatic environments.

3. Halogenated Aliphatic Hydrocarbons. Transport and fate of halogenated aliphatics are generally dominated by volatilization, so that their ultimate fate typically involves atmospheric processes. Most of the data available on rates of volatilization are valid only for comparisons (relative rates) between compounds.

4. Halogenated Ethers and Selected Monocyclic Aromatics. For several groupings of compounds, including the haloethers, phenols, phthalates, and benzene and its derivatives, it is typical that only one or two members of each group have been studied extensively. Extrapolation of environmental behavior to other members of the groupings was performed when feasible, but wide variations in chemical and physical properties limit the accuracy of such extrapolations.

5. Polycyclic Aromatic Hydrocarbons. The behavior of the polycyclic aromatic hydrocarbons was found to be a function of the number of rings present, and these compounds were grouped accordingly. In general, it appears that the important processes for these compounds are adsorption onto particulates, sedimentation, and subsequent biodegradation.

6. Nitrophenols, Nitrosamines, and Miscellaneous Compounds. For several groups of compounds, almost no environmental data were found. These groups include the nitrophenols, the nitrosamines, and various other nitrogen-containing compounds. In many of these cases, environmental scenarios could be developed from research studies conducted for purposes other than the determination of environmental behavior, and the scenarios could be used to indicate the relative importance of the processes considered.

An annotated table of conclusions for each of the 129 priority pollutants is presented in Section 4.3.

4.2 Recommendations

Based on the conclusions presented above, the general recommendation is made that the state of knowledge of environmental transport and fate of these (and other) pollutants should be improved through studies directed specifically towards definition of their environmental behavior. In addition, unavailable physical constants and process rates should be determined. Some of the more important areas of needed research are listed below.

1. Metal-organic relationships and their effects on metal transport in surface waters should be defined.

2. Definitive studies on the importance of volatilization of pollutants from water relative to the other transport and fate processes should be conducted for specific pollutants and groups.

3. A determination should be made of the importance of toxic products resulting from reactions of the pollutants in the environment and in water treatment facilities.

4. Further work is recommended on the development and validation of fate models, so that the data generated by the above studies can be used effectively in predicting the environmental fate of chemicals.

4.3 Summary of Conclusions

An annoted table of conclusions for each of the 129 priority pollutants, by chemical group, is presented in Table 4-1. Two ratings are presented for each compound and related fate and transport processes. The first rating (Yes, No, or Uncertain) is a statement of importance, and the second is a numerical rating dealing with the depth of available supportive data. These ratings were assigned by the major author of the chapter on each compound, or group of compounds, and involved a certain degree of subjective judgment. The application of these ratings may therefore vary slightly with each chemical group.

Table 4-1 condenses the large amount of information reviewed in each pollutant chapter into a single summary line statement about the water-related fate and transport of 129 priority pollutants. For a specific compound, therefore, the reader is encouraged to consult the chapter devoted to that compound before making final judgments.

TABLE 4-1

SUMMARY OF CONCLUSIONS FOR THE TRANSPORT AND FATE OF PRIORITY POLLUTANTS:

A. Metals and Inorganics

Chapter No.	Chemical	Is the Process Important for Aquatic Transport? (See Key Below)			Is the Process Important in Determining Aquatic Fate? (See Key Below)			
		Volatilization	Sorption	Transport Downstream	Photolysis	Chemical Speciation	Bioaccumulation	Biotransformation/ Biodegradation
5	Antimony	UNCT(2)	YES(2)	YES(2)	NO(3)	YES(1)	NO(2)	YES(3)
6	Arsenic	YES(1)	YES(1)	YES(1)	NO(3)	YES(1)	YES(2)	YES(1)
7	Asbestos	NO(3)	NO(2)	YES(1)	NO(3)	NO(2)	NO(3)	NO(3)
8	Beryllium	NO(3)	YES(3)	YES(3)	NO(3)	YES(2)	UNCT(2)	NO(3)
9	Cadmium	NO(2)	YES(1)	YES(1)	NO(3)	YES(1)	YES(1)	NO(3)
10	Chromium	NO(3)	YES(1)	YES(2)	NO(3)	YES(2)	YES(1)	NO(3)
11	Copper	NO(3)	YES(1)	YES(1)	NO(2)	YES(1)	YES(1)	NO(3)
12	Cyanide	YES(1)	NO(2)	NO(2)	YES(1)	UNCT(2)	NO(2)	YES(1)
13	Lead	UNCT(1)	YES(1)	YES(1)	UNCT(1)	YES(1)	YES(1)	YES(1)
14	Mercury	YES(1)	YES(1)	YES(1)	YES(2)	YES(1)	YES(1)	YES(1)
15	Nickel	NO(3)	YES(1)	YES(1)	NO(3)	YES(2)	NO(2)	NO(3)
16	Selenium	UNCT(2)	YES(1)	YES(1)	NO(3)	YES(2)	UNCT(1)	YES(1)
17	Silver	NO(3)	YES(1)	YES(1)	NO(2)	YES(1)	UNCT(1)	NO(3)
18	Thallium	NO(3)	YES(1)	YES(1)	NO(2)	YES(1)	UNCT(2)	NO(3)
19	Zinc	NO(3)	YES(1)	YES(1)	NO(3)	YES(1)	YES(1)	NO(3)

Key:

For each chemical and related process, two ratings are presented. The first is a statement of importance and can be one of the following: YES, NO, or UNCT (for uncertain). The second is a numerical rating, dealing with available supporting data, explained below:

(1). There are environmental data available to support this conclusion.

(2). There are no direct conclusive environmental data; some laboratory data can be extrapolated to support conclusions.

(3). There are no supporting data available; evidence is drawn from theoretical calculations, estimates, results for similar chemicals, and inferences.

TABLE 4-1 (Cont.)

SUMMARY OF CONCLUSIONS FOR THE TRANSPORT AND FATE OF PRIORITY POLLUTANTS:

B. Pesticides, PCBs, and Related Compounds

Chapter No.	Chemical	Is the Process Important for Aquatic Transport? (See Key Below)			Is the Process Important in Determining Aquatic Fate? (See Key Below)			
		Volatilization	Sorption	Transport Downstream	Photolysis/ Oxidation	Hydrolysis	Bioaccumulation	Biotransformation/ Biodegradation
20	Acrolein	UNCT(2)	NO(2)	UNCT(2)	UNCT(2)	NO(1)	UNCT(2)	YES(2)
21	Aldrin	UNCT(2)	YES(2)	UNCT(2)	UNCT(2)	NO(1)	YES(1)	YES(2)
22	Chlordane	UNCT(2)	UNCT(2)	UNCT(2)	UNCT(2)	NO(1)	YES(1)	UNCT(2)
23	DDD	YES(2)	YES(1)	UNCT(2)	UNCT(2)	UNCT(1)	YES(1)	UNCT(2)
24	DDE	YES(2)	YES(1)	UNCT(2)	UNCT(2)	NO(1)	YES(1)	UNCT(2)
25	DDT	YES(2)	YES(1)	UNCT(2)	UNCT(2)	UNCT(1)	YES(1)	UNCT(2)
26	Dieldrin	UNCT(2)	YES(2)	UNCT(2)	UNCT(2)	NO(1)	YES(1)	UNCT(2)
27	Endosulfan and Endosulfan Sulfate	UNCT(3)	YES(3)	UNCT(3)	UNCT(2)	YES(1)	UNCT(2)	YES(2)
28	Endrin and Endrin Aldehyde	UNCT(2)	UNCT(2)	UNCT(2)	UNCT(2)	NO(1)	YES(1)	UNCT(2)
29	Heptachlor	UNCT(2)	NO(2)	UNCT(2)	UNCT(2)	YES(1)	UNCT(1)	NO(1)
30	Heptachlor Epoxide	UNCT(2)	YES(1)	UNCT(2)	UNCT(2)	NO(1)	YES(1)	YES(2)
31	Hexachlorocyclohexane (α, β, δ isomers)	UNCT(2)	UNCT(2)	UNCT(2)	NO(1)	NO(1)	UNCT(1)	YES(2)
32	γ-Hexachlorocyclohexane (Lindane)	UNCT(2)	UNCT(2)	UNCT(1)	NO(1)	NO(1)	UNCT(1)	YES(2)
33	Isophorone	UNCT(3)	NO(3)	YES(3)	UNCT(2)	NO(1)	UNCT(2)	UNCT(2)
34	TCDD	UNCT(2)	YES(1)	YES(3)	NO(2)	NO(1)	YES(1)	UNCT(2)
35	Toxaphene	UNCT(2)	YES(1)	YES(2)	NO(2)	NO(1)	YES(1)	UNCT(1)
36	Polychlorinated Biphenyls	YES(2)	YES(1)	UNCT(3)	UNCT(3)	NO(3)	YES(1)	NO(1)
37	2-Chloronaphthalene	UNCT(3)	UNCT(3)	UNCT(3)	UNCT(2)	NO(3)	UNCT(2)	YES(2)

Key:

For each chemical and related process, two ratings are presented. The first is a statement of importance and can be one of the following: YES, NO, or UNCT (for uncertain). The second is a numerical rating, dealing with available supporting data, explained below:

(1). Quantitative (rate constants, half-lives) data are available to support conclusions.

(2). Qualitative description only; there are no direct environmental data, however, some laboratory data can be extrapolated to support conclusions.

(3). There are no supporting data available; evidence is drawn from theoretical calculations, estimates, results for similar chemicals, and inferences.

TABLE 4-1 (Cont.)

SUMMARY OF CONCLUSIONS FOR THE TRANSPORT AND FATE OF PRIORITY POLLUTANTS:

C. Halogenated Aliphatic Hydrocarbons

Chapter No.	Chemical	Is the Process Important for Aquatic Transport? (See Key Below)			Is the Process Important in Determining Aquatic Fate? (See Key Below)			
		Volatilization	Sorption	Transport Downstream	Photolysis/ Oxidation	Hydrolysis	Bioaccumulation	Biotransformation/ Biodegradation
38	Chloromethane	YES(2)	NO(3)	UNCT(3)	NO(3)	NO(1)	NO(3)	NO(3)
39	Dichloromethane	YES(2)	NO(2)	UNCT(3)	NO(2)	NO(1)	NO(3)	NO(3)
40	Trichloromethane	YES(2)	NO(2)	UNCT(3)	NO(2)	NO(1)	NO(3)	NO(3)
41	Tetrachloromethane	YES(2)	NO(2)	UNCT(3)	NO(3)	NO(1)	UNCT(2)	NO(3)
42	Chloroethane	YES(2)	NO(2)	UNCT(3)	NO(3)	NO(1)	NO(3)	NO(3)
43	1,1-Dichloroethane	YES(2)	NO(3)	UNCT(3)	NO(3)	NO(3)	NO(3)	NO(3)
44	1,2-Dichloroethane	YES(2)	NO(3)	UNCT(3)	NO(3)	NO(3)	NO(3)	UNCT(2)
45	1,1,1-Trichloroethane	YES(2)	NO(2)	UNCT(3)	NO(2)	NO(3)	NO(3)	NO(3)
46	1,1,2-Trichloroethane	YES(2)	NO(3)	UNCT(3)	NO(2)	NO(3)	NO(3)	NO(3)
47	1,1,2,2-Tetrachloroethane	UNCT(2)	NO(3)	UNCT(3)	NO(2)	NO(3)	UNCT(3)	NO(3)
48	Hexachloroethane	UNCT(2)	UNCT(3)	NO(3)	NO(3)	UNCT(3)	UNCT(3)	UNCT(3)
49	Chloroethene	YES(2)	NO(2)	NO(3)	NO(2)	UNCT(3)	NO(2)	NO(2)
50	1,1-Dichloroethene	YES(2)	NO(3)	UNCT(3)	NO(3)	NO(3)	NO(3)	NO(3)
51	1,2-trans-Dichloroethene	YES(2)	NO(3)	UNCT(3)	NO(3)	NO(3)	NO(3)	NO(3)
52	Trichloroethene	YES(2)	NO(2)	UNCT(3)	NO(2)	NO(2)	UNCT(2)	UNCT(3)
53	Tetrachloroethene	YES(2)	NO(2)	UNCT(3)	NO(2)	NO(2)	UNCT(2)	UNCT(3)
54	1,2-Dichloropropane	YES(3)	UNCT(3)	UNCT(3)	NO(3)	UNCT(3)	UNCT(3)	UNCT(3)
55	1,3-Dichloropropene	YES(2)	UNCT(3)	UNCT(3)	NO(3)	UNCT(3)	NO(3)	UNCT(3)
56	Hexachlorobutadiene	UNCT(2)	YES(2)	NO(3)	NO(3)	UNCT(3)	YES(2)	UNCT(3)
57	Hexachlorocyclopentadiene	YES(3)	YES(3)	NO(3)	YES(2)	YES(1)	YES(2)	NO(2)
58	Bromomethane	YES(3)	NO(3)	UNCT(3)	NO(3)	YES(1)	NO(3)	NO(3)
59	Bromodichloromethane	UNCT(3)	UNCT(3)	UNCT(3)	UNCT(3)	NO(1)	UNCT(3)	UNCT(3)
60	Dibromochloromethane	UNCT(3)	UNCT(3)	UNCT(3)	UNCT(3)	NO(1)	UNCT(3)	UNCT(3)
61	Tribromomethane	YES(3)	UNCT(3)	UNCT(3)	UNCT(3)	NO(1)	UNCT(3)	UNCT(3)
62	Dichlorodifluoromethane	YES(3)	UNCT(3)	UNCT(3)	NO(3)	NO(2)	UNCT(3)	UNCT(3)
63	Trichlorofluoromethane	YES(3)	UNCT(3)	UNCT(3)	NO(3)	NO(2)	UNCT(3)	UNCT(3)

Key:

For each chemical and related process, two ratings are presented. The first is a statement of importance and can be one of the following: YES, NO, or UNCT (for uncertain). The second is a numerical rating, dealing with available supporting data, explained below:

(1). Quantitative (rate constants, half-lives) data are available to support conclusions.

(2). Qualitative description only; there are no direct environmental data, however, some laboratory data can be extrapolated to support conclusions.

(3). There are no supporting data available; evidence is drawn from theoretical calculations, estimates, results for similar chemicals, and inferences.

TABLE 4-1 (Cont.)

SUMMARY OF CONCLUSIONS FOR THE TRANSPORT AND FATE OF PRIORITY POLLUTANTS:

D. Halogenated Ethers

Chapter No.	Chemical	Is the Process Important for Aquatic Transport? (See Key Below)			Is the Process Important in Determining Aquatic Fate? (See Key Below)			
		Volatilization	Sorption	Transport Downstream	Photolysis/ Oxidation	Hydrolysis	Bioaccumulation	Biotransformation/ Biodegradation
64	Bis(chloromethyl)ether	NO(2)	NO(2)	NO(3)	NO(2)	YES(1)	NO(1)	NO(2)
65	Bis(2-chloroethyl)ether	YES(3)	NO(3)	UNCT(3)	NO(3)	NO(3)	NO(3)	NO(3)
66	Bis(2-chloroisopropyl)ether	YES(3)	NO(3)	UNCT(3)	NO(3)	UNCT(3)	NO(3)	UNCT(3)
67	2-Chloroethyl vinyl ether	YES(3)	NO(3)	UNCT(3)	NO(3)	UNCT(1)	NO(3)	UNCT(3)
68	4-Chlorophenyl phenyl ether	UNCT(2)	UNCT(2)	UNCT(3)	UNCT(3)	NO(3)	UNCT(1)	UNCT(2)
69	4-Bromophenyl phenyl ether	UNCT(3)	UNCT(3)	UNCT(3)	UNCT(3)	NO(3)	UNCT(3)	UNCT(3)
70	Bis(2-chloroethoxy)methane	NO(2)	NO(2)	YES(3)	NO(2)	UNCT(3)	NO(3)	UNCT(3)

Key:

For each chemical and related process, two ratings are presented. The first is a statement of importance and can be one of the following: YES, NO, or UNCT (for uncertain). The second is a numerical rating, dealing with available supporting data, explained below:

(1). Quantitative (rate constants, half-lives) data are available to support conclusions.

(2). Qualitative description only; there are no direct environmental data, however, some laboratory data can be extrapolated to support conclusions.

(3). There are no supporting data available; evidence is drawn from theoretical calculations, estimates, results for similar chemicals, and inferences.

TABLE 4-1 (Cont.)

SUMMARY OF CONCLUSIONS FOR THE TRANSPORT AND FATE OF PRIORITY POLLUTANTS:

E. Monocyclic Aromatics

Chapter No.	Chemical	Is the Process Important for Aquatic Transport? (See Key Below)			Is the Process Important in Determining Aquatic Fate? (See Key Below)			
		Volatilization	Sorption	Transport Downstream	Photolysis/ Oxidation	Hydrolysis	Bioaccumulation	Biotransformation/ Biodegradation
71	Benzene	YES(1)	UNCT(3)	UNCT(3)	NO(2)	NO(3)	NO(3)	UNCT(2)
72	Chlorobenzene	YES(2)	UNCT(3)	UNCT(3)	NO(3)	NO(3)	UNCT(2)	UNCT(2)
73	1,2-Dichlorobenzene	YES(2)	UNCT(3)	UNCT(3)	NO(3)	NO(3)	UNCT(2)	UNCT(2)
74	1,3-Dichlorobenzene	UNCT(3)	UNCT(3)	UNCT(3)	NO(3)	NO(3)	YES(3)	UNCT(3)
75	1,4-Dichlorobenzene	UNCT(3)	UNCT(3)	UNCT(3)	NO(3)	NO(3)	YES(3)	UNCT(3)
76	1,2,4-Trichlorobenzene	UNCT(3)	UNCT(3)	UNCT(3)	NO(3)	NO(3)	YES(3)	UNCT(3)
77	Hexachlorobenzene	UNCT(3)	YES(2)	UNCT(3)	NO(3)	NO(3)	YES(1)	NO(3)
78	Ethylbenzene	YES(2)	UNCT(3)	UNCT(3)	NO(3)	NO(3)	NO(3)	UNCT(3)
79	Nitrobenzene	UNCT(3)	UNCT(3)	UNCT(3)	UNCT(3)	NO(3)	NO(3)	UNCT(3)
80	Toluene	YES(2)	UNCT(3)	UNCT(3)	NO(3)	NO(3)	NO(3)	UNCT(3)
81	2,4-Dinitrotoluene	NO(3)	YES(2)	UNCT(3)	YES(2)	NO(3)	UNCT(3)	UNCT(3)
82	2,6-Dinitrotoluene	NO(3)	YES(2)	UNCT(3)	YES(2)	NO(3)	UNCT(3)	UNCT(3)
83	Phenol	UNCT(2)	NO(2)	UNCT(2)	YES(2)	NO(2)	NO(2)	YES(1)
84	2-Chlorophenol	NO(3)	NO(3)	UNCT(3)	UNCT(3)	NO(3)	UNCT(2)	UNCT(3)
85	2,4-Dichlorophenol	NO(3)	NO(3)	UNCT(3)	NO(3)	NO(3)	UNCT(3)	YES(2)
86	2,4,6-Trichlorophenol	NO(3)	UNCT(3)	UNCT(3)	NO(3)	NO(3)	UNCT(3)	UNCT(3)
87	Pentachlorophenol	NO(3)	YES(1)	YES(1)	YES(1)	NO(3)	YES(1)	YES(1)
88	2-Nitrophenol	NO(2)	YES(2)	UNCT(3)	YES(3)	UNCT(3)	NO(3)	NO(1)
89	4-Nitrophenol	NO(1)	YES(1)	UNCT(3)	YES(3)	UNCT(3)	NO(3)	NO(1)
90	2,4-Dinitrophenol	NO(2)	YES(3)	UNCT(3)	YES(3)	UNCT(3)	NO(3)	UNCT(2)
91	2,4-Dimethyl phenol	NO(3)	UNCT(3)	UNCT(3)	YES(3)	NO(2)	UNCT(3)	UNCT(3)
92	p-Chloro-m-cresol	NO(3)	NO(3)	UNCT(3)	YES(3)	NO(3)	NO(3)	UNCT(3)
93	4,6-Dinitro-o-cresol	NO(3)	YES(3)	UNCT(3)	YES(3)	NO(3)	UNCT(3)	UNCT(3)

Key:

For each chemical and related process, two ratings are presented. The first is a statement of importance and can be one of the following: YES, NO, or UNCT (for uncertain). The second is a numerical rating, dealing with available supporting data, explained below:

(1). Quantitative (rate constants, half-lives) data are available to support conclusions.

(2). Qualitative description only; there are no direct environmental data, however, some laboratory data can be extrapolated to support conclusions.

(3). There are no supporting data available; evidence is drawn from theoretical calculations, estimates, results for similar chemicals, and inferences.

TABLE 4-1 (Cont.)

SUMMARY OF CONCLUSIONS FOR THE TRANSPORT AND FATE OF PRIORITY POLLUTANTS:

F. Phthalate Esters and Polycyclic Aromatic Hydrocarbons

Chapter No.	Chemical	Is the Process Important for Aquatic Transport? (See Key Below)			Is the Process Important in Determining Aquatic Fate? (See Key Below)			
		Volatilization	Sorption	Transport Downstream	Photolysis/ Oxidation	Hydrolysis	Bioaccumulation	Biotransformation/ Biodegradation
94	Phthalate Esters:							
	• Dimethyl	NO(3)	UNCT(2)	YES(1)	NO(3)	UNCT(2)	UNCT(2)	UNCT(2)
	• Diethyl	NO(3)	UNCT(2)	YES(1)	NO(3)	NO(3)	UNCT(2)	UNCT(2)
	• Di-n-butyl	NO(3)	YES(1)	YES(1)	NO(3)	NO(3)	UNCT(2)	UNCT(2)
	• Di-n-octyl	NO(3)	UNCT(2)	UNCT(2)	NO(3)	NO(3)	UNCT(2)	UNCT(2)
	• Bis(2-ethylhexyl)	NO(3)	YES(1)	YES(1)	NO(3)	NO(3)	YES(1)	YES(1)
	• Butyl benzyl	UNCT(3)	UNCT(3)	UNCT(3)	NO(3)	NO(3)	UNCT(2)	YES(3)
	Polycyclic Aromatic Hydrocarbons:							
95	• Acenaphthene	NO(3)	YES(3)	UNCT(3)	YES(3)	NO(3)	NO(3)	YES(3)
	• Acenaphthylene	NO(3)	YES(3)	UNCT(3)	YES(3)	NO(3)	NO(3)	YES(3)
	• Fluorene	NO(3)	YES(3)	UNCT(3)	YES(3)	NO(3)	NO(3)	YES(3)
	• Naphthalene	UNCT(3)	UNCT(3)	UNCT(3)	YES(3)	NO(3)	NO(2)	YES(1)
96	• Anthracene	UNCT(3)	YES(2)	UNCT(3)	YES(1)	NO(3)	NO(2)	YES(1)
	• Fluoranthene	NO(3)	YES(2)	UNCT(3)	YES(3)	NO(3)	NO(2)	YES(2)
	• Phenanthrene	NO(3)	YES(2)	UNCT(3)	YES(3)	NO(3)	NO(2)	YES(2)
97	• Benzo[a]anthracene	NO(3)	YES(2)	UNCT(3)	YES(1)	NO(3)	NO(2)	YES(2)
	• Benzo[b]fluoranthene	UNCT(3)	YES(2)	UNCT(3)	YES(3)	NO(3)	NO(3)	YES(2)
	• Benzo[k]fluoranthene	UNCT(3)	YES(2)	UNCT(3)	YES(3)	NO(3)	NO(3)	YES(3)
	• Chrysene	UNCT(3)	YES(2)	UNCT(3)	YES(3)	NO(3)	NO(3)	YES(3)
	• Pyrene	UNCT(3)	YES(2)	UNCT(3)	YES(3)	NO(3)	NO(3)	YES(3)
98	• Benzo[ghi]perylene	UNCT(3)	YES(2)	UNCT(3)	UNCT(3)	NO(3)	UNCT(3)	UNCT(3)
	• Benzo[a]pyrene	UNCT(3)	YES(1)	UNCT(3)	YES(1)	NO(3)	UNCT(3)	YES(1)
	• Dibenzo[a]anthracene	UNCT(3)	YES(3)	UNCT(3)	UNCT(3)	NO(3)	UNCT(3)	UNCT(3)
	• Indeno[1,2,3-cd]pyrene	UNCT(3)	YES(3)	UNCT(3)	UNCT(3)	NO(3)	UNCT(3)	UNCT(3)

Key:

For each chemical and related process, two ratings are presented. The first is a statement of importance and can be one of the following: YES, NO, or UNCT (for uncertain). The second is a numerical rating, dealing with available supporting data, explained below:

(1). Quantitative (rate constants, half-lives) data are available to support conclusions.

(2). Qualitative description only; there are no direct environmental data, however, some laboratory data can be extrapolated to support conclusions.

(3). There are no supporting data available; evidence is drawn from theoretical calculations, estimates, results for similar chemicals, and inferences.

TABLE 4-1 (Cont.)

SUMMARY OF CONCLUSIONS FOR THE TRANSPORT AND FATE OF PRIORITY POLLUTANTS:

C. Nitrosamines and Miscellaneous Compounds

Chapter No.	Chemical	Is the Process Important for Aquatic Transport? (See Key Below)			Is the Process Important in Determining Aquatic Fate? (See Key Below)			
		Volatilization	Sorption	Transport Downstream	Photolysis/ Oxidation	Hydrolysis	Bioaccumulation	Biotransformation/ Biodegradation
99	Dimethyl nitrosamine	NO(3)	NO(3)	UNCT(3)	YES(2)	NO(3)	NO(3)	NO(2)
100	Diphenyl nitrosamine	NO(3)	UNCT(3)	UNCT(3)	UNCT(3)	NO(3)	UNCT(3)	UNCT(3)
101	Di-n-propyl nitrosamine	NO(3)	NO(3)	UNCT(3)	YES(2)	NO(3)	NO(3)	NO(2)
102	Benzidine	NO(1)	YES(1)	UNCT(3)	YES(1)	NO(2)	NO(2)	UNCT(2)
103	3,3'-Dichlorobenzidine	NO(1)	YES(1)	UNCT(3)	YES(1)	NO(3)	YES(1)	NO(1)
104	1,2-Diphenylhydrazine	NO(1)	YES(2)	UNCT(3)	UNCT(2)	NO(2)	YES(3)	UNCT(3)
105	Acrylonitrile	YES(2)	NO(3)	UNCT(3)	NO(3)	NO(3)	NO(3)	UNCT(3)

Key:

For each chemical and related process, two ratings are presented. The first is a statement of importance and can be one of the following: YES, NO, or UNCT (for uncertain). The second is a numerical rating, dealing with available supporting data, explained below:

(1). Quantitative (rate constants, half-lives) data are available to support conclusions.

(2). Qualitative description only; there are no direct environmental data, however, some laboratory data can be extrapolated to support conclusions.

(3). There are no supporting data available; evidence is drawn from theoretical calculations, estimates, results for similar chemicals, and inferences.

SECTION II: METALS AND INORGANICS

Chapters 5-19

5. ANTIMONY

5.1 Statement of Probable Fate

The fate of antimony in the aquatic environment is determined by a number of factors including pH, Eh, sorptive interactions, and biologically mediated methylation. Due to the relatively high solubility of the antimonite and antimonate ions, most of the antimony introduced into the aquatic environment is probably transported in solution to the oceans. Coprecipitation with iron and aluminum oxides, adsorption by mineral surfaces, and bioaccumulation may, however, be responsible for removing some antimony from solution. Biologically mediated methylation or reduction to stibine (SbH_3) may occur in reducing environments, resulting in remobilization of antimony. The relative importance of each of these processes varies widely among watersheds; but, in general, transport of dissolved antimony to the oceans is the most probable dominant fate.

5.2 Identification - Geochemistry of Antimony

Antimony is an element occurring in concentrations of about 0.2-0.5 ppm in the earth's crust (A.D. Little, Inc. 1976). Important minerals of antimony are the native element Sb; stibnite Sb_2S_3; kermesite Sb_2S_2O; serarmonite, Sb_2O_3; jamesonite, $2PbS \cdot Sb_2S_3$; boulangerite $5PbS \cdot 2Sb_2S_3$; and the sulfantimorids of copper, silver, and nickel. Important artificial compounds include stibine, SbH_3 (a noxious poisonous gas), the chlorides $SbCl_3$ and $SbCl_5$, the sulfides Sb_2S_3 and Sb_2S_5, and the oxides Sb_2O_3 and Sb_2O_5.

Antimony has chalcophilic properties, and thus combines readily with sulfides. Antimony shows no marked preference for mafic or silicic rocks. Antimony becomes enriched in the early stages of magmatic differentiation in sulfide bodies. In addition, antimony accumulates in late-stage granitic pegmatites, together with niobrium and tantalum oxides, in granodiorites, and hydrothermal sulfide deposits. Antimony is also present in galena (a lead ore), in amounts up to 1%, where it replaces either the lead or the sulfur. Antimony may also substitute for arsenic in many minerals.

Little is known about the behavior of antimony during weathering. The antimony sulfides may be converted to the corresponding oxides, and it probably occurs in both hydrolysate and oxidate sediments. Antimony may accumulate with heavy elements in carbonaceous shales or become sorbed on clays and hydrous oxides. Thus, it may be enriched in manganese oxide sediments and black shales.

Antimony has an atomic number of 51 and an atomic weight of 121.75. In its compounds, it has a valence of +5, +3, or -3. When in the +3 state it has metallic characteristics. Antimony's chemical properties are analogous to those of arsenic, which is directly above it in the periodic table, and forms compounds with a number of other elements, such as oxygen, hydrogen, sulfur, and the halogens (Weast 1977).

Antimony's CAS number is 7440-36-0; its TSL number is A167-6664.

5.3 Summary of Fate Data

5.3.1 Photolysis

Antimony compounds may undergo photochemical reactions, but none of these appear to be important in determining aquatic fate. Stibine (SbH_3) reacts with sulfur at 100°C in the presence of light to form antimony sulfide. Under the same conditions, stibine reacts with selenium to form antimony selenide (A.D. Little, Inc. 1976). Antimony trioxide can act as a photocatalyst for the oxidation of organic matter by ultraviolet light, producing organic peroxides (Markham et al. 1958.)

5.3.2 Chemical Speciation

The chemical properties of antimony resemble those of bismuth and arsenic. Antimony loses its 2(s) and 3(p) electrons readily, and may exist in the oxidation states -3, +3, +5, and 0, although the existence of simple Sb^{+3} or Sb^{+5} ions is improbable. In reducing environments, stibine (SbH_3) may be formed. Stibine is a gas at room temperature, and it is quite soluble in water (5,000 mg/l). It is not stable in aerobic waters and is hydrolyzed to form the oxide. The formation of stibine in bed sediments (which usually offer a reducing environment) may result in remobilization of antimony which had been removed from solution by adsorption, coprecipitation, etc.

Under moderately oxidizing conditions, antimony has a valence of +3, and it is found in solution as the hydrated trioxide, $Sb_2O_3(H_2O)_n$. Unlike arsenic, which forms arsenious acid (H_3AsO_3) under mildly oxidizing conditions, the lower valence acid of antimony is unknown; however, the antimonites are well defined salts (Cotton and Wilkinson 1972). The higher acid, H_3SbO_4, does exist, although it does not appear to dissociate completely to the SbO_4^{-3} ion even in the most alkaline conditions (Cotton and Wilkinson 1972). This form of antimony, in which the element exhibits a valance of +5, is found only in highly oxidizing environments.

Antimony salts, added to aqueous media, are hydrolyzed to the oxide or antimonic acid forms. Although the hydrolysis products are usually less soluble than the original salts, the solubility is still sufficient to keep antimony in solution, except for cases of extremely heavy loading. When the system is no longer saturated, any antimony that precipitated out as the oxide will go back into solution.

The oxides, i.e., antimonite and antimonate forms, which are stable in the redox range typically observed in natural waters, all have sufficient solubility to keep antimony in solution at the levels of concentration normally found in natural waters. The calcium, magnesium, and sodium salts of the antimonates and antimonites are probably not a significant control on antimony solubility; but, by analogy to arsenic, some of the trace metal compounds may exhibit limited solubility. Thus, one could speculate that the presence of heavy metals (e.g., copper) in solution may reduce the mobility of antimony.

5.3.3 Volatilization

Antimony may be volatilized when in the form of stibine or its methylated derivatives. Stibine can be formed by reduction of antimony in the sediments. Although biomethylation of antimony has not been demonstrated, there are no obvious thermodynamic or kinetic obstacles (Parris and Brinkman 1975, 1976). Moreover, the elements Sn, Pb, As, Se, Te, which surround antimony in the periodic table, are subject to biomethylation, suggesting that biomethylation pathways could exist for antimony (Parris and Brinkman 1975, 1976). Stibine is rapidly oxidized in air or oxic water to form Sb_2O_3. It is likely then, that most of the stibine formed in the sediments reacts in the water column to produce the oxide, resulting in remobilization of antimony.

The methylated forms of antimony are also subject to oxidation. Parris and Brinkman (1976) estimate the rate of oxidation of trimethylstibine as greater than 10^{-2} M^{-1} s^{-1}. The product of this reaction, $(CH_3)_3SbO$, is much more soluble than trimethylstibine; and, therefore, this oxidation would probably tend to reduce volatility. The rapid rate of oxidation implies that, if trimethylstibine is formed in natural systems, much of it would be oxidized before it volatilized and only a small amount of the volatile antimony compounds formed by either abiotic or biotic mechanisms would be liberated to the atmosphere.

5.3.4 Sorption

The extent to which sorption reduces the aqueous transport of antimony is unknown, but it is clear that sorption processes are normally the most important mechanisms resulting in the removal of antimony from solution. Antimony apparently has an affinity for clay and other mineral

surfaces. Coprecipitation of antimony with hydrous iron, manganese, and aluminum oxides may exert a significant control on antimony mobility in areas where there is active precipitation of these metals. Crecelius et al. (1975) studied the metal concentrations of Puget Sound, Washington, and found that, in uncontaminated areas, most of the antimony in the sediments was bound to extractable iron and aluminum compounds. Antimony bound in such forms would probably be susceptible to remobilization via bioaccumulation, reduction, or biomethylation. On the other hand, antimony in heavily contaminated areas was found mainly in stable, unextractable forms. These forms might include the oxide or insoluble metal antimonates or antimonites. Crecelius et al. (1975) found that less than 10% of the antimony in sediments from both the contaminated and uncontaminated sediments was bound to easily oxidizable organic matter. Since antimony has an anionic character in aqueous solution, it probably has little affinity for complexation with humic and fulvic acids, which are important complexing agents for metals.

Maxfield et al. (1974), in their study of heavy metals in the Coeur d' Alene River of Idaho, found that antimony was concentrated and evenly distributed throughout the sediment. They suggested that, although antimony is being adsorbed by all types of particulate matter, it is not being strongly bound in the sediments. The high levels of antimony that are characteristic of this region are due to former antimony mining activities; and the antimony found in the sediments probably entered the system, not in the dissolved state, but rather on particulate matter. Maxfield et al. (1974) concluded that the results suggest that antimony is leaving the sediments; but since this is a diffusion controlled process, it proceeds slowly.

Strohal et al. (1975) investigated antimony in the sediments of the North Adriatic Sea. They found that the fixation rate of antimony on various inorganic particles is rather small. They found, however, that antimony could be accumulated by organic matter, especially humic acids. Unfortunately, sorption processes of antimony have not been studied in enough detail to quantify the role of sorption in its aquatic fate.

5.3.5 Bioaccumulation

Antimony is only slightly bioaccumulated and has been little studied in aquatic organisms. Leatherland et al. (1973) found low levels of antimony in various fishes and invertebrates collected off the northwest coast of Africa; antimony was generally present in higher concentrations in invertebrates than in fish. Aquatic organisms from the Danube River and Danube Canal in Vienna, Austria, were found to contain only background

levels of antimony (Rehwoldt et al. 1975). Similar results were obtained in clams, mussels, and shrimp by Bertine and Goldberg (1972). Table 5-1 summarizes known bioconcentration factors for antimony.

Table 5-1

Bioconcentration Factors for Antimony

Taxon	Bioconcentration Factor[a]	Reference
Freshwater fish	40	Chapman et al. 1968
Freshwater invertebrates	16,000	Chapman et al. 1968
Marine fish	40	Chapman et al. 1968
Marine invertebrates	16,000	Chapman et al. 1968

a. Concentration factors are defined by the ratio of the concentration of the element in the organism in ppm (wet weight) divided by the concentration of the element in water (ppm).

5.3.6 Biotransformation

It has been reported that a species of bacteria, Stibiobacter senarmontii, utilizes the energy released by metabolically induced oxidation of antimony (Lyalikova 1974), but the distribution and ecological importance of this organism is unknown. As previously mentioned, biomethylation of antimony has not been demonstrated, but it is thought that this process could occur in the environment (Parris and Brinkman 1976).

5.4 Data Summary

Although the aquatic fate of antimony has not been comprehensively studied, it appears that most of the antimony introduced into aquatic environments is probably transported in solution to the oceans. Sorption processes act as temporary sinks for antimony, but bioaccumulation, reduction to stibine, and possibly biomethylation may act to remobilize antimony in bed sediments. There is a possibility that heavy metals in solution could react with antimonite (H_3SbO_3, $H_2SbO_3^-$, $HSbO_3^{-2}$, SbO_3^{-3}) or antimonate (H_3SbO_4, $H_2SbO_4^-$, $HSbO_4^{-2}$) species to form insoluble compounds, greatly reducing the mobility of antimony, but the importance of such reactions is unknown. The aquatic fate of antimony is summarized in Table 5-2.

Table 5-2

Summary of Aquatic Fate of Antimony

Environmental Process	Summary Statement	Confidence of Data
Photolysis	Not important.	Low
Chemical Speciation[a]	Antimony is present as the soluble oxide or antimonite salt in most natural waters. In reducing environments, volatile SbH_3 may be formed. Most species of antimony are soluble and mobile in the aquatic environment.	Medium
Volatilization	Important where SbH_3 is stable.	Medium
Sorption[a]	Antimony is adsorbed by clays and organic materials.	Low
Bioaccumulation	Very slight.	Medium
Biotransformation[a]	Biomethylation may occur.	Low

a. All of the noted environmental processes are important; however, their relative importance with respect to each other is uncertain for determining final fate.

5.5 Literature Cited

A.D. Little, Inc. 1976. Literature study of selected potential environmental contaminants; antimony and its compounds. pp.5-15. PB 251-438. 147p.

Bertine, K.K. and E.D. Goldberg. 1972. Trace elements in clams, mussels, and shrimp. Limnol. Oceanogr. 17(6):877-884.

Chapman, W.H., H.L. Fisher, and M.W. Pratt. 1968. Concentration factors of chemical elements in edible aquatic organisms. Lawrence Radiation Laboratory. Livermore, Calif. UCRL-50564. 46p.

Cotton, F.A. and G. Wilkinson. 1972. Advanced inorganic chemistry. pp.367-402. Inter-Science Publishers, New York. 1145p.

Crecelius, E.A., M.H. Bothner, and R. Carpenter. 1975. Geochemistries of arsenic, antimony, mercury, and related elements in sediments of Puget Sound. Environ. Sci. Technol. 9(4):325-333.

Leatherland, T.M., J.D. Burton, F. Culkis, M.J. McCartney, and R.J. Morris. 1973. Concentrations of some trace metals in pelagic organisms and of mercury in northeast Atlantic Ocean water. Deep-Sea Res. 20:679-685.

Lyalikova, N.N. 1974. Stibiobacter senarmontii, a new microorganism oxidizing antimony. Mikrobiologiya 43(6):941-948. (Abstract only). CA 1975. 82:135404y.

Markham, M.C., M.C. Hannan, L. Liu, C. Coffey, and B. Jones. 1958. Photochemical properties of antimony trioxide. J. Phys. Chem. 62(8):989-992.

Maxfield, D., J.M. Rodriguez, M. Buettner, J. Davis, L. Forbes, R. Kovacs, W. Russel, L. Schultz, R. Smith, J. Stanton, and C.M. Wai. 1974. Heavy metal pollution in the sediments of the Coeur d' Alene River delta. Environ. Pollut. 7:1-6.

Parris, G.E. and F.E. Brinkman. 1975. Reactions which relate to the environmental mobility of arsenic and antimony. I. Quarternization of trimethylarsine and trimethylstibine. J. Org. Chem. 40:3801-3803.

Parris, G.E. and F.E. Brinkman. 1976. Reactions which relate to the environmental mobility of arsenic and antimony. II. Oxidation of trimethylarsine and trimethylstibine. Environ. Sci. Technol. 10(12):1128-1134.

Rehwoldt, R., D. Karimian-Tehenani, and H. Altmann. 1975. Measurement and distribution of various heavy metals in the Danube River and Danube Canal aquatic communities in the vicinity of Vienna, Austria. Sci. Total Environ. 3:341-348.

Strohal, P., D. Huljer, S. Lubic, and M. Picer. 1975. Antimony in the coastal marine environment, North Adriatic. Estuarine and Coastal Marine Science 3:119-123.

Weast, R.C. (ed.). 1977. Handbook of chemistry and physics, 58th edition. CRC Press, Cleveland, Ohio. 2398p.

6. ARSENIC

6.1 Statement of Probable Fate

The fate of arsenic in the aquatic environment depends largely on prevailing pH and Eh conditions. Arsenic is extremely mobile in the aquatic environment and cycles through the water column, sediments and biota. Although the equilibrium chemistry of arsenic has been extensively discussed in the literature, no information regarding the kinetics of arsenic reactions in the environment was found. It appears that, in most cases, the sediments and the oceans are the primary sinks for arsenic in the aquatic environment.

6.2 Identification - Geochemistry of Arsenic

Arsenic is considered to be a rare but ubiquitous element in the earth's crust. The average abundance of crustal arsenic has been established at 5 ppm (Weast 1977). Arsenic is the third member of group VB of the periodic system, which also includes nitrogen, phosphorus, antimony, and bismuth. In some of its chemical reactions, arsenic behaves much like phosphorus and antimony.

In the natural environment, four oxidation states are possible for arsenic: the-3 state, the metallic (0) state, and the +3 and +5 states. The metallic state is not uncommon for the element in certain types of mineral deposits. The +3 and +5 states are common in a variety of complex minerals and in dissolved salts in natural waters. The -3 stae is present in gasecus AsH_3 (arsine) which may form under some natural conditions. Because of its multiple oxidation states and its tendency to form soluble complexes, the geochemistry of arsaenic is intricate and not well characterized. The element most commonly associated with arsenic in nature is sulfur (Boyle and Jonasson 1973).

In all, there are 100 or more arsenic bearing minerals known to occur in nature. The principal arsenic minerals are arsenopyrite (FeAsS), niccolite (NiAs), cobaltite (CoAsS), tennantite ($Cu_{12}As_4S_{13}$), enargite (Cu_3AsS_4), native arsenic (As), orpiment (As_2S_3), realgar (AsS), prousite (Ag_3AsS_3), scorodite ($(Fe,Al)(AsO_4)\cdot 2H_2O$), bendantite ($PbFe_3(AsO_4)(SO_4)(OH)_6$), olivenite ($Cu_2AsO_4OH$), mimetite ($Pb_5(PO_4,AsO_4)_3Cl$), arsenolite ($As_2O_3$), erythrite ($Co_3(AsO_4)_2\cdot 8H_2O$), and annabergite ($Ni_3(AsO_4)_2\cdot 2H_2O$). Arsenic also occurs in minor quantities in practically all the common sulfides and in a great variety of secondary oxidation products, particularly in sulfates and phosphates (Boyle and Jonasson 1973). The generalized geochemical cycle of arsenic is shown in Figure 6-1.

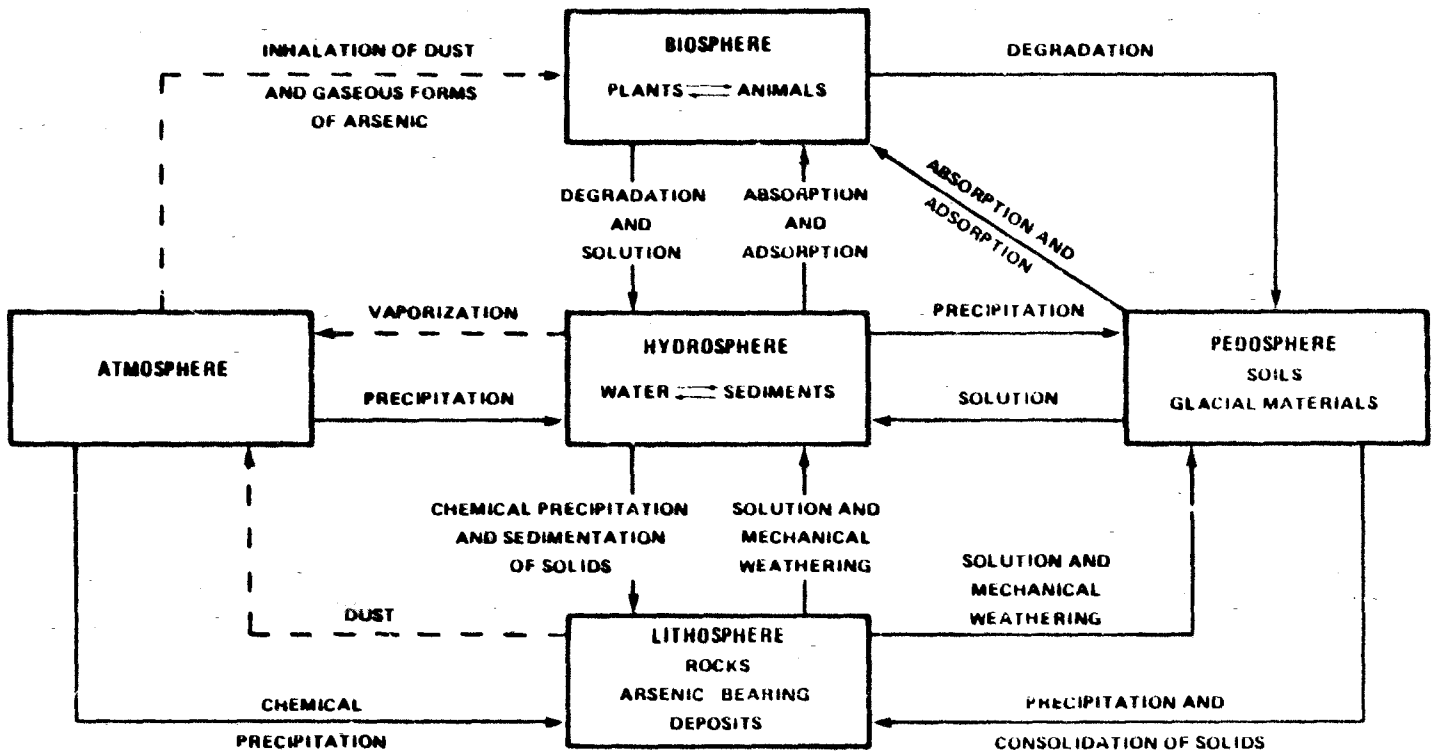


Figure 6-1 The generalized geochemical cycle of arsenic. From Boyle and Jonasson (1973).

Arsenic has no aqueous cationic chemistry other than in organic quaternary salts (Cotton and Wilkinson 1972). The oxo acids, arsenious acid (H_3AsO_3) and arsenic acid (H_3AsO_4), are the prevalent forms of arsenic in aerobic waters. Arsenic can form complexes with a number of organic compounds, most of which increase solubility.

The atomic number of arsenic is 33; its atomic weight is 74.91; density is 5.72 (20°C); melting point (28 atm.) is 817°C; and boiling point is 613°C (Weast 1977).

The CAS number of arsenic is 7440-38-2; the TSL number is A-1418-8227.

6.3 Summary of Fate Data

6.3.1 Photolysis

No evidence was found that photolysis is an important mechanism in determining the fate of arsenic compounds.

6.3.2 Chemical Speciation

In aquatic systems, arsenic has an unusually complex chemistry with oxidation-reduction, ligand exchange, precipitation, and adsorption reactions all taking place. Arsenic is stable in four oxidation states (+5, +3, 0, -3) under Eh conditions occurring in aquatic systems. Arsenic metal occurs only rarely and the -3 oxidation state is stable only at extremely low Eh values. Since the valence state of arsenic is extremely important in determining toxicity (the +3 state is much more toxic than the +5 state; National Academy of Sciences 1976) as well as complexation behavior, the chemical speciation of arsenic is very important when considering its aquatic fate.

Wagemann (1978) examined the typical concentrations of major and minor ionic constituents in freshwater systems in an attempt to find the possible controls on total dissolved arsenic in freshwater. He selected four metals (Ba, Cr, Fe, Ca) as possible controlling factors and studied their metal arsenates more closely in the laboratory. Barium ion, at typical freshwater concentrations, was the most likely freshwater constituent that would be capable of holding total dissolved arsenic to rather low concentrations. Based on these studies, an Eh-pH diagram (Figure 6-2), which summarizes theoretical arsenic speciation in freshwater environments, was developed.

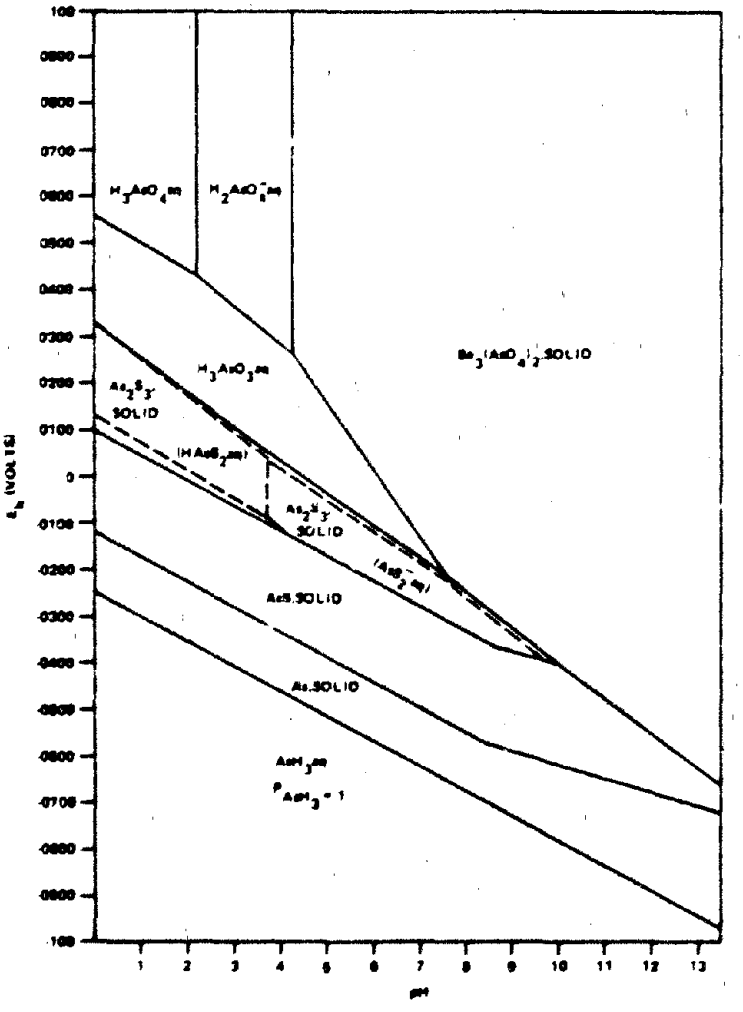


Figure 6-2 Eh-pH diagram for arsenic at 25°C and 1 atm. pressure, showing the fields of stability for the most important arsenic species in the presence of 10^{-3}M of total arsenic, 10^{-3}M of total sulfur and 2.2×10^{-7}M of total barium. Dashed lines define domains for species enclosed in parentheses. From Wagemann (1978).

Andreae (1978) analyzed seawater from the Southern California coast and terrestrial waters from several locations in the United States for four arsenic species: arsenite, arsenate, monomethylarsonic acid, and dimethylarsinic acid. Generally, arsenate was dominant, but in waters of the photic zone, the other species were found in significant concentrations. A positive correlation was evident between the concentrations of arsenite and methylated arsenicals and biological activity. These results indicate that the speciation of arsenic in natural waters is significantly influenced by the biota. In the waters below the euphotic zone, arsenate concentrations increased with depth, suggesting regeneration from biological material. Inasmuch as arsenate is the thermodynamically stable form of arsenic under the conditions prevalent in most natural waters, the non-equilibrium species reflect the biological activity in natural waters.

These results were confirmed by the work of Waslenchuk and Windom (1978) in estuaries and Waslenchuk (1979) in rivers. Waslenchuk and Windom (1978) found that in estuaries the only detectable species was arsenate which remained in solution as fresh and salt water mixed. Complexes occurred between arsenic and low molecular weight dissolved organic matter. These complexes presumably prevented adsorptive and coprecipitative interactions with the sediments and allowed the arsenic to travel to the ocean in a dissolved form. Arsenic which enters the estuary associated with particulates, however, apparently remained so and accumulated in the sediments.

Waslenchuk (1979) found that the levels of dissolved arsenic in rivers in the southeast of the United States are controlled by the availability of arsenic, by rainwater dilution, by the extent of complexation with dissolved organic matter, and perhaps by the metabolic activity of aquatic plants. Arsenic complexation by dissolved organic matter prevents adsorptive interactions between the arsenic and solid-phase organic and inorganic materials. Despite high arsenate solubility, arsenate concentration is limited to levels below saturation, due to reactions which remove the free arsenate ion from solution. The particulate arsenic load may be as important as the dissolved load with respect to material transport in rivers. Only the dissolved load, however, is delivered to the ocean. It appears further that those biologically mediated reactions which result in arsenic species disequilibria, in the ocean and lakes, have an insignificant effect on arsenic speciation in rivers.

6.3.3 Volatilization

Volatilization of arsenic may be a significant process in extremely reducing environments where arsine (AsH_3) is formed, but under normal circumstances, it is not an important mechanism in determining the fate of arsenic after the element's introduction to the aqueous environment.

Arsine is probably oxidized rapidly in aerobic waters or the atmosphere (Parris and Brinkman 1975, 1976).

Methylated arsine derivatives may have more potential for volatilization. Trimethylarsine is quite volatile at room temperature (varor pressure 322 torr) and is oxidized to more soluble products very s owly. Parris and Brinkman (1976) reported a rate constant of less than $10^{-2}{}_M{}^{-1}{}_s{}^{-1}$ for oxidation of $(CH_3)_3As$ by dissolved oxygen. In the gas phase, the rate constant for oxidation by oxygen was $10^{-6}{}_M{}^{-1}{}_s{}^{-1}$. Thus, trimethylarsine can travel considerable distances without undergoing chemical change, even in aerobic systems.

6.3.4 Sorption

Cycling of arsenic in the aquatic environment is dominated by adsorption and desorption to sediments. Arsenic may be sorbed onto clays, aluminum hydroxide, iron oxides, and organic material (Ferguson and Gavis 1972; Jackson et al. 1978). In areas where phosphate minerals occur, arsenate may isomorphously substitute for phosphate (Hem 1970). Under most conditions, coprecipitation or sorption of arsenic with hydrous oxides of iron is probably the prevalent process in the removal of dissolved arsenic. The oxyanions of both arsenic and arsenous acid can coprecipitate with hydrous iron and manganese oxides (Ferguson and Gavis 1972).

Gupta and Chen (1978) studied the adsorption of As(III) and As(V) onto alumina, bauxite, and carbon under various pH and salinity conditions in the laboratory. The results indicate that: (1) the rate of adsorption and the extent of arsenic removal decrease with increasing salinity; (2) pentavalent arsenic species have a greater adsorptive affinity for the materials tested than do trivalent species; (3) alumina and bauxite are much more effective adsorbents than carbon; and (4) adsorption decreases with increasing pH above pH 9 for As(III) and above pH 7 for As(V). These data show that adsorption will be most important in aerobic, acidic, fresh waters. As conditons become more reducing, alkaline, and/or saline, arsenic is less likely to be adsorbed and more likely to remain dissolved.

At Tacoma, Washington, a smelter discharges large amounts of As_2O_5 into the air and Puget Sound. Sediments near the smelter contain high levels of arsenic (up to 10,000 ppm). Surface seawater samples taken next to the smelter contained a maximum 1200 ppb arsenic. The concentration decreased very rapidly with distance to about 4 ppb within one mile. Crecelius et al. (1975) explained this phenomenon by the rapid absorption of arsenic into the sediments of Puget Sound. Crecelius (1975) estimated that for Lake Washington, which received high loadings of arsenic, approxi-

nately 55% of the arsenic entering the lake was removed to the sediments. About 60% of the arsenic in the sediments was extractable with the iron-manganese compounds, indicating that sorption or coprecipitation was the primary removal process. Of the riverine input to the lake, 65% of the arsenic was dissolved and 35% was associated with particles. Since much of the arsenic entering the lake originated from the nearby smelter and was probably chemically bound to particles which subsequently settled to the sediments, it is quite possible that in uncontaminated environments, less arsenic would be removed to the sediments and a greater proportion of the arsenic in the sediments would be associated with the extractable iron-manganese compounds.

La Peintre (1954) demonstrated that arsenate species are coprecipitated or adsorb onto hydrous iron oxide. Shnyukov (1963) observed that iron ores are always enriched with arsenic, owing to the high adsorptive capacity of the hydrous iron oxides and the fact that ferric arsenate is very insoluble. Arsenate species are adsorbed by aluminum hydroxide and by clays; however, bauxite and silicates are usually only moderately enriched in arsenic (Onishi and Sandell 1955). It appears, therefore, that adsorption of arsenic by sediments is one of the controlling mechanisms for its fate in the aquatic environment.

6.3.5 Bioaccumulation

Although arsenic is toxic, a number of studies have shown that it is bioaccumulated. Arsenic is accumulated by fish both from water and from food, but reported concentration factors for arsenic in aquatic organisms are generally quite low (Table 6-1).

Reay (1973) studied the arsenic levels in an arsenic-rich river, the Waikato (New Zealand), and related bioaccumulation of arsenic by aquatic plants to the total amount transported by the river. By estimating total production (ecological) and the amount of arsenic transported by the river, the author estimated that only 3-4% of the annual arsenic input to the river was bioaccumulated, with much of the balance being discharged to the sea and the remainder settling out with sediment at impoundments.

In a microcosm experiment, Isensee *et al.* (1973) investigated the bioaccumulation of two organic arsenicals, cacodylic acid and dimethylarsine, for a total of 32 days in a model ecosystem that contained algae, snails, daphnia, and fish. Fish exhibited the least accumulation, with a bioconcentration factor of 21 for cacodylic acid and 34 for dimethylarsine. Snails accumulated the compounds to a greater extent (the bioconcentration factor ranged from 110 to 446), and the two planktonic components concentrated arsenic the most, with bioconcentration factors ranging from 730 to

Table 6-1

Bioconcentration Factors for Arsenic

Taxon	Bioconcentration Factor[a]	Reference
Freshwater Plants	333 6000	Chapman et al. 1968 Reay 1973
Freshwater Invertebrates	333	Chapman et al. 1968
Freshwater Fish	333	Chapman et al. 1968
Marine Plants	333	Chapman et al. 1968
Marine Invertebrates	333	Chapman et al. 1968
Marine Fish	333	Chapman et al. 1968

a. Bioconcentration factors are the ratio derived from the concentration of the element in the aquatic organism (in ppm wet weight) divided by the concentration of the element in water (in ppm).

2175. It was concluded that the arsenic compounds did not show a tendency to biomagnify (increase in concentration as trophic level increases); and after 32 days, about 30% of the original arsenic in solution was incorporated by the biota.

Sorensen (1976a) exposed green sunfish (Lepomis cyanellus) to various concentrations of arsenic (as sodium arsenate) in water and measured the accumulation. There appeared to be a relationship between exposure concentration and arsenic accumulation, but the data were not statistically correlated. In further experiments green sunfish were exposed to sodium arsenate under varying temperature and exposure intervals (Sorensen 1976b). Arsenic uptake by liver, gut and muscle increased with arsenic concentration in water and with temperature and exposure interval. Dead sunfish did not passively accumulate arsenic and no useful method was found for confirming arsenic-caused fish kills. Biological half-life for arsenic in gut and liver was about seven days.

Gilderhus (1966) observed the arsenic uptake by young and adult bluegills (Lepomis marcochirus) placed in ponds that had been treated with various concentrations of sodium arsenate as a herbicide. After sixteen weeks exposure, whole adult bluegills contained arsenic levels very similar to the concentration of arsenic remaining in the pond after that period. Immature bluegills attained arsenic concentrations nearly twice those present in adults. By the end of the experiment, 20 to 80 percent of the arsenic applied to the ponds remained in solution.

Sandhu (1977) measured arsenic content of fish and water in a pond accidentally sprayed with an arsenical herbicide. Arsenic levels in the pond reached 2.5 mg As/l; fish accumulated up to 12.4 µg As/g in muscle, representing a concentration factor of only five. Lake Michigan plankton and benthos were found to contain 6.0 and 6.6 µg As/g, respectively (Seydel 1972). Lake Superior plankton contained about 30 percent less. The arsenic concentrations present in phytoplankton and zooplankton were similar.

In general, fat contains more arsenic than other tissue fractions. Fish muscle tissue also accumulates arsenic; however, the biological half-life of arsenic is only seven days in green sunfish. Shellfish concentrate arsenic to a much greater extent than fish, and marine organisms contain more arsenic than freshwater species.

6.3.6 Biotransformation

Arsenic has been shown to undergo a number of biologically mediated transformations in aquatic environments, most of which involve methyl-

ation to derivatives of arsine (Johnson 1972; Wood 1975; Zingaro and Irgolic 1975). Arsenic forms stable bonds with sulfur and carbon in organic compounds, and it is the affinity of trivalent arsenic for sulfhydryl groups, most notably in amino acids, which accounts for the primary mode of arsenic toxicity (National Academy of Sciences 1976). Pentavalent arsenic is not reactive with sulfhydryl groups, but since some organisms are capable of reducing arsenate to arsenite, biological reduction in natural waters could cause an increase in the ratio of arsenite to arsenate (Braman and Foreback 1973).

In methylation studies, McBride and Wolfe (1971) demonstrated that Methanobacterium reduced and methylated arsenate under anaerobic conditions to dimethylarsine. A methyl donor, methylcobolamin in this case, was necessary. Cox and Alexander (1973) demonstrated that three species of fungi, found in sewage sludge, could produce trimethylarsine. Two of the fungi were able to form trimethylarsine from mono- or dimethylarsine, while the third was able to produce trimethylarsine from arsenite and arsenate as well. In general, more trimethylarsine was produced in acidic media than under neutral conditions. The methylarsines can be produced by a number of yeasts, bacteria, and fungi. This literature has been reviewed by Ferguson and Gavis (1972) and Woolson (1977).

The biological function of the methylation of arsenic is not known, but Braman and Foreback (1973) speculate that methylation may be a detoxification mechanism since most of the organic metabolites are considerably less toxic than arsenite. Alternatively, methylation of arsenic could be purely adventitious. In an anaerobic environment, it may be energetically preferable for organisms to transmethylate metals rather than to synthesize methane. Only aerobic metabolism has been found to yield methylarsines and methylation may occur in the aerobic upper layer of the sediment. The probable mobility of methylarsines from the sediments to solution and to the aquatic food chain plus the increased anthropogenic discharges of arsenic could bring about ever increasing arsenic concentrations in the aquatic environment. This cyclic behavior of arsenic in biological systems has been summarized in Figure 6-3.

6.4 Data Summary

Arsenic is extremely mobile in the aquatic environment. Although a number of studies have described the equilibrium chemistry of arsenic, the rates of most of these reactions are unknown. It is evident that once in the aquatic system, arsenic cycles through several components, i.e., the water column, the sediments, the biota, and the atmosphere. Figure 6-4 summarizes this cyclical nature of arsenic.

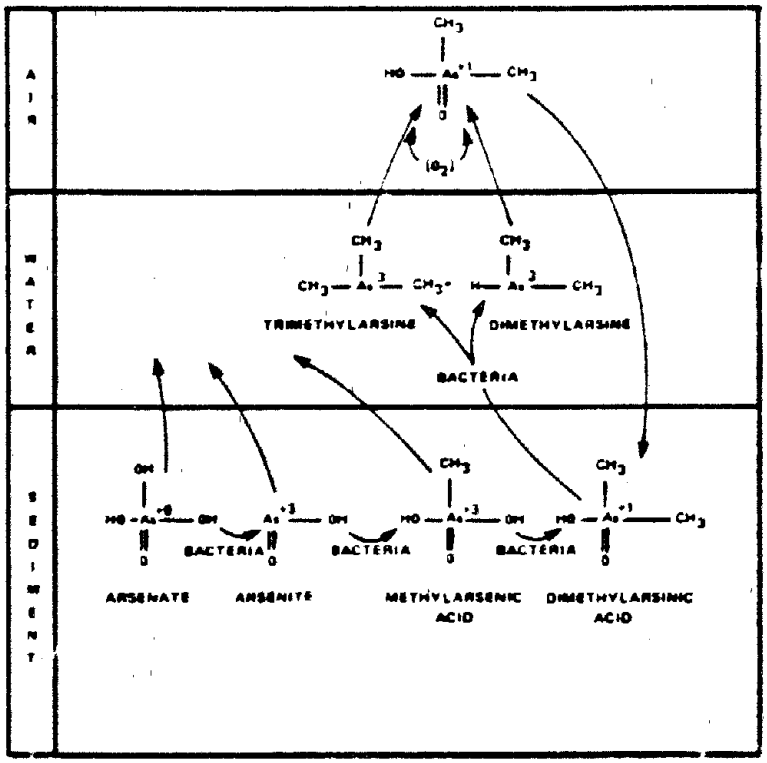


Figure 6-3 The biologic arsenic cycle in the aquatic environment. From Wood (1975).

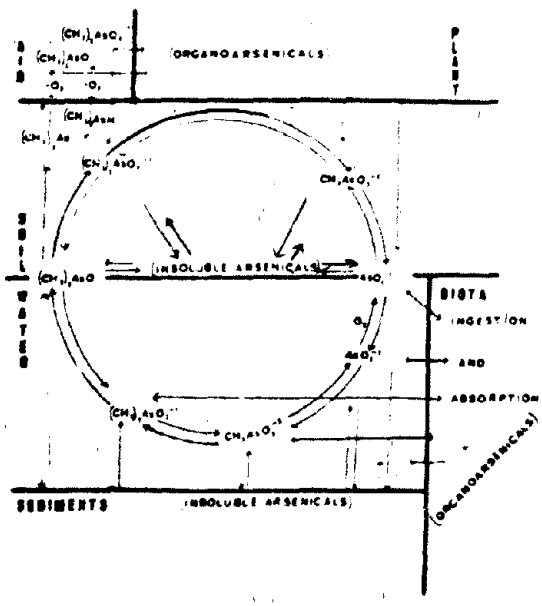


Figure 6-4 Cycle of arsenic through different environmental compartments. From Woolson (1977).

Obviously, the fate of arsenic in the aquatic environment is a complex problem, depending on a number of factors including Eh, pH, metal sulfide and sulfide ion concentrations, presence of phosphorus minerals, iron concentration, temperature, salinity, and distribution and composition of the biota. It appears that, in most cases, the sediment is the major sink for arsenic, but that mobilization by bacteria and other benthic organisms returns much of this arsenic to the cycle. Much, if not most, of the arsenic introduced to the aquatic ecosystem is eventually transported in solution to the oceans. Table 6-2 summarizes the aquatic fate of arsenic.

Table 6-2

Summary of Aquatic Fate of Arsenic

Environmental Process	Summary Statement	Confidence or Data
Photolysis	Not an important process.	Medium
Chemical Speciation[a]	Important in determining arsenic distribution and mobility. Interconversions of +3 and +5 state and organic complexation are most important.	High
Volatilization[a]	Important when biological activity or highly reducing conditions produce AsH_3 or methylarsenics.	High
Sorption[a]	Sorption onto clays, iron oxides, and organic material are a controlling mechanism for the fate of arsenic in the aquatic environment.	High
Bioaccumulation[a]	Appears to be most significant in lower trophic levels. High toxicity lowers overall accumulation by aquatic organisms.	Medium
Biotransformation[a]	Arsenic is metabolized by a number of organisms to organic arsenicals, thereby increasing arsenic mobility in the environment.	High

a. All of the noted environmental processes are important; however, their relative importance with respect to each other is uncertain for determining final fate.

6.5 Literature Cited

Andreae, M.O. 1978. Distribution and speciation of arsenic in natural waters and some marine algae. Deep-Sea Research 25(4):391-402.

Boyle, R.W. and I.R. Jonasson. 1973. The geochemistry of arsenic and its use as an indicator element in geochemical prospecting. J. Geochem. Expl. 2:251-296.

Braman, R.S. and C.C. Foreback. 1973. Methylated forms of arsenic in the environment. Science 182:1247-1249.

Chapman, W.H., H.L. Fisher, and M.W. Pratt. 1968. Concentration factors of chemical elements in edible aquatic organisms. Lawrence Radiation Laboratory, Livermore, Calif. UCRL-50564. 46p.

Cotton, F.A. and G. Wilkinson. 1972. Advanced inorganic chemistry. pp.367-402. Interscience Publishers, New York. 1145p.

Cox, D.P. and M. Alexander. 1973. Production of trimethylarsine gas from various arsenic compounds by three sewage fungi. Bull. Environ. Contam. Toxicol. 9:84-88.

Crecelius, E.A. 1975. The geochemical cycle of arsenic in Lake Washington and its relation to other elements. Liminol. Oceanogr. 20(3):441-451.

Crecelius, E.A., M.H. Bothner, and R. Carpenter. 1975. Geochemistries of arsenic, antimony, mercury, and related elements in sediments of Puget Sound. Environ. Sci. Technol. 9(4):325-333.

Ferguson, J.F. and J. Gavis. 1972. A review of the arsenic cycle in natural waters. Water Res. 6:1259-1274.

Gilderhus, P.A. 1966. Some effects of sublethal concentrations of sodium arsenate on bluegills and the aquatic environment. Trans. Am. Fish Soc. 95(3):289-296.

Gupta, S. and K.Y. Chen. 1978. Arsenic removal by adsorption. J. Water Pollut. Control Fed. 50(3):493-506.

Hem, J.D. 1970. Study and interpretation of the chemical characteristics of natural water. pp.206-207. U.S.G.S. Water Supply Paper 1473. Washington, D.C. 363p.

Isensee, A.R., P.C. Kearney, E.A. Woolson, G.E. Jones, and V.P. Williams. 1973. Distribution of alkyl arsenicals in model ecosystem. Environ. Sci. Technol. 7(9):841-845.

Jackson, K.S., I.R. Jonasson, and G.B. Skippen. 1978. The nature of metals-sediment-water interactions in freshwater bodies, with emphasis on the role of organic matter. Earth-Science Reviews 14:97-146.

Johnson, D.L. 1972. Bacterial reduction of arsenate in seawater. Nature 240:44-45.

La Peintre, M. 1954. Solubilization par les eaux naturelles de l'arsenic lié au fer dans les roches sedimentaries. Comt. Rend. Acad. Sci. (France) 239:359-360.

McBride, B.C. and R.S. Wolfe. 1971. Biosynthesis of dimethylarsine by Methanobacterium. Biochemistry 10:4312-4317.

National Academy of Sciences. 1976. Arsenic. pp.6-121. U.S. Environmental Protection Agency, Research Triangle Park, N.C. NTIS PB 262 167. 480p.

Onishi, H. and E.B. Sandell. 1955. Geochemistry of arsenic. Geochim. Cosmochim. Acta 7:1-33.

Parris, G.E. and F.E. Brinckman. 1975. Reactions which relate to the environmental mobility of arsenic and antimony I. Quarternization of trimethylarsine and trimethylstibine. J. Org. Chem. 40:3801-3803.

Parris, G.E. and F.E. Brinckman. 1976. Reactions which relate to the environmental mobility of arsenic and antimony II. Oxidation of trimethylarsine and trimethylstibine. Environ. Sci. Technol. 10(12):1128-1134.

Reay, P.F. 1973. The accumulation of arsenic from arsenic-rich natural waters by aquatic plants. J. Appl. Ecology 9(2):557-565.

Sandhu, S.S. 1977. Study on the post-mortem identification of pollutants in the fish killed by water pollution: detection of arsenic. Bull. Environ. Contam. Toxicol. 17(3):373-378.

Seydel, I.S. 1972. Distribution and circulation of arsenic through water, organisms and sediments of Lake Michigan. Arch. Hydrobiol. 71(1):17-30.

Shnyukov, E.F. 1963. Arsenic in the cimmerian iron ores of the Azov-Black Sea region. Geochemistry (USSR) 163:87-93.

Sorensen, E.M.B. 1976a. Thermal effects on the accumulation of arsenic in green sunfish, Lepomis cyanellus. Arch. Environ. Contam. Toxicol.

Sorensen, E.M.B. 1976b. Toxicity and accumulation of arsenic in green sunfish, Lepomis cyanellus exposed to arsenate in water. Bull. Environ. Contam. Toxicol. 15(6):756-761.

Wagemann, R. 1978. Some theoretical aspects of stability and solubility of inorganic arsenic in the freshwater environment. Water Res. 12:139-145.

Waslenchuk, D.G. and H.L. Windom, 1978. Factors controlling the estuarine chemistry of arsenic. Estuarine Coastal Mar. Sci. 7:455-464.

Waslenchuk, D.G. 1979. The geochemical controls on arsenic concentrations in southeastern United States rivers. Chem. Geol. 24:315-325.

Weast, R.C. (ed.). 1977. Handbook of chemistry and physics, 58th edition. CRC Press, Cleveland, Ohio. 2398p.

Wood, J.M. 1975. Metabolic cycles for toxic elements in the environment - a study of kinetics and mechanism. pp.105-112. in Heavy metals in the aquatic environment. P.A. Krenkel (ed.). Pergamon Press, Oxford, England. 352p.

Woolson, E.A. 1977. Fate of arsenicals in different environmental substrates. Environ. Health Perspect. 19:73-81.

Zingaro, R.A. and K.J. Irgolic. 1975. The methylation of arsenic compounds. Science 187:765.

7. ASBESTOS

7.1 Statement of Probable Fate

Asbestos is mineralogically stable and is not prone to significant chemical or biological degradation in the aquatic environment. After introduction into surface waters, asbestos remains in suspension until physical degradation or chemical coagulation allows it to settle into the sediment layer.

7.2 Identification - Geochemistry of Asbestos

Asbestos is a generic term for a variety of hydrated silicate minerals which have one common attribute, namely, the ability to be separated into relatively soft, silky fibers. Although the name is ordinarily associated with those varieties which have technologic importance, it has often been applied to all minerals which fit the above description. The term "asbestos" as used in this report, refers to the definition of asbestos fibers currently used by the Environmental Protection Agency. The more general term "asbestiform minerals" denotes minerals of this type without reference to size, form, or usage.

The definition of asbestos currently used by the EPA is from the notice of proposed rule-making for "Occupational Exposure to Asbestos" published in the Federal Register (Oct. 9, 1975; pp. 47652, 47660) by the U.S. Occupational Safety and Health Administration (OSHA). In this notice, the naturally occurring minerals chrysotile, amosite, crocidolite, tremolite, anthophyllite, and actinolite are classified as "asbestos" if the individual crystallites or crystal fragments have the following dimensions: length - greater than 5 micrometers; maximum diameter - less than 5 micrometers; and a length to diameter ratio of 3 or greater. Any products containing any of these minerals in this size range are also designated as "asbestos" (Campbell et al. 1977).

The known varieties of asbestiform minerals can be divided into two main classes on the basis of their crystal structures: serpentine and amphibole. The sole member of the serpentine class is chrysotile asbestos, which is by far the most common of the asbestiform minerals. It accounts for more than 95 percent of the asbestos fiber produced today (Speil 1974). There are five recognized asbestiform varieties of amphibole: crocidolite, amosite, anthophyllite, tremolite, and actinolite. Although the amphiboles are common rock-forming minerals, the asbestiform varieties are much less abundant than chrysotile. The physical and chemical properties

of the asbestiform minerals which are responsible for their commercial importance can be directly related to their crystal structure and chemical composition. Therefore, an attempt will be made in this report to elucidate the structure and composition of these minerals.

7.2.1 Mineralogy of Commercial Asbestos

The commercial deposits of asbestos contain one of the following minerals:

chrysotile	$Mg_3Si_2O_5(OH)_4$
amosite	$(Fe(II)\ Mg)_7Si_8O_{22}(OH)_2$
crocidolite	$Na_2(Fe(II),Mg)_3Fe(III)_2Si_8O_{22}(OH)_2$
fibrous anthophyllite	$(Mg,Fe)_7Si_8O_{22}(OH)_2$
fibrous tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$
fibrous actinolite	$Ca_2(Mg,Fe(II))_5Si_8O_{22}(OH)_2$

Tremolite, actinolite, and anthophyllite are presently of little commercial importance (Ross 1978).

In addition to being compositionally different, the five amphibole forms of commercial asbestos have completely different crystal structures from that of chrysotile. The structure of chrysotile (Figure 7-1) consists of double layers, each consisting of a layer of linked SiO_4 tetrahedra that are coordinated to a second layer of linked $MgO_2(OH)_4$ octahedra through the sharing of oxygen atoms; the composite double layer rolls up, in the same manner as a window shade, to form long hollow tubes. The diameters of the individual tubes are approximately 25 nm; the length-to-diameter ratio can vary from 5 to 10 to well over 10,000 (Ross 1978). These individual tubes are easily separated because the bonding between the tubes is weak and is due only to van der Waals forces.

The structures of the amphibole minerals (Figure 7-2), on the other hand, are composed of strips or ribbons of linked polyhedra, which join together to form the three-dimensional crystals. The individual strips are composed of three elements - two double chains of linked $(Si,Al)O_4$ tetrahedra that form a sandwich with a strip of linked MgO_6 or FeO_6. These structures are easily broken into fibers due to their chain defects, which are also called Wadsley defects (Franco et al. 1977). These defects are caused by the formation of expanded "I-beams" that are composed of triple, quadruple, etc., chains of linked SiO_4 tetrahedra rather than the double chains found in all other amphibole crystal structures. If these "I-beams" are expanded indefinitely, the resulting strip becomes identical with the single talc layer of composition or $Mg_6Si_8O_{20}(OH)_4$; these expanded "I-beams" intermix with the regular amphibole structure to produce the fibrous cleavage planes of the amphibole asbestiform minerals.

7.2.2 Formation of Asbestos

Modes of origin can be inferred from the stability relationships among talc, anthophyllite, enstatite, forsterite, antigorite, and chrysotile given by Hemley et al. (1977). Their mineral stability fields at 1 kbar H_2O, in terms of crystallization temperature and molality of aqueous silica, are given in Figure 7-3. This figure shows a number of relationships pertinent to the problem of formation of asbestos minerals. As the temperature decreases, forsterite (Mg-rich olivine) can react to form antigonite or chrysotile depending on the silica concentration in the aqueous solution to which the olivine-bearing rock is exposed. At silica concentrations near the quartz saturation curve, the forsterite or anthophyllite can undergo alteration to one of the amphibole asbestiform minerals (depending on the metal cation concentrations), or directly to talc. Figure 7-4 shows the stability fields of forsterite, enstatite, anthophyllite, talc and the amphibole asbestiform minerals. The fibrous nature of the amphibole asbestiform minerals can be explained if the alteration process of a chain silicate (anthophyllite) to a sheet silicate (talc) proceeds by reforming the double chain at the unit-cell level. In this manner, the fibrous nature of amphibole asbestiform minerals appears to be related to the crystal growth mechanism; i.e., the crystallites may nucleate at many centers and grow as individual fibers only a few tens of nanometers thick (Branco et al. 1977). Thus, the presence of "Wadsley" defects may be the result of rapid growth and, in addition, may hinder growth in a direction perpendicular to the fiber axis.

7.2.3 Chemical Reactivity

Asbestos has often been touted as an indestructable mineral; in reality, however this is far from the case. Experiments on thermal effects and the acid leaching of asbestos have been summarized by Speil and Leineweber (1969) and have only a peripheral relation to the aquatic fate of asbestos; but the following laboratory experiments are definitely germane with regard to degradation in ambient surface waters.

Choi and Smith (1972) observed the kinetics of the dissolution of chrysotile in water over a temperature range of 5 to 45°C. A parallelism was noted between the rate of dissolution of magnesium from the chrysotile and the rate of pH drift. The rate of the dissolution reaction was directly proportional to the specific surface area of the asbestos minerals. It was noted that magnesium cations may be continuously liberated from the chrysotile fibers, leaving behind an intact silica structure. This original structure could then readsorb metal cations, since it will develop a highly negative charge. In general, however, this readsorption of metal cations is not observed; the smaller the particle, the faster the magnesium is liberated from the asbestos structure. Moreover, the reaction is temperature sensitive only in the initial stages of contact between chrysotile and water.

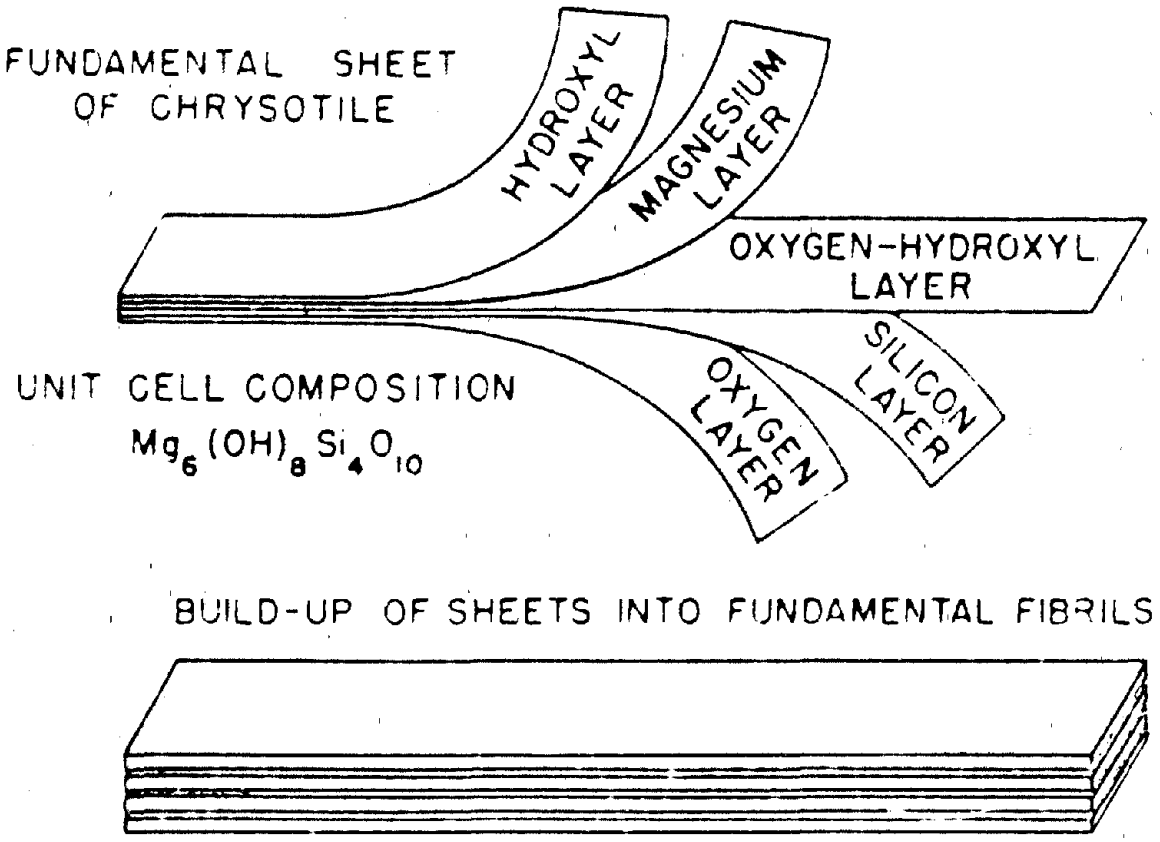


Figure 7-1 The structure of chrysotile. From Speil and Leineweber (1969).

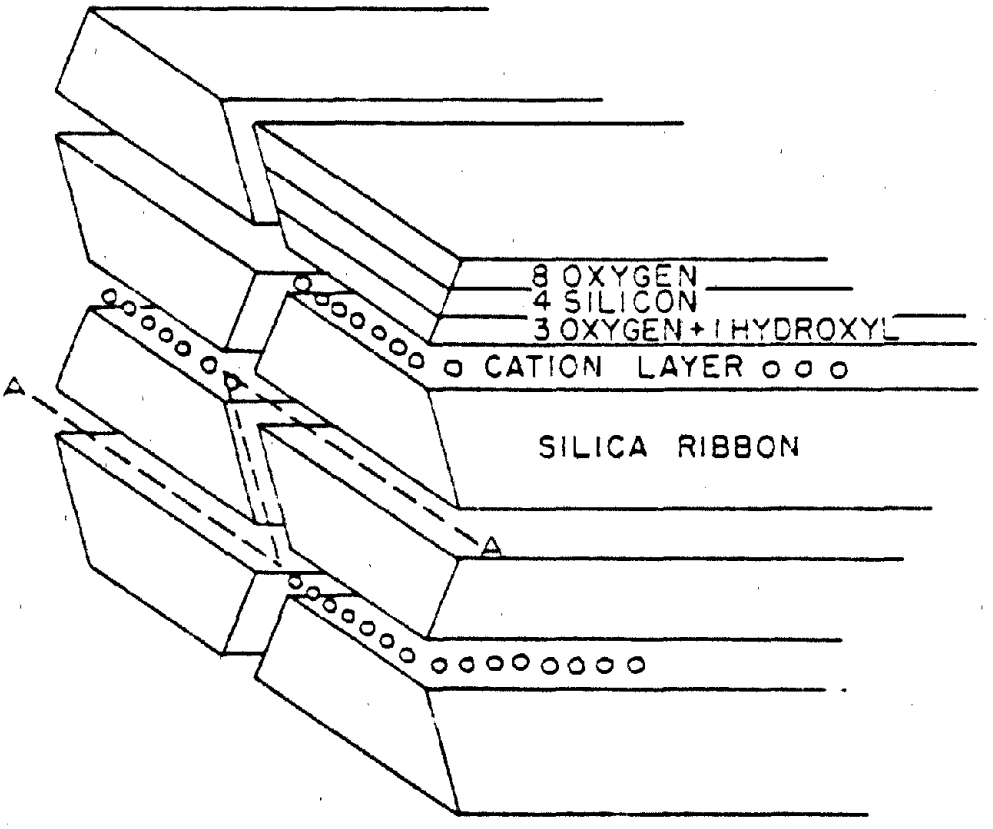


Figure 7-2 The structure of the amphibole asbestiform minerals. From Speil and Leineweber (1969).

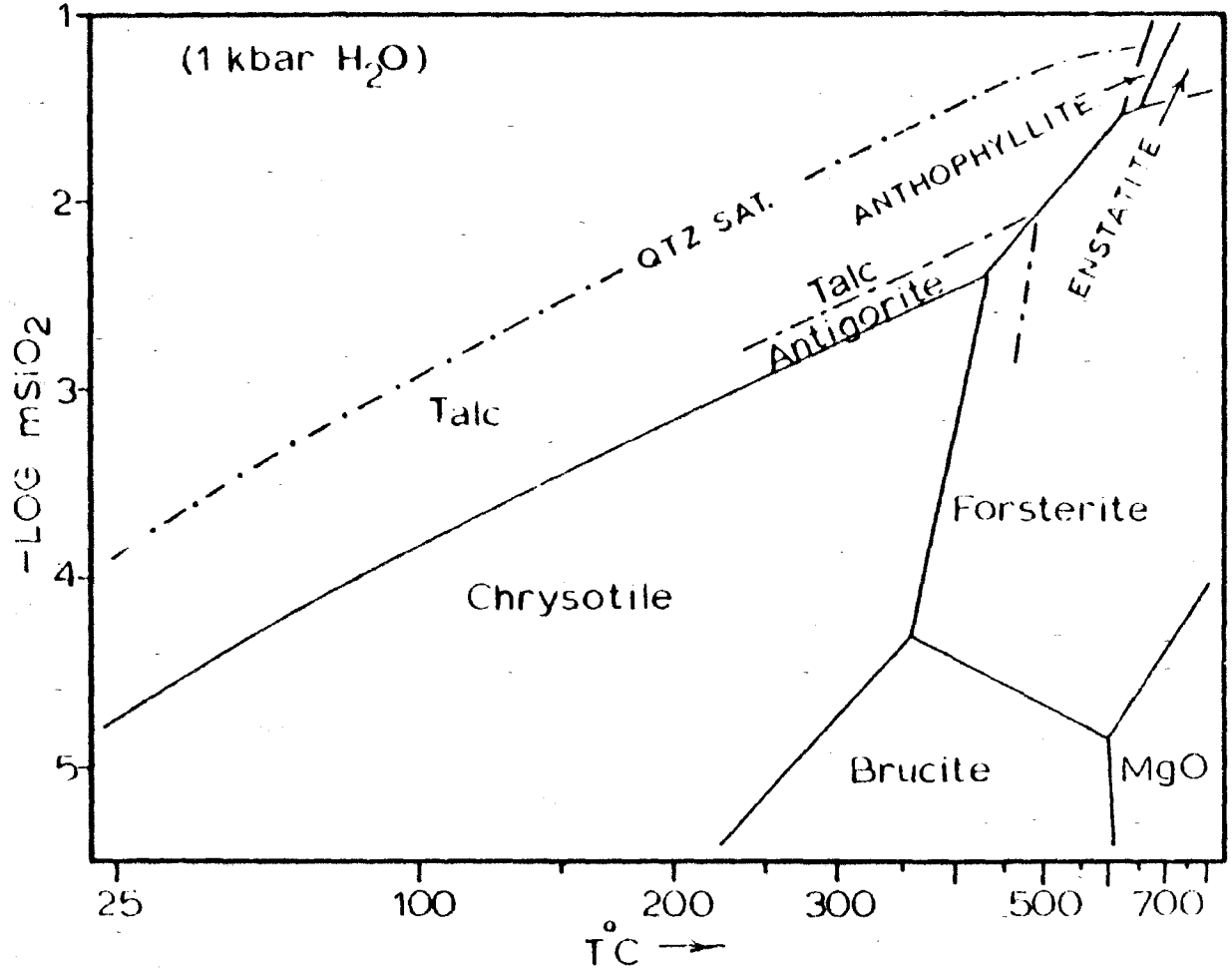


Figure 7-3 Mineral stability fields in the $MgO-SiO_2-H_2O$ system at 1 kbar H_2O. Modified from Hemley et al. (1977).

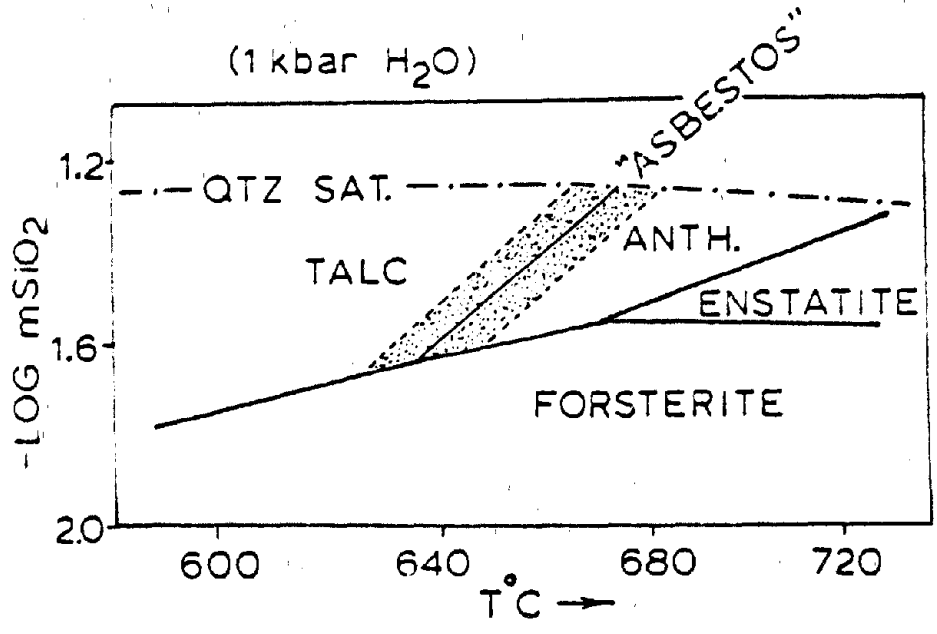


Figure 7-4 Mineral stability fields in the $MgO-SiO_2-H_2O$ system in the region of amphibole asbestos formation.[2] Modified from Hemley et al. (1977).

Hostetler and Christ (1968), in a laboratory study of the dissolution of chrysotile in water, determined an activity product of chrysotile in water at 25°C of $10^{-51.0}$. These results suggest that chrysotile is slowly soluble in water under conditions of continuous extraction. How useful these results are in the environment can only be determined through further experimentation. For instance, Chowdhury (1975) studied the leaching of asbestos in distilled water and at body temperature (37°C). He found that, for all practical purposes, amosite and crocidolite were inert under these conditions. Nonetheless, although he was unable to reach a chemical equilibrium after two months of leaching, a significant amount of the chrysotile had dissolved (1,000 μmol of Mg/g asbestos had been leached). He found further that under a dynamic system, after the magnesium had leached out, the silica skeleton began flaking apart, thereby eliminating the asbestos structure.

Langer et al. (1978) investigated the effect of milling (done to produce industrial useful fibers) on the chemical structure of asbestos. The milling altered the crystallinity of the chrysotile which appeared to include shifts in interlayer bonding between the magnesium and silica sheets and changes in hydroxyl configuration. The changes would theoretically increase the leachability of chrysotile in water and might replicate the effect that transport in the aquatic environment would have on the individual asbestos fiber.

7.2.4 Asbestos in Lake Superior

Tailings from taconite mining, dumped into Lake Superior by the Reserve Mining Company at Silver Bay, Minnesota, have provided the opportunity to study the transport of asbestos in the aquatic environment. These tailings contained more than 50 percent quartz and about 40 percent amosite (the Cummingtonite -Grunerite series - mean chemical composition $(Fe_5Mg_2)Si_8O_{22}(OH)_2$). These tailings were dumped into the lake at the rate of about 60,000 - 70,000 metric tons per day in a water slurry of about 2.4×10^6 m^3/day (Cook 1973) and have been detected in the drinking water of Duluth, Minnesota (about 75 miles distance). Although the asbestos fibers are traveling great distances in the water column, they are being coagulated and sedimented in the western part of the lake near the tailing delta (Kramer 1976). If this process were not going on, according to the calculations of Kramer (1976), 3.5×10^6 fibers/liter should be found distributed evenly throughout the volume of Lake Superior. In actuality, however, only 1×10^6 fibers/liter are present in the eastern part of Lake Superior. Kramer (1976) found, as well, that the greater the distance from the tailings themselves, the richer in magnesium the asbestos became. This effect was attributed to the magnesium-rich asbestos having a more negative zeta potential which would prevent coagulation and sedimentation. It appears, therefore, that the fate of asbestos in the aquatic environment depends upon little understood geochemical mechanisms, which are a function of the surface chemistry and the detailed mineralogy of the fiber.

The CAS number for asbestos is 1332-21-4; for chrysotile, 12001-29-5; for anthophyllite, 17068-78-9; for actinolite, 13768-00-8; for amosite, 12172-73-5; for crocidolite, 12001-28-4; for tremolite, 14567-73-8. The TSL number for asbestos is A152-4265 and for asbestos fibers A152-4672.

7.3 Summary of Fate Data

7.3.1 Photolysis

Asbestos, as a mineral, is not affected by photolytic processes. It is possible however, that some of the more than sixty organic compounds observed to be adsorbed to asbestos fibers (Hilborn et al. 1974) might be susceptible to photolysis. The importance of such a process is presently uncertain.

7.3.2 Chemical Speciation

Asbestos, as a mineral group, is almost indestructable in the aquatic environment, as has been discussed in the identification section. Asbestos is, therefore, resistant to the processes of chemical speciation such as oxidation/reduction, hydrolysis, etc. Differences in chemical speciation, however, are observed in the amount of trace constituents in the asbestos fibers. Cralley et al. (1968) analyzed asbestos for trace metals and found up to 1482 µg/g of nickel, 1378 µg/g chromium; 54 µg/g cobalt and 444 µg/g manganese in chrysotile fibers. They found as well that the degree of solubility of the same metal varied considerably by source and type of asbestos.

Lockwood (1974) analyzed nine Canadian chrysotile samples for trace metals and found 2-14 µg/g beryllium, 3-10 µg/g cadmium, 202-771 µg/g chromium, 36-78 µg/g cobalt, 9-26 µg/g copper, 325-1065 µg/g manganese, 299-1187 µg/g nickel and 35-71 µg/g thallium in the asbestos samples. Similiar results were found by Korda et al. (1977) in their study of trace elements in the Reserve Mining Company's taconite dumpings in Lake Superior.

Hilborn et al. (1974) observed more than 60 different organic compounds in reference standard asbestos. The principal organic materials were alkanes, polycyclic aromatic hydrocarbons and amino acids. Harington (1962) investigated the benzopyrene content of asbestos because of its activity as a carcinogen. In a later study, Harington (1965) proposed that the majority of the organic matter originated from algae and bacteria that were present during the formation of the asbestos that was being mined. He also suggested that the asbestos is filtering organic matter out of the aqueous solutions found in most ore bodies. It is not clear whether these trace constituents are important to the overall aquatic fate of asbestos.

The trace metals and organic material, however, may have a great effect on the biological systems with which the asbestos comes in contact.

7.3.3 Volatilization

The importance of the transport of asbestos from the surface of aquatic environments by wind-activated aerosol formation is presently indeterminate. The mobilization of asbestos from the surface of highways and soils into the atmosphere by the action of wind has been observed in urban air (Holt and Young 1973; Aiste et al. 1976). Unfortunately, such studies have not been conducted from the surfaces of asbestos-containing water bodies.

7.3.4 Sorption

It appears that asbestos does not have an adsorptive affinity for the solids normally found in natural water systems; however, some materials, notably trace metals and organic compounds, have an affinity for asbestos minerals. The charge-dependent behavior of asbestos can be described by the concept of the zeta potential, the isoelectric point (IEP) and the zero point of charge (ZPC) (for a detailed description of these concepts see Parks 1967). The zeta potential is a measure of the surface charge of a solid in mV. The ZPC is the pH at which the solid surface charge from all sources is zero. The IEP is a ZPC arising from interaction of H^+, OH^-, the solid and water alone. The ZPC of a complex oxide such as asbestos is approximately the weighted average of the IEPs of its components. Predictable shifts in ZPC occur in response to specific adsorption and to changes in cation coordination, crystallinity, hydration state, cleavage habit, surface composition, and structural charge or ion exchange capacity.

Prasad and Pooley (1973) investigated the electrokinetic properties of amphibole asbestos dust samples in comparison with quartz dust. They found that the isoelectric-point of amosite was found at a pH of 3.1 and that of crocidolite was at a pH of 3.3 (Figures 7-5 and 7-6). The zeta potential of these amphibole asbestos minerals, due to the formation of the fibers, is a function of the combined face and edge charge. The face charge will be due to the silica in the structure while the edge charge is due to the layers of metal cations sandwiched between the layers of silica. Due to differences in fracture, when the fibers are being produced, it is likely that there will sometimes be a variation in the ratio of face to edge charges. It is evident from the results that amphibole asbestos has a net negative charge, i.e., the sum of the negatively charged silica surfaces and the positively charged edges of the metal cationic layers is negative. This net charge is very much lower than the actual value of charge per unit area on the fiber-face surface. The amphibole asbestos is, therefore, capable of adsorbing both cationic and anionic species, the former much more extensively than the latter.

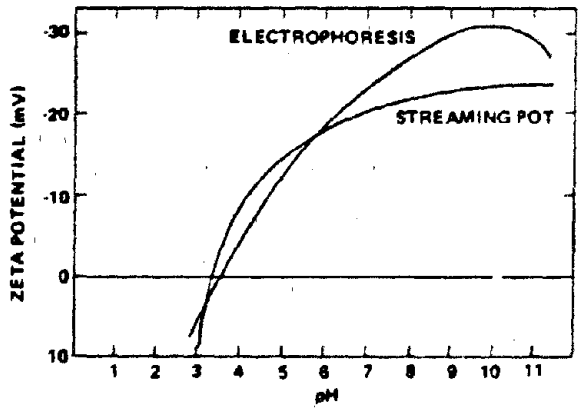


Figure 7-5 Variation of zeta potential with pH for amosite using the streaming potential and electrophoresis techniques. From Prasad and Pooley (1973).

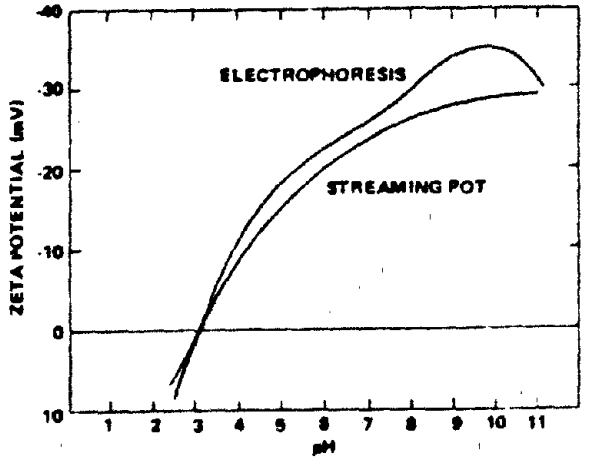


Figure 7-6 Variation of zeta potential with pH for crocidolite using streaming potential and electrophoresis techniques. From Prasad and Pooley (1973).

Chowdhury and Kitchener (1975), in a study of the zeta potentials of natural and synthetic chrysotiles, found a wide variety of zeta potentials. Strongly positive values were found in samples containing an excess of magnesium in the form of brucite $Mg(OH)_2$. Synthetic chrysotile and natural samples containing little or no brucite, gave moderately positive zeta potentials over the pH range of 3-11. Feebly positive or weakly negative zeta potentials were found in chrysotiles which had undergone weathering (due to natural leaching of the brucite layer). Since the pH and the ambient concentration of Mg^{+2} ions near the surface are the main controlling factors of the chrysotile zeta potential, and since chrysotile's brucite layer is susceptible to leaching in aqueous solution, the zeta potential of chrysotile is a constantly changing value. These results explain the temporary colloidal stability of dilute suspensions of chrysotile in environmental media and the mutual coagulation of chrysotile and amphibole asbestos slurries.

This effect of the colloidal stability of chrysotile was first described by Naumann and Dresher (1968). They found that, due to the positive zeta potential of chrysotile in environmental media, low viscosity suspensions could be prepared by means of the inherent charge of the chrysotile surfaces. This charge however, is so small in pure chrysotile that dispension was obtained only with short fibers and low fiber concentrations (1 percent). By increasing the concentration of certain metallic salts, however, it was found that low viscosity suspensions could be prepared under almost any environmental condition. These observations suggest that the presence of trace metals will produce a suspension of chrysotile asbestos in water which will persist until sufficient magnesium has leached from the chrysotile structure to degrade the suspension. Furthermore, it is probable that under certain conditions asbestos will persist in the water column until its concentration becomes high enough to destroy the suspension or until leaching of the brucite layer decays the zeta potential to a point where it will become negative.

These suspensions of asbestos might be susceptible to settling under certain environmental conditions. Although no specific data are available on settling rates of asbestos, several analytic models of the physical processes in aquatic environments have been developed in recent years. Examples include calculations of vertical eddy diffusivity within a nepheloid layer (Feely 1976), dissolution of diatoms (Lol and Lerman 1975), and suspended sediment transport (Nihoul 1977). Many of the analytic models have relied on Stokes Law, in itself an analytic solution to the problems of a sphere settling in an unbonded Newtonian fluid (Sverdrup et al. 1964). The work of Neihof and Loeb (1972, 1974) and Chase (1979) on the electrochemical characteristics of natural particulates and their settling behavior in natural water systems suggests that the Stokesian assumption may not be appropriate for charged particles. It appears to be

impossible at present to describe the settling behavior of asbestos in aquatic systems more definitely than to say that asbestos will stay in suspension for quite a long time.

7.3.5 Bioaccumulation

No evidence was found regarding the bioaccumulation of asbestos in aquatic organisms. Asbestos in city drinking water (Levy et al. 1976) has been found to be linked with certain gastrointestinal cancers in humans, and asbestos in food and water (Cunningham et al. 1977) has been found to have a similiar effect in rats. The release of metal ions from ingested asbestos (Chowdhury 1975) might lead to an accumulation of the heavy metals in some aquatic organisms. The importance of these processes is indeterminate at this time.

7.3.6 Biotransformation

Asbestos is considered to be non-degradable by aquatic organisms.

7.4 Data Summary

Although there has been little study of asbestos in aquatic environmental systems, it appears that asbestos is refractory in the aquatic environment. Therefore, asbestos, once introduced into the aquatic environment, will remain in the water column until surface charge coagulation or changes in flow regime allow it to settle out of the system. Table 7-1 summarizes the aquatic fate of asbestos.

Table 7-1

Summary of Aquatic Fate of Asbestos

Environmental Process	Summary Statement	Confidence of Data
Photolysis	Does not occur.	High
Chemical Speciation[a]	Some dissolution of chrysotile is observed; trace metal and organic materials in the structure might have an effect on the fate of asbestos in biological systems.	Medium
Volatilization	Not a significant process.	High
Sorption[a]	The sorptive capacity of asbestos (as defined by IEP and ZPC) has great effect on colloid behavior of asbestos.	Medium
Bioaccumulation	Not observed in aquatic organisms.	Low
Biotransformation	Does not occur in aquatic organisms.	High

a. All of the noted environmental processes are important; however, their relative importance with respect to each other is uncertain for determining final fate.

7.5 Literature Cited

Alstie, J., D. Watson, and J. Bagg. 1976. Airborne asbestos in the vicinity of a freeway. Atmos. Environ. 10:583-589.

Campbell, W.J., R.L. Blake, L.L. Brown, E.E. Cather, and J.J. Sjoberg. 1977. Selected silicate minerals and their asbestiform varieties: mineralogical definitions and identification-characterization. U.S. Bureau of Mines Information Circular 8751, Washington, D.C. 56p.

Chase, R.R.P. 1979. Settling behavior of natural aquatic particulates. Limnol. Oceanogr. 24(3):417-426.

Choi, I. and R.W. Smith. 1972. Kinetic study of dissolution of asbestos fibers in waters. J. Colloid Interface Sci. 40(2):253-262.

Chowdhury, S. 1975. Kinetics of leaching of asbestos minerals at body temperatures. J. Appl. Chem. Biotechnol. 25:347-353.

Chowdhury, S. and J.A. Kitchener. 1975. The zeta-potentials of natural and synthetic chrysotiles. Internat. J. Mineral Processing 2:277-285.

Cook, P.M. 1973. Distribution of taconite tailings in Lake Superior water and public water supplies. U.S. Environmental Protection Agency. National Water Quality Laboratory. Second Progress Report, July, 1973. Duluth, Minnesota. 88p.

Cralley, L.J., R.G. Keenan, R.E. Kupel, R.E. Kinsen, and J.R. Lynch. 1968. Characterization and solubility of metals associated with asbestos fibers. Amer. Ind. Hyg. Assoc. J. 29:569-573.

Cunningham, H.M., C.A. Moodie, G.A. Lawrence, and R.D. Pontefract. 1977. Chronic effects of ingested asbestos in rats. Arch. Environ. Contam. Toxicol. 6:507-513.

Feeley, R.A. 1976. Evidence for aggregate formation in a nepheloid layer and its possible role in the sedimentation of particulate matter. Marine Geol. 20:7-13.

Franco, M.A., J.L Hutchinson, D.A. Jefferson, and J.M. Thomas. 1977. Structural imperfection and morphology of crocidolite (blue asbestos). Nature 266:520-521.

Harington, J.S. 1962. Natural occurrence of oils containing 3,4-benzopyrene and related substances in asbestos. Nature 193:43.

Harington, J.S. 1965. Chemical studies of asbestos. Ann. N.Y. Acad. Sci. 132:31-47.

Hemley, J.J., J.W. Montoya, D.R. Shaw, and R.W. Luce. 1977. Mineral equilibria in the $MgO-SiO_2-H_2O$ system: II. Talc -antigorite -forsterite -anthophyllite - enstatite stability relations and some geologic implications in the system. Am. J. Sci. 277:353-383.

Hilborn, J., R.S. Thomas, and R.C. Lao. 1974. The organic content of international reference samples of asbestos. Sci. Total Environ. 3:129-140.

Holt, P.F. and D.K. Young. 1973. Asbestos fibres in the air of towns. Atmos. Environ. 7:481-483.

Hostetler, P.B. and C.L. Christ. 1968. Studies in the system $MgO-SiO_2-CO_2-H_2O(I)$: The activity-product constant of chrysotile. Geochim. Cosmochim. Acta 32:485-497.

Korda, R.J., T.E. Henzler, P.A. Helmke, M.M. Jimenez, L.A. Haskin, and E.M. Larsen. 1977. Trace elements in samples of fish, sediment, and taconite from Lake Superior. J. Great Lakes Res. 31(1-2):148-154.

Kramer, J.R. 1976. Fibrous cummingtonite in Lake Superior. Can. Mineral. 14:91-98.

Langer, A.M., M.S. Wolff, A.N. Rohl, and I.J. Selikoff. 1978. Variation of properties of chrysotile asbestos subjected to milling. J. Toxicol. Environ. Health 4:173-188.

Levy, B.S., E. Sigurdson, J. Mandel, E. Landon, and J. Pearson. 1976. Investigating possible effects of asbestos in city water: surveillance of gastrointestinal cancer incidences in Duluth, Minnesota. Amer. J. Epidemol. 103(4):362-368.

Lockwood, T.H. 1974. The analysis of asbestos for trace metals. Amer. Ind. Hyg. Assoc. J. 35:245-251.

Lol, D. and A. Lerman. 1975. Size spectra of biogenic particles in ocean water and sediments. J. Geophys. Res. 80:423-430.

Naumann, A.W. and W.H. Dresher. 1968. Colloidal suspensions of chrysotile asbestos surface charge enhancement. J. Colloid Interface Sci. 27(1):133-140.

Neihof, R.A. and G.I. Loeb. 1972. The surface charge of particulate matter in seawater. Limnol. Oceanogr. 17:7-16.

Neihof, R.A. and G.I. Loeb. 1974. Dissolved organic matter in sea water and the electric charge of immersed surfaces. J. Mar. Res. 32:5-12.

Nihoul, J.C. 1977. Turbulent boundary layer bearing silt in suspension. Phys. Fluids 20:5197-5202.

Parks, G.A. 1967. Aqueous surface chemistry of oxides and complex oxide minerals. pp.121-160. in Equilibrium concepts in natural water systems. W. Stumm (ed.). Advances in Chemistry Series 67. American Chemical Society, Washington, D.C. 344p.

Prasad, N.A. and F.D. Pooley. 1973. Characteristics of amphibole asbestos dust surfaces in aqueous media with reference to quartz. J. Appl. Chem. Biotechnol. 23:675-687.

Ross, M. 1978. The "asbestos" minerals: definitions, description, mode of formation, physical and chemical properties, and health risk to the mining community. Workshop on asbestos: definitions and measurement methods. National Bureau of Standards, Special Publication 506, Gaithersburg, Md. p.49-63.

Speil, S. 1974. Chrysotile in water. Environ. Health Perspect. 9:161-163.

Speil, S. and J.R. Leineweber. 1969. Asbestos minerals in modern technology. Environ. Res. 2:166-208.

Sverdrup, H.V., M.W. Johnson, and R.H. Fleming. 1964. The oceans: their physics, chemistry, and general biology. pp.956-958. Prentice-Hall, Inc., Englewood, Cliffs, N.J. 1565p.

8. BERYLLIUM

8.1 Statement of Probable Fate

Beryllium has a very low aqueous solubility and is probably precipitated or adsorbed onto solids soon after introduction to the aqueous environment. Complexing agents may solubilize beryllium, but ambient water quality data suggest that the concentration of this element in heavily polluted waters is quite low. Apparently, beryllium in natural water systems is found predominately in particulate rather than dissolved form.

8.2 Identification - Geochemistry of Beryllium

Beryllium is a naturally occuring element, found in the earth's crust at an average concentration of 2.5 ppm (Weast 1977). Beryllium is found chiefly as the minerals beryl ($Be_3Al_2Si_6O_{18}$), bromellite (BeO), chrysoberyl ($BeAl_2O_4$) and beryllonite ($NaBePO_4$). The chemical behavior of beryllium is similiar to that of magnesium (Cotton and Wilkinson 1972). In crystalline compounds, beryllium exists as bivalent ions of relatively small radius (0.35 Å). Two natural nuclides of beryllium are known, ^{9}Be and ^{10}Be, the latter being produced by the action of cosmic rays in the atmosphere.

Analyses of surface, ground, and rain waters have shown that, in general, beryllium concentrations are well below 1 µg/l. Meehan and Smythe (1967) reported that the maximum beryllium concentration in 20 rain water samples and 56 river water samples (from 5 different Australian rivers) was 0.18 µg/l. In a study of beryllium in ground water, drinking water, and surface water, Reichert (1973) found that even in the heavily polluted Rhine and Main Rivers (Germany), the concentration was below 0.02 µg/l. Hem (1970) estimates that the average concentration of beryllium in fresh surface waters is less than 1 µg/l.

Beryllium is concentrated in silicate minerals relative to sulfides. In common crystalline rocks, the element is enriched in the feldspar minerals relative to ferromagnesium minerals and apparently replaces the silicon ion; 85-98% of the total crustal beryllium may be bound in the feldspar structures (Beus 1966). Beryllium is thought to become concentrated in the later stages of magmatic differentiation. The greatest known concentrations of beryllium are found in certain pegmatite bodies, where crystals of beryl account for a few percent of the total pegmatite volume, and may be found in several of the strata of zoned-dykes. The element is sometimes concentrated in hydrothermal veins, and some granitic rocks contain sufficient amounts to permit the crystallization of small amounts of beryl. During the weathering of crystalline rocks and during sedimentation processes, beryllium appears to follow the course of aluminum, and it becomes enriched in some bauxite deposits, clays, and deep-sea sediments.

Beryllium has a complicated coordination chemistry and can form complexes, oxycarboxylates, and chelates with a variety of materials (Bertin and Thomas 1971). In aqueous solution, beryllium does not exist as actual Be^{+2} ions, but as hydrated complexes (Cotton and Wilkinson 1972). Complexing of beryllium may result in soluble beryllium concentrations in excess of those predicted on the basis of conventional thermodynamic considerations.

Beryllium, atomic number 4, is among the lightest of elements with an atomic weight of 9.012. It is a member of the alkaline earth elements, and, except for its metallic state, always has a valence of +2. The metal has a specific gravity of 1.85, a melting point of 1278°C, and a boiling point of 2970°C (Weast 1977).

The CAS number of beryllium is 7440-41-7, and the TSL number is A267-0214.

8.3 Summary of Fate Data

8.3.1 Photolysis

No data were found regarding photolysis of beryllium compounds. Photolysis is probably not an important process in the aquatic fate of beryllium.

8.3.2 Chemical Speciation

Beryllium is the smallest of the group II metals - the crystal radius of the divalent ion is only 0.31 Å. The small ionic radius and the resultant large surface charge-density are dominant influences on the chemistry of beryllium. Thus, beryllium forms stable compounds with small anions, such as fluoride and oxide, because unusually close approaches to their ionic centers are possible. The highly hydrated state of beryllium ion in acidic solution and the amphoteric nature of beryllium are all further consequences of the small size and high surface charge-density of the beryllium ion (Drury *et al.* 1978).

Soluble beryllium salts are hydrolyzed to form insoluble beryllium hydroxide, $Be(OH)_2$ (Cotton and Wilkinson 1972). The solubility of $Be(OH)_2$ is quite low in the pH range of most natural waters. A pH-log (species) diagram constructed for a simple system in which the solubility of $Be(OH)_2$ is controlled by dissolution into Be^{+2} and $HBeO_2^-$ indicates that beryllium will have minimal solubility at about pH 7.5 (Figure 8-1).

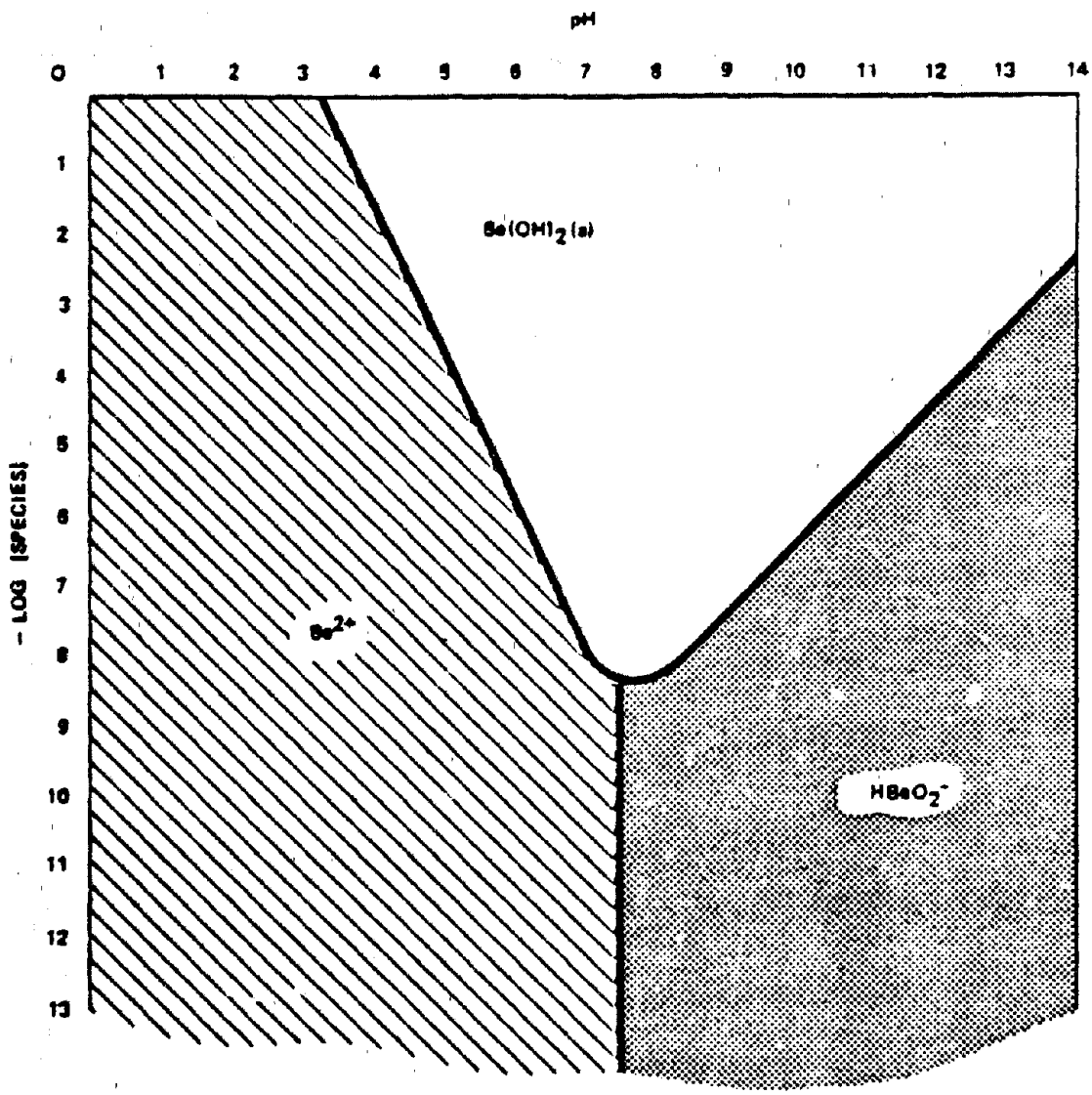


Figure 8-1 pH-log (species) diagram for $Be(OH)_2$, Be^{+2} and $HBeO_2^-$. From Cotton and Wilkinson (1972).

Formation of complexes with hydroxide ions may increase the solubility somewhat, especially at higher pH where polynuclear hydroxide complexes may form (Hem 1970). It is probable, however, that in most natural environments, beryllium is present in particulate rather than dissolved form (Hem 1970). This is substantiated by empirical data which indicate that, even in polluted rivers, dissolved beryllium levels are very low.

8.3.3 Volatilization

Although inhalating the airborne dust is the most widely known hazard associated with beryllium, no evidence was found that biomethylation or other processes result in volatilization of beryllium from aquatic systems.

8.3.4 Sorption

No data were found on the adsorption of beryllium. Nonetheless, due to its geochemical similarity to aluminum, one would expect that at low pH, beryllium would tend to be adsorbed onto clay mineral surfaces while at high pH, it should be complexed in some insoluble compounds. Beryllium should be present in particulate (either sorbed or precipitated) rather than in dissolved form in most natural environments.

8.3.5 Bioaccumulation

Little work has been completed concerning the biological pathways of beryllium in water. Tarzwell and Henderson (1960) have demonstrated that beryllium is highly toxic to warmwater fishes in soft water. Slonim (1973) measured ^{7}Be uptake by guppies (Poecilia reticulata) in a static freshwater system. Levels were highest in the viscera and intestinal tract, followed by kidney and ovary. Uptake was directly related to beryllium concentration in water, inversely related to fish size, and not related to fish age. Water hardness was inversely related to beryllium toxicity but did not appear to influence beryllium uptake by guppies. Thus, the body burden of beryllium is not the controlling factor governing toxicity. It was suggested that beryllium, present in a particular target organ, may be related to toxic response.

Cowgill (1973), in a study of biogeochemical cycles in a freshwater glacial lake in Connecticut, found no evidence of bioaccumulation or food chain magnification. He found that beryllium seemed to be concentrated in the stalks of aquatic plants, with lower quantities in the flowers and leaves.

Although beryllium has a low solubility in water, it is possible that benthos could accumulate beryllium from sediment and thereby transfer the metal to higher organisms via the food chain. Although beryllium toxicity decreases with increasing water hardness, beryllium uptake appears to be unaffected by increasing hardness. There is a general paucity of information (Table 8-1) concerning the accumulation of beryllium by aquatic plants and animals.

Table 8-1

Bioconcentration Factors for Beryllium

Taxon	Bioconcentration Factor[a]	Reference
Freshwater Plants	100	Chapman et al. 1968
Freshwater Invertebrates	100	Chapman et al. 1968
Freshwater Fish	100	Chapman et al. 1968
Marine Plants	100	Chapman et al. 1968
Marine Invertebrates	100	Chapman et al. 1968
Marine Fish	100	Chapman et al. 1968

a. Bioconcentration factors are the ratio derived from the concentration of the element in the aquatic organism (in ppm wet weight) divided by the concentration of the element in water (in ppm).

8.3.6 Biotransformation

No data were found relative to aquatic fate on biotransformation of beryllium or its compounds.

8.4 Data Summary

Beryllium has a very low aqueous solubility under normal pH conditions due to the formation of insoluble $Be(OH)_2$. Adsorption probably further reduces the concentration of dissolved beryllium. Formation of soluble complexes may tend to increase the solubility of this element, but it appears that under most circumstances, beryllium is associated with the particulate rather than the dissolved components of natural water systems. The aquatic fate of beryllium is summarized in Table 8-2.

Table 8-2

Summary of Aquatic Fate of Beryllium

Environmental Process	Summary Statement	Confidence of Data
Photolysis	Not an important fate.	Low
Chemical Speciation[a]	Beryllium is hydrolyzed to form insoluble compounds. A controlling mechanism for beryllium in the aquatic environment.	Medium
Volatilization	Not an important fate.	Low
Sorption[a]	Probably adsorbed by clays and other mineral surfaces at low pH.	Low
Bioaccumulation	Slight accumulation by aquatic organisms. No food chain magnification in evidence.	Medium
Biotransformation	Unreported.	Low

a. All of the noted environmental processes are important; however, their relative importance with respect to each other is uncertain for determining final fate.

8.5 Literature Cited

Bertin, F. and G. Thomas. 1971. Sur la chimie de coordination du béryllium. Bull. Soc. Chim. France. 10:3467-3498.

Beus, A.A. 1966. Distribution of beryllium in granites. Geochemistry (USSR) 5:432-437.

Chapman, W.H., H.L. Fisher, and M.W. Pratt. 1968. Concentration factors of chemical elements in edible aquatic organisms. Lawrence Radiation Laboratory, Livermore, Calif. UCRL-50564. 46p.

Cotton, F.A. and G. Wilkinson. 1972. Advanced inorganic chemistry. pp.245-254. Interscience Publishers, New York. 1145p.

Cowgill, U.M. 1973. Biogeochemical cycles for the chemical elements in Nymphaea odorata Ait. and the aphid Rhopalosiphum nymphaeae (L.) living in Linsley Pond. Sci. Total Environ. 2:259-303.

Drury, J.S., C.R. Shriver, E.B. Lewis, L.L. Towill, and A.S. Hammons. 1978. Reviews of the environmental effects of pollutants: VI Beryllium. pp.8-38. Oak Ridge National Laboratory, Oak Ridge, Tenn. PB 290-966. 198p.

Hem, J.D. 1970. Study and interpretation of the chemical characteristics of natural water. p.194. U.S.G.S. Water Supply Paper 1473. Washington, D.C. 363p.

Meehan, W.R. and L.E. Smythe. 1967. Occurence of beryllium as a trace element in environmental materials. Environ. Sci. Technol. 1(10):839-844.

Reichert, J.K. 1973. Beryllium, ein toxisches element in der mensch-lichen umgebung unter besonder berücksichtigung seines vorkommens in gewässern. Vom Wasser 41:209-215.

Slonim, A.R. 1973. Acute toxicity of beryllium sulfate to the common guppy. J. Water Pollut. Control Fed. 45(10):2110-2121.

Tarzwell, C.M. and C. Henderson. 1960. Toxicity of less common metals to fishes. Ind. Wastes 5:12.

Weast, R.C. (ed.) 1977. Handbook of chemistry and physics, 58th edition. CRC Press, Cleveland, Ohio. 2398p.

9. CADMIUM

9.1 Statement of Probable Fate

Compared to the other heavy metals, cadmium is relatively mobile in the aquatic environment and may be transported in solution as either hydrated cations or as organic or inorganic complexes. In most natural surface waters, the affinity of complexing ligands for cadmium probably follows the order: humic acids $> CO_3^{2-} > OH^- \geq Cl^- \geq SO_4^{2-}$.
In polluted waters, complexing with organic materials is the most important factor in determining the aquatic fate and transport of cadmium. Sorption processes account for the removal of dissolved cadmium to bed sediments and are increasingly effective as pH increases. Adsorption onto organic materials, mineral surfaces, co-precipitation with hydrous metal oxides, and isomorphous substitution in carbonate minerals can all result in reductions in aqueous cadmium concentration. Cadmium is strongly accumulated by organisms at all trophic levels.

9.2 Identification - Geochemistry of Cadmium

Cadmium is a relatively rare element that is concentrated in zinc-bearing sulfide ores (Zn/Cd ratio is usually 100 to 200) and, consequently, is found in all zinc-containing products. It is found at an average concentration of 0.15 ppm in the earth's crust (Weast 1977). Most fresh waters contain less than 1 ppb cadmium. The chemistry of cadmium in surface and ground waters has been reviewed by Hem (1972), giving calculations of equilibrium solubilities with the hydroxides or carbonates as solid phases. Most natural waters are undersaturated with respect to these phases, i.e., only 20 percent have cadmium concentrations in reasonable agreement with calculated solubilities that assume $CdCO_3$ to be the equilibrium solid phase. Cadmium levels in sea waters average about 0.15 ppb.

Cadmium has an atomic weight of 112.41. Metallic cadmium has a melting point of 320.0°C, a boiling point of 765°C, specific gravity of 8.642, and a vapor pressure of 1 mm at 394°C (Weast 1977). The geochemistry of cadmium has been extensively reviewed by Wakita and Schmitt (1970).

Cadmium's CAS number is 7440-43-9; its TSL number is A344-2245.

9.3 Summary of Fate Data

9.3.1 Photolysis

No evidence was found indicating that photolysis is an important mechanism in determining the fate of cadmium compounds in the aquatic environment.

9.3.2 Chemical Speciation

In natural waters cadmium can be found in several chemical forms, for example, as simple aquated ions, as metal-inorganic complexes, or as metal-organic complexes. An understanding of the chemical speciation of cadmium in any given situation is based upon theoretical calculations of hydrolysis, oxidation/reduction and organic complexation. A short presentation of this material will be given after which the chemical speciation of cadmium in various aquatic environments will be discussed.

Cadmium forms complexes with OH^- such as $CdOH^+$, $Cd(OH)_2(aq.)$, $Cd(OH)_3^-$, and $Cd(OH)_4^{2-}$. A distribution diagram for cadmium hydroxide complexes is shown as Figure 9-1 (Weber and Posselt 1974). As is evident from the diagram, almost all of the soluble cadmium is in the divalent cation form up to about pH 9. The solubility of cadmium decreases as pH increases due to formation of solid $Cd(OH)_2$, according to the reaction:

$$Cd^{2+} + 2\ OH^- \rightleftharpoons Cd(OH)_2\downarrow$$

Patterson et al. (1977) studied the removal of dissolved cadmium by hydroxide and carbonate precipitation. A comparison of experimentally determined $Cd(OH)_2$ solubility with the calculated solubility curve is shown as Figure 9-2. The diagram shows that, even at the optimal pH for precipitation, the equilibrium solubility of cadmium is still approximately 1 mg/l.

Since it seemed possible that carbonate could be a more effective control on cadmium solubility than precipitation as the hydroxide, Patterson et al. (1977) investigated the use of a carbonate system as a possible treatment technology. The results of adding carbonate as Na_2CO_3 with $C_T = 10^{-1.2}$ M and $C_T = 10^{-2.7}$ M are shown as Figures 9-3 and 9-4, respectively. The treatment time was 4 hours. Although the dissolved cadmium concentrations are still quite high in the carbonate systems at pH > 10, they are considerably lower than in the hydroxide system.

Cadmium is always found in the +2 valence state in water (Cotton and Wilkinson 1972). Therefore, redox potential has little direct effect on cadmium. Under reducing conditions and in the presence of sulfur, however, cadmium may react to form the insoluble sulfide. The log K_{sp} (log solubility product constant) for cadmium sulfide is 5.73 (Huang et al. 1977) for the following reaction:

$$CdS_{(s)} + 2H^+ \rightleftharpoons Cd^{2+} + H_2S(aq)$$

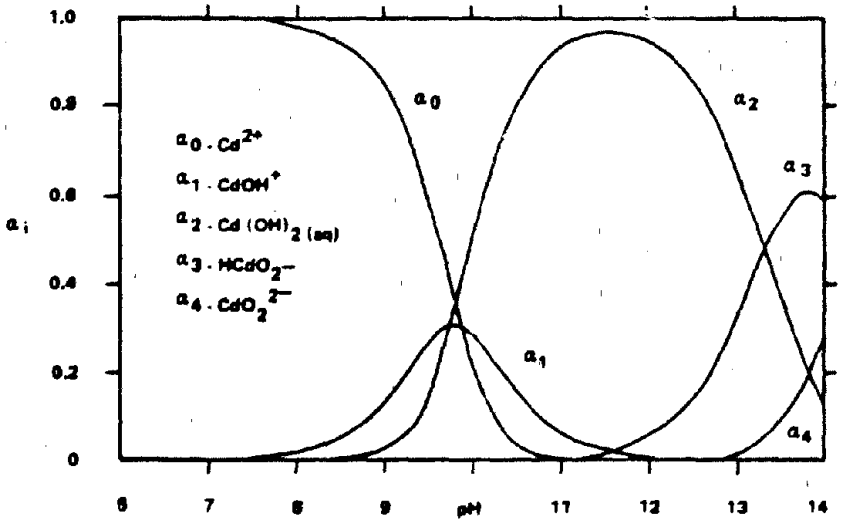


Figure 9-1 Distribution diagram for cadmium hydroxide complexes. From Weber and Posselt (1974).

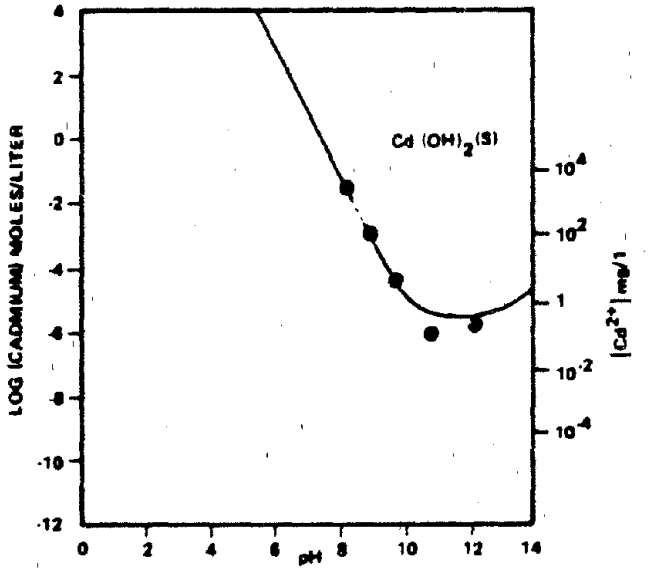


Figure 9-2 Comparison of cadmium hydroxide solubility data with theoretical solubility curve. From Patterson et al. (1977).

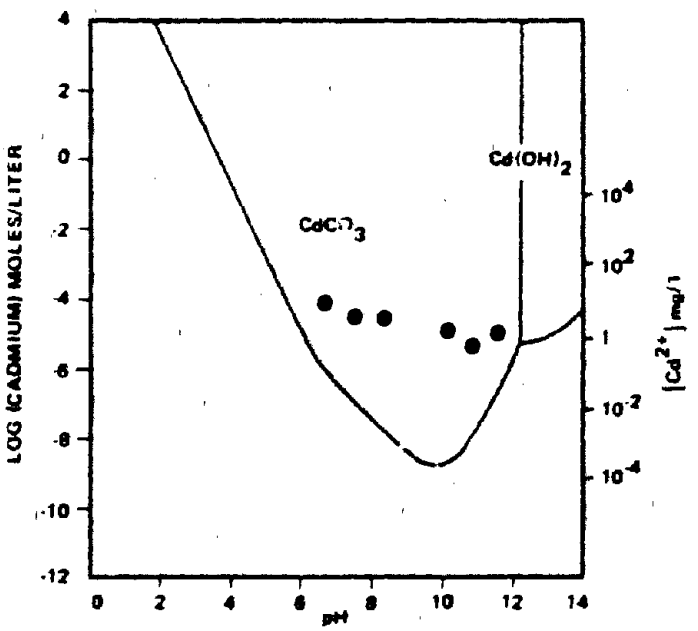


Figure 9-3 Comparison of cadmium solubility data with theoretical phase diagram ($C_T = 10^{-1.2}$ mol/l). From Patterson et al. (1977).

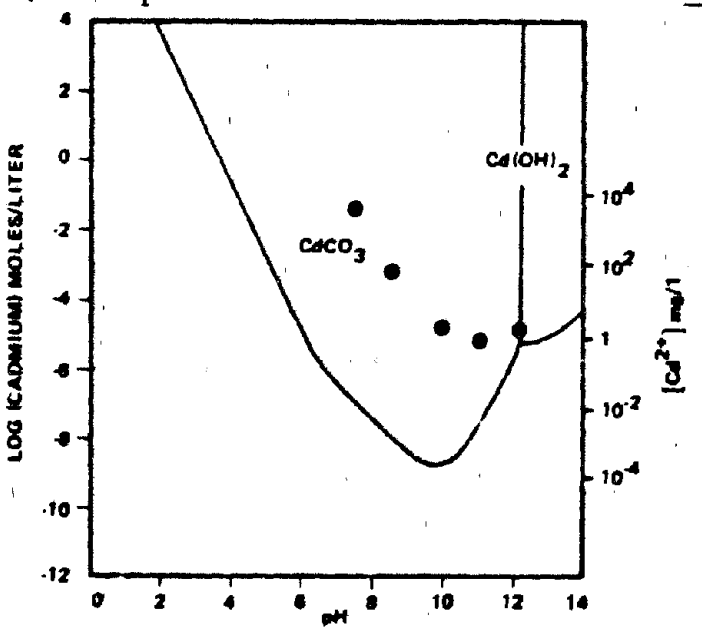


Figure 9-4 Comparison of cadmium carbonate solubility data with theoretical phase diagram ($C_T = 10^{-2.7}$ mol/l). From Patterson et al. (1977).

Under acidic conditions, CdS is more soluble. In the sediments, in anaerobic digestion of waste water, and in other reducing environments where sulfur is available, the solubility of cadmium may be controlled by formation of CdS (Holmes et al. 1974).

Long and Angino (1977) developed a theoretical model to study the chemical speciation of cadmium in aqueous solutions and the response of cadmium to variations in ionic strength and complexation. Association of cadmium with the ligands OH^-, Cl^-, CO_3^{2-}, SO_4^{2-} and HCO_3^- were considered at pH values from 3.5 to 11.0 at 25°C in differing seawater-freshwater mixtures. The results are summarized in Figure 9-5. In general, the relative importance of the various ligand-cadmium complexes can be predicted from a comparison of their stability constants. Unfortunately, this model does not take into account metal-organic complexes, and it is, therefore, useful only in unpolluted, relatively organic-free waters.

Gardiner (1974a), in his study of the speciation of cadmium in natural waters, found that a substantial portion of the total cadmium in river and lake water will usually be present as the divalent cadmium ion, the concentration of which will be inversely related to the pH and the concentration of organic material present in the water. Humic substances usually account for most of the complexation, followed in importance by the carbonates. O'Shea and Mancy (1978), in their study of the effect of pH and hardness on cadmium speciation, found that the effect of pH and hardness was insignificant in trace metal-inorganic interactions. Hardness and pH were quite important, however, in trace metal-humic acid interactions. Increasing the pH increased the exchangeable cadmium while an increase in hardness led to a most pronounced decrease in the extent of the humic acid interaction. Metals responsible for hardness apparently inhibit the exchangeable interactions between metals and humic materials in ways that are not yet fully understood.

Guy and Chakrabarti (1976), in their study of metal-organic interactions in natural waters, found that humic acids in solution and other natural complexing agents can maintain cadmium ions in a bound form at a pH as low as 3. The release of cadmium from sediments is, therefore, apparently controlled by a combination of ion exchange and complex formation whereby the stability of the metal-organic complex determines the amount of metal solubilized.

In summation, the transport of cadmium in the aquatic environment is controlled by the speciation of the ion. Although it appears that in most unpolluted waters cadmium will exist mainly as a divalent cation, organic material will have a pervasive effect on the chemical form in which

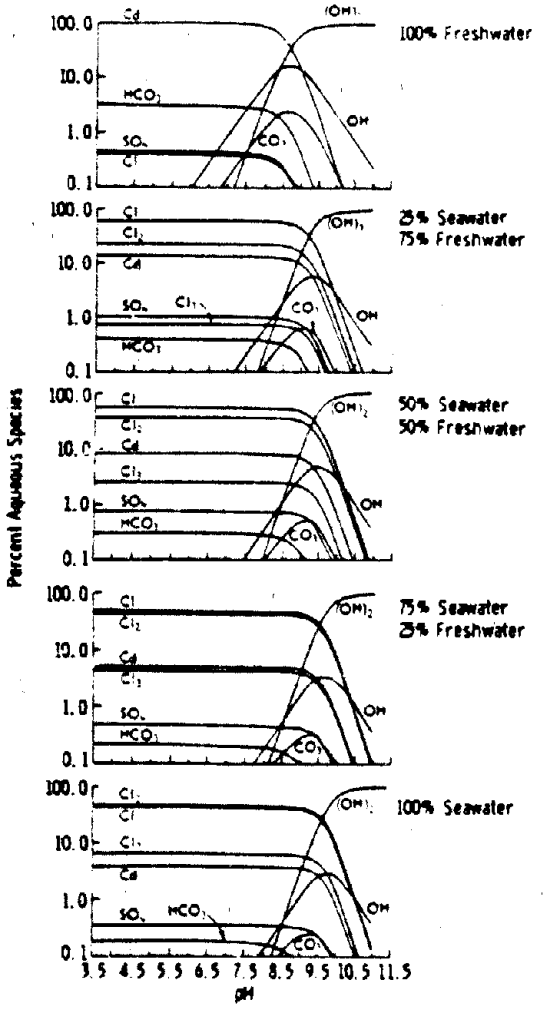


Figure 9-5 Cadmium speciation in seawater-freshwater mixtures (Long and Angino 1977).

cadmium will be present in industrialized urban areas. In most fresh water systems, the affinity of complexing ligands for cadmium appears to follow the order of: humic acids > CO_3^{2-} > OH^- ≥ Cl^- ≥ SO_4^{2-}. Nonetheless, there is as yet insufficient information to present a comprehensive model for the transport and sorption of cadmium based upon these and similar interactions.

9.3.3 Volatilization

Cadmium is not known to form volatile compounds in the aquatic environment. Unlike mercury, which is directly below cadmium in the periodic table and, therefore, chemically similar, biological methylation of cadmium has not been reported. The instability of alkyl cadmium compounds in the presence of water or oxygen (Cotton and Wilkinson 1972) probably precludes their formation in aqueous ecosystems.

9.3.4 Sorption

Although sorption processes affect cadmium to a lesser extent than most of the other heavy metal pollutants, sorption by mineral surfaces, hydrous metal oxides, and organic materials probably removes more cadmium from solution than does precipitation. Various studies place different emphasis on the relative contributions of sorption to clays, sorption to organic matter, co-precipitation with hydrous iron, aluminum, and manganese oxides, and isomorphous substitution in carbonate minerals. All studies indicate that cadmium concentrations in bed sediments are generally at least an order of magnitude higher than in overlying waters (Gardiner 1974b; Kubota *et al.* 1974; Perhac 1974a, 1974b; Helz *et al.* 1975; Steele and Wagner 1975; Farrah and Pickering 1977; Schell and Nevissi 1977; Suzuki *et al.* 1979).

Suzuki *et al.* (1979), in their study of a polluted Japanese river, found that the cadmium content of the sediment is directly proportional to the ignition loss of the sediment indicating that the organic material is mainly responsible for the accumulation of cadmium in organically polluted river sediments. Moreover, laboratory studies on the river sediments demonstrated that cadmium sorption could be correlated with the amount of organic matter present in the sediment by a Freundlich-type equilibrium relation:

$$O.M. = k\, C^{1/n}$$

where O.M. is organic matter as measured by ignition loss, C is concentration of cadmium in the aqueous phase, and k and n are experimentally deter-

mined equilibrium constants. These results suggest that in the transport of cadmium, suspended solids of high organic content play a dominant role in polluted waters.

Gardiner (1974b), in a laboratory study of the adsorption of cadmium on mud solids, particles of clay and silica, and humic material, found that the adsorption of cadmium on mud solids is of major importance in controlling the concentration of cadmium in fresh water. He found that concentration factors for mud varied between 5,000 and 50,000 depending on the type of solid, its state of subdivision, the concentration of metal ion and complexing ligands present, as well as the temperature, pH, and hardness of the water. It appeared further that humic material was at all times the major component of sediment responsible for adsorption.

In contrast, Perhac (1974b) found that most of the cadmium in the bottom sediments of an unpolluted Tennessee stream was associated with carbonates and (to a lesser extent) iron oxides, and therefore hypothesized that cadmium occurs in cation lattice sites within the carbonate minerals. Isomorphous substitution of cadmium for calcium in such minerals could probably occur; the crystal ionic radius for cadmium(II) is 0.97 Å, and the radius for calcium(II) is 0.99 Å (Weast 1977). It is pertinent that Perhac's (1972; 1974a) studies of metal distribution in unpolluted streams show that most of the cadmium transported in the water column is in the dissolved state (77.4-95.4 percent). Minor amounts are transported with the coarse particulates (3.5-21.9 percent), and only a small fraction is transported with colloids (0.5-6.0 percent). Even though the concentration in colloids is greatest, the concentration in coarse particulates intermediate, and the concentration as dissolved species is the lowest, the mass of water transported in the stream so greatly outweighs the mass of suspended particles that the greatest transport (by mass) is in the dissolved state. Perhac's (1974b) assertion that the carbonate minerals and iron oxides can control cadmium mobility is corroborated by Steele and Wagner (1975), who found that most of the cadmium in Buffalo River (Arkansas) sediments was in the form of mineral clasts, although a minor amount was associated with metal oxides.

Ramamoorthy and Rust (1978), in their study of Ottawa River sediments, found that, although the sediment was composed mainly of well sorted sand, it was an efficient sink for heavy metals. They discovered that this was due to the significant amount of organic material added to the sediments by the commercial use of the river for logging. The mobility and persistence of the cadmium itself was in part dependent on the extent of its sorption onto the sediments while its redistribution was a function of desorption processes at the sediment-water interface. Both sorption and

desorption were controlled by the nature of total heavy metal loading, the sediment type and the surface water characteristics.

The adsorption of cadmium onto soils and silicon and aluminum oxides was studied by Huang et al. (1977). The results of this laboratory study indicate that adsorption is strongly pH-dependent, increasing as conditions become more alkaline (see Figure 9-6). When the pH is below 6-7, cadmium is desorbed from these materials. Cadmium has considerably less affinity for the absorbents tested than do copper, zinc, and lead, and thus might be expected to be more mobile in the environment than these materials.

Another relevant observation of Huang et al. (1977) was that addition of anions to the dissolved cadmium caused an increase in adsorption (Figure 9-7). Humic acid was most effective in this regard, followed by nitrilotriacetate, tartrate, glycine, and phosphate, respectively. Huang et al. (1977) suggest that the anions complex the cadmium and that subsequent adsorption of the organo-cadmium compounds by hydrous solids occurs through specific chemical bonds (e.g., "sharing of free electrons available from the metal-ligand complexes and hydrogen bond").

The mode by which cadmium is sorbed to the sediments is important in determining its disposition toward remobilization. Cadmium found in association with carbonate minerals, precipitated as stable solid compounds, or co-precipitated with hydrous iron oxides would be less likely to be mobilized by resuspension of sediments or biological activity. Cadmium adsorbed to mineral surfaces (e.g., clay) or organic materials would be more easily bioaccumulated or released in the dissolved state when sediments are disturbed, such as during flooding.

Although it is widely reported that dissolved cadmium concentrations decrease with distance from the source and sediment concentrations are concomitantly enriched, several authors have reported a remobilization phenomenon in which sorbed cadmium is subsequently released due to salinity (Helz et al. 1975) and redox effects (Holmes et al. 1974; Lu and Chen 1977). Kubota et al. (1974) showed that the cadmium concentration of Lake Cayuga was higher than the concentration in tributary streams, suggesting remobilization from sediments. Such remobilization may have occured due to a reduction in pH in the lake water relative to most of its tributaries; unfortunately, pH values for the lake were not reported.

It appears, therefore, that sorption processes are important in determining cadmium transport, partitioning, and potential for remobilization. In unpolluted waters, exchange of cadmium for calcium in the lattice structure of carbonate minerals can remove cadmium from solution. Thus,

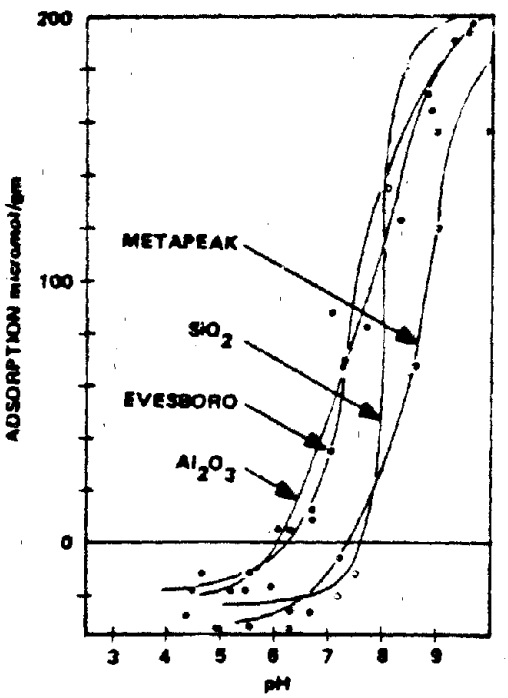


Figure 9-6 Adsorption of cadmium on various solids (from Huang et al. 1977). Concentration of solids = 5 g/l; $[Cd^{2+}] = 10^{-3}$ M = 110 mg/l; ionic strength = 10^{-7} M (NaCl).

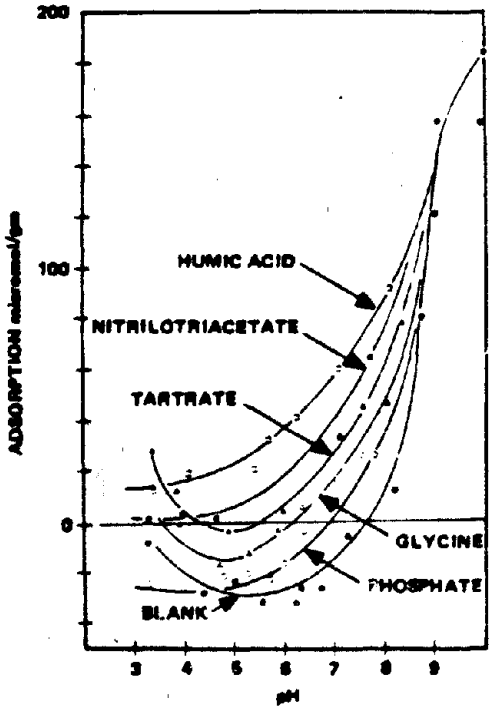


Figure 9-7 Effect of anions on the adsorption of cadmium by Metapeak soil. In addition to the experimental conditions shown in the caption of Figure 9-6, the anion concentration was 10^{-4} M except for humic acid which was added at 50 mg/l (from Huang et al. 1977).

co-precipitation with hydrous iron, aluminum, and manganese oxides can be the controlling factors in these unpolluted waters. In polluted or organic-rich waters, however, the adsorption of cadmium by humic substances and other organic complexing agents will be the controlling factor in determining transport, partitioning, and potential for remobilization.

9.3.5 Bioaccumulation

Cadmium is strongly accumulated by all organisms. Because of its chemical kinship to zinc, cadmium may displace zinc in certain enzymes, thereby disrupting normal metabolic function.

Cadmium has been reported to accumulate in the tissue of aquatic and marine organisms at concentrations hundreds to thousands of times higher than in the water column (Eisler et al. 1962; Friberg et al. 1971; Huckabee and Blaylock 1973; Kelso and Frank 1974; Valiela et al. 1974; Kinkade and Erdman 1975). Fish accumulate cadmium most readily in the liver, kidneys, and intestines, followed by the gills and the remainder of the body (Cearley and Coleman 1972; Huckabee and Blaylock 1973).

Several surveys of the concentration of cadmium in various marine and fresh water biota have been completed. Lovett et al. (1972) examined concentration levels in fish from various New York State fresh water lakes and streams. Maximum concentration levels exceeded 0.1 ppm Cd but most fish contained less than 0.02 ppm Cd. Martin and Broenkow (1975) reported that mixed phytoplankton and zooplankton collected off Baja California near San Diego averaged 13.2 ppm Cd (dry weight basis); samples collected from other coastal areas never exceeded 7.5 ppm Cd.

Reported microcosm and field studies differ in the relative concentration factors for cadmium in biota. Lu et al. (1975) found that bioaccumulation of cadmium was strongly correlated with the cation exchange capacity of test soils in their microcosm. As cation exchange capacity increased, levels of cadmium in the biota decreased. Fish (Gambusia affinis) accumulated less cadmium than algae, snails, mosquito larvae, or sorghum. The invertebrates accumulated more cadmium than algae or sorghum in two out of three test soils; but in the soil with the least cation exchange capacity, algae accumulated cadmium about 4 times as much as either of the invertebrates. Bioconcentration factors (concentration in organism ÷ concentration in water) calculated from the data of Lu et al. (1975) range from about 10^2 to 10^4.

The influence of hardness on uptake of cadmium by a microcosm containing an alga, a rooted plant, snails, catfish, and guppies was studied by Kinkade and Erdman (1975). They found that initial uptake of

cadmium was faster in hard than in soft water but that the total concentration of cadmium was greater in the organisms that were placed in soft water. The relative bioaccumulation factors descended in the following order: rooted plant > alga > guppies > snails > catfish.

Pascoe and Mattey (1977) exposed three-spined sticklebacks to a range of cadmium levels in water (0.001-100 mg Cd/l) for up to 79 days. Sticklebacks accumulated cadmium at all concentrations tested; however, the concentration factor was inversely and linearly related to exposure concentration. Concentration factors ranged from 311 at the lowest exposure to 0.51 at the highest. All of the concentrations tested were lethal to sticklebacks.

Cadmium is readily accumulated through both food and water by fresh water organisms, and either source of uptake can result in the development of toxic symptoms by fishes. Fish tissues appear to reach equilibrium with respect to cadmium after 8-20 weeks' exposure, depending upon the water temperature (Phillips and Russo 1978). Cadmium uptake increases with increasing water temperature and decreasing salinity. There is an indication that sex may determine the rate of cadmium accumulation in some fish species due, perhaps, to some sex-related metabolic differences. Fish accumulate highest cadmium concentrations in the kidneys and liver and little in the edible portions. Bioconcentration factors for cadmium are summarized in Table 9-1.

9.3.6 Biotransformation

No evidence was found in the reviewed literature for biomethylation of cadmium. Biologically produced ligands may affect the mobility of cadmium in aquatic environments, especially under eutrophic conditions. Cadmium also can be complexed *in vivo* by polydentate ligands that are normally involved in the binding sites of essential metal ions such as iron, manganese, cobalt, zinc and copper (Fulkerson and Goeller 1973).

9.4 Data Summary

Cadmium is mobile in the aquatic environment relative to most other heavy metals. It occurs as the divalent metal cation in acidic and circumneutral water, and it forms complexes with organic material in highly polluted waters and complexes with carbonate and hydroxide ions at higher pH values. The formation of complexes with humic substances is important because these complexes are more easily assimilated by the sediments than the hydrated divalent cation. Sorption processes are the most important factor in reducing the aquatic load and transport velocity of cadmium. Cadmium is less mobile in alkaline than in acidic waters. Sorption to

Table 9-1

Bioconcentration Factors for Cadmium

Taxon	Concentration Factor[a]	Reference
Marine Plants	1,000	Chapman et al. 1968
Marine Invertebrates	250,000	Chapman et al. 1968
Marine Fish	3,000	Chapman et al. 1968
Freshwater Plants	1,000	Chapman et al. 1968
Freshwater Invertebrates	4,000	Chapman et al. 1968
Freshwater Fish	3,000	Chapman et al. 1968

a. Concentration factors are defined by the ratio of the concentration of the element in the organism in ppm (wet weight) divided by the concentration of the element in water (ppm).

organic materials and clay minerals, co-precipitation with hydrous metal oxides and substitution in carbonate minerals all affect the distribution and fate of cadmium. Cadmium, although highly toxic, is concentrated by all organisms. The aquatic fate of cadmium is summarized in Table 9-2.

Table 9-2

Summary of Aquatic Fate of Cadmium

Environmental Process	Summary Statement	Confidence of Data
Photolysis	Not an important process.	High
Chemical Speciation[a]	In most unpolluted waters the majority of the cadmium will exist as the hydrated divalent cation. In polluted waters, complexation with organic material will be most important. Affinity of ligands for cadmium follows the order of humic acids $>CO_3^{2-}>OH^- \geq Cl^- \geq SO_4^{2-}$.	Medium
Volatilization	Not an important process.	High
Sorption[a]	Various sorption processes reduce the mobility of cadmium and result in the enrichment of suspended and bed sediments relative to the water column. In unpolluted waters, sorption onto clay minerals, and hydrous iron and manganese oxides are controlling factors. In polluted waters, sorption onto organic materials is the controlling factor.	High
Bioaccumulation[a]	Biota strongly accumulate Cd with concentration factors ranging from 10^2 to 10^4 or more. Bioaccumulation is greater in soft than hard water.	High
Biotransformation	No biomethylation in evidence. Organic ligands of biological origin may affect solubility and adsorption.	Medium

a. All of the noted environmental processes are important; however, their relative importance with respect to each other is uncertain for determining final fate.

9.5 Literature Cited

Cearley, J.E. and R.L. Coleman. 1972. Cadmium toxicity and bioaccumulation in largemouth bass and bluegill. Bull. Environ. Contam. Toxicol. 11(2):146-151.

Chapman, W.H., H.L. Fisher, and M.W. Pratt. 1968. Concentration factors of chemical elements in edible aquatic organisms. Lawrence Radiation Laboratory. Livermore, Calif. UCRL-50564.

Cotton, F.A. and G. Wilkerson. 1972. Advanced inorganic chemistry. pp.503-527. Inter-Science Publishers, New York. 1145p.

Eisler, R., G.E. Zaroogian, and R.J. Hennekey. 1962. Cadmium uptake by marine organisms. J. Fish. Res. Bd. Canada. 29:1367-1369.

Farrah, H. and W.F. Pickering. 1977. Influence of clay solute interactions on aqueous heavy metal ion levels. Water Air Soil Pollut. 8:189-197.

Friberg, L., M. Piscator, and G. Nordberg. 1971. Cadmium in the environment: a toxicological and epidemiological appraisal. pp.4-16 - 4-41. U.S. Environmental Protection Agency, Durham, N.C. (NTIS PB 199 795) 319p.

Fulkerson, W. and H.E. Goeller. (eds). 1973. Cadmium: the dissipated element. pp. 279-323. Oak Ridge National Laboratory, Oak Ridge, Tennessee. ORNL-NSF-EP-21. 472p.

Gardiner, J. 1974a. The chemistry of cadmium in natural waters - I. A study of cadmium complex formation using the cadmium specific-ion electrode. Water Research. 8(1):23-30.

Gardiner, J. 1974b. The chemistry of cadmium in natural waters - II. The adsorption of cadmium on river muds and naturally occurring solids. Water Research. 8:157-164.

Guy, R.D. and C.L. Chakrabarti. 1976. Studies of metal-organic interactions in model systems pertaining to natural waters. Can. J. Chem. 54:2600-2611.

Helz, G.R., R.J. Huggett, and J.M. Hill. 1975. Behavior of Mn, Fe, Cu, Zn, Cd, and Pb discharged from a wastewater treatment plant into an estuarine environment. Water Research. 9:631-636.

Hem, J.D. 1972. Chemistry and occurrence of cadmium and zinc in surface and ground waters. Water Resources Research. 8:661-671.

Holmes, C.W., E.A. Slade, and C.J. McLerram. 1974. Migration and redistribution of zinc and cadmium in a marine estuarine ecosystem. Environ. Sci. Technol. 8(3):255-259.

Huang, C.P., H.A. Elliott, and R.M. Ashmead. 1977. Interfacial reactions and the fate of heavy metals in soil-water systems. Jour. Water Poll. Control Fed. 49(5):745-756.

Huckabee, J.W. and B.G. Blaylock. 1973. Transfer of mercury and cadmium from terrestrial to aquatic ecosystems. Adv. Exp. Med. Biol. 40:125-160.

Kelso, J.R. and R. Frank. 1974. Organochlorine residue, mercury, copper, and cadmium in yellow perch, white bass, small mouth bass, in Long Point Bay, Lake Erie. Trans. Am. Fish. Soc. 103(3):577-581.

Kinkade, M.L. and H.E. Erdman. 1975. The influence of hardness components (Ca^{+2} and Mg^{+2}) in water on the uptake and concentration of cadmium in a simulated fresh water environment. Environ. Res. 10(2):308-313.

Kubota, J., E.L. Mills, and R.T. Ogleoby. 1974. Lead, Cd, Zn, Cu, and Co in streams and lake waters of Cayuga Lake Basin, New York. Environ. Sci. Techol. 8(3):243-248.

Long, D.T. and E.E. Angino. 1977. Chemical speciation of Cd, Cu, Pb, and Zn in mixed fresh water, seawater, and brine solutions. Geochim. Cosmochim. Acta. 41:1183-1191.

Lovett, R.J., W.H. Gutenmann, I.S. Pakkak, W.D. Youngs, D.J. Lisk, G.E. Burdick, and E.J. Harris. 1972. A survey of the total cadmium content of 406 fish from 49 New York State fresh waters. J. Fish Res. Bd. Can. 29(9):1283-1290.

Lu, J. C. S. and K.Y. Chen. 1977. Migration of trace metals in interfaces of seawater and polluted surficial sediments. Environ. Sci. Technol. 11(2):174-182.

Lu, P.Y., R.L. Metcalf, R. Furman, R. Vogel, and J. Hassett. 1975. Model ecosystem studies of lead and cadmium and of urban sewage sludge containing these elements. J. Environ. Quality 4(4):505-509.

Martin, J.H. and W.W. Broenkow. 1975. Cadmium in plankton: elevated concentrations off Baja California. Science. 190:884-885.

O'Shea, T.A. and K.H. Mancy. 1978. The effect of pH and hardness metal ions on the competitive interaction between trace metal ions and inorganic and organic complexing agents found in natural waters. Water Research. 12:703-711.

Pascoe, D. and D.L. Mattey. 1977. Studies on the toxicity of cadmium to the three-spined stickleback, Gastensteus aculeatus L. J. Fish. Biol. 11(2):207-215.

Patterson, J.W., H.E. Allen, and J.J. Scala. 1977. Carbonate precipitation for heavy metal pollutants. Jour. Water Poll. Control Fed. 49(12):2397-2410.

Perhac, R.M. 1972. Distribution of Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn in dissolved and particulate solids from two streams in Tennessee. Jour. Hydrol. 15:177-186.

Perhac, R.M. 1974a. Water transport of heavy metals in solution and by different sizes of particulate solids. Univ. of Tenn. Water Res. Research Ctr., Knoxville, Tenn. Project No. 023. 41p.

Perhac, R.M. 1974b. Heavy metal distribution in bottom sediments and wastes in the Tennessee River - Loudon Lake Reservoir system. Univ. of Tenn. Water Res. Research Ctr. Knoxville, Tenn. Research Report No. 40. 22p.

Phillips, A.R. and R.C. Russo. 1978. Metal bioaccumulation in fishes and aquatic invertebrates: a literature review. pp.13-20. U.S. Environmental Protection Agency, Duluth, Minn. (EPA 600/3-78-103). 115p.

Ramamoorthy, S. and B.R. Rust. 1978. Heavy metal exchange processes in sediment-water systems. Environ. Geol. 2(3):165-172.

Schell, W.R. and A. Nevissi. 1977. Heavy metals from waste disposal in Central Puget Sound. Environ. Sci. Technol. 11(9):887-893.

Steele, K.F. and G.H. Wagner. 1975. Trace metal relationships in bottom sediments of a fresh water stream - The Buffalo River, Arkansas. Jour. Sed. Pet. 45(1):310-319.

Suzuki, M.,T. Yamada, T. Miyazaki, and K. Kawazoe. 1979. Sorption and accumulation of cadmium in the sediment of the Tama River. Water Research. 13(1):57-63.

Valiela, I., M.D. Banus, and J.M. Teal. 1974. Response of salt marsh bivalves to enrichment with metal containing sewage sludge and retention of lead, zinc, and cadmium by marsh sediments. Environ. Pollut. 7(2):149-157.

Wakita, H. and R.A. Schmitt. 1970. Cadmium in: Handbook of geochemistry. (K.H. Wedepohl, ed). Vol. II, Chap. 2, Springer-Verlag, New York. 23p.

Weast, R.C. ed. 1977. CRC Handbook of chemistry and physics, 58th Edition, CRC Press, Cleveland, Ohio. 2398p.

Weber, W.J. and H.S. Posselt. 1974. Equilibrium models and precipitation reactions for cadmium(II) in: Aqueous environmental chemistry of metals (A.J. Rubin, ed). Ann Arbor Science Publishers, Ann Arbor, Mich.

10. CHROMIUM

10.1 Statement of Probable Fate

Chromium exists in two oxidation states in aqueous systems: Cr(III) and Cr(VI). The hexavalent form is quite soluble, existing in solution as a complex anion, and is not sorbed to any significant degree by clays or hydrous metal oxides. It is, however, sorbed strongly to activated carbon. Hexavalent chromium is a moderately strong oxidizing agent and reacts with reducing materials to form trivalent chromium. Trivalent chromium reacts with aqueous hydroxide ion to form the insoluble chromium hydroxide ($Cr(OH)_3$). Precipitation of this material is thought to be the dominant fate of chromium in natural waters. Sorption processes also result in removal of dissolved chromium to the bed sediments. Chromium forms complexes with a variety of organic materials. The importance of these materials in solubilizing trivalent chromium is unknown, but is probably not significant. Chromium is bioaccumulated by aquatic organisms and passage of chromium through the food chain has been demonstrated.

10.2 Identification - Geochemistry of Chromium

Chromium, a transition element, occurs in nature principally as the trivalent ion Cr^{+3}, although valence states ranging from -2 to +6 have been reported. Chromium is found in concentrations of about 10-100 ppm in the crust and about 0.001-0.8 ppm in river waters (National Academy of Sciences 1974). The principal chromium-bearing minerals belong to the chromite spinel group with the general formula $(Mg, Fe)O(Cr,Al,Fe)_2O_3$. Depending on the degree of substitution in the Al, Fe, Cr series, the chromites contain from 13 to 65 percent Cr_2O_3 (Towill et al. 1978). A variety of chromium compounds are prepared from these chromites. Most of these compounds contain chromium in the stable trivalent and hexavalent oxidation states.

The geochemistry of chromium is dominated by the ability of the trivalent ion Cr(III), with a radius of 0.64 Å to substitute for Fe(III) (0.67 Å) and Al(III) (0.56 Å) during crystallization. Chromium typically is precipitated from magmas at an early stage, either in the chromite spinels or in silicate minerals, especially clinopyroxene. Chromite is generally resistant to chemical weathering. Due to its high specific gravity, it may be mechanically concentrated in laterites or heavy mineral placers. The chromium-bearing silicates release chromium which is then incorporated into shales and schists. Little chromium becomes solubilized, and thus, geological precipitates and evaporates have a low chromium content.

Chromium, atomic number 24, has an atomic weight of 51.996 (Weast 1977). The metal has a melting point of 18.57°C, a boiling point of 2672°C and a specific gravity of 7.20 at 20°C (Weast 1977).

Chromium forms thousands of chromium (III) complexes, almost all of which are hexacoordinate (Cotton and Wilkinson 1972). In aqueous solutions, the principal characteristic of these complexes is their relative kinetic inertness, even under conditions where they are thermodynamically unstable (Cotton and Wilkinson 1972). The importance of complexation in determining aquatic fate is unknown, but it is probably not significant relative to oxidation, precipitation, and sorption reactions discussed below.

The CAS number of chromium is 7440-47-3; the TSL number is A 431-4218.

10.3 Summary of Fate Data

10.3.1 Photolysis

No data were found that would indicate that photolysis of chromium compounds plays an important role in determining aquatic fate.

10.3.2 Chemical Speciation

The inorganic chemistry of chromium has been well studied and documented; however, its biological and environmental interactions are obscure and poorly characterized. This dichotomy is the direct result of the chemical complexity of the element and the extremely low concentrations of chromium found in the environment. Chromium occurs in valence states ranging from -2 to +6. The tripositive state (the most stable form) exhibits a strong tendency to form hexacoordinate octahedral complexes with a great variety of ligands such as water, ammonia, urea, halides, sulfates, ethylenediamine, and organic acids. In neutral and basic solutions, trivalent chromium forms polynuclear compounds in which adjacent chromium atoms are linked through OH or O bridges. These compounds may eventually precipitate as $Cr_2O_3(nH_2O)$. Hexavalent chromium compounds have greater economic importance as well as biological and environmental significance due to its high toxicity. All stable hexavalent chromium compounds are oxy-species (such as CrO_3, CrO_4^{-2}, and $CrO_2Cl_3^{-1}$) which strongly oxidize organic matter on contact. The other valence states of chromium are too unstable to be significant in the aquatic environment.

Trivalent chromium is the most stable form under redox conditions normally found in natural waters and sediments, and when in solution at pH greater than 5, quickly precipitates due to formation of the insoluble hydroxide or oxide (National Academy of Sciences 1974; Cotton and Wilkinson 1972).

Hexavalent chromium, Cr(VI), is a strong oxidizing agent, and is always found in aqueous solution as a component of a complex anion. The anionic form varies according to pH, and may be chromate (CrO_4^{-2}), hydrochromate ($HCrO_4^-$), or dichromate ($Cr_2O_7^{-2}$). Dichromate concentration is not significant unless pH values are well below those observed in most natural waters. Thus, hexavalent chromium present in most natural waters (pH>6.5) will be in the form of the chromate ion, CrO_4^{-2}. All of the anionic forms are quite soluble, and are thus quite mobile in the aquatic environment (Towill et al. 1978).

Schroeder and Lee (1975), in a laboratory study on the transformation of chromium in natural waters, found that Cr(III) and Cr(VI) are readily interconvertible under natural conditions. Their results indicated that Cr(VI) can be reduced by Fe(II), dissolved sulfides, and certain organic compounds with sulfhydryl groups, while Cr(III) can be oxidized by a large excess of MnO_2 and at a slower rate by O_2 under natural water conditions. Moreover, if aquatic conditions favor Cr(VI), then chromium will accumulate as soluble forms in waters; if, however, Cr(III) is favored, then the accumulation will occur in the sediments.

This environmental accumulation of Cr(III) in the sediments has been noted by several authors (Nelson and Hanshild 1970; Bruland et al. 1974; Perhac 1974; Morel et al. 1975; Rehwoldt et al. 1975; Steele and Wagner 1975; Namminga and Wilhm 1977) and can be explained by the hydrolysis of Cr(III) complexes to insoluble hydroxide forms, especially $Cr(OH)_3$.

It appears, therefore, that chemical speciation plays a dominant role in the fate of chromium in the aquatic environment. Conditions favorable to Cr(VI) will keep chromium in a soluble form in the water, while conditions favorable to Cr(III) will lead to precipitation and adsorption of chromium in the sediments.

10.3.3 Volatilization

No data were found that would indicate that volatilization of chromium compounds plays an important role in determining aquatic fate.

10.3.4 Sorption

Hexavalent chromium is not adsorbed to any significant degree by clays, ferric hydroxide, or ferric and manganese oxides (Kharkar et al. 1968). It is efficiently removed by activated carbon (Linstedt et al. 1971), and thus may have some affinity for organic materials in natural waters.

The fractional extraction of sediments indicates that surface adsorption, which is a relatively weak binding process, does not account for most of the chromium associated with sediments. Furthermore, there is generally a strong inverse correlation between chromium concentration and sediment grain size (Nelson and Haushild 1970; Perhac 1974; Steele and Wagner 1975). Besides precipitation, several sorption mechanisms have been postulated to explain these observations.

Steele and Wagner (1975) noted that there was a good correlation between extractable chromium and extractable iron in sediments from an Arkansas river, and suggested that incorporation of chromium into hydrous iron oxides was probably the reason for this. Their extraction technique used aqua regia, which is undoubtedly capable of solubilizing $Cr(OH)_3$, as well as the chromium incorporated with the hydrous iron oxides. Also, the fact that chromium is mineralogically associated with iron implies that chromium introduced into the stream by weathering would be precipitating out in the same areas as iron. Thus, another way to explain the results would be that the correlation between Cr and Fe is not due to removal of dissolved Cr by precipitating Fe, but is a result of the fact that $Cr(OH)_3$ is precipitated in the same areas as $Fe(OH)_3$. Coprecipitation of these materials may increase the speed with which chromium is removed from solution.

Perhac (1974) found that very little chromium in sediments was bound up in iron oxides. He extracted the iron oxides with sodium dithionite, which reduces the ferric iron to ferrous iron and thus destroys the hydrous iron oxide coatings. $Cr(OH)_3$ would probably not be solubilized by such an extraction procedure.

A pertinent observation was reported by Griffin et al. (1977) in their laboratory study on the effect of pH on the adsorption of chromium by clay minerals. Since this study was carried out in soils, direct extrapolation cannot be made to the aquatic environment; however, the physicochemical generalizations should be applicable. They found that adsorption of Cr(VI) decreased as pH increased and that the $HCrO_4^-$ ion was the Cr(VI) species predominantly adsorbed. The adsorption of Cr(III), however, increased as the pH increased. About 30 to 300 times more Cr(III) than Cr(VI) was adsorbed by clays, and the amounts of Cr(III) adsorbed corresponded to cation exchange adsorption of hydrolyzed Cr(III) species. These results suggest that while Cr(VI) is highly mobile, Cr(III) will be quickly immobilized into the sediments.

Gibbs (1973) studied transport of trace metals in the Yukon and Amazon Rivers. He concluded that chromium was transported primarily in crystalline sediments, with transport as dissolved species and biological solids running a distant second and third. If chromium is indeed trans-

ported to any appreciable degree in crystalline sediments, it is possible that it is due to isomorphous substitution of Cr(III) for Al(III) and Fe(III). The importance of this process to the environmental transport of chromium is still unclear.

In summary, it appears that Cr(III) and Cr(VI) are only weakly adsorbed into inorganic solids, although Cr(III) is adsorbed more strongly that Cr(VI). Sorption of Cr(III) may be ancillary to precipitation of $Cr(OH)_3$.

10.3.5 Bioaccumulation

Chromium is an essential nutrient (National Academy of Sciences 1974), and it is accumulated in aquatic and marine biota to levels much higher than in ambient water. Levels in biota, however, are usually lower than levels in the sediments.

Namminga and Wilhm (1977) studied heavy metal partitioning between water, sediments, and chironomid larvae (a benthic invertebrate). They found an average chromium concentration of 1.1 µg/l in water, 7.64 µg/g in sediments and 2.96 µg/g in chironomids. Bioconcentration factors for chironomids to water are thus about 3,000, and for chironomids to sediments, about 0.39. Rehwoldt et al. (1975) found similar relationships among water, sediments, and biota in the Danube River.

Patrick and Loutit (1976) examined the ability of bacteria to mobilize metals by accumulating them and passing them up the food chain. Tubificid worms (benthic) were fed bacteria that had accumulated chromium and retained some of the element. Tubificids are apparently able to excrete chromium more effectively than the bacteria, because the concentrations in the worms were lower than concentrations in the bacterial cells. Nevertheless, the experiment proved that chromium can be passed on through the food chain. Accumulation of metals by benthic species may result in chromium mobilization through the biota.

Fromm and Stokes (1962) found that rainbow trout took 10 days to reach whole-body equilibrium concentration upon exposure to hexavalent chromium levels below 0.01 mg Cr/l. Fish exposed to chromium concentrations of 0.05 mg/l and higher, however, continued to accumulate chromium linearly in time until the test was terminated after 30 days. In a laboratory study, Buhler et al. (1977) analyzed two groups of rainbow trout raised in two natural waters differing in chromium content. The trout accumulated chromium rapidly during the first day of exposure but did not accumulate much more chromium during further exposure for 22 days. Apparently, an equilibrium condition was rapidly reached. The trout contained chromium levels in proportion to the chromium in their environment.

Baptist and Lewis (1969) studied the transfer of radiolabeled Cr(III) in an estuarine food chain consisting of phytoplankton, brine shrimp, post-larval fish, and mummichog. Chromium was transferred through the food chain through each trophic level, with concentrations declining as trophic level increased. Theoretical calculations indicated that, in general, the food chain was a more efficient pathway for uptake of chromium than direct uptake from seawater.

Distribution of chromium in water, sediment, seston (suspended abiotic and biotic material), phytoplankton, mollusks, annelids, and fish in Narragansett Bay, R.I., was studied by Phelps et al. (1975). The highest concentrations of chromium were found in the sediments, followed by the seston. Phytoplankton concentrated chromium to a greater extent than other organisms, with the lowest levels being found in bottom-feeding fish.

Some bioconcentration factors reported for chromium are given in Tale 10-1. The range in concentration ratios probably reflects not only differences among taxa, but also differences in ambient water concentrations of chromium.

10.3.6 Biotransformation

No data were collected concerning the importance of biodegradation of chromium compounds on aquatic fate. There has been some speculation that chromium could be methylated in reducing environments (Anon. 1977), but no evidence was found that this process occurs in natural or experimental systems. Under anaerobic conditions, there is a possibility that Cr(VI) species such as $HCrO_4^-$ (hydrochromate) and CrO_4^{-2} (chromate) could be utilized by bacteria and other anaerobes as an oxygen source (Adams et al. 1975). Chemical reduction to Cr(III) with concomitant loss of oxygen would be indistinguishable from this effect, and certainly occurs in such environments. Biogenic complexing agents may have some effect on chromium distribution, especially in eutrophic systems which typically have high concentrations of organic material.

10.4 Data Summary

Most of the trivalent chromium in the aquatic environment is hydrolyzed and precipitates as $Cr(OH)_3$. Sorption processes and bioaccumulation will remove the remaining Cr(III) from solution. Under certain natural water conditions, chromium can exist in the hexavalent form. Cr(VI) exists as an oxyanion in aqueous solution and is quite soluble. It has little affinity for clays and other inorganic surfaces, although it is strongly sorbed by activated carbon. It is very toxic to aquatic organisms. Processes relating to chemical speciation are important in determining the aquatic fate of chromium, which is summarized in Table 10-2.

Table 10-1

Bioconcentration Factors for Chromium

Taxon	Bioconcentration Factor[a]	Reference
Freshwater fish	200	Chapman et al. 1968
Freshwater invertebrates	2,000	Chapman et al. 1968
Freshwater plants	4,000	Chapman et al. 1968
Marine fish	400	Chapman et al. 1968
Marine invertebrates	2,000	Chapman et al. 1968
Marine plants	2,000	Chapman et al. 1968
Benthic algae	1,600	National Academy of Sciences 1974
Phytoplankton	2,300	National Academy of Sciences 1974
Zooplankton	1,900	National Academy of Sciences 1974
Mollusc viscera	440	National Academy of Sciences 1974
Crustacean muscle	100	National Academy of Sciences 1974
Fish muscle	70	National Academy of Sciences 1974

a. Concentration factors are defined by the ratio of the concentation of the element in the organism in ppm (wet weight) divided by the concentration of the element in water (ppm).

Table 10-2

Summary of Aquatic Fate of Chromium

Environmental Process	Summary Statement	Confidence of Data
Photolysis	Not an important process.	Medium
Chemical Speciation[a]	An important consideration in the aquatic fate of chromium. Controls the intertransformation of Cr(VI) to Cr(III). Cr(VI) remains soluble, while Cr(III) will hydrolyze and precipitate as $Cr(OH)_3$.	Medium
Volatilization	Not an important process.	Medium
Sorption[a]	Cr(III) is adsorbed weakly to inorganic materials. Cr(VI) may be adsorbed by organic materials.	Medium
Bioaccumulation[a]	As an essential nutrient, chromium is bioaccumulated by a variety of aquatic organisms. May be transferred via the food chain.	High
Biotransformation	Probably not important.	Low

a. All of the noted environmental processes are important; however, their relative importance with respect to each other is uncertain for determining final fate.

10.5 Literature Cited

Adams, C.E., Jr., W. Eckenfelder, Jr., and B.L. Goodman. 1975. The effects and removal of heavy metals in biological treatment. pp. 277-292. in Heavy Metals in the Aquatic Environment. P.A. Krenkel (ed.). Pergamon Press, Oxford, England. 352p.

Anon. 1977. Tracking trace metals in the biosphere. Chem. Eng. News 55(16):23.

Baptist, J.P. and C.W. Lewis. 1969. Transfer of ^{65}Zn and ^{51}Cr through an estuarine food chain. pp. 420-430. Proc. 2nd Nat. Symp. on Radioecology. U.S. Atomic Energy Commission Conf. 670503. 631p.

Bruland, K.W., K.K. Bertine, M. Koide, and E.D. Goldberg. 1974. History of metal pollution in Southern California coastal zone. Environ. Sci. Technol. 8(5):425-432.

Buhler, D.R., R.M. Stokes, and R.S. Caldwell. 1977. Tissue accumulation and enzymatic effects of hexavalent chromium in rainbow trout (Salmo gairdneri). J. Fish. Res. Bd. Can. 34(1):9-18.

Chapman, W.H., H.L. Fisher, and M.W. Prett. 1968. Concentration factors of chemical elements in edible aquatic organisms. Lawrence Radiation Laboratory, Livermore, Calif. UCRL-50564. 46p.

Cotton, F.A. and G. Wilkinson. 1972. Advanced inorganic chemistry. pp. 830-845. Interscience Publishers, New York. 1145p.

Fromm, P.O. and R.M. Stokes. 1962. Assimilation and metabolism of chromium by trout. J. Water Pollut. Control Fed. 34(11):1151-1155.

Gibbs, R.J. 1973. Mechanisms of metal transport in rivers. Science 180:71-73.

Griffin, R.A., A.K. Au, and R.R. Frost. 1977. Effect of pH on adsorption of chromium from landfill-leachate by clay minerals. J. Environ. Sci. Health A12(8):431-449.

Kharkar, D.P., K.K. Turekian, and K.K. Bertine. 1968. Stream supply of dissolved Ag, Mo, Sb, Se, Cr, Co, Rb, and Cs to the oceans. Geochim. Cosmochim. Acta 32:285-298.

Linstedt, K.D., C.P. Houck, and J.T. O'Connor. 1971. Trace-element removals in advanced wastewater treatment processes. J. Water Pollut. Control Fed. 43(7):1507-1513.

Morel, F.M.M., J.C. Westall, C.R. O'Melia, and J.J. Morgan. 1975. Fate of trace metals in Los Angeles County wastewater discharge. Environ. Sci. Technol. 9(8):756-761.

Namminga, H. and J. Wilhm. 1977. Heavy metals in water, sediments, and chironomids. J. Water Pollut. Control Fed. 49(7):1725-1731.

National Academy of Sciences. 1974. Chromium. pp. 86-89. U.S. Government Printing Office, Washington, D.C. 155p.

Nelson, J.L. and W.L. Haushild. 1970. Accumulation of radionuclides in bed sediments of the Columbia River between the Hanford reactor and McNay Dam. Water Resources Res. 6(1):130-137.

Patrick, F.M. and M. Loutit. 1976. Passage of metals in effluents through bacteria to higher organisms. Water Res. 10:333-335.

Perhac, R.M. 1974. Heavy metal distribution in bottom sediments and water in the Tennessee River-Loudon Lake Reservoir system. Univ. of Tenn. Water Resources Research Center, Knoxville, Tenn., Research Report No. 40. 22pp.

Phelps, D.K., G. Telek, and R.L. Lapan, Jr. 1975. Evaluation of the distribution of heavy metals in the food chain. Ing. Ambientale 4(3):321-328. (Italian) (Abstract only). CA 1976. 84:131057f.

Rehwoldt, R., D. Karimain-Teheranie, and H. Altmann. 1975. Measurement and distribution of various heavy metals in the Danube River and Danube Canal: aquatic communities in the vicinity of Vienna, Austria. Sci. Total Environ. 3:341-348.

Schroeder, D.C. and G.F. Lee. 1975. Potential transformations of chromium in natural waters. Water Air Soil Pollut. 4:355-365.

Steele, K.F. and G.H. Wagner. 1975. Trace metal relationships in bottom sediments of a freshwater stream. The Buffalo River, Arkansas. J. Sed. Pet. 45(1):310-319.

Towill, L.E., C.R. Shriner, J.S. Drury, A.S. Hammons, and J.W. Holleman. 1978. Reviews of the environmental effects of pollutants: III. Chromium. pp. 12-36. Oak Ridge National Laboratory, Oak Ridge, Tenn. PB 282 796 285p.

Weast, R.C. (ed.). 1977. Handbook of chemistry and physics, 58th edition. CRC Press, Cleveland, Ohio. 2398p.

11. COPPER

11.1 Statement of Probable Fate

Several processes determine the fate of copper in the aquatic environment: complex formation, especially with humic substances; sorption to hydrous metal oxides, clays, and organic materials; and bioaccumulation. The formation of complexes with organic ligands modifies the solubility and precipitation behavior of copper such that solid copper species probably do not precipitate under normal circumstances. Furthermore, complexed copper is more easily adsorbed by clay and other surfaces than the free (hydrated) cation. The aquatic fate of copper is highly dependent on such variables as pH, Eh, concentrations of organic materials and adsorbents, availability of precipitating iron and manganese oxides, biological activity, and competition with other heavy metals.

Sorption of copper by precipitating hydrous iron and manganese oxides is an effective control on dissolved copper concentrations where these metals are being actively weathered or otherwise introduced into unpolluted aquatic environments. In organic rich environments, typical of polluted natural waters, the effective control on dissolved copper concentrations will be the competition between organic complexing in solution and sorption onto clay and particulate organic material.

Copper is strongly bioaccumulated and is an essential trace element; however, high concentrations of Cu(II) ion are toxic to aquatic organisms. Biological activity, as a source of organic ligands, plays an important part in determining the aquatic fate of copper.

11.2 Identification - Geochemistry of Copper

Copper is a metallic element and a member of the first transition series. It exists in the lithosphere primarily as a sulfide, both as the simple sulfide and as a great variety of complex sulfide minerals that include other metals. By far the most abundant of the copper minerals is chalcopyrite ($CuFeS_2$), although metallic copper, chalcocite (Cu_2S), and bornite (Cu_5FeS_4) are also found in economically important deposits.

Copper is present in concentrations averaging about 4 ppm in limestones, 55 ppm in igneous rocks, 50 ppm in sandstones and 45 ppm in shales (Krauskopf 1972). The marked concentrations of copper in shales and sandstones suggest that copper in the lithosphere exists largely as adsorbed ions, fine grained particles or as one of many discrete sedimentary copper minerals. Generally, these minerals occur only as sparse tiny grains that are widely disseminated throughout the sedimentary rocks.

Reactions leading to precipitation of definite copper compounds, however, are probably not common in most sediments and, almost certainly, are less effective than adsorption as a general mechanism for removing copper from solution. Copper is most strongly adsorbed by the surfaces available in neutral waters. Because Cu^{+2} forms so readily during weathering, and because it can persist in acidic oxidizing solutions at fairly high concentrations, copper is considered to be among the more mobile of the heavy metals in surface environments. The distance it can travel is limited largely by its strong adsorption to many kinds of surfaces. Ferric hydroxide, for example, is quite an effective adsorbent of Cu^{+2}, provided the pH is above the isoelectric point of the hydroxide (Hem and Skougstand 1960).

Copper, atomic number 29, has an atomic weight of 63.546 (Weast 1977). It forms salts and complexes with valences of +1, +2, and, very rarely, +3 (Cotton and Wilkinson 1972). The electrochemical properties of copper are well known.

The CAS number for copper is 7440-50-8, and its TSL number is A546-0888.

11.3 Summary of Fate Data

11.3.1 Photolysis

Although some copper complexes are photosensitive, no evidence was found indicating that photolysis is an important mechanism in determining the aquatic fate of this metal.

11.3.2 Chemical Speciation

In aqueous solution, copper is present as Cu(II), since the only cuprous (valence +1) compounds stable in oxic waters are those that are highly insoluble (e.g., CuCl or CuCN)(Cotton and Wilkinson 1972). Although most cupric salts are not considered to be readily water-soluble, there are several exceptions, including cupric chloride ($CuCl_2$), cupric nitrate ($Cu(NO_3)_2$) and cupric sulfate ($CuSO_4$).

Copper has a pronounced tendency to form complexes with both organic and inorganic ligands. Stiff (1971a, 1971b) found that, at pH values and inorganic carbon concentrations characteristic of natural waters, most of the copper in solution is present as complexes of cupric carbonate rather than as the (hydrated) divalent cupric ion. Stiff (1971a), in a laboratory study of unpolluted waters, found that the copper in these waters would most likely be present as complexes of cupric carbonate. Stiff (1971b) extended this study to polluted waters and showed

that the predominant species of soluble copper in polluted environments would be complexes with cyanide, amino acids, and humic substances as well as the complex carbonates and the (hydrated) divalent cupric ion. In a related field study reported by Stiff (1971b), it was demonstrated that much of the copper present in polluted English rivers was associated with suspended solids and that soluble copper consisted almost entirely of complexed organic forms.

Sylva (1976) examined the speciation of copper(II) in fresh water with respect to inorganic and organic complexation and adsorption and precipitation. It was found that these processes are capable of reducing the level of soluble copper to very low values even in the presence of high levels of total copper. Hydrolysis and precipitation dominate the chemistry of copper(II) at pH values expected in most natural water systems wherever there is a limited amount of organic complexing agents (Figure 11-1). The most significant process by which divalent, hydrated copper(II) is removed from unpolluted water is the precipitation of malachite ($Cu_2(OH)_2CO_3$). The rate of this precipitation, however, is very slow at low copper levels and the equilibrium situation may not always be reached or even approached because of fluctuating conditions. The effect of the presence of organic complexing agents can change the system to such an extent as to alter greatly the results plotted in Figure 11-1, especially at the lower pH values. Thus, the speciation of copper(II) can vary considerably from one natural water system to another and also within one given system over a period of time.

Long and Angino (1977) developed a theoretical model to study the chemical speciation of copper in aqueous solutions and the response of copper to variations in ionic strength and complexation. Association of copper with the ligands OH^-, Cl^-, CO_3^{-2}, SO_4^{-2} and HCO_3^- was considered at pH values from 3.5 to 11.0 at 25°C in differing seawater-freshwater mixtures. The results are summarized in Figure 11-2. In general, the relative importance of the various ligand-copper complexes can be predicted from a comparison of their stability constants. This model, however, does not take into account metal-organic complexes and it is, therefore, useful only in unpolluted, relatively organic-free waters.

In most surface waters, organic materials prevail over inorganic ions in complexing copper. Ramamoorthy and Kushner (1975) demonstrated that almost all of the heavy-metal binding capacity of Ottawa River water was due to organic substances. They calculated an empirical equilibirum constant from the equation:

$$K = \frac{[\text{Metal ion bound}]}{[\text{Metal ion unbound}][\text{River component unbound}].}$$

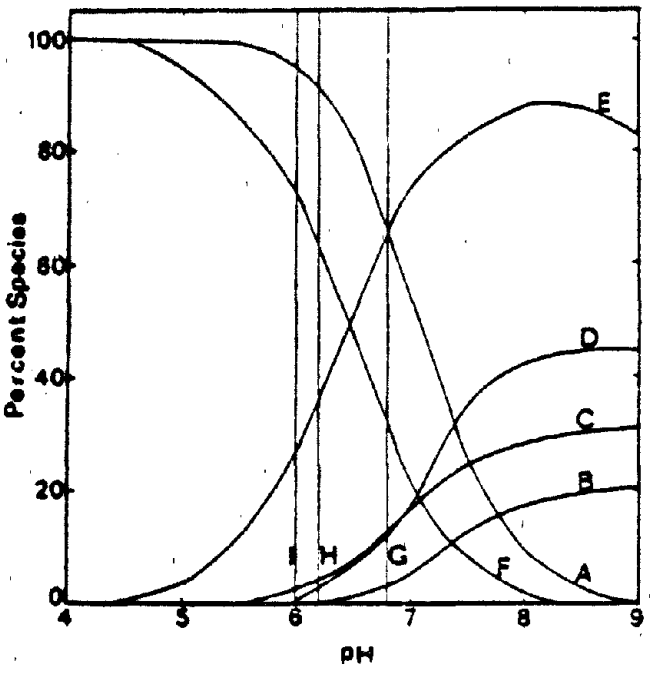


Figure 11-1 Speciation of copper(II)(total concentration 2 ppm) and carbonates as a function of pH. (A) Cu^{+2}. (B) $Cu_2(OH)_2^{+2}$. (C) $CuOH^+$. (D) $CuCO_3$. (E) HCO_3^-. (F) H_2CO_3. (G) pH at which $Cu(OH)_2$ will precipitate. (H) pH at which $Cu_3(OH)_2(CO_3)_2$ (azurite) will precipitate. (I) pH at which $Cu_2(OH)_2CO_3$ (malachite) will precipitate. From Sylva (1976).

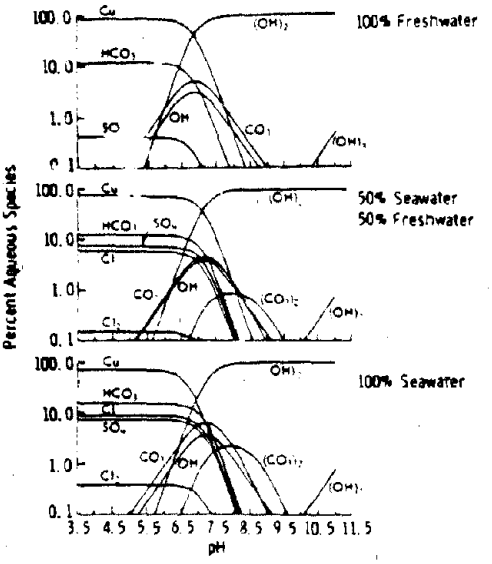


Figure 11-2 Chemical speciation of copper in seawater-freshwater mixtures. From Long and Angino (1977).

The value of K for copper was $5.01 \pm 1.38 \times 10^3$ and the calculated concentration of the river binding component was 2.54×10^{-5}M.

Lopez and Lee (1977), in their study of a heavily copper-polluted, organic-depleted lake in Michigan found that the predominance of soluble copper species followed the order: $Cu(OH)^+ > Cu^{+2} > CuCO_3^\circ$. It appeared further that copper concentration in this lake was controlled by hydrous oxides of iron and manganese and not by the solubility of copper compounds.

Hem (1975) calculated the predominance of dissolved copper species and the stability fields for solid copper compounds in a system with total dissolved carbon equal to 10^{-3}M and total dissolved sulfur equal to 10^{-4}M. The Eh-pH diagrams for this system are shown as Figure 11-3 and 11-4.

The strong tendency of copper to form complexes has important ramifications in its precipitation and sorption behavior and is a most important process for considering the aquatic fate of copper.

11.3.3 Volatilization

No evidence was found to indicate that volatilization of copper compounds is an important aquatic fate.

11.3.4 Sorption

Copper has a strong affinity for hydrous iron and manganese oxides, clays, carbonate minerals, and organic matter. Sorption to these materials, both suspended in the water column and in the bed sediments, results in relative enrichment of the solid phase and reduction in dissolved levels.

Hem and Skougstad (1960) demonstrated that coprecipitation of copper with the hydrous oxides of iron effectively scavenges copper from solution. These materials form a coating on solid surfaces in the water, and as they precipitate, copper and other metals tend to be attracted due to the negative zeta-potential usually exhibited by the hydrous iron oxide (Jenne 1968). Copper may thus be incorporated into the lattice structure of the hydrous iron oxide coating, this process being known as coprecipitation. Thus, the hydrous iron (and to a lesser extent, manganese) oxides can control the mobility of copper in natural waters. Jenne (1968), and more recently Lee (1975), have presented convincing evidence that such hydrous metal oxides are important controls on the mobility of copper and some other metals in unpolluted aqueous and soil environments. In reducing or acidic environments, such as in richly organic bed sediments, these oxides can be dissolved, resulting in remobilization of sorbed or copreci-

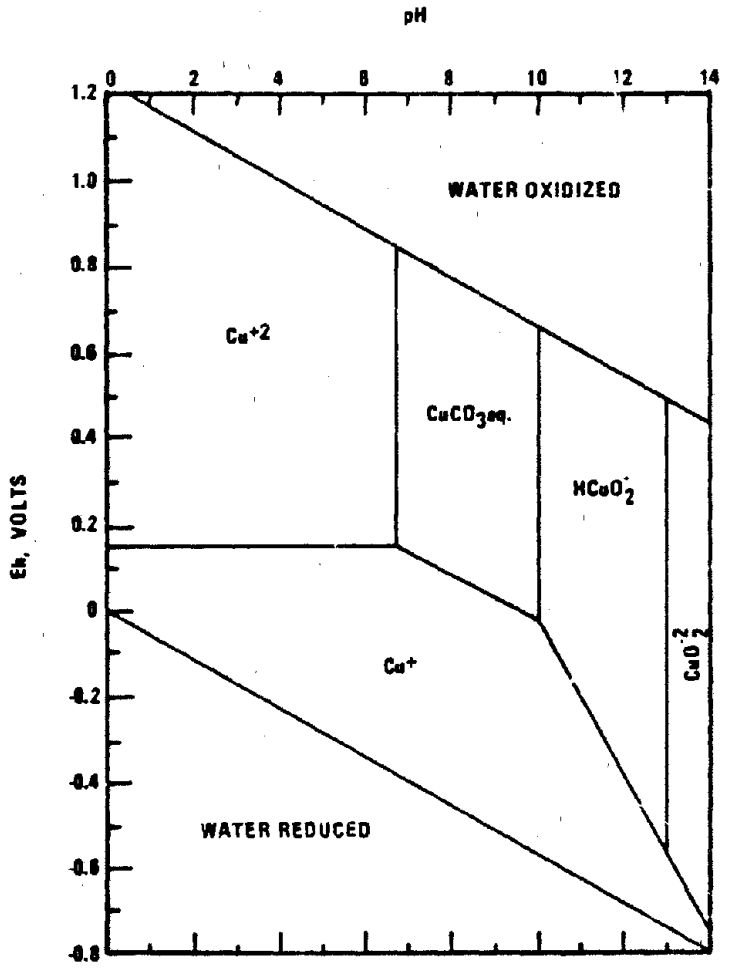


Figure 11-3 Eh-pH diagram showing areas of dominance of five species (solute) of copper at equilibrium at 25°C and 1 atm. System Cu-H_2O-C-S; total dissolved $C=10^{-3.00}$ moles/l; total dissolved $S=10^{-4.00}$ moles/l. From Hem (1975).

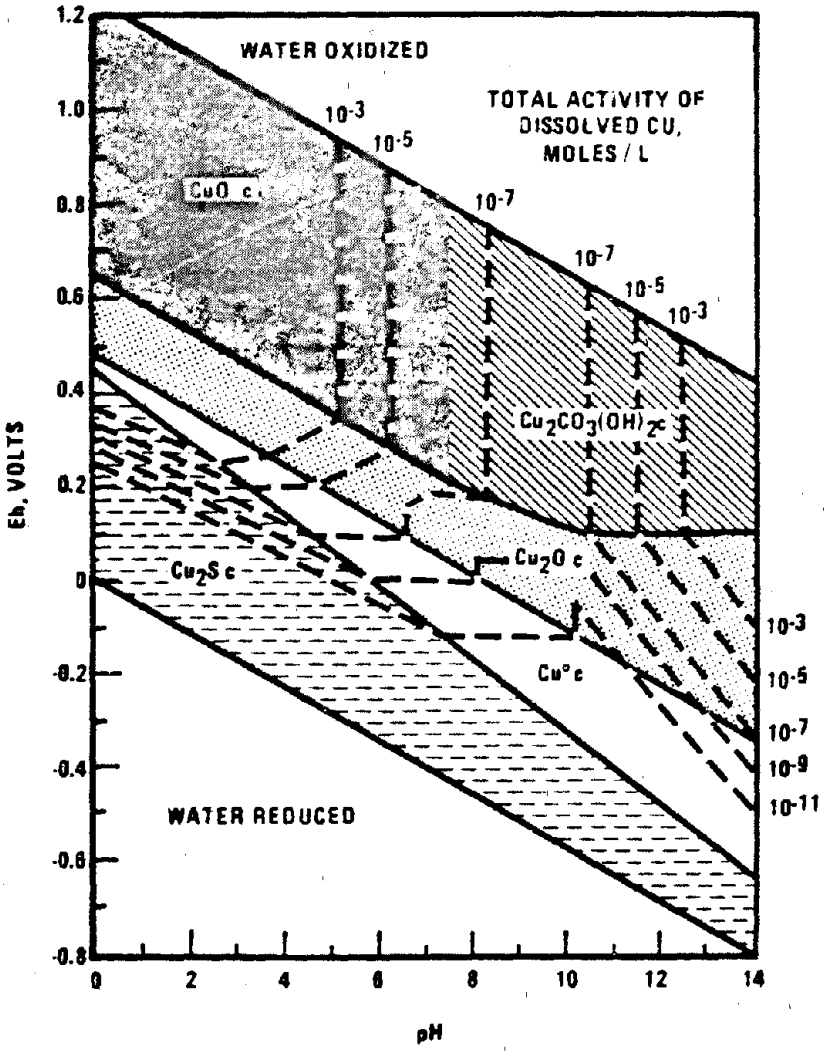


Figure 11-4 Eh-pH diagram showing fields of stability of solids and total equilibrium activity of dissolved copper at 25°C and 1 atm. System Cu-H_2O-C-S; total dissolved C=$10^{-3.00}$ moles/l; total dissolved S=$10^{-4.00}$ moles/l. From Hem (1975).

pitated metals. Several investigations have given evidence for this process by reporting a high correlation in the sediments of natural streams between copper content and iron and manganese content (Carpenter et al. 1975; Steele and Wagner 1975; Collins 1973). There is substantiation, therefore, that coprecipitation of copper by hydrous iron and manganese oxides is an important process for removing copper from solution in some natural waters.

Copper is adsorbed to clay and mineral surfaces (Huang et al. 1977) and organic materials (Rashid 1974; Baker-Blocker et al. 1975). Huang et al. (1977) demonstrated that adsorption of copper to soils and aluminum and silicon oxides is strongly pH-dependent, as shown in Figure 11-5. Furthermore, the addition of various anions significantly increased adsorption. Humic acid was particularly effective in this regard (see Figure 11-6). Huang et al. (1977) hypothesized that the enhanced adsorption due to the anions resulted from formation of a metal-ligand bond, followed by adsorption to the hydrous solids through specific chemical bonds such as "sharing of free electrons available from the metal-ligand complexes." Thus, the ease with which copper forms complexes with organic and inorganic ligands (as discussed in Section 11.3.2) undoubtedly facilitates its adsorption by solids in natural waters. Payne and Pickering (1975), in their laboratory study on the removal of Cu(II) species from aqueous solution by kaolinite clay suspensions, found that the extent of copper removal was increased by the presence of ligands. They found that the important processes for determining the extent of copper adsorption were solution pH, the nature of the ligands present and the order of contact of the species. They also reported that, in the presence of organic ligands at a pH>6, there was virtually a total removal of copper. In the highly calcareous Lake Monona, Wisconsin, 6.8×10^5 kg (1.5×10^6 lbs.) of copper sulfate has been added over the last 50 years as an algicide. Sanchez and Lee (1973) showed that most of the copper in bed sediments from this lake was found in the crystal structure of carbonate minerals. These investigators hypothesized that copper substitutes for calcium and magnesium atoms in the carbonate lattice structure.

Ramamoorthy and Rust (1978), in their study of heavy metal exchange processes in the organic-rich sediments from the Ottawa River, Canada, found that the ability of the sediments to sorb copper ions was directly related to the amount of organic materials present. Unless strong leaching agents (in this study NaCl and NTA at about 10^{-4}M concentration) are present, the mobility of copper ions is low and they persist in the sediments for a considerable period of time. Therefore, relative to freshwater environments, marine ecosystems should be subject to greater desorption of copper into the aqueous phase because of chloride complexing and a reduced degree of bonding to sediment particles. Nonetheless, because of

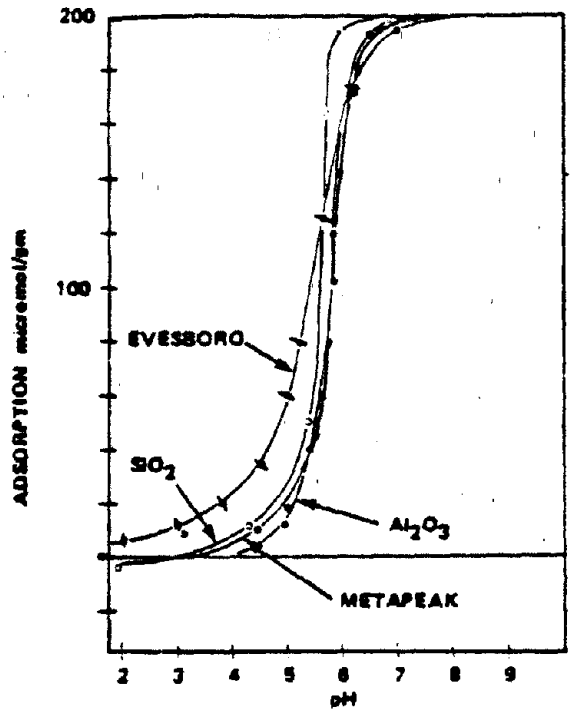


Figure 11-5 Adsorption of copper on four solid suspensions after 24 hour exposure.

Concentration of solids - gm/l
$[Cu_T]$ - 10^{-3}M
Ionic strength - 10^{-1}M (NaCl)

The upper limit of the graph, 200 μmol/gm, represents 100% adsorption. From Huang et al. (1977).

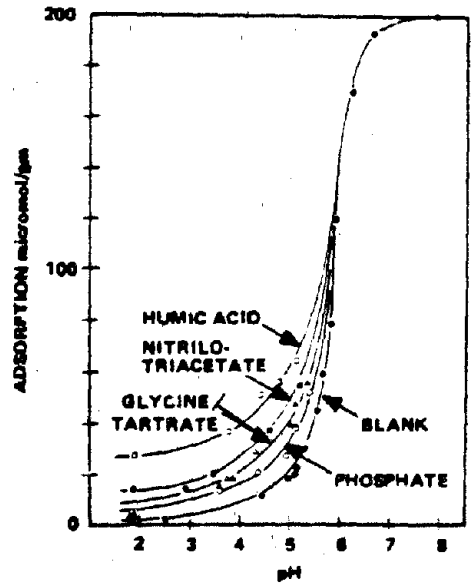


Figure 11-6 Effect of anions on the adsorption of copper by Metapeak soil. In addition to the experimental conditions shown in Figure 11-5, the anion concentration was 10^{-4}M except for humic acid, which was 50 mg/l. From Huang et al. (1977).

the somewhat static nature of marine depositional environments, it is possible that chloride-complexed copper can remain in interstitial waters and escape only slowly into the overlying water column.

Jackson and Skippen (1978), in a laboratory study of the dispersion of heavy metals via organic acids at the sediment-water boundary, demonstrated that the organic acids increased the solubility of copper in the presence of clay. Hence, an influx of soluble organic matter into stream water will favor the prolonged dispersion of copper in solution. Furthermore, humic and fulvic acids, when in excess of the copper ions, have the potential to retain copper in solution in competition with hydrolysis and sorption onto clay. Some of this effect might be due solely to the lowering of pH which will decrease copper sorption; however, the greatest effect is probably that of competition for clay adsorption sites and of organic-copper complexing reactions. While these observations appear to conflict with those discussed earlier, they can be rationalized by recognizing the differences in effects that will be mediated by soluble organic compounds as opposed to particulate organic matter as described by Huang et al. (1977) and Payne and Pickering (1975). Jackson and Skippen (1978) also reported that, although humic and fulvic acids are capable of remobilizing copper from a clay-sorbed phase and its associated metal hydroxide precipitates, the desorption of copper is so kinetically inhibited as to be almost nonexistent.

In summary, sorption processes are quite active and efficient in scavenging dissolved copper and in controlling its mobility in natural unpolluted streams. In unpolluted waters, the effectiveness of these processes varies according to pH, Eh, and the occurrence of potential sorption surfaces. In water polluted with soluble organic material, however, sorption appears to be rather ineffective, thus favoring the prolonged dispersion of copper in solution. The presence of organic acids also can lead to the mobilization of copper from the sediments to solution.

11.3.5 Bioaccumulation

As an essential nutrient, copper is accumulated by all plants and animals. Table 11-1 lists bioconcentration factors (concentration in organism/concentration in ambient water) for some aquatic and marine species.

Since copper is strongly bioaccumulated, and because biogenic ligands play such an important role in complexing copper (which affects precipitation and sorption behavior), biological activity is a major factor in determining the distribution and occurence of copper in the ecosystem. Kimball (1973) studied seasonal fluctuations in copper concentration in a pond and found that concentrations were higher in fall and winter months

Table 11-1

Bioconcentration Factors for Copper

Taxon	Bioconcentration Factor[a]	Reference
Algae		
Scenedesmus guadricarda	12	Khobot'ev *et al.* 1976
Anabaena variabilis	300	Khobot'ev *et al.* 1976
Scenedesmus sp.	2400	Stokes *et al.* 1973
Chlorella sp.	2400	Stokes *et al.* 1973
Bacteria	630-1567	Patrick and Loutit 1976
Plants, Marine and Fresh	1000	Chapman *et al.* 1968
Invertebrates		
Marine	1670	Chapman *et al.* 1968
Freshwater	1000	Chapman *et al.* 1968
Molluscs	30,000	Raymont 1972
Insects	546	Namminga and Wilhm 1977
Fish		
Marine	667	Chapman *et al.* 1968
Freshwater	200	Chapman *et al.* 1968

a. Bioconcentration factors are the ratio derived from the concentrations of the element in the aquatic organism (in ppm of wet weight) divided by the concentration of the element in water (in ppm).

than in spring and summer months. Namminga and Wilhm (1977) observed the same phenomenon in an Oklahoma stream. Kimball (1973) concluded that the reason for the seasonal fluctuation was that copper became concentrated in vegetation during the growing season, and was released from leaf litter and decaying aquatic plants in the fall. Another possible explanation is that, in the warmer months, there is a greater rate of decomposition of organic material with concomitant release of humic substances. As previously discussed, these substances can either adsorb copper directly or complex it, thus making it more available for adsorption on solids. Probably both of these hypotheses are operative and complement each other in causing elevated levels of copper in fall and winter as compared to spring and summer.

In their study of heavy metals in an Oklahoma stream, Namminga and Wilhm (1977) found that chironomid larvae (benthic insect forms) concentrated copper relative to the water column and the sediment matrix which they inhabit. The concentration of copper measured in water, sediments, and larvae was 4.1 µg/l, 1.8 µg/g, and 1.91 µg/g, respectively, yielding a bioconcentration factor of 546 from water and 1.1 from sediments.

Nehring (1976) suggested that it may be possible to detect instances of intermittently acute copper pollution in streams by monitoring copper levels in aquatic insects. Some stream insects, including the mayfly (Ephemerella grandis) and the stonefly (Pteronarcys californica), were more resistant to copper toxicity than fish, and copper residue accumulation affected the insects' copper exposure history.

In a food chain consisting of copper-enriched sediment, bacteria, and tubificid worms, copper levels increased with increasing trophic level (Patrick and Loutit 1976). Windom et al. (1973) found, however, that for several North Atlantic fish species, copper level was inversely related to trophic position. Similarly, Cross et al. (1973) observed no increase in copper content with age among bluefish (Pomatomes saltatrix) and morids (Antinora rostrata) collected off the North Carolina coast.

Since copper is toxic to aquatic life at high concentrations, especially high concentrations of the divalent copper ion and its hydroxy complexes, Brungs et al. (1973) measured copper uptake at several copper concentrations by the brown bullhead (Ictaluris nebalosus). They hoped to establish an autopsy technique useful for confirming copper-caused fish kills. No useful relationship was found; moreover, lethal exposure preceded by subacute exposure resulted in higher tissue copper levels than in fish having experienced only the lethal conditions. Bullheads accumulated copper at all water concentrations equalling or exceeding 27 µg Cu/l. Copper concentrations in liver and gill tissues most accurately reflected the copper exposure conditions. Equilibrium concentrations were reached in these tissues after 30 days' exposure.

Data in Table 11-1 also indicate that copper is not biomagnified; concentration ratios for fish (higher trophic levels) are lower than concentration levels for algae (primary producers, i.e., lowest trophic level). The apparent lack of biomagnification is not uncommon with the heavy metals. Furthermore, since copper is an essential nutrient, all organisms have active transport mechanisms for it, and there is no reason to believe that differences in the physiological ability to excrete copper should be related to trophic level.

11.3.6 Biotransformation

No evidence was found to indicate that there is any biotransformation process for copper compounds which would have a significant bearing on the fate of copper in aquatic environments.

11.4 Data Summary

Copper exhibits a very complex behavior in the aquatic environment. Sorption processes are probably most important in controlling copper distribution and include: coprecipitation/sorption by hydrous iron and manganese oxides; ion exchange in the crystal lattice structure of carbonate minerals; adsorption to clays and other mineral surfaces; and adsorption to organic solids. Sorption appears to be more important than precipitation in most circumstances.

Both organic and inorganic ligands complex copper. Under normal conditions, most of the copper in solution is in complexed form. These complexes alter the behavior of copper to the extent that it is generally more soluble in natural waters than would be predicted by conventional analysis employing thermodynamic equilibria, and it has a greater adsorptive affinity for hydrous solids than uncomplexed forms.

Seasonal fluctuations have been observed in aqueous copper concentrations with higher levels in fall and winter and lower levels in spring and summer. This probably reflects changes in bioaccumulation patterns: during the growing season, copper is taken up by biota; during fall and winter, decomposing leaf litter and aquatic vegetation release copper. The availability of biogenic ligands (e.g., humic and fulvic acids) is probably greater during the warmer part of the year, and this may enhance adsorption of copper. At present, it is impossible to estimate how much of the copper introduced into the aquatic environment is partitioned into bed sediments and biota and how much is transported by the water column to the oceans. This undoubtedly varies widely with local conditions.

Table 11-2 summarizes the aquatic fate information described above.

Table 11-2

Summary of Aquatic Fate of Copper

Environmental Process	Summary Statement	Confidence of Data
Photolysis	Not an important process.	Medium
Chemical Speciation[a]	In most unpolluted waters, the majority of copper will exist as the carbonate complex. In polluted waters, complexation with organic material will be most important.	Medium
Volatilization	Not an important process.	High
Sorption[a]	Various sorption processes reduce the mobility of copper and result in the enrichment of suspended and bed sediments relative to the water column. In unpolluted waters, sorption onto clay minerals, and hydrous iron and manganese oxides are controlling factors. In polluted waters, sorption onto organic materials is the controlling factor.	High
Bioaccumulation[a]	Biota strongly accumulate copper. Copper is apparently not biomagnified.	High
Biotransformation	Some copper complexes may be metabolized. Organic ligands are important in sorption and complexation processes.	Medium

a. All of the noted environmental processes are important; however, their relative importance with respect to each other is uncertain for determining final fate.

11.5 Literature Cited

Baker-Blocker, A., E. Callender, and P.D. Josephson. 1975. Trace-element and organic carbon content of surface sediments from Grand Traverse Bay, Lake Michigan. Geol. Soc. Amer. Bull. 86:1358-1362.

Brungs, W.A., E.N. Leonard, and J.M. McKim. 1973. Acute and long-term accumulation of copper by the brown bullhead, Ictaluris nebulosus. J. Fish. Res. Bd. Can. 30(4):583-586.

Carpenter, R.H., T.A. Pope, and R.L. Smith. 1975. Fe-Mn oxide coatings in stream sediment geochemical surveys. J. Geochem. Explor. 4:349-363.

Chapman, W.H., H.L. Fisher, and M.W. Pratt. 1968. Concentration factors of chemical elements in edible aquatic organisms. Lawrence Radiation Laboratory, Livermore, Calif. UCRL-50564. 46p.

Collins, B.I. 1973. The concentration control of soluble copper in a mine tailings stream. Geochim. Cosmochim. Acta. 37:69-75.

Cotton, F.A. and G. Wilkerson. 1972. Advanced inorganic chemistry. pp.903-922. Inter-Science Publishers, New York. 1145p.

Cross, F.A., L.H. Hardy, N.Y. Jones, and R.T. Barber. 1973. Relation between total body weight and concentrations of manganese, iron, copper, zinc, and mercury in white muscle of bluefish (Pomatonuis saltatrix) and a bathyl-demersal fish Antimora rostrata. J. Fish. Res. Bd. Can. 30(9):1287-1291.

Hem, J.D. and M.W. Skougstand. 1960. Co-precipitation effects in solutions containing ferrous, ferric, and cupric ions. p.104. U.S. Geological Survey Water Supply Paper 1459-E, Washington, D.C. 110p.

Hem, J.D. 1975. Discussion of "Role of hydrous metal oxides in the transport of heavy metals in the environment" by G.F. Lee. pp.149-153. in Heavy metals in the aquatic environment. P.A. Krenkel (ed.). Pergamon Press, Oxford, England. 352p.

Huang, C.P., H.A. Elliott, and R.M. Ashmead. 1977. Interfacial reactions and the fate of heavy metals in soil-water systems. J. Water Pollut. Control Fed. 49(5):745-756.

Jackson, K.S. and G.B. Skippen. 1978. Geochemical dispersion of heavy metals via organic complexing: a laboratory study of copper, lead, zinc, and nickel behavior at a simulated sediment-water boundary. J. Geochem. Explor. 10:117-138.

Jenne, E.A. 1968. Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and waters: the significant role of hydrous Mn and Fe oxides. pp.337-387. in Trace inorganics in water. R.F. Gould (ed.). Advances in Chem. Series 73. American Chemical Society, Washington, D.C. 396p.

Khobot'ev, V.G., V.I. Kapkov, E.G. Rikhadze, N.V. Turanina, and N.A. Shidlovskaga. 1976. Copper uptake by algae from copper-containing compounds and the effect of this process on their salt metabolism. Gidiobiol. Zh. 12(1):40-46 (Russian) (Abstract only). CA 1976. 85:42023r.

Kimball, K.D. 1973. Seasonal fluctuations of ionic copper in Knight's Pond, Massachusetts. Liminol. Oceanogr. 18(1):169-172.

Krauskopf, K.B. 1972. Geochemistry of micronutrients. pp. 7-40. in Micronutrients in agriculture. Mortvedt, J.J., P.M. Giordano, and W.L. Lindsay (eds.). Soil Science Society of America, Inc. Madison, Wisconsin. 649p.

Lee, G.F. 1975. Transport of heavy metals in the environment. pp. 137-147. in Heavy metals in the aquatic environment. P.A. Krendel (ed.). Pergamon Press Oxford, England. 352p.

Long, D.T. and E.E. Angino. 1977. Chemical speciation of Cd, Cu, Pb, and Zn in mixed freshwater, seawater, and brine solutions. Geochim. Cosmochim. Acta. 41:1183-1191.

Lopez, J.M. and G.F. Lee. 1977. Environmental chemistry of copper in Torch Lake, Michigan. Water Air Soil Pollut. 8:373-385.

Namminga, H. and J. Wilhm. 1977. Heavy metals in water, sediments and chironomids. J. Water Pollut. Control Fed. 49(7):1725-1731.

Nehring, R.B. 1976. Aquatic insects as biological monitors of heavy metal pollution. Bull. Environ. Contam. Toxicol. 15(2):147-154.

Patrick, F.M. and M. Loutit. 1976. Passage of metals in effluents through bacteria to higher organisms. Water Res. 10(4):333-335.

Payne, K. and W.F. Pickering. 1975. Influence of clay-solute interactions on aqueous copper ion levels. Water Air Soil Pollut. 5:63-69.

Ramamoorthy, S. and D.J. Kushner. 1975. Heavy metal binding components of river water. J. Fish. Res. Bd. Can. 32:1755-1766.

Ramamoorthy, S. and B.R. Rust. 1978. Heavy metal exchange processes in sediment-water systems. Environ. Geol. 2(3):165-172.

Rashid, M.A. 1974. Adsorption of metals on sedimentary and peat humic acids. Chem. Geol. 13:115-123.

Raymont, J.E.G. 1972. Pollution in Southhampton water. Proc. Roy. Soc. Ser. B. 180(106):451-468. (Abstract only). CA 1973. 78:144603f.

Sanchez, I. and G.F. Lee. 1973. Sorption of copper on Lake Monorna sediments - effect of NTA on copper release from sediments. Water Res. 7:587-593.

Steele, K.F. and G.H. Wagner. 1975. Trace metal relationships in bottom sediments of a fresh water stream - The Buffalo River, Arkansas. J. Sed. Pet. 45(1):310-319.

Stiff, M.J. 1971a. Copper/bicarbonate equilibria in solutions of bicarbonate ion at concentrations similar to those found in natural waters. Water Res. 5:171-176.

Stiff, M.J. 1971b. The chemical states of copper in polluted fresh water and a scheme of analysis to differentiate them. Water Res. 5:585-599.

Stokes, P.M., T.C. Hutchinson, and K. Kraute. 1973. Heavy metal tolerance in algae isolated from polluted lakes near the Sudbury, Ontario smelters. Water Pollut. Res. Can. 8:178-201. (Abstract only). CA 1975. 83:202492m.

Sylva, R.N. 1976. The environmental chemistry of copper(II) in aquatic systems. Water Res. 10:798-792.

Weast, R.C. (ed.). 1977. CRC Handbook of chemistry and physics. 58th Ed. CRC Press, Cleveland, Ohio. 2398p.

Windom, H., R. Stickney, R. Smith, D. White, and F. Taylor. 1973. Arsenic, cadmium, copper, mercury, and zinc in some species of North Atlantic finfish. J. Fish. Res. Bd. Can. 30(2):275-279.

12. CYANIDES

12.1 Statement of Probable Fate

Cyanides are a diverse group of compounds whose fate in the aquatic environment varies widely. Hydrogen cyanide, the most common and most toxic of the cyanides, may be destroyed by biodegradation or can be removed from solution by volatilization or adsorption. Cyanide ion (CN^-) can react with a variety of metals to form insoluble metal cyanides. If cyanide ion is present in excess, complex metallocyanides may be formed. The latter compounds are quite soluble and can be transported in solution. The fate of low molecular weight organic cyanides (nitriles) is expected to parallel the fate of hydrogen cyanide.

12.2 Identification - Environmental Chemistry of Cyanides

Cyanides are defined as organic or inorganic compounds which contain the -CN group. Hydrogen cyanide (HCN) is lighter than air and diffuses rapidly. Free HCN is very reactive and occurs only rarely in nature; it is usually prepared commercially from ammonia and methane at elevated temperatures with a platinum catalyst. Hydrogen cyanide is soluble in all proportions in water. It is quite volatile, having a vapor pressure of 100 torr at -178°C; 360 torr at 7°C; 658.7 torr at 21.9°C; and 760 torr at 26.7°C (boiling point) (Towill et al. 1978). Cyanide ion forms complexes with a variety of metals, especially those of the transition series. Ferricyanides and ferrocyanides have a variety of industrial uses but do not release cyanide unless exposed to ultraviolet light. Thus, sunlight can lead to the mobilization of cyanide in waters containing iron cyanides. Cyanogen [$(CN)_2$] is a flammable gas of high toxicity which has a vapor pressure of about 5 atm. at 20°C (Towill et al. 1978). It reacts slowly with water to produce HCN, cyanic acid, and other compounds. Cyanates contain the -OCN radical. Inorganic cyanates, which are formed industrially by the oxidation of cyanide salts, hydrolyze in water to form ammonia and bicarbonate ion. Alkyl cyanates trimerize readily (when sufficiently concentrated) to form cyanurates. Alkyl isocyanates contain the -NCO radical and are formed from cyanates; they, too, are readily hydrolyzed. Thiocyanates (-SCN radical) are formed from cyanides and sulfur-containing materials and are more stable than cyanates. Solutions of thiocyanates form free hydrogen cyanide in acidic media. Nitriles are organic compounds that have a cyanide group as a substituent. The nitriles are generally much less toxic than the free hydrogen cyanide or the metal cyanides. Cyanohydrins [$R_2C(OH)CN$] are toxic compounds which can decompose with the release of HCN or CN^- under environmental conditions.

In general, the cyanides occur in water as (1) free hydrocyanic acid (HCN), (2) simple cyanides (alkali and alkaline earth cyanides), (3) easily decomposable complex cyanides such as $Zn(CN)_2$, and (4) relatively stable complex cyanides such as $[Fe(CN)_6]^{-3}$, $[Fe(CN)_6]^{-4}$, and $Co(CN)_4$. The complex nickel and copper cyanides assume an intermediate position between the easily decomposable and relatively stable compounds.

The CAS number for cyanide ion is 57-12-5; its TSL number is A568-9315.

The CAS number for HCN is 74-90-8; its TSL number is A948-9671.

12.3 Summary of Fate Data

12.3.1 Photolysis

The photodecomposition of ferrocyanide and ferricyanide solutions and the resultant cyanide residuals in test solutions were observed by Bandish and Bass (1922) and Schwarz and Tede (1927). This effect was corroborated for river waters at concentration levels of 2 mg/l with both potassium ferrocyanide and ferricyanide by Burdick and Lipschuetz (1948). A 5-hour exposure of 100 mg/l potassium ferrocyanide to sunlight produced a cyanide ion level of 6 mg/l. No rate constants were calculated which would help assess the importance of this photodecomposition as an environmental fate.

Hydrogen cyanide is very resistant to photolysis by wavelengths of light reaching the earth's surface (Frank and Bard 1977). In the presence of titanium dioxide (TiO_2) powder, however, photocatalytic oxidation of cyanide ion proceeds at significant rates in both high intensity artificial sunlight and unfocused sunlight. Frank and Bard (1977) demonstrated that, with TiO_2 powder present, more than 99% of a 1 mM (26 mg/l) solution of cyanide ion was oxidized by exposure to sunlight for two days. In the absence of TiO_2 powder, little or no oxidation occurred.

The significance of photolysis on the aquatic fate of the cyanides has not been fully investigated, although it is possible that the photolysis of the metallocyanides could result in the release of cyanide ion (Broderius, 1977). This process could be important in aquatic environments downstream from metallocyanide discharges.

12.3.2 Chemical Speciation

Hydrogen cyanide can be oxidized to isocyanic acid (HNCO) in the presence of strong oxidizing agents. This material can then be hydrolyzed via the following reaction (Towill *et al.* 1978):

$$H - N = C = O \xrightarrow{H_2O} H_2N - \overset{O}{\overset{\|}{C}} - OH \xrightarrow{H_2O} NH_3 + H_2O + CO_2$$

Hydrolysis can also result in the destruction of HCN and the nitriles, but it probably occurs so slowly as to be non-competitive with other processes. HCN is hydrolyzed via the following reactions (Khorkin et al. 1967):

$$HCN \rightleftharpoons HCN: \qquad HCN: + H_2O \rightleftharpoons H - \overset{O}{\overset{\|}{C}} - NH_2 + H_2 \rightleftharpoons NH_4^+ + HCOO^-$$

The tautomerization of HCN to HCN: is the rate determining step, with the subsequent steps occurring rapidly at room temperature (Kreible and McNally 1929; Kreible and Peiker 1933; Khorkin et al. 1967). Hydrolysis of HCN in strongly acidic solutions (pH<1) proceeds readily, with half-lives on the order of 10 to 1000 hours, depending on the acid used and its concentration (Kreible and McNally 1929). At lower acid concentrations, the reaction is much slower, requiring several hundred hours to produce measurable hydrolysis (Kreible and Peiker 1933).

Cyanide ion can also be hydrolyzed under alkaline conditions, yielding formate ion and ammonia. Alkaline hydrolysis is first-order with respect to cyanide ion concentration. Rate constants for decomposition of HCN range from $2 \times 10^{-8} sec^{-1}$ to $2 \times 10^{-6} sec^{-1}$ at temperatures between 33°C and 65°C (Wiegand and Tremelling 1972). The relatively slow rates reported for both acidic and basic hydrolysis of HCN and cyanide ion indicate that this process is not competitive with volatilization and biodegradation.

The nitriles can also be hydrolyzed, but their reactivity varies greatly depending on the R group of the R-CN molecule (Towill et al. 1978). Kreible and Noll (1939) studied acid hydrolysis of several nitriles and found that the reactivity decreased in the order $CH_3CHOHCN > CH_3CH_2CN > CH_3CN$, $CH_2OHCH_2CN > (COOH)CH_2CN$. HCN was more reactive than all of the above nitriles. This implies that hydrolysis of nitriles in the aquatic environment is slow, in most cases, and is probably not competitive with other processes.

12.3.3 Volatilization

Hydrogen cyanide (HCN) is highly volatile, exerting a vapor pressure of 360 torr at 7°C. In most natural waters, almost all of the free cyanide in solution is present as HCN, with the remainder present as CN^-. The relationship of pH to percent HCN is shown below (Towill et al. 1978).

pH	Percentage of Total Free Cyanide as HCN
<7	>99
8	93.3
9	58
10	13

Unpublished data developed by Dr. S.J. Broderius of the University of Minnesota-St. Paul (Broderius 1977) indicate that volatilization of HCN is a relatively swift process. Ten 8-liter natural water samples were spiked with HCN and left open to the laboratory atmosphere (with no wind) in battery jars. Initial cyanide concentration and concentration after 6 hours were measured. The relationship between rate of HCN loss and initial concentration of free cyanide (as HCN) was observed to be first order. Half-lives of 22 to 111 hours were calculated for the conditions extant to St. Paul, Minnesota. When the experiment was performed outdoors, so that the solutions were exposed to moderate winds, the rate of HCN loss increased by a factor of 2 to 2.5. The concentrations of cyanide in this experiment ranged from 25 to 200 µg/l.

In a duplicate experiment, samples from the ten natural waters were again spiked with HCN but not exposed to the atmosphere. Cyanide loss was much smaller indicating that volatilization was the predominant process. It should be noted, however, that such concentrations of cyanide would probably retard biodegradation, or at least cause a lag in biological action by organisms capable of metabolizing cyanide. Nonetheless, these unpublished results indicate that volatilization is important as a fate of free cyanide (uncomplexed by metals) in the environment. The rate of volatilization is, of course, affected by a number of parameters including temperature, pH, mixing characteristics of the water, wind speed and ice cover.

A more rigorous experiment, but one which applies less directly to natural aquatic conditions, was performed by Raef et al. (1977a). The fate of cyanide in aerobic microbial systems (e.g., secondary sewage treatment) was studied with respect to adsorption, biodegradation, reaction with glucose, and stripping (volatilization effected by air forced through the system). In the stripping experiments, an air-flow of 2 cc min^{-1} was passed through 6 liters of 10 mg/l cyanide solution (pH 7.0, 30°C). After 50 minutes, the amount of cyanide in the reaction vessel had declined from 60 mg to about 55 mg. The amount of cyanide continued to decline until, after 375 minutes, only about 35 mg remained (Figure 12-1). Addition of biological solids had little effect on the stripping rate, although there was an initial decrease when solids were introduced. This reduction in rate was probably due to adsorption onto the solids. In comparison to the other processes investigated, stripping was more effective in removing cyanide than either adsorption or biodegradation. It is difficult, however, to generalize these results to natural aquatic systems.

12.3.4 Sorption

Cyanides are sorbed by a variety of materials, including clays (Cruz et al. 1974), biological solids (Raef et al. 1977a), activated carbon (Dardan and Popa 1939), and sediments (Kordakov and Vasillev 1971). In

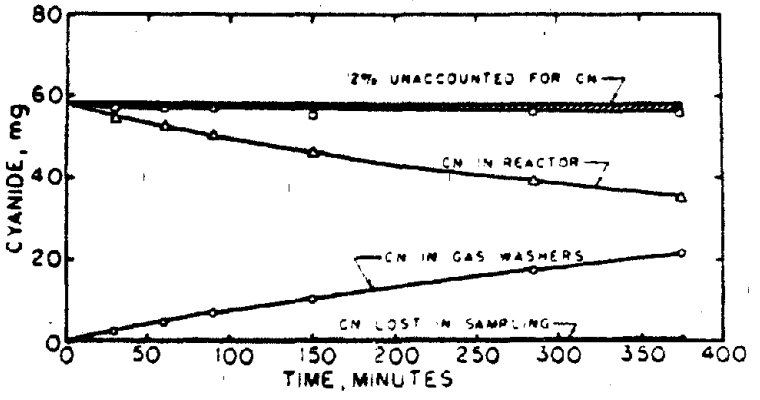


Figure 12-1 Stripping of cyanide from a reactor vessel containing 6 liters of 10 mg/l cyanide solution. From Rael et al. (1977a).

comparison to many refractory organic pollutants, hydrogen cyanide is not strongly partitioned into the sediments or suspended adsorbents, primarily due to its high solubility in water.

Cyanides are fairly mobile in the soil environment (Alesii and Fuller 1976), indicating that adsorption is probably not a significant control on mobility in most aquatic environments where sorbents are much less concentrated. Alesii and Fuller (1976) reported that cyanide mobility is least where soils exhibit low pH, high concentrations of free iron oxides, and positively charged particles (e.g., kaolin, chlorite, gibbsite). Mobility is greatest at high pH, high concentrations of free $CaCO_3$ (high negative charge) and low clay content.

Cruz et al. (1974) studied the adsorption of HCN by montmorillonitic clays. The data showed that adsorption is fairly weak and is decreased by the presence of water. Thus, in the aquatic environment, adsorption to montmorillonitic clays is probably not an important fate process.

Biological solids sorb cyanides, but, as with the other sorbents, the amount thus bound is probably insignificant in comparison to the amounts volatilized or biodegraded. Raef et al. (1977a) demonstrated that, with an initial cyanide concentration of 20 mg/l and a biological solids concentration of 6000 mg/l (dry weight), a non-flocculating bacterial culture did not remove any cyanide from solution. In a similar experiment, addition of 7260 mg/l (dry weight) of a flocculant culture of heterogeneous bacteria reduced cyanide concentration from 16 mg/l to 14.1 mg/l after one hour. The absence of strong sorptive effects led the investigators to conclude that adsorption probably plays an insignificant role in the overall removal of cyanide observed in biological treatment plants (Raef et al. 1977a).

Although it appears that sorption is not important in determining the fate of HCN, more data are required before the importance of sorption on the fate of the metal cyanides and nitriles can be adequately assessed.

12.3.5 Bioaccumulation

In biological systems, hydrogen cyanide interferes with the enzymes associated with cellular oxidation. It is either quickly metabolized or the organism dies. Thus, there is little potential for bioaccumulation of hydrogen cyanide.

Many plants synthesize and accumulate cyanogenic glycosides (Gewitz et al. 1976). When the tissues of these plants are crushed, hydrolytic enzymes are released, which in turn cause the destruction of the cyanogenic glycosides to evolve cyanide.

Broderius (1973) reported the bioaccumulation of metal cyanide complexes in fish. Copper cyanide concentrations ranged from undetectable to 303.9 µg per gram for various bluegill tissues, with the liver/gall bladder fraction exhibiting greatest bioaccumulation. Likewise, silver cyanide was accumulated in concentations up to 168.4 µg per gram. It is difficult to assess the environmental importance of metal cyanide bioaccumulation, other than to note that the metal cyanides are generally less toxic than HCN. Chronic toxic effects of the metal cyanides are undoubtedly enhanced by such bioaccumulation.

12.3.6 Biotransformation

Hydrogen cyanide, metallocyanide complexes, and nitriles are all subject to biodegradation. Although few data are available on biodegradation of cyanides in surface water, the literature is replete with references to degradation in anaerobic and aerobic sewage treatment. It has been demonstrated that activated sludge treatment can result in virtually complete removal of cyanide (Ludzack and Schaffer 1962; Kostenbalder and Flecksteiner 1969), but Raef et al. (1977b) showed that most of the loss of cyanide in such systems is due to stripping (volatilization). Biodegradation was of secondary importance, and adsorption accounted for a minor amount of cyanide removal. The pronounced difference in biological densities and physico-chemical conditions (nutrient concentrations, dissolved gases, etc.) between natural surface water systems and sewage treatment processes make it very difficult to extrapolate the above results to the aquatic environment. It is evident, however, that biodegradation of cyanides does occur in natural waters, and the importance of this process varies according to such factors as cyanide concentrations, pH, temperature, concentration of microbes, availability of nutrients, and whether the microbes are acclimated to cyanide.

The ability to metabolize hydrogen cyanide or its salts appears to be nearly universal. A bacterium has been isolated that is capable of using cyanide as its sole source of carbon and nitrogen (Ware and Painter 1955), but most organisms can only tolerate very low concentations. Typical metabolic pathways for degradation of cyanide include production of thiocyanate, reaction with hydroxocobalamin to form cyanocobalamin, combination with amino acids, and oxidation to carbon dioxide and formate ion (Towill et al. 1978).

Of the numerous experiments that have been performed regarding the biochemistry of cyanide metabolism, one of the most salient was that of Hardy and Knight (1967). In this experiment, nitrogen-fixing enzymes were extracted from the bacteria Azotobacter vinelandii and Clostridium pasteurnianum. Under reducing conditions, these enzymes reduced HCN to CH_4, NH_3, and possibly small amounts of CH_3NH_2. Adenosine triphosphate (ATP) was required for the reaction, and it was necessary for the enzymes

to be extracted from cells grown in N_2, rather than ammonia or urea. Apparently the same enzymes that catalyze the reduction of N_2 to NH_3 and NO_2 to N_2 are responsible for the reduction of HCN (and azide). Hydrogen cyanide is synthesized by a variety of organisms including bacteria (Lorck 1948; Wissing 1974; Castric 1975), fungi (Hutchinson 1973); and a millipede (Duffey and Blum 1977).

Nitriles can also be biodegraded. Some of the low molecular weight nitriles can be used by microbes as their sole source of carbon and nitrogen. The bacterium Nocardia rhodochrous can metabolize acetonitrile, propionitrile, hydroacrylonitrile, butyronitrile, and succinonitrile (DiGeronimo and Antoine 1976). Biodegradation of nitriles is sometimes a two-step enzymatically mediated hydrolysis with an amide as the intermediate product, and ammonia and the corresponding carboxylic acid as end products (Fukuda et al. 1971; DiGeronimo and Antoine 1976; Mimura et al. 1969).

In Pseudomonas, the biodegradation process may involve several additional intermediates. Firmin and Gray (1976) showed that acetonitrile is metabolized via the following pathway in Pseudomonas: acetonitrile ⟶ acetamide ⟶ acetate ⟶ tricarboxylic acid intermediates. This pathway apparently exists in higher plants as well. The authors speculated that higher aliphatic nitriles could also be metabolized by enzymatically mediated hydrolysis combined with α - and β - oxidation.

It is evident from the literature that the cyanides can be biodegraded. The rapidity of this process varies widely in the laboratory, however, and it is difficult to generalize these results to environmental conditions. In natural surface waters, biodegradation is an important fate, but more work needs to be done before the quantitative aspects of this process can be determined.

12.4 Data Summary

The data on the fate of cyanides in the aquatic environment are inconclusive, and can only be interpreted with caution. It appears, however, that volatilization and biodegradation are the dominant processes affecting HCN and the nitriles. Adsorption can also result in removal of those cyanides from solution. The simple metal cyanides are insoluble and probably accumulate in the bed sediments. Complex metallocyanides are transported in solution by the water column. Changes in the concentration ratio of metals to cyanide can alter the behavior of the metal-cyanide compounds. If the metals become more prevalent, formation of simple metal cyanides is favored; if cyanide becomes more prevalent, the complexed forms occur. Some of the metallocyanide complexes can be photolyzed by sunlight, possibly resulting in diurnal fluctuation in free cyanide levels where these complexes are present. Table 12-1 summarizes the aquatic fate of cyanides.

Table 12-1

Summary of Aquatic Fate of Cyanide

Environmental Process	Summary Statement	Confidence of Data
Photolysis[a]	Can cause breakdown of some metallocyanide complexes.	Medium
Chemical Speciation	Chemical transformations occur very slowly in most aquatic environments.	Medium
Volatilization[a]	At pH<10 most of the free cyanide will be HCN which is quite volatile. A most important process in the aquatic environment.	Medium
Sorption	Cyanides are sorbed by organic materials and to a lesser extent clay minerals. Not an important process.	Low
Bioaccumulation	Cyanides are not bioaccumulated.	Medium
Biotransformation[a]	Cyanides are biodegraded at low concentrations by almost all organisms. A very important process for the aquatic fate of cyanides.	Medium

a. All of the noted environmental processes are important; however, their relative importance with respect to each other is uncertain for determining final fate.

12.5 Literature Cited

Alesii, B.A. and W.H. Fuller. 1976. The mobility of three cyanide forms in soils. pp. 213-223. in Residual Management by Land Disposal. W.H. Fuller (ed.). Environmental Protection Agency, Cincinnatti, Ohio. PB 256768 268p.

Bandish, O. and L.W. Bass. 1922. Eisen ab licht-chemisher katalyzator. I. Uber die zursetzing von ferrocyankalium in tageslicht. Ber. Deut. Chem. Gesell. 55:2698-2706.

Broderius, S.J. 1973. Determination of molecular hydrocyanic acid in water and studies of the chemistry and toxicity to fish of metal-cyanide complexes. Ph.D. Dissertation, Oregon State Univ., Corvallis, Ore. 287p. Available from Univ. Microfilms International, No. 73-21299, Ann Arbor, Michigan.

Broderius, S.J. 1977. Personal communication concetning the fate of cyanides in the aquatic environment. EPA Grant R805291, Dec. 8, 1977. Univ. of Minnesota, St. Paul.

Burdick, G.E. and M. Lipschuetz. 1948. Toxicity of ferro- and ferricyanide solutions to fish and determinations of the cause of mortality. Trans. Amer. Fish Soc. 78:192-202.

Castric, P.A. 1975. Hydrogen cyanide, a secondary metabolite of Pseudomonas aerogmosi. Can. Jour. Microbiol. 21:613-618.

Cruz, M., A. Kaiser, P.G. Rowxhat, and J.J. Fripiat. 1974. Absorption and transformation of HCN on the surface of copper and calcium montmorillonite. Clays Clay Mineral. 22:417-425.

Dardan, D. and S. Popa. 1939. Influence of alkalinity on the absorbing power of activated carbon for warfare gases: phosgene, chlorine, chloropicrin, and HCN. Compt. Rend. Inst. Sci. Roumanie 3:675-682 (Abstract only). CA 1941. 36:6695.

DiGeronimo, M.J. and A.D. Antoine. 1976. Metabolism of acetonitrile and propionitrile by Nocardia rhodochrous LL100-21. Appl. Environ. Microbiol. 31(6):900-906.

Duffey, S.S. and M.S. Blum. 1977. Phenol and guaiacol: biosynthesis, detoxification, and function in a polydesinid millipede, Oxidus grocillus. Insect. Biochem. 7:57-65.

Firmin, J.L. and D.O. Gray. 1976. The biochemical pathway for the breakdown of methyl cyanide (acetonitrile) in bacteria. Biochem. J. 158:223-229.

Frank, S.N. and A.J. Bard. 1977. Heterogenous photocatalyst oxidation of cyanide ion in aqueous solutions at titanium dioxide powder. J. Amer. Chem. Soc. 99(1):303-304.

Fukuda, Y., M. Fukui, T. Harrada, and Y. Izumi. 1971. Formation of α-aminonitrile by cell suspensions of a strain of Corynelsacterium. J. Ferment. Technol. 49:1011-1016.

Gewitz, H.S., E.K. Pistorius, H. Voss, and B. Vennesland. 1976. Cyanide formation in preparations from Chlorella vulgaris Beijerink: effect of sonication and amygdalin addition. Planta. 131:145-148.

Hardy, R.W.F. and E. Knight, Jr. 1967. ATP-dependent reduction of azide and HCN by N_2-fixing enzymes of Azotobacter rinelandii and Clostriduim pasteurianum. Biochem. Biophys. Acta 139:69-90.

Hutchinson, S.A. 1973. Biological activities of fungal metabolites. Am. Rev. Phytopathol. 11:233-246.

Khorkin, A.A., O.N. Temkin, and R.M. Flid. 1967. Kinetics of the acid hydrolysis of hydrocyanic acid. Russian J. Phys. Chem. 41(2):150-152.

Kostenbalder, P.D. and J.W. Flecksteiner. 1969. Biological oxidation of coke plant weak ammonia liquor. J. Water Pollut. Control Fed. 41(1):199-207.

Kordakov, V.A. and B.F. Vasillev. 1971. Physicochemical processes in the elimination of heavy metal ions and cyanides from industrial wastewaters. Tor. Naveh. Issled. Prackt. Ingt. Okogashch. Rud. Tsvet. Metal. 7:49-58 (Russian) (Abstract only). CA 1973. 78:163698h.

Kreible, V.K. and J.G. McNally. 1929. The hydrolysis of hydrogen cyanide by acids. J. Amer. Chem. Soc. 51:3368-3375.

Kreible, V.K. and A.L. Peiker. 1933. The hydrolysis of hydrogen cyanide by acids II. J. Amer. Chem. Soc. 55:2326-2331.

Kreible, V.K. And C.I. Noll. 1939. The hydrolysis of nitriles with acids. J. Amer. Chem. Soc. 61:560-563.

Lorck, H. 1948. Production of hydrocyanic acid by bacteria. Physiol. Plant. 1:142-146.

Ludzack, F.J. and R.B. Schaffer. 1962. Activated sludge treatment of cyanide, cyanate, and thiocyanate. J. Water Pollut. Control Fed. 34(4):320-341.

Mimura, A., T. Kawano, and Y. Yamaga. 1969. Application of microorganisms to petrochemical industry. I. Assimilation of nitrile compounds by microorganisms. J. Ferment. Technol. 47:631-638.

Raef, S.F., W.G. Characklis, M.A. Kossich, and C.H. Ward. 1977a. Fate of cyanide and related compounds in aerobic microbiol systems. I. Chemical reaction with substrate and physical removal. Water Res. 11:477-483.

Raef, S.F., W.G. Characklis, M.A. Kossich, and C.H. Ward. 1977b. Fate of cyanide and related compounds in aerobic microbial systems. II. Microbial degradation. Water Res. 11:485-492.

Schwarz, R. and K. Tede. 1927. Uber die photochemie der komplexverbindungen. III. Die hexacyanokomplexe des dreiwertigen essins, kabalts, chroms, and mangans. Ber. Deut. Chem. Gesell. 60:69-72.

Towill, L.E., J.S. Drury, B.L. Whitfield, E.B. Lewis, E.L. Galyan, and A.S. Hammons. 1978. Reviews of the environmental effects of pollutants. V. Cyanide. pp. 11-33. Oak Ridge National Laboratory, Oak Ridge, Tenn. PB 289 920. 190p.

Ware, G.C. and H.A. Painter. 1955. Bacterial utilization of cyanide. Nature 175 (4464):900.

Wiegand, G.H. and M. Tremelling. 1972. The kinetics and mechanism of the decomposition of potassium cyanide in aqueous alkaline medium. Hydrolysis of the simplest nitrile, HCN. J. Org. Chem. 37(6):914-916.

Wissing, F. 1974. Cyanide formation from oxidation of glycine by a Pseudomonas species. J. Bacteriol. 117:1289-1294.

13. LEAD

13.1 Statement of Probable Fate

Sorption processes are effective in reducing the concentration of soluble lead in natural waters and result in enrichment of bed sediments near the source. The equilibrium solubility of lead with carbonate, sulfate, and sulfide is low. In severely contaminated areas, precipitation may be important in controlling the mobility of this metal, but under most circumstances, sorption predominates. The tendency for lead to form complexes with naturally occurring organic materials (e.g., humic and fulvic acids) increases its adsorptive affinity for clays and other mineral surfaces. Benthic microbes can methylate lead to form tetramethyl lead which is volatile and more toxic than inorganic lead. Biomethylation may, in this manner, also provide a mechanism for remobilization of lead in the bed sediments. Bioaccumulation of weakly sorbed lead phases also may result in remobilization. Lead is generally not biomagnified; bioconcentration factors tend to decrease as the trophic level increases.

13.2 Identification - Geochemistry of Lead

Lead is a naturally occurring element and is a major constituent of more than 200 identified minerals. Most of these are very rare, and only three are found in sufficient abundance to form mineable deposits: galena (PbS) the simple sulfide, angelesite ($PbSO_4$) the sulfate, and cerrusite ($PbCO_3$) the carbonate. By far the most abundant is galena which is the primary constituent of the sulfide ore deposits from which most lead is presently mined.

Ores of lead, as well as those of zinc, are often closely associated in deposits formed by replacement of limestone or dolomite. Lead ore is commonly present together with ores of copper, zinc, silver, arsenic, and antimony in complex vein deposits, but lead ore also may occur in a variety of igneous, metamorphic, and sedimentary rocks.

Lead, atomic number 82, atomic weight 207.19, is a member of the group IV elements (Weast 1977). Lead exists in three oxidation states, 0, +2, and +4. Although neither metallic lead nor the common lead minerals is classified as soluble in water, they can both be solubilized by some acids; in contrast, some of the lead compounds produced industrially are considerably water soluble. Therefore, natural compounds of lead are not usually mobile in normal ground or surface water because the lead leached from ores becomes adsorbed by ferric hydroxide or tends to combine with carbonate or sulfate ions to form insoluble compounds (Hem 1976a).

The average abundance of lead in the earth's crust is approximately 15 ppm (Lovering 1976) which is equivalent to one-half ounce of lead per ton of rock. Shales and unconsolidated sediments have a mean lead abundance close to the crustal average, showing the fairly even distribution of lead in the environment.

The CAS number for lead is 7439-92-1; the TSL number is B049-0641.

13.3 Summary of Fate Data

13.3.1 Photolysis

Although no evidence was found concerning the photolysis of organo-lead complexes in natural waters, photolysis of these compounds in the atmosphere has a great bearing on the form of lead which will enter the aquatic environment. For example, Hirschler and Gilbert (1964) report that the chief constituents of the inorganic lead compounds leaving the exhaust system of automobiles burning leaded fuels are two forms of PbClBr, $NH_4Cl \cdot 4PbClBr$ and $2NH_4Cl \cdot PbClBr$. The species PbClBr (lead bromochloride) appears to be stable at ordinary temperatures and is isomorphous with $PbCl_2$ and $PbBr_2$. Both $PbCl_2$ and $PbBr_2$ darken on exposure to sunlight with the release of halogen. The ultimate products of the photolysis of these lead compounds in the atmosphere would be PbO and the halogens. Since the majority of the lead emitted to the environment originates from the tailpipes of automobiles, these photolytic processes are quite important. Also of importance, as Pierrard (1969) has pointed out, is that the halogens produced from the photolysis of the lead halides may be involved in chain reaction mechanisms with such atmospheric pollutants as CO, NO, and SO_2.

13.3.2 Chemical Speciation

An outstanding characteristic of lead is its tendency to form complexes of low solubility with the major anions of natural environmental systems. The hydroxide, carbonate, sulfide, and (more rarely) the sulfate of lead may act as solubility controls. Throughout most of the natural environment, the divalent form, Pb^{+2}, is the stable ionic species of lead. The more oxidized solid PbO_2, in which lead has a +4 charge, is stable only under highly oxidizing conditions, and probably has very little significance in the aquatic environment (Cotton and Wilkerson 1972). If sulfur activity is very low, metallic lead can be a stable phase in alkaline or circumneutral reducing conditions.

Huang *et al.* (1977) calculated the equilibrium solubility of lead as a function of pE for a system with total carbonate and total sulfur concentrations of 10^{-3} M at pH 7. Figure 13-1 shows the solubility of lead

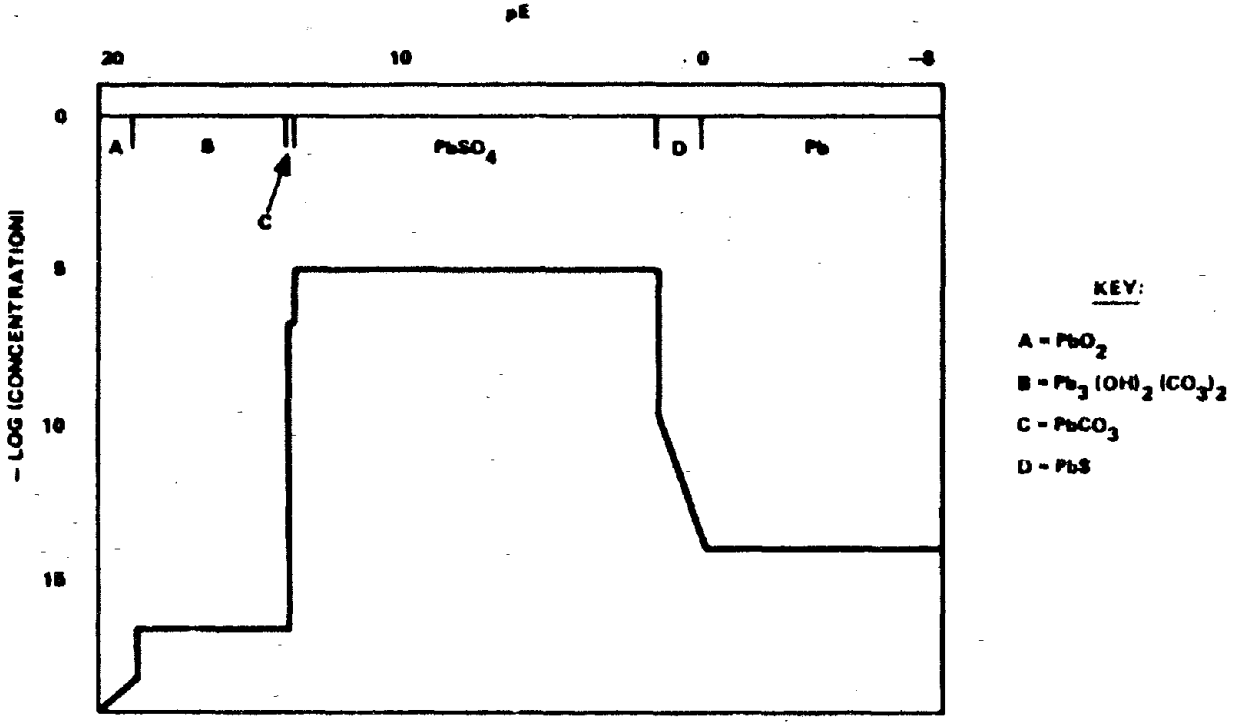


Figure 13-1 Solubility of lead as a function of pE. Modified from Huang et al. (1977).

and the controlling solid species for pE from +20 to -8. At pH 7, $PbSO_4$ controls solubility over much of the pE range encountered in natural waters.

Hem (1976b) calculated the fields of stability for solid species of lead based on the available thermodynamic data; these results are summarized in Figure 13-2 and Figure 13-3. Although these figures are useful in depicting equilibrium behavior, they are limited in that they do not take into account environmental interactions with organic compounds and other trace elements and, therefore, may be misleading with respect to fate and transport in normal surface waters. Hem (1976a) looked at the equilibrium distribution between lead in solution and lead adsorbed on cation exchange sites in sediments. He calculated these distributions using equations representing selecticities of substrate for lead over H^+, Ca^{+2}, and Na^+ and the stabilities of lead solute species. Included in the calculations were total concentrations of major ions, cation exchange capacity of the substrate, and pH. The cation exchange behavior of lead in natural systems could be predicted with this model if enough supporting information were available. The available information for describing natural stream sediments, however, is inadequate for accurate use of this model. In general, Hem's model suggests that in most natural environments, sorption processes would more effectively scavenge dissolved lead than precipitation.

Long and Angino (1977) developed a theoretical model to study the chemical speciation of lead in aquatic environments and the response of lead to variations in ionic strength and complexation. Association of lead with the ligands OH^-, Cl^-, CO_3^{-2}, SO_4^{-2}, and HCO_3^- was considered at pH values from 3.5 to 11.0 at 25°C in differing seawater-freshwater mixtures. The results are summarized in Figure 13-4. In general, the relative importance of the various ligand-lead complexes can be predicted from a comparison of their stability constants; however, since this model does not take into account metal-organic complexes, it is useful only in unpolluted, relatively organic-free waters.

Dissolved lead may be hydrolyzed to form $Pb(OH)_2$. Patterson et al. (1977) studied the formation of $Pb(OH)_2$ versus $PbCO_3$ to determine the feasibility of treating lead-containing waters with carbonates. They found that $PbCO_3$ controls lead solubility at pH < 11.5. Even small concentrations of inorganic carbonate due to dissolution of atmospheric CO_2 are sufficient to reduce the solubility of lead to concentrations below those predicted on the basis of hydrolysis alone. It should be noted that lead concentrations were reduced nearly to the computed solubility limits within four hours; thus, precipitation of lead carbonate can occur quickly.

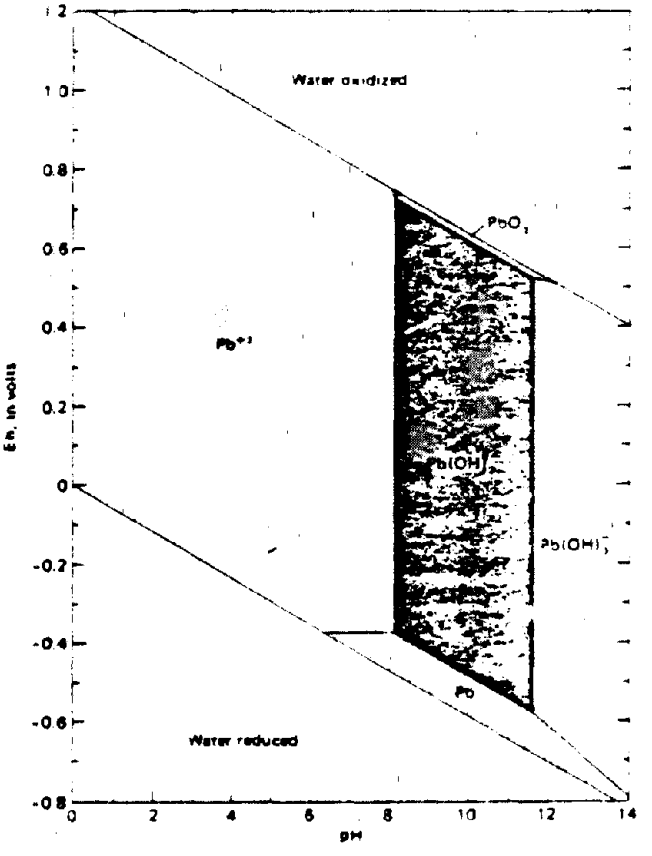


Figure 13-2 Fields of stability for solid species and dominant solute species in system Pb + H_2O as functions of pH and redox potential. Dissolved lead activity is $10^{-8.32}$ mol/l at 25°C and 1 atm. pressure. From Hem (1976b).

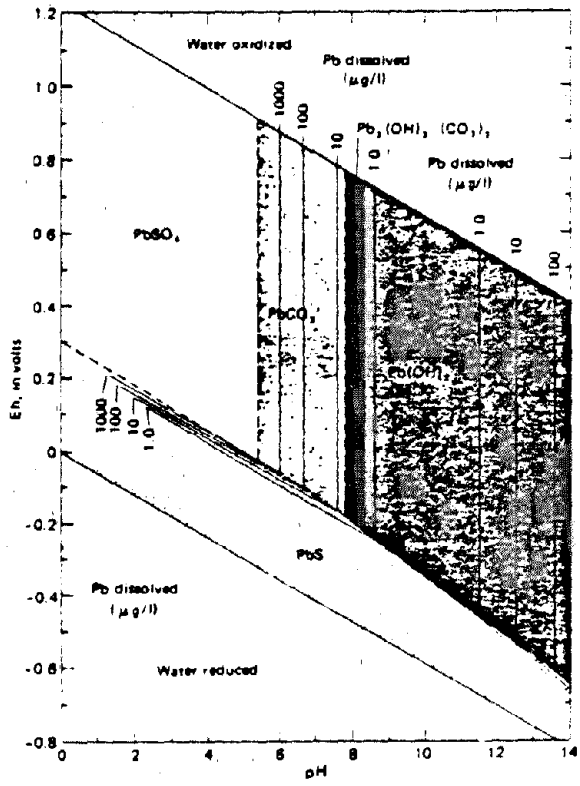


Figure 13-3 Fields of stability for solids and solubility of lead in system Pb + CO_2 + S + H_2O at 25°C and 1 atm. pressure. Ionic strength 0.005. From Hem (1976b).

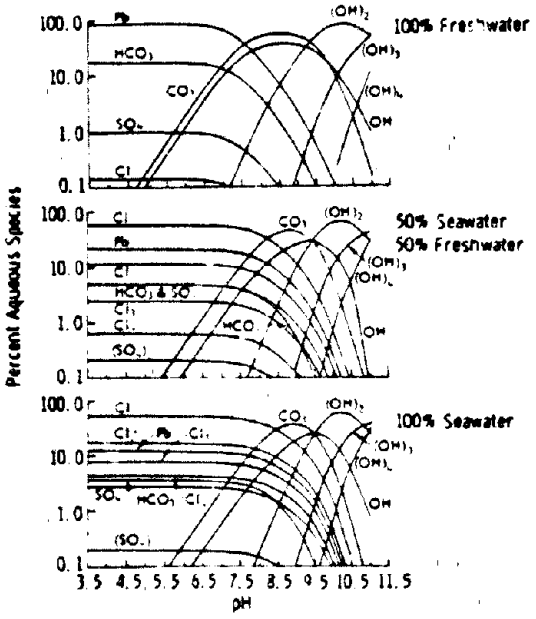


Figure 13-4 Chemical speciation of lead in seawater-freshwater mixtures. From Long and Angino (1977).

At the low concentration in which lead is normally found in the aquatic environment, almost all of the lead in the dissolved phase may be complexed by the ligands of river water. By using an ion-specific electrode, Ramamoorthy and Kushner (1975) determined that lead binding capacity was predominantly due to organic compounds. Inorganic complexes were not important, since evaporating the water samples, ashing the residue, and reconstituting the ash in water resulted in complete loss of the binding capacity. (In waters with a high carbonate concentration, however, binding by HCO_3^- or CO_3^{-2} is important).

Guy and Chakrabarti (1976), in their study of metal-organic interactions in natural waters, found that humic acids in solution and other organic complexing agents can maintain lead ions in a bound form at a pH as low as 3. O'Shea and Mancy (1978), in their study of the effect of pH and hardness on lead speciation, found that the effects of pH and hardness metals were insignificant in lead-inorganic interactions. They were important, however, in lead-humic acid interactions. Increasing the pH increased the concentration of exchangeable lead complexes while an increase in hardness tends to decrease the extent of the humic acid-lead interaction. Metals responsible for hardness apparently inhibit the exchangeable interactions between metals and humic materials in ways that are not fully understood.

Jackson and Skippen (1978) investigated the behavior of lead and organic materials at a simulated sediment-water boundary. The interactions involved sorption by clays, organic complexing, carbonate reactions, hydrolysis, and desorption of lead from clay and metal hydroxides. They found that organic acids decreased the solubility of lead in the presence of clay, particularly at acidic pH values. This organic complexing is probably due to colloidal coagulation. The organic acids, moreover, proved capable of remobilizing lead from the solid phase. There is, however, a general kinetic hindrance to this desorption, particularly at basic pH values.

In summation, the transport of lead in the aquatic environment is influenced by the speciation of the ion. Although lead will exist mainly as the divalent cation in most unpolluted waters and become sorbed into particulate phases, organic material in polluted waters will have a great effect on the chemical form in which lead will be present.

13.3.3 Volatilization

The relatively volatile tetramethyl lead ($(CH_3)_4Pb$) can be produced by microorganisms in lake sediments from inorganic ($Pb(NO_3)_2$ and $PbCl_2$) and organic ($(CH_3)_3PbOOCCH_3$) lead compounds (Wong *et al.* 1975). Analysis of air in flasks that contained anaerobic lake sediments

inoculated with these compounds showed that tetramethyl lead thus produced can be volatilized. Under these experimental conditions, addition of 10 mg of lead as trimethyl lead acetate resulted in volatilization of weekly increments of 125 µg, 642 µg, 550 µg, and 256 µg of tetramethyl lead during the first four weeks (Wong et al. 1975). Nevertheless, the importance of volatilization of tetramethyl lead is uncertain. Although the rate of destruction of tetramethyl lead in aerobic waters is unknown, this compound is probably not stable in oxidizing environments. When a layer of aerobic water lies between the reducing sediments and the atmosphere, volatilization may not be important.

13.3.4 Sorption

Sorption processes appear to exert a dominant effect on the distribution of lead in the environment. Several investigators have reported that in aquatic and estuarine systems, lead is removed to the bed sediments in close proximity to its source, apparently due to sorption onto the sediments (Helz et al. 1975; Valiela et al. 1974). Different sorption mechanisms have been invoked by different investigators, and the relative importance of these mechanisms varies widely with such parameters as geological setting, pH, Eh, availability of ligands, dissolved and particulate iron concentration, salinity, composition of suspended and bed sediments, and initial lead concentration.

Pita and Hyne (1975) studied the depositional environment of lead in reservoir sediments and found that almost all of the lead in the sediments was in the fraction with specific gravity between 2.0 and 2.9. This fraction contains the clays. The authors suggested that formation of organo-lead complexes may play an important role in adsorption, noting that "the same type of organic matter (negatively charged or polar) which tends to form organo-metallic compounds would also tend to adhere to clay minerals and would occur in the 2.0 to 2.9 specific gravity portion." The paucity of lead in sediments with specific gravity less than 2.0 indicated that adsorption onto organic material not active in complex formation was insignificant; the lack of lead in the denser fraction (sp. gr. > 2.9) indicated that precipitation was not important. The relative dominance of adsorption over precipitation is corroborated by calculations made by Hem (1976a), which indicate that precipitation is important only under relatively alkaline conditions.

The adsorption of lead to soils and oxides was studied by Huang et al. (1977). The data indicate that adsorption is highly pH-dependent, but above pH 7, essentially all of the lead is in the solid phase (Figure 13-5). It should be noted that at low pH, lead is negatively sorbed (repelled from the adsorbent surface). The addition of organic complexing agents increased the affinity for adsorption (Figure 13-6). Therefore, the

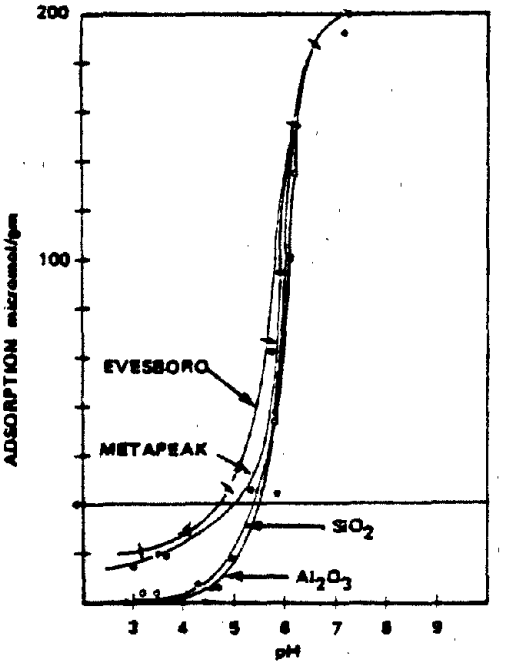


Figure 13-5 Adsorption of lead on various solids. The soil-water system consisted of 5 gm/l solid, 10^{-3}M Pb, and 0.1M NaCl (thus adsorption of 200 µM/gm = 100% removal). From Huang et al. (1977).

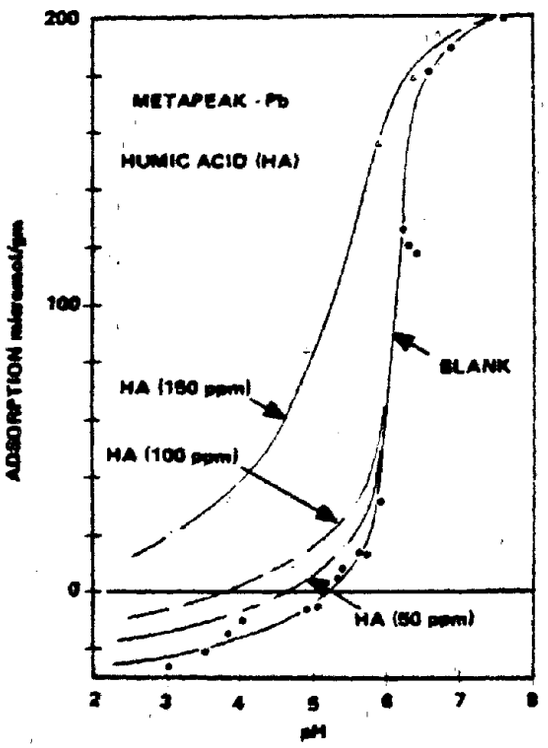


Figure 13-6 Effect of humic acid on the adsorption of lead by metapeak soil. Soil added at 5 gm/l, initial $[Pb^{2+}] = 10^{-3}$M, ionic strength = 10^{-1}M (NaCl). From Huang et al. 1977.

tendency for lead to be adsorbed probably reflects the fact that lead is strongly complexed by organic materials in the aquatic environment (Ramamoorthy and Kushner 1975). Huang et al. (1977) speculate that the increased adsorption is due to the ability of the metal-ligand complexes to share free electrons, thus facilitating sorption to electrophilic solid surfaces.

Similar studies have been carried out in seawater environments. For example, Patterson et al. (1976), in their study of sewage effluent entering polluted coastal waters, found that virtually all the lead in the sewage was contained in the particulate phase before it entered the ocean but that about 11 percent was made freely available within a day by cation exchange when the sewage was mixed with seawater. Further exposure of the sewage to seawater, however, did not facilitate the release of more lead. Lu and Chen (1977), in their laboratory study of the migration of trace metals from polluted sediment into seawater, found that the release of lead from the sediment increased as the redox conditions became more oxidizing. Moreover, after long-term incubation under aerobic conditions, lead concentrations were far below equilibrium concentration. This latter observation is indicative of the substantial sorption processes which lead undergoes in aquatic sediments.

Ramamoorthy and Rust (1978) found that the sorption of lead by Ottawa River bed sediments can be fitted to the linear form of Langmuir's equations. They reported that the partition coefficient of lead between sediment and solution is not greatly changed by the presence of other heavy metals, provided that the latter has the same order of concentration. If the concentration of one cation exceeds the other by more than a factor of 10, however, significant desorption of the less concentrated ion takes place on a mass action basis.

There are significant differences reported not only in the mode of binding to bed sediments, but also in the distribution of lead among phases in the water column. Some authors report that lead is transported predominantly in the particulate phase rather than the dissolved phase (Kubota et al. 1974; Schell and Nevissi 1977); others report that the amount in the dissolved phase is about equal to that in the particulate phase (Angino et al. 1974); and still others find that more lead is transported in the dissolved phase than in the suspended material (Pita and Hyne 1975). There is general agreement, however, that residence in lakes and impoundments causes a reduction in dissolved lead levels even when lead is initially present in concentrations below calculated solubility limits (Kubota et al. 1974; Pita and Hyne 1975). Thus, sorption processes appear to be effective in reducing dissolved lead levels and result in enrichment of bed sediments. It appears that, under most conditions, adsorption to clay and other mineral surfaces, coprecipitation/sorption by hydrous iron oxides, and incorpora-

tion into cationic lattice sites in crystalline sediments are the important sorption processes.

Several authors, notably Jenne (1968), Lee (1975), and Hohl and Stumm (1976), have hypothesized that the sorption of heavy metals by hydrous iron and manganese oxides is a major control on the mobility of these pollutants in the aquatic environment. On the basis of a high correlation between the lead, iron and manganese concentration in sediments, Angino et al. (1974) suggested that sorption by iron and manganese oxides is the dominant sorption process in several Kansas streams. Gaddle and Laitmen (1973) demonstrated that hydrous iron oxides have a high sorption capacity for lead, sorbing as much as 0.28 moles lead per mole iron at pH 6. The ability of hydrous iron oxides to sorb lead increases with increasing pH. At pH 8.1, 91 percent of the added lead was sorbed. When the pH drops, however, lead may be desorbed. Although the relative importance of individual sorption processes varies widely, it appears that, in most circumstances, lead is effectively removed to the sediments by sorption .

13.3.5 Bioaccumulation

Bioaccumulation of lead has been demonstrated for a variety of organisms. Table 13-1 lists bioconcentration factors reported by various sources.

Microcosm studies indicate that lead is not biomagnified. Lu et al. (1975) studied the fate of lead in three ecosystems differing only in their soil substrate. The ecosystems contained algae, snails, mosquito larvae, mosquito fish, and microorganisms. Lead was concentrated most by the mosquito larvae and least by the fish. Furthermore, body burdens and aqueous lead concentration appeared to be strongly correlated to the percentage of organic matter and cation exchange capacity of the soils, indicating that the availability of lead in the systems was controlled by adsorption to the soils. Since pH was the same for all three soils, precipitation/dissolution of inorganically bound lead was probably not responsible for the differences in lead availability and uptake.

Merlini and Pozzi (1977a) measured lead uptake in pumpkinseed sunfish (Leponis giblosus) exposed to ^{203}Pb at pH 6.0 and 7.5 Fish at the lower pH accumulated three times as much lead as fish kept at pH 7.5. Gill, liver, and fin accumulated the most lead and muscle the least. The authors attributed the increased lead uptake at low pH to the increasing concentration of divalent lead with decreasing pH. In another experiment, Merlini and Pozzi (1977b) found a direct correlation between lead accumulation by pumpkinseed sunfish and the concentration of ionic lead in water at various concentrations of total lead. Results suggest that the conditions existing in the majority of natural waters render most lead unavailable for accumulation by aquatic animals.

Table 13-1

Bioconcentration Factors for Lead

Taxon	Bioconcentration Factor[a]	Reference
Freshwater plants	200	Chapman et al. 1968
Freshwater invertebrates	200	Chapman et al. 1968
Freshwater fish	60	Chapman et al. 1968
Marine plants	200	Chapman et al. 1968
Marine invertebrates	200	Chapman et al. 1968
Marine fish	60	Chapman et al. 1968

a. Bioconcentration factors are the ratio derived from the concentration of the element in the aquatic organism (in ppm wet weight) divided by the concentration of the element in water (in ppm).

Patrick and Loutit (1976) studied uptake of lead by benthic bacteria and subsequent transfer to tubificid worms. The concentration factor for bacteria was approximately 360. Concentration of lead by tubificids was 0.77 times the amount fed them in the bacteria, indicating that the tubificids can clear lead more easily than the bacteria. The fact that the bacteria could concentrate lead indicates that lead in the sediments can be remobilized by bioaccumulation.

Based upon available information, fish accumulate very little lead in edible tissues; however, oysters and mussels are capable of accumulating high levels of lead. Decreasing pH increases the availability of divalent lead, the principal form accumulated by aquatic animals.

13.3.6 Biotransformation

As previously discussed, lead can be methylated by microorganisms present in lake sediments. The volatile compound resulting from biomethylation, i.e., tetramethyl lead, probably leaves the sediments and is either oxidized in the water column or enters the atmosphere. In any event, biomethylation represents a process which enables lead in the bed sediments to be reintroduced to the aqueous or atmospheric environment. In addition, biogenic ligands can play a significant role in complexing lead, especially in polluted waters, and will thereby have a significant impact on the aquatic fate of lead.

13.4 Data Summary

The dominant mechanism controlling the fate of lead appears to be sorption. Precipitation of $PbSO_4$, $PbCO_3$, and PbS and bioaccumulation may also be important. At low pH values, sorption and precipitation are not nearly as effective in removing lead from solution, so that lead is much more mobile in acidic waters than at higher pH values. In alkaline and circumneutral waters, removal of lead by sorption and precipitation may occur relatively quickly. Table 13-2 summarizes the fate data.

Table 13-2

Summary of Aquatic Fate of Lead

Environmental Process	Summary Statement	Confidence of Data
Photolysis[a]	Important in determining the form of lead entering the aquatic environment. Importance within natural waters is undeterminable.	Medium
Chemical Speciation[a]	Determines which solid species controls solubility in unpolluted waters. Over most of the normal pH range, $PbCO_3$ and $PbSO_4$ control solubility in aerobic conditions. PbS and Pb control solubility in anaerobic conditions. In polluted waters, organic complexation is most imortant.	Medium
Volatilization	Probably not important in most aquatic environments.	Medium
Sorption[a]	Adsorption to inorganic solids, organic materials, and hydrous iron and manganese oxides usually controls the mobility of lead.	High
Bioaccumulation[a]	Lead is bioaccumulated by aquatic organisms. Bioconcentration factors are within the range of 10^2 - 10^3.	High
Biotransformation[a]	Biomethylation in sediments can remobilize lead.	Medium

a. All of the noted environmental processes are important; however, their relative importance with respect to each other is uncertain for determining final fate.

13.5 Literature Cited

Angino, E.E., L.M. Magnuson, and T.C. Maugh. 1974. Mineralogy of suspended sediment and concentration of Fe, Mn, Ni, Zn, Cu, and Pb in water and Fe, Mn, and Pb in suspended load of selected Kansas streams. Water Resources Res. 10(6):1187-1191.

Chapman, W.H., H.L. Fisher, and M.W. Pratt. 1968. Concentration factors of chemical elements in edible aquatic organisms. Lawrence Radiation Laboratory, Livermore, Calif. UCRL-50564. 46p.

Cotton, F.A. and G. Wilkerson. 1972. Advanced inorganic chemistry. pp.309-338. Interscience Publishers, New York. 1145p.

Gaddle, R.R and H.A. Laitmen. 1973. Study of the sorption of lead by hydrous ferric oxide. Environ. Letters. 5(4):223-235.

Guy, R.D. and C.L. Chakrabarti. 1976. Studies of metal-organic interactions in model systems pertaining to natural waters. Can. J. Chem. 54:2600-2611.

Helz, G.R., R.J. Huggett, and J.M. Hill. 1975. Behavior of Mn, Fe, Cu, Zn, Cd, and Pb discharged from a wastewater treatment plant into an estuarine environment. Water Res. 9(7):631-636.

Hem, J.D. 1976a. Geochemical controls on lead concentrations in stream water and sediments. Geochim. Cosmochim. Acta. 40:599-609.

Hem, J.D. 1976b. Inorganic chemistry of lead in water. pp.5-11. in Lead in the environment. T.G. Lovering (ed.). U.S. Geological Survey Professional Paper 957, Washington, D.C. 90p.

Hirschler, A. and L.F. Gilbert. 1964. Nature of lead in automobile exhaust gas. Arch. Environ. Health. 8:297-313.

Hohl, H. and W. Stumm. 1976. Interaction of Pb^{2+} with hydrous γ-Al_2O_3. J. Colloid Interface Sci. 55(2):281-288.

Huang, C.P., H.A. Elliott, and R.M. Ashmead. 1977. Interfacial reactions and the fate of heavy metals in soil-water system. J. Water Pollut. Control Fed. 49(5):745-756.

Jackson, K.S. and G.B. Skippen. 1978. Geochemical dispersion of heavy metals via organic complexing: a laboratory study of copper, lead, zinc, and nickel behavior at a simulated sediment-water boundary. J. Geochem. Explor. 10:117-138.

Jenne, E.A. 1968. Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and waters: the significant role of hydrous Mn and Fe oxides. pp.337-387 in Trace inorganics in water. R.A. Baker (ed.). Advances in Chemistry Series 73. American Chemical Society, Washington, DC. 396p.

Kubota, J., E.L. Mills, and R.T. Oglesby. 1974. Pb, Cd, Zn, Cu, and Co in streams and waters of Cayuga Lake Basin. Environ. Sci. Technol. 8(3):243-248.

Lee, G.F. 1975. Role of hydrous metal oxides in the transport of heavy metals in the environment. pp.137-148. in Heavy metals in the aquatic environment. P.A. Krenkel (ed.). Pergamon Press, Oxford, England. 352p.

Long, D.T. and E.E. Angino. 1977. Chemical speciation of Cd, Cu, Pb, and Zn in mixed freshwater, seawater, and brine solutions. Geochim. Cosmochim. Acta. 41:1183-1191.

Lovering, T.G. (ed.). 1976. Lead in the environment. U.S. Geological Survey Professional Paper 957. Washington, D.C. 90p.

Lu, J.C.S. and K.Y. Chen. 1977. Migration of trace metals in interfaces of seawater and polluted surficial sediments. Environ. Sci. Technol. 11(2):174-182.

Lu, P.Y., R.L. Metcalf, R. Furman, R. Vogel, and J. Hassett. 1975. Model ecosystem studies of lead and cadmium and of urban sewage sludge containing these elements. J. Environ. Qual. 4(4):505-509.

Merlini, M. and A. Pozzi. 1977a. Lead and freshwater fishes: part 1 -lead accumulation and water pH. Environ. Pollut. 12:168-172.

Merlini, M. and A. Pozzi. 1977b. Lead and freshwater fishes: part 2 -ionic lead accumulation. Environ. Pollut. 13:119-126.

O'Shea, T.A. and K.H. Mancy. 1978. The effect of pH and hardness metal ions on the competitive interaction between trace metal ions and inorganic and organic complexing agents found in natural waters. Water Res. 12:703-711.

Patrick, F.M. and M. Loutit. 1976. Passage of metals in effluents, through bacteria to higher organisms. Water Res. 10:333-335.

Patterson, C., D. Settle, and B. Glover. 1976. Analysis of lead in polluted coastal seawater. Marine Chem. 4(4):305-319.

Patterson, J.W., H.E. Allen, and J.J. Scala. 1977. Carbonate precipitation for heavy metal pollutants. J. Water Pollut. Control Fed. 49(12):2397-2410.

Pierrand, J.M. 1969. Photochemical decomposition of lead solids from automobile exhaust. Environ. Sci. Technol. 3(1):48-51.

Pita, F.W. and N.J. Hyne. 1975. The depositional environment of zinc, lead, and cadmium in reservoir sediments. Water Res. 9:701-706.

Ramamoorthy, S. and D.J. Kushner. 1975. Heavy metal binding components of river water. J. Fish. Res. Bd. Can. 32:1755-1766.

Ramamoorthy, S. and B.R. Rust. 1978. Heavy metal exchange processes in sediment-water systems. Environ. Geol. 2(3):165-172.

Schell, W.R. and A. Nevissi. 1977. Heavy metals from waste disposal in Central Puget Sound. Environ. Sci. Techol. 11(9):887-893.

Valiela, I., M.D. Banes, and J.M. Teal. 1974. Response of salt marsh bivalves to enrichment with metal containing sewage sludge and retention of Pb, Zn and Cd by marsh sediments. Environ. Pollut. 7(2):149-157.

Weast, R.C. (ed.). 1977. CRC handbook of chemistry and physics. 58th edition. CRC Press, Cleveland, Ohio. 2398p.

Wong, P.T.S., Y.K. Chan, and P.L. Luxon. 1975. Methylation of lead in the environment. Nature. 253:263-264.

14. MERCURY

14.1 Statement of Probable Fate

Mercury's major removal mechanism from a natural water system is adsorption onto the surfaces of particulate phases and subsequent settling to the bed sediment. The overwhelming majority of any dissolved mercury is removed in this manner within a relatively short time, generally in the immediate vicinity of the source. Much smaller portions of the dissolved mercury are ingested by the aquatic biota or transported by current movement and dilution. Secondary transformations of mercury in the sediments can occur; these include precipitation as HgS and methylation by bacteria. Since the mercury itself is not destroyed, these inorganic and organic forms of mercury may then release ionic or metallic mercury into the water column as part of a recycling process. Resuspension of sediments by turbulence or the activity of benthic organisms can also release these compounds of mercury directly into the water column. The primary sink for mercury released to the environment is thus the sediments.

14.2 Identification - Geochemistry of Mercury

Mercury is able to exist in the natural environment in three oxidation states: as the native element itself, in the +1 (mercurous) state, and in the +2 (mercuric) state. The nature of the species which will occur in a given assemblage, or predominate in solution, depends upon the redox potential and pH of the environment.

It is difficult to estimate the abundance of mercury in the earth's crust. Fleischer (1970) reported that concentrations vary between 5 and 1000 ppb in common natural materials. Considerably higher concentrations have been measured in specific formations in mercury-rich regions of the world. Erickson (1960) estimated that about 10^{10} metric tons of rock are weathered each year. Using an average mercury content for rocks of 80 ppb, this would mean that about 800 metric tons of mercury are released from rock every year. Since typical soils do not contain higher concentrations of mercury than does its underlying rock, some of this weathered mercury must reach the aquatic environment.

Mercury has an atomic weight of 200.59, a melting point of -38.37°C, and a boiling point range of 356-358°C. At 20°C, its specific gravity is 13.546 and its vapor pressure is 0.0012 torr (Weast 1977). The solubility of metallic mercury in pure water has been determined by Sanemasa (1975) to be 19.2 µg/l and 81.3 µg/l at 5°C and 30°C, respectively.

Superimposed upon the inorganic movements of mercury in the aquatic environment is the biological mercury cycle. This cycle is summarized in Figure 14-1. These interconversions of mercury compounds maintain a dynamic system of reversible reactions which lead to a steady-state concentration of methyl mercury in sediments and waters. This process will be discussed in greater detail later in this report.

The chemical abstract number of mercury is 7439-97-6; its TSL number is B 100-9715.

14.3 Summary of Fate Data

14.3.1 Photolysis

Photolysis seems to be of significance to the chemical speciation of mercury in the atmosphere and perhaps in the aquatic environment. A photolytic breakdown of dimethyl mercury in the atmosphere to methyl mercury has been suggested (Williston 1968; Holm and Cox 1974; Johnson and Braman 1974) as well as photodecomposition of phenyl mercury compounds in both the atmosphere and natural waters (Zepp et al. 1973). Because of the limited amount of information on this subject, however, it is not clear what impact this process might have on the overall fate of mercury in the aquatic environment.

14.3.2 Chemical Speciation

Under the usual conditions of temperature and pressure that occur in the aquatic environment, mercury can be present in any one of three different oxidation states. The most reduced of these forms is the metal, which is a liquid at ordinary temperatures and which has a tendency to vaporize. The other two forms are the mercurous ion, Hg^{+1}, and the mercuric ion, Hg^{+2}. On the basis of commonly available thermodynamic data (cf. Hem 1970; Gavis and Ferguson 1972) it can be seen that mercury forms many solute species. Some of these complex ions have considerable aqueous solubility while others are quite insoluble. Mercury forms many stable organic complexes and is generally much more soluble in organic liquids than in water. Figure 14-2 shows the solid and liquid forms of mercury that will be stable in the normal range of environmental conditions. Figure 14-3 shows the aqueous mercury species under the same conditions as Figure 14-2.

Within a moderately oxidizing environment above pH 5, the predominant mercury species will be elemental mercury. The solubility of this material is nearly constant under all conditions in which the liquid metal is stable. Mildly reducing conditions, which are likely to occur in many sediments, can cause the mercury to be precipitated as the sulfide,

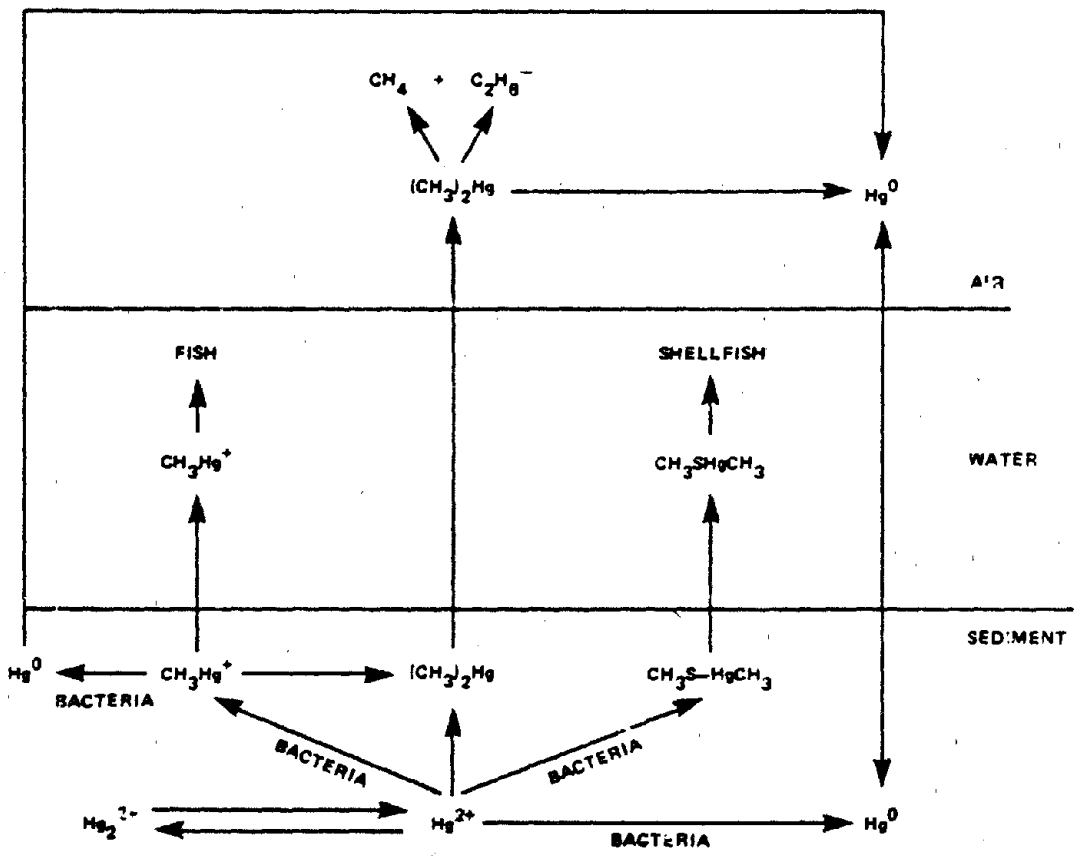


Figure 14-1 The biological mercury cycle in the aquatic environment. Modified from Wood, 1974.

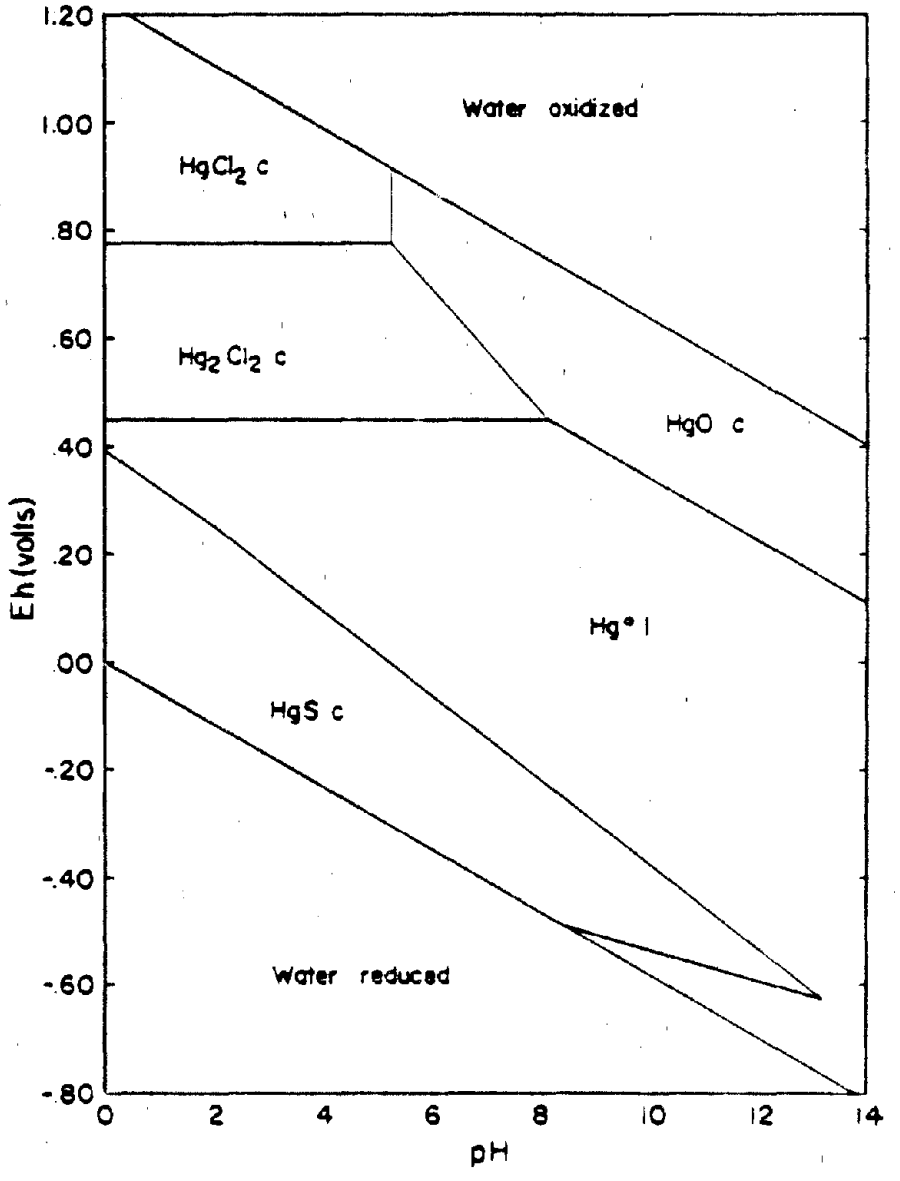


Figure 14-2 Fields of stability for solid (c) and liquid (l) mercury species at 25°C and atmospheric pressure. System includes water that contains 36 ppm chlorine and 96 ppm sulfur as SO_4^{-2} (Hem 1970).

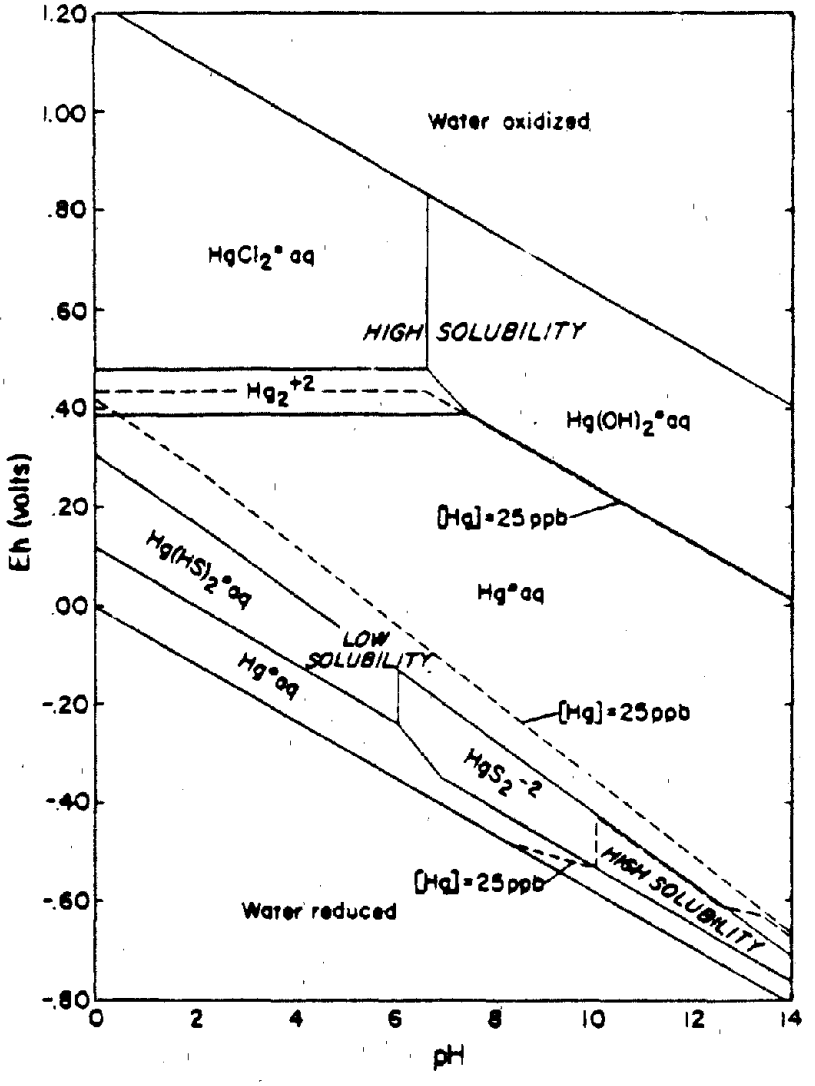


Figure 14-3 Fields of stability for aqueous mercury species at 25°C and 1 atmosphere pressure. System is the same as used for Figure 14-2. Hem (1970).

cinnabar, which has an extremely low aqueous solubility. In aquatic environments that are high in chloride, the solubility of mercury in oxygenated solutions may be greatly increased by the formation of charged mercuric chloride complexes (Garvis and Ferguson 1972).

Equally as important as the thermodynamic parameters which are depicted in Figures 14-2 and 14-3 are the processes which produce the organic complexes of mercury. Mercury exhibits an affinity for sulfhydryl groups (-SH) which are present in the many proteins that contain the amino acid cysteine as a component part. Mercury also forms complexes with organic amino groups, which are present in proteins, amino acids, and their derivatives.

Two types of alkylated mercury compounds are formed in the environment. In compounds with a single carbon-mercury bond, the compound thus formed acts as a substituted salt and is reasonably water-soluble. An example is methyl mercuric chloride (CH_3HgCl) which becomes CH_3Hg^+ ion and Cl^- ion in solution. The other type involves covalent attachment of two carbon atoms to the mercury. Although they are considered insoluble, dialkyl, covalent mercury compounds may appear in natural waters at trace levels. An example is dimethyl mercury (CH_3HgCH_3) which is volatile and is undissociated in solution. The chemistry of methyl mercury species and equilibria in aqueous solution have been discussed in detail by Burrows et al. (1974) and Rabenstein et al. (1975).

14.3.3 Volatilization

Metallic mercury, with its uniquely high vapor pressure relative to other metals, can enter the atmosphere from the aquatic environment as several different gaseous compounds. This factor makes volatilization important for the aquatic fate of mercury. The rate of vaporization of mercury and certain of its inorganic compounds decreases in the sequence $Hg > Hg_2Cl_2 > HgCl_2 > HgS > HgO$ according to the data of Koksay and Bradshaw (1969).

Presumably, the microbial methylation of mercury would enhance the evaporative loss of mercury. Although monomethyl mercury compounds are the principal product of biological methylation rather than the non-ionizable dimethyl mercury (Jensen and Jernelov 1969), a net increase in volatility should result. Because of limited quantitative data available on the subject of the volatilization of mercury compounds from natural waters, it is not clear what impact volatilization will have on the overall fate of mercury in the aquatic environment.

14.3.4 Sorption

Mercury shows a tenacious affinity for surfaces of many types. The problems of storing dilute aquatic mercury samples in glass vessels

have been well known for years. In natural samples, a major portion of the total mercury has been found associated with the particulates (Hinkle and Learned 1969). Studies on the addition of mercury to a variety of natural samples have led to the same conclusion. Carr and Wilkniss (1972) found that radioactive mercury, when added to stored samples, was rapidly apportioned onto the particulate phases with half-lives for adsorption of less than one to fifty hours. This experiment indicated that the adsorbed species are probably not methylated mercury compounds. The work of Kudo et al. (1977b) supports this contention by demonstrating that there is no significant isotopic exchange between $^{203}HgCl_2$ and CH_3HgCl or $CH_3{}^{203}HgCl$ and $HgCl_2$.

Loring (1975) has demonstrated that the concentrations of mercury in the sediments of the Gulf of St. Lawrence are highest immediately adjacent to the source rocks with concentrations decreasing as one proceeds seaward in Saguenay Fjord. The mercury is enriched, however, in the sediments relative to the source rocks. This distribution indicates a direct movement from the source through the aquatic environment to the sediments since physical transfer of source-rock to the sediment would not produce the observed enrichment.

Ramamoorthy and Rust (1976) studied mercury sorption onto the bed sediments of the Ottawa River in a laboratory study. By varying Hg^{2+} concentrations and pH at a constant temperature, they found that sorption rates were highest in organic-rich sands, and it appeared that sediment binding capacity was most closely related to organic content. They found that mercury sorption was little affected by pH. Desorption rates were low, e.g., less than 1 percent Hg was leached from the sediment after 70 hours agitation in distilled water. Several other investigators have reported similiar results with the sediments of other areas, e.g., Thomas (1972) with Lake Ontario, Pillay et al. (1972) with Lake Erie, Kudo et al. (1977a) on methyl mercury in the Ottawa River, and Creceluis et al. (1975) in Puget Sound. Moreover, the theoretical work of MacNaughton and James (1974), on adsorption of aqueous mercury complexes, indicated that the adsorption of inorganic mercury on the inorganic oxide components of sediments is likely to be very small.

Reimers and Krenkel (1974), in their study of mercury adsorption and desorption on sediments, reported that at a constant pH, the adsorption of inorganic mercury is affected by aquatic chloride concentration, with the percent loss in capacity depending upon the constituents of the sediment. The sedimentary materials studied exhibited a capacity to sorb methyl mercury that followed the order:

organics >> illite >> montmorillonite >> sand

They found, as well, that inorganic mercury is bound strongly enough by sediments to be transported by sedimentary mobilization.

In summary, it is evident from environmental studies and theoretical considerations, that mercury adsorption onto the sediments is probably the most important process for determining the fate of mercury in the aquatic environment.

14.3.5 Bioaccumulation

Due to the recent concern over the danger to human health from the eating of mercury-containing fish, the bioaccumulation of mercury has been well studied in the aquatic environment. Mercury is acquired by organisms through direct contact in air and/or water and through the food chain (Phillips and Russo 1978).

Bacteria common to most natural waters have been proven to be capable of converting many mercury compounds to methyl mercury (Jensen and Jernelov 1969; Bisogni and Lawrence 1975). Therefore, virtually any mercury compound entering the water may become a bioaccumulation hazard if the environmental conditions are favorable for biomethylation.

Ramamoorthy et al. (1977) have measured the uptake of mercury from water by both bacteria and sediments. Bacteria accumulated mercury much more rapidly than sediment, taking up nearly 20 times as much mercury as sediment after 72 hours. Loss of mercury from the system during the experiment was attributed to the bacterial conversion of divalent mercury to the volatile metallic mercury. This loss did not occur in sterilized control samples.

Kudo (1976) exposed guppies to water over a ^{203}Hg-enriched sediment bed and measured mercury uptake by the fish. Mercury uptake by the guppies was compensated within the system by increased mobilization of mercury from sediment into water. The half-life of mercury in the sediment under these conditions was estimated to be 12-20 years. Over one-half of the mercury present in the fish was organic, suggesting that conditions were such that mercury was being methylated. Kramer and Neidhart (1975) measured mercury uptake from water in guppies using inorganic mercury and methyl mercury. Methyl mercury was more readily accumulated and retained than inorganic mercury and the rates of uptake increased with exposure level. The accumulative half-life for methyl mercury was 70 days, a much lower value than that reported by other workers. These observations support the hypothesis that inorganic mercury is not the major source of mercury for bioaccumulation by fish in most natural enviroments.

Potter et al. (1975) reported on the mercury content of various tissues from fish and invertebrates collected from Lake Powell, Arizona.

Muscle contained the highest mercury level of any tissue for most species (e.g., largemouth bass and carp) while in trout, the vital organs all exceeded the muscular mercury levels. Apparently, modes of uptake, retention, and elimination vary among species. Factors which were believed to influence the observed levels of mercury in plants and animals at different trophic levels included age, surface area, metabolism, habitat, and activity.

In summary, methyl mercury is the form of mercury present in most fish tissue, and it is the most readily accumulated and retained form of mercury in aquatic biota. Methyl mercury is readily accumulated by fish both from their food and through the water. Although conflicting evidence exists regarding the relative importance of these two sources of mercury to fish, most reports suggest that both sources can be significant. Upon entering the biological system, methyl mercury is very difficult to eliminate. Most studies imply that the depurative half-life of methyl mercury in aquatic organisms is between one and three years (Phillips and Russo 1978). Bioconcentration factors for mercury are summarized in Table 14-1.

14.3.6 Biotransformation

Mercury, as an element, is not intrinsically altered by chemical reaction, but does take part in biologically mediated reactions which drastically alter its mobility and toxicity. Iverson et al. (1975) showed that certain bacteria are capable of transforming mercuric ion and phenylmercuric acetate to volatile elemental mercury, and Spangler et al. (1973) have described a process whereby methyl mercury is demethylated.

Bisogni and Lawrence (1975) described the influences of inorganic mercury concentration and speciation, pH, microbial activity, and redox potential on mercury methylation rates. In general, the more inorganic mercury present, the more methyl mercury will be produced. At a circumneutral pH, the primary product of mercury methylation is methyl mercury. Methylation can occur under both aerobic and anaerobic conditions, although more mercury methylation occurs when more bacteria are present. Therefore, highly organic sediments which favor bacterial growth have a higher methylation potential than inorganic sediments. Wood (1974) pointed out that all the mercury in natural waters could participate in a system of microbially catalyzed reactions and chemical equilibria to produce steady state concentrations of dimethyl mercury, methyl mercuric ion, metallic mercury, mercuric ion and mercurous ion.

Upon entering an aqueous system, virtually any mercurial compound may be microbially converted to methyl mercury. Conditions reported to enhance the methylation process include large amounts of available mercury, large numbers of bacteria, absence of strong complexing agents such as

Table 14-1

Bioconcentration Factors for Mercury

Marine Plants	1,000
Marine Invertebrates	100,000
Marine Fish	1,670
Freshwater Plants	1,000
Freshwater Invertebrates	100,000
Freshwater Fish	1,000

Concentration factors are based on the concentration of elements in the aquatic organism (expressed in ppm of wet weight) divided by the concentration of the element in water (expressed in ppm); from Chapman et al. 1968.

sulfide, circumneutral pH, high temperature, and a moderately aerobic environment. Demethylation processes also occur but apparently only when methyl mercury levels become excessive (Fagerstrom and Jernelov 1972).

The conversion, in aquatic environments, of inorganic mercury compounds to methyl mercury implies that recycling of mercury from sediment to water to air and back could be a rapid process. Bacteria can act not only as mediators of methylation, but can also preferentially accumulate large amounts of mercury. Although the sediment is probably the most important sink for mercury, methylation by bacteria could reduce the mercury content of overlying waters resulting in the mobilization of inorganic mercury from the sediments.

14.4 Data Summary

The environmental fate of mercury has been well reviewed in several papers (Gavis and Ferguson, 1972; Kothny 1973; Krenkel 1973, 1974; National Academy of Sciences 1978).

Mercury is strongly sorbed to inorganic and organic particulates. Deposition of mercury-laden sediments in reducing zones can result in precipitation of the sulfide. Biomethylation of mercury in the sediments can result in remobilization. Since dimethyl mercury has a low solubility in water and is a gas at room temperature, volatilization may occur. Mercury is strongly bioaccumulated. Table 14-2 summarizes the aquatic fate of mercury.

Table 14-2

Summary of Aquatic Fate of Mercury

Environmental Process	Summary Statement	Confidence of Data
Photolysis[a]	Important in the breakdown of airborne mercurials, might be important in some aquatic environments.	Medium
Chemical Speciation[a]	Controls volatility of metallic mercury by conversion to complexed species. In reducing sediments HgS will precipitate and may constitute a major chemical sink.	High
Volatilization[a]	Important to the movement of mercury compounds in and out of the aquatic environment.	High
Sorption[a]	Sorption processes result in the strong partitioning of mercury into suspended and bed sediments. Sorption is strongest into organic materials.	High
Bioaccumulation[a]	Bioaccumulation has been proven to occur via numerous mechanisms. Most are connected to methylated forms of mercury.	High
Biotransformation[a]	Mercury can be metabolized by bacteria to methyl and dimethyl forms which are quite mobile in the environment.	High

a. All of the noted environmental processes are important; however, their relative importance with respect to each other is uncertain for determining final fate.

14.5 Literature Cited

Bisogni, J.J. and A.W. Lawrence. 1975. Kinetics of mercury methylation in aerobic and anaerobic aquatic environments. Jour. Water Poll. Control Fed. 47(1):135-152.

Burrows, W.D., R.S. Reimers, and E.B. Shin. 1974. Chemistry of mercury in the environment. pp 251-264 in Mercury: environmental considerations, part II. P.A. Krenkel (ed) CRC Critical Reviews in Environmental Control 251-339p.

Carr, R.A. and P.E. Wilkniss. 1973. Mercury: short term storage of natural waters. Environ. Sci. Technol. 7:62-63.

Chapman, W.H., H.L. Fisher, and M.W. Pratt. 1968. Concentration factors of chemical elements in edible organisms. Lawrence Radiation Laboratory, Livermore, Calif. UCRL-50564. 46p.

Creceluis, E.A., M.H. Bothner, and R. Carpenter. 1975. Geochemistries of arsenic, antimony, mercury, and related elements in sediments of Puget Sound. Environ. Sci. Technol. 9(4):325-333.

Erickson, E. 1960. The yearly circulation of chloride and sulfur in nature. Tellus. 12:63-109.

Fagerstrom, T. and A. Jernelov. 1972. Some aspects of the quantitative ecology of mercury. Water Res. 6:1193-1202.

Fleischer, M. 1970. Summary of the literature in the inorganic geochemistry of mercury. pp.6-13 in Mercury in the environment. U.S. Geological Survey Professional Paper 713, Washington, D.C. 67p.

Gavis, J. and J.F. Ferguson. 1972. The cycling of mercury through the environment. Water Res. 6:989-1008.

Hem, J.D. 1970. Chemical behavior of mercury in aqueous media. pp. 19-24 in Mercury in the environment. U.S. Geological Survey Professional Paper 713, Washington, D.C. 67p.

Hinkle, M.E. and R.E. Learned. 1969. Determination of mercury in natural waters by collection on silver screens. pp.251-255. U.S. Geological Survey Professional Paper 650D, Washington, D.C. 299p.

Holm, H.W. and M.F. Cox. 1974. Mercury in aquatic systems: methylation, oxidation -reduction, and bioaccumulation. (EPA 660/3-74-021). U.S. Environmental Protection Agency, Washington, D.C. 38p.

Iverson, W.P., C. Huey, F.E. Brinckman, K.L. Jewett, and W. Blair. 1975. Biological and nonbiological transformations of mercury in aquatic systems pp.193-195 in Heavy metals in the aquatic environment, P.A. Krenkel (ed.) Pergamon Press, Oxford, England. 352p.

Jensen, S. and A. Jernelov. 1969. Biological methylation in aquatic organisms. Nature. 223:753-754.

Johnson, D.L. and R.S. Bramen. 1974. Distribution of atmospheric mercury near ground. Environ. Sci. Technol. 8(12):1003-1009.

Koksay, M. and P.M.D. Bradshaw. 1969. Secondary dispersion of mercury from cinnabar and stibnite deposits, West Turkey. Colorado School Mines Quart. 64(1):33-356.

Kothney, E.L. 1973. The three-phase equilibrium of mercury in nature. pp.48-80 in Trace Elements in the Environment. R.T. Gould (ed.) Advances in Chemistry Series No. 123, American Chemical Society. Washington, D.C. 245p.

Kramer, H.J. and B. Neidhart, 1975. The behavior of mercury in the system water-fish. Bull. Environ. Contam. Toxicol. 14(6):699-704.

Krenkel, P.A. (ed). 1973. Mercury: environmental considerations, part I. CRC Critical Reviews in Environmental Control. pp.303-373.

Krenkel, P.A. (ed). 1974. Mercury: environmental considerations, part II. CRC Critical Reviews in Environmental Control. pp.251-339.

Kudo, A. 1976. Mercury transfer from bed sediments to freshwater fish (guppies). J. Environ. Qual. 5(4):427-430.

Kudo, A., H. Akagi, D.C. Mortimer, and D.R. Miller. 1977a. Equilibrium concentrations of methylmercury in Ottawa River sediments. Nature. 270:419-420.

Kudo, A., A. Hirokatsu, D.C. Mortimer, and D.R. Miller. 1977b. Isotopic organic and inorganic mercury exchange in river water. Environ. Sci Technol. 11:907-908.

Loring, D.H. 1975. Mercury in the sediments of the Gulf of St. Lawrence. Can. J. Earth Sci. 12:1219-1237.

MacNaughton, M.G. and R.O. James. 1974. Adsorption of aqueous mercury(II) complexes at the oxide/water interface. J. Colloid Interface Sci 47(2):431-440.

National Academy of Sciences. 1978. An assessment of mercury in the environment. Washington, D.C. 185p.

Phillips, G.R and R.C. Russo. 1978. Metal bioaccumulation in fishes and aquatic invertebrates. U.S. Environmental Protection Agency, Environmental Reserach Laboratory, Duluth, Minn. (EPA 600/3-78-103). 116p.

Pillay, K.K.S., C.C. Thomas, Jr., J.A. Sondel, and C.M. Hyche. 1972. Mercury pollution of Lake Erie ecosphere. Environ. Res. 5:172-181.

Potter, L., D. Kidd, and D. Standiford. 1975. Mercury levels in Lake Powell, bioamplification of mercury in man-made desert reservoir. Environ. Sci. Technol. 9(1):41-46.

Rabenstein, D.C., C.A. Evans, M.C. Tourangeau, and M.T. Fairhurst. 1975. Methylmercury species and equilibria in aqueous solution. Anal. Chem. 47:338-341.

Ramamoorthy, S. and B.R. Rust. 1976. Mercury sorption and desorption characteristics of some Ottawa River sediments. Can. J. Earth Sci. 13:530-536.

Ramamoorthy, S., S. Springthorpe, and D.J. Kushner. 1977. Competition for mercury between river sediment and bacteria. Bull. Environ. Contam. Toxicol. 17(5):505-511.

Reimers, R.S. and P.A. Krenkel. 1974. Kinetics of mercury adsorption and desorption in sediments. Jour. Water Poll. Control Fed. 46(2):352-365.

Sanemasa, I. 1975. The solubility of elemental mercury vapor in water. Bull. Chem. Soc. Japan. 48:1795-1798.

Spangler, W.J., J.L. Spigarelli, J.M. Rose, and H.M. Miller. 1973. Methylmercury; bacterial degradation in lake sediments. Science. 1890:192-193.

Thomas, R.L. 1972. The distribution of mercury in the sediments of Lake Ontario. Can. J. Earth Sci. 9:636-651.

Weast, R.C. (ed). 1977. CRC Handbook of Chemistry and Physics. 58th Edition. CRC Press, Cleveland, Ohio. 2398p.

Williston, S.H. 1968. Mercury in the atmosphere. J. Geophysical Res. 73(22):7051-7055.

Wood, J.M. 1974. Biological cycles for toxic elements in the environment. Science. 183:1049-1052.

Zepp, R.G., N.L. Wolfe,. and J.A. Gordon. 1973. Photodecomposition of phenylmercury compounds in sunlight. Chemosphere. 3:93-99.

15. NICKEL

15.1 Statement of Probable Fate

Nickel appears to be a relatively mobile heavy metal. Although sorption and precipitation do not appear to be as effective as they are with many of the other heavy metals, sorption processes can scavenge nickel from solution. Nickel has an affinity for organic materials and hydrous iron and manganese oxides. The latter materials are probably the dominant control on the mobility of nickel in the aquatic environment.

Most of the common aqueous ligands form moderately soluble compounds with nickel. An exception is nickel sulfide, which can be formed in reducing environments and is quite insoluble. Under aerobic conditions, however, the hydroxide, carbonate, sulfate, and halide compounds are sufficiently soluble to allow toxic levels of nickel to persist in solution. Although nickel is bioaccumulated, the concentration ratios reported for most freshwater organisms indicate that partitioning into biota is not a dominant fate process.

15.2 Identification - Geochemistry of Nickel

Nickel is a naturally occurring element and is found in the earth's crust in average concentrations of 80 ppm (Weast 1977). Nickel is usually divalent in its compounds which are predominantly ionic in character. Nickel compounds with valences of 0, +1, +3, and +4 have been reported, but these are extremely rare and not important in a discussion of the chemistry of nickel in the aquatic environment. Nickel forms compounds with sulfate, chloride, nitrate, carbonate, oxide, hydroxide, and with organic ligands (Cotton and Wilkinson 1972).

Nickel is siderophilic and will alloy itself with metallic iron whenever such a phase is present. Nickel is only slightly miscible in iron and the two phases separate at low temperatures. The earth's core is thought to be a nickel-iron alloy (barysphere) with a Fe/Ni ratio of about 11:1. The weathering of nickel-rich bedrock gives rise to iron-, nickel-, and silica-rich solutions. Ionic nickel is very stable in aqueous solutions and is capable of migration over long distances. The high affinity of nickel for sulfur accounts for its occurrence in magmatic or metamorphic segregates of sulfide bodies. These sulfide segregates constitute the large nickel ore body at Sudbury, Ontario, which provides well over a third of the world's mining production of nickel (Corrich 1973). Nickel is a transition element, atomic number 28, atomic weight 58.71 (Weast 1977).

Nickel's CAS number is 007440020; its TSL number is QR 59500.

15.3 Summary of Fate Data

15.3.1 Photolysis

No evidence was found to suggest that the photochemistry of nickel compounds affects the aquatic fate of nickel.

15.3.2 Chemical Speciation

Nickel is almost always found in the divalent oxidation state in aquatic systems (Cotton and Wilkinson 1972). Under reducing conditions and in the presence of sulfur, the insoluble sulfide is formed. Under aerobic conditions and pH below 9, the compounds nickel forms with hydroxide, carbonate, sulfate, and naturally occurring organic ligands are sufficiently soluble to maintain aqueous Ni^{+2} concentrations above 10^{-6}M (60µg/l). Above pH 9, precipitation of the hydroxide or carbonate exhibits some control on nickel mobility.

Hydrolysis of aqueous nickel to the hydroxide, $Ni(OH)_2$, is significant only under basic conditions. Patterson et al. (1977) compared the precipitation behavior of nickel carbonate and nickel hydroxide in the context of treatment of nickel-bearing waste effluents. Although precipitation as the hydroxide was found to be the more efficient treatment, the lowest nickel concentration attained at pH values below 9 was 15 mg/l. This level is quite high with regard to its toxicity and indicates that precipitation is not an effective control on nickel under most conditions.

Furthermore, humic acids in natural waters alter the solubility and precipitation behavior of nickel. Rashid and Leonard (1973) exposed nickel carbonate to humic acid and found that complexation with humic acid solubilized much of the nickel. Approximately 200 mg of nickel was released per gram of humic acid added. Addition of humic acid did not solubilize nickel sulfide. When humic acid was added to solutions that contained nickel and some natural inorganic ligands (either sulfide, carbonate, or hydroxide), the quantity of nickel required to cause precipitation increased dramatically. Humic acids are ubiquitous in natural waters and may be expected to increase the solubility of nickel under natural conditions to the point that precipitation is probably not a significant fate.

15.3.3 Volatilization

No evidence was found to suggest that volatilization of nickel compounds occurs from the aquatic environment.

15.3.4 Sorption

Sorption of nickel by hydrous iron and manganese oxides and organic material probably exerts the major control on the mobility of

nickel in the aquatic environment. Nickel, however, is a highly mobile metal and is sorbed only to a small extent. Lee (1975) presented cogent evidence for the importance of hydrous iron and manganese oxides in controlling nickel concentrations in aquatic environments. When these oxides precipitate, nickel is attracted to the negative zeta potential they usually exhibit and can become incorporated into the crystal lattice structure of the dewatering oxides. Some analyses of bottom sediments have corroborated this hypothesis, showing a strong correlation between nickel concentration and iron and manganese concentrations (Angino et al. 1974; Steele and Wagner 1975).

Gibbs (1973) found that most of the nickel in the Amazon and Yukon River systems was associated with suspended particulates, organic material, or coprecipitated with hydrous iron and manganese oxides. In contrast to Gibbs' (1973) results, Perhac (1972, 1974a) found that almost all of the nickel transported by two Tennessee streams was in the dissolved form. The reason for this discrepancy is probably the fact that about 90% of the solids in the streams studied by Perhac were dissolved solids, so that there were very few suspended particles available for coprecipitation/sorption reactions. Suspended solids probably compose a greater fraction of the total solids in Gibb's study, providing a substrate for coprecipitation or sorption. Perhac's (1974b) analyses of bed sediments indicated that much of the sedimentary nickel was incorporated in the crystalline structures of carbonate minerals. Thus, isomorphous substitution of nickel for other cations in lattice sites may be another process affecting the distribution and mobility of nickel.

The partitioning of nickel into dissolved and particulate fractions is undoubtedly related to the abundance of suspended material, competition with organic material, and concentrations of iron and manganese. Hydrous iron and manganese oxides precipitate as a coating on suspended particles, and attract nickel and other metals.

Suspended organic matter may be a good adsorbent for nickel. Rashid (1974) used colloidal humic substances to adsorb nickel and found that of the nickel thus bound, only 26% could be extracted by ammonium acetate. Iron chloride added to the solution extracted 76%, showing that precipitating hydrous iron oxides probably attract nickel more strongly than organic matter. The importance of these competing processes is strongly affected by the relative abundance of sorbents (organic matter, hydrous metal oxides) in the water column and sediments. Although organic matter can adsorb nickel, Adams et al. (1975) reported that sewage treatment by primary digestion and activated sludge removed less than 45% of the nickel that was present. Organic material obviously abounds in such environments, and yet apparently little nickel is adsorbed.

Jackson and Skippen (1978) found, in a recent laboratory study, that organic acids increase the solubility of nickel in the presence of clay. Fulvic and humic acids were shown to be capable of remobilizing nickel from all solid phases, although the reaction appears to be kinetically hindered, especially at basic pH values.

Although data on the sorption of nickel in the aquatic environment are somewhat limited, a few general conclusions can be reached. In natural, unpolluted waters, for example, it would appear that sorption processes are at least moderately effective in limiting the mobility of nickel in the aquatic environment. In the more organic-rich, polluted waters, it would appear that little sorption, if any, of nickel takes place. In either case, the lack of other controls probably makes incorporation into bed sediments an important fate of nickel in surface waters. It would appear, however, that much of the nickel entering the aquatic environment will be transported to the oceans.

15.3.5 Bioaccumulation

Nickel is bioaccumulated by some aquatic organisms, but most concentration factors are less than 10^3. Tong (1974) showed that nickel does not bioaccumulate in lake trout, Salvelinus namaycush. Friedrich and Filice (1976) studied the accumulation of nickel by the mussel (Mytilkus edulis) in artificially prepared seawater under static conditions. No significant accumulation was noted after four weeks' exposure to 0.03 mg Ni/l, but significant uptake was noted at all concentrations exceeding 0.056 mg Ni/l; rates of nickel elimination were not measured.

In a study of the accumulation of iron, zinc, lead, copper, and nickel by algae collected near a zinc smelting plant, it was found that nickel exhibited the lowest concentration factor for all metals tested (Trollope and Evans 1976). Skaar et al. (1974) demonstrated that uptake of nickel by the diatom Phaesdactylum tricornutum is strongly dependent on metabolic state and is affected by the phosphate concentration in the water.

Wright (1976) observed nickel concentrations exceeding 7.0 µg Ni/g in muscle from marine fishes collected from the northeast coast of England, and Romeril and Davis (1976) reported that European eels (Anguilla anguilla) maintained in Treat River water averaged (dry basis) 21 µg Ni/g in muscle and 16 in liver.

In general, nickel is not accumulated in significant amounts by aquatic organisms. Concentration factors for organisms shown to accumulate nickel are given in Table 15-1.

Table 15-1

Bioconcentration Factors for Nickel

Taxon	Bioconcentration Factor[a]	Reference
Freshwater plants	100	Chapman et al. 1968
Freshwater invertebrates	100	Chapman et al. 1968
Freshwater fish	40	Chapman et al. 1968
Marine plants	250	Chapman et al. 1968
Seaweeds	550 - 2,000	Stumm and Morgan 1970
Algae	2,000 - 40,000	Stumm and Morgan 1970
Marine plankton	<20 - 8,000	Stumm and Morgan 1970
Marine sponges	420	Stumm and Morgan 1970
Marine invertebrates	259	Chapman et al. 1968
Marine fish	100	Chapman et al. 1968
Skipjack tuna	50	Stumm and Morgan 1970

a. Concentration factors are defined by the ratio of the concentration of the element in the organism in ppm (wet weight) divided by the concentration of the element in water (ppm).

15.3.6 Biotransformation

No data was found in the available literature to suggest that nickel is involved in any biological transformation in the aquatic environment.

15.4 Data Summary

The mobility of nickel in the aquatic environment is controlled largely by the capability of various sorbents to scavenge it from solution. Although data is limited, it appears that in pristine environments, hydrous oxides of iron and manganese control nickel's mobility via coprecipitation and sorption. In polluted environments, the more prevalent organic material will keep nickel soluble. In reducing environments, insoluble nickel sulfide may be formed. Although nickel is bioaccumulated, the concentration factors are such as to suggest that partitioning into the biota is not a dominant fate process. Nickel is one of the most mobile of the heavy metals in the aquatic environment. The aquatic fate of nickel is summarized in Table 15-2.

Table 15-2

Summary of Aquatic Fate of Nickel

Environmental Process	Summary Statement	Confidence of Data
Photolysis	Not an important process.	Medium
Chemical Speciation[a]	In aerobic environments below pH 9, soluble compounds are formed with hydroxide, carbonate, sulfate and organics. Above pH 9, precipitation of the hydroxide or carbonate will occur. In reducing environments, NiS will precipitate. Not a regulating factor in most waters.	Medium
Volatilization	Not an important process.	Medium
Sorption[a]	Nickel is the most mobile of the heavy metals. Coprecipitation with hydrous metal oxides, sorption into organic material, and ion exchange with crystalline minerals are the dominant factors which affect its mobility.	High
Bioaccumulation	Reported bioconcentration factors are on the order of 10^2-10^3. Not a dominant process.	Medium
Biotransformation	Not an important process.	Medium

a. All of the noted environmental processes are important; however, their relative importance with respect to each other is uncertain for determining final fate.

15.5 Literature Cited

Adams, C.E., Jr., W.W. Eckenfelder, Jr., and B.L. Goodman. 1975. The effects and removal of heavy metals in biological treatment. pp.277-292. in Heavy metals in the aquatic environment. P.A. Krenkel (ed.). Pengamon Press, Oxford, England. 352p.

Angino, E.E., L.M. Magnuson, and T.C. Waugh. 1974. Mineralogy of suspended sediment and concentration of Fe, Mn, Ni, Zn, Cu, and Pb in water and Fe, Mn, and Pb in suspended load of selected Kansas streams. Water Resources Res. 10(6):1187-1191.

Chapman, W.H., H.L. Fisher, and M.W. Pratt. 1968. Concentration factors of chemical elements in edible aquatic organisms. Lawrence Radiation Laboratory, Livermore, Calif. UCRL-50564. 46p.

Corrich, J.D. 1973. Nickel. pp.1-15. in 1973 Bureau of Mines Minerals Yearbook. U.S. Department of the Interior, Washington, D.C. 396p.

Cotton, F.A., and G. Wilkinson. 1972. Advanced inorganic chemistry. pp.890-903. Interscience Publishers, New York. 1145p.

Friedrich, A.R. and F.P. Filice. 1976. Uptake and accumulation of the nickel ion by Mytilus edulis. Bull. Environ. Contam. Toxicol. 16(6):750-8755.

Gibbs, R.J. 1973. Mechanisms of trace metals transport in rivers. Science. 180:71-73.

Jackson, K.S. and G.B. Skippen. 1978. Geochemical dispersion of heavy metals via organic complexing: a laboratory study of copper, lead, zinc, and nickel behavior at a simulated sediment - water boundary. J. Geochem. Explor. 10:117-138.

Lee, G.F. 1975. Role of hydrous metal oxides in the transport of heavy metals in the environment. pp.137-149. in Heavy metals in the aquatic environment. P.A. Krenkel (ed.). Pergamon Press, Oxford, England. 352p.

Patterson, J.W., H.E. Allen, and J.J. Scala. 1977. Carbonate precipitation for heavy metal pollutants. J. Water Pollut. Control Fed. 49(12):2397-2410.

Perhac, R.M. 1972. Distribution of Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn in dissolved and particulate solids from two streams in Tennessee. J. Hydrol. 15:177-186.

Perhac, R.M. 1974a. Water transport of heavy metals in solution and by different sizes of particulate solids. Univ. of Tenn. Water Resources Res. Ctr. Project 23. Knoxville, Tenn. 41p.

Perhac, R.M. 1974b. Heavy metal distributions in bottom sediments and water in the Tennessee River - Loudan Lake reservoir system. Univ. of Tenn. Water Resources Res. Ctr. Project 40. Knoxville, Tenn. 18p.

Rashid, M.A., and J.D. Leonard. 1973. Modifications in the solubility and precipitation behavior of various metals as a result of their interaction with sedimentary humic acid. Chem. Geol. 11:89-97.

Rashid, M.A. 1974. Adsorption of metals on sedimentary and peat humic substances. Chem. Geol. 13:115-123.

Romeril, M.G. and M.H. Davis. 1976. Trace metal levels in eels grown in power station cooling water. Aquaculture. 8:139-140.

Skaar, H., B. Rystal, and A. Jensen. 1974. The uptake of ^{63}Ni by the diatom Phoeodactylum ricornutum. Physiol. Plantum. 32:352-358.

Steele, K.F. and G.H. Wagner. 1975. Trace metal relationships in bottom sediments of a freshwater stream - The Buffalo River, Arkansas. J. Sed. Pet. 45(1):310-319.

Stumm, W., and J.J. Morgan. 1970. Aquatic chemistry. p.289. Wiley Interscience, New York. 583p.

Tong, S.S.C. 1974. Trace metals in Lake Cayuga lake trout (Salvelinas namayaush) in relation to age. J. Fish. Res. Bd. Can. 31:1974-1976.

Trollope, D.R. and B. Evans. 1976. Concentrations of copper, iron, lead, nickel and zinc in freshwater algal blooms. Environ. Pollut. 11:109-116.

Weast, R.C. (ed.). 1977. Handbook of chemistry and physics, 58th edition. CRC Press, Cleveland, Ohio. 2398p.

Wright, D.A. 1976. Heavy metals in animals from the northeast coast. Mar. Pollut. Bull. 7(2):36-38.

16. SELENIUM

16.1 Statement of Probable Fate

In aerobic waters, selenium is present in the selenite (H_2SeO_3, $HSeO_3^-$, SeO_3^{-2}) or selenate (H_2SeO_4, $HSeO_4^-$, SeO_4^{-2}) oxidation state of 4+ or 6+. These chemical species are very soluble, and most of the selenium discharged into the aquatic environment is probably transported in these forms to the oceans. Under reducing conditions, selenium can form metal selenides either by direct reaction with metals or through substitution for sulfur in metal sulfides. Most of the metal selenides, however, have a very low solubility in water.

Selenium has a sorptive affinity for hydrous metal oxides, clays and organic materials. Sorption by bed sediments or suspended solids can result in enrichment of selenium concentrations in the bed sediments. Sorption or precipitation with hydrous iron oxides is probably the major control on mobility of selenium in aerobic waters.

Selenium can be methylated by a variety of organisms, including benthic microflora. In a reducing environment, hydrogen selenide (H_2Se) may be formed. Both the methylated forms and H_2Se are volatile and may escape to the atmosphere. Formation of volatile selenium compounds in the sediments can remobilize sorbed selenium.

16.2 Identification - Geochemistry of Selenium

Selenium is able to exist in the natural environment in four oxidation states; the elemental form, the +6 state (selenate oxyanion), the +4 state (selenite oxyanion) and the -2 state (selenide ion). The nature of the species which will occur in a given assemblage or predominate in solution depends upon the redox potential and pH of the environment. This will be discussed in greater detail later in this report under chemical speciation.

Selenium is considered to be a non-metal, and it is a member of the Group VI elements. Selenium occurs in igneous rocks in concentrations of approximately 0.05 ppm; in shale, 0.6 ppm; in sandstone, 0.05 ppm; and in limestone, 0.08 ppm (National Research Council 1976). Most of the selenium found in natural waters results from the weathering of seleniferous rock; anthropogenic discharges of selenium generally appear to be in the same ranges as those encountered in seleniferous regions. Areas of the U.S. with soil and rocks that contain high levels of selenium are the Rocky Mountain states and the mid-western tier states (Rosenfeld and Beath 1964).

Geochemically, selenium resembles sulfur. Sulfide or elemental sulfur deposits very often contain significant amounts of selenium. Metal sulfides have been found to contain selenium occasionally at levels of over 20 percent (Davidson 1960). Jarasite and barite, two sulfate minerals, have also been found to contain selenium, but at relatively low levels. Crude sulfur often contains selenium at well over 1 percent. Deposits of sulfur-containing minerals are often geochemically secondary in nature, and when selenium occurs in them, it has probably been leached from some other material and redeposited.

Selenium probably occurs as a free element or, more likely, as a metal selenide, in unweathered rocks. It is apparently readily oxidized during the weathering of crustal materials. In areas of acidic soils, selenium is probably present as the selenite anion which is firmly bound in iron oxide colloids; while in alkaline soils, it should oxidize further to the very soluble selenate anion. Selenium, atomic number 34, atomic weight 78.96, has an elemental melting point of 217°C and a boiling point of 684.9°C (Weast 1977).

The CAS number of selenium is 7782-49-2; its TSL number is B562-1046.

16.3 Summary of Fate Data

16.3.1 Photolysis

Although the photoconductive and photovoltaic properties of selenium are of prime importance in the commercial applications of selenium, no data were found to suggest that photolysis reactions play an important role in determining the aquatic fate of the selenium present in the aquatic environment.

16.3.2 Chemical Speciation

As previously noted, selenium is stable in four valence states: -2, 0, +4, and +6. The positive oxidation states are present in oxyanions and organo-selenium compounds, the bond types of which exhibit a covalent character (Cotton and Wilkinson 1972). The inorganic forms govern the physical chemistry of selenium in solution. Coleman and Delevaux (1957) calculated the stability of a selenium-selenite-selenate system (total Se was 10^{-6}M which is equivalent to 80 ug/l) under various Eh-pH conditions (Figure 16-1). As is evident from the stability diagram, elemental selenium is stable in a wide range of redox and pH values, being favored by low pH and reducing conditions. In aerobic conditions, selenium is in the form of the soluble $HSeO_3^-$, SeO_3^{-2}, and SeO_4^{-2} anions.

The major features of selenium chemistry that affect its movement, toxicity, and deficiency in the environment are associated with changes in

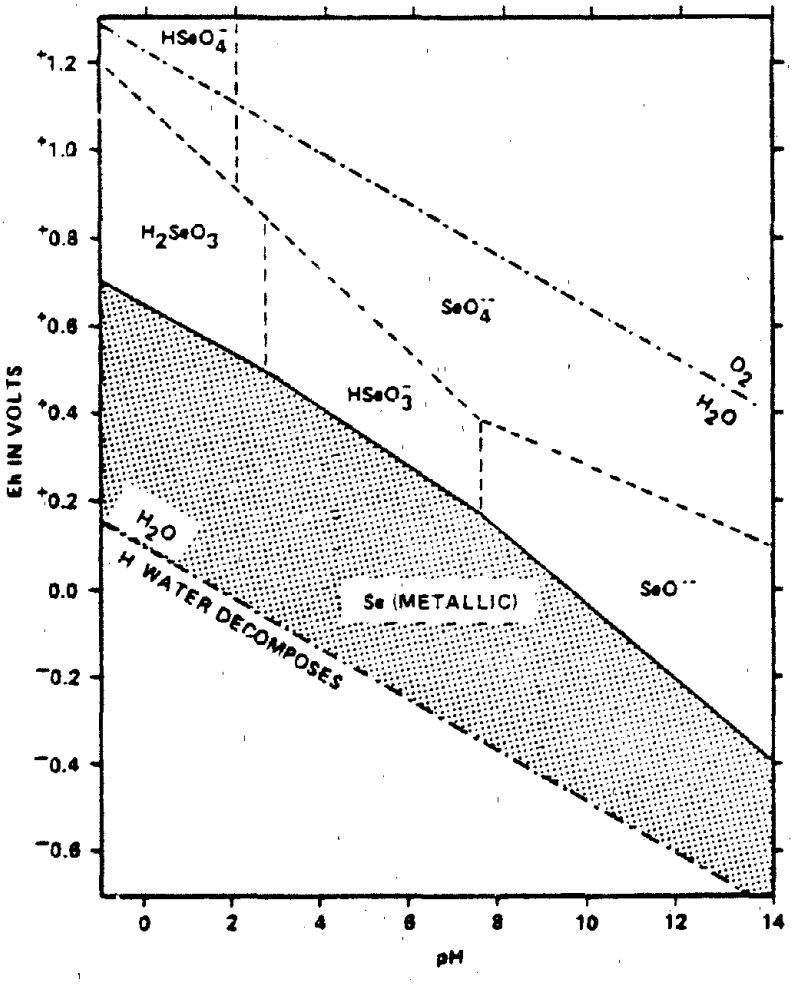


Figure 16-1 Stability Field of Selenium, (Temperature 25°C, pressure 1 atm, Concentration of Se 10^{-6}M). From Coleman and Delevaux (1957).

its oxidation state and the resulting difference in chemical properties. Therefore, during the following discussion, each oxidation state will be discussed in turn.

Properties of selenate selenium (+6 oxidation state). Selenic acid (H_2SeO_4) is a strong acid; its salts exhibit similar solubilities as the sulfates of the same metals (Rosenfeld and Beath 1964). Soluble selenates would be expected in alkaline environments and even though one would expect selenate to be converted to selenite or elemental selenium in acidic environments, this conversion appears to be kinetically inhibited (Lakin 1973). Because of its stability at alkaline pH, its solubility and its ready availability to plants, selenate appears to be the most dangerous form of selenium as far as potential environmental pollution is concerned.

Properties of selenite selenium (+4 oxidation state). Selenious acid (H_2SeO_3) is a weak acid, and any dissolved selenite would be present predominantly as the biselenite ion in water between pH 3.5 and 9.0 (Coleman and Delevaux 1957). Most selenite salts are less soluble than the corresponding selenates (National Research Council 1976). Of special relevance, with respect to the aquatic environment, is the very low solubility of ferric selenites (Geering et al. 1968). Another characteristic of selenite (of importance to environmental cycling of selenium) is the property of selenite to rapidly become reduced to elemental selenium under acidic conditions by mild reducing agents, such as ascorbic acid or SO_2 (Rosenfeld and Beath 1964). The probability that selenite will either form insoluble compounds, adsorbates with ferric oxides, or be reduced to insoluble elemental selenium minimizes the possibility for its transport in the aquatic environment.

Properties of elemental selenium (0 oxidation state). Various allotropic forms of elemental selenium are reviewed and their solubility in various reagents is tabulated in Rosenfeld and Beath (1964). The electronic and photoelectric properties of elemental selenium are responsible for many industrial uses of the element. The extreme insolubility of elemental selenium in aqueous systems is of primary importance in any discussion of the fate of selenium in the aquatic environment. Insoluble elemental selenium appears to be a major sink for selenium that can be considered to be inert in the aquatic environment and is quite important for determining the overall fate of the element.

Properties of selenide selenium (-2 oxidation state). Hydrogen selenide is a fairly strong acid, and it is highly toxic. This compound rapidly decomposes, however, to form elemental selenium, and it is thus of minor importance to the overall fate of selenium in the aquatic environment.

Organic chemistry of selenium. Important features of the organic chemistry of selenium were reviewed in the proceedings of a symposium edited by Klayman and Gunther (1973). As far as the aquatic environment is concerned, the important feature of the organic chemistry of selenium is that essentially all of the relevant compounds contain selenium in the -2 oxidation state. These compounds will decompose in the environment to form elemental selenium which will be insoluble and relatively inert to further chemical reaction.

16.3.3 Volatilization

Methylation of selenium occurs in mammals, plants, and microbes (Stadtman 1974). The selenium compounds thus produced are volatile and may escape to the atmosphere. Quantitative data, however, are lacking on this process in the aquatic environment.

Of the studies performed on selenium methylation, the one most applicable to aquatic fate was reported by Chau et al. (1976) who demonstrated that microbes present in lake sediments in the Sudbury, Ontario region could methylate organic and inorganic selenium compounds including sodium selenite and sodium selenate. The ability of aquatic microflora to produce gaseous dimethyl selenide or dimethyl diselenide from additions of 5 mg/l sodium selenite or sodium selenate was observed in 11 of 12 sediment samples. It is noteworthy that 4 of the 12 sediment samples evolved methylated selenides even without added selenium (sediment concentrations of selenium for these four samples ranged from 0.48 µg/g to 20.48 µg/gm). Calculations from the data presented by Chau et al. (1976) show that for the four cultures in which volatile organic selenium was produced from selenium in the sediments, the highest ratio of volatilized selenium to initially sedimented selenium was 1.6×10^{-3}. The duration of the experiment was one week. Clearly, biomethylation with subsequent volatilization may be an important fate process for selenium.

Volatile selenium compounds can also be formed by inorganic means. For example, volatile H_2Se can be formed under reducing conditions; however, because of the lack of quantitative data, the importance of this latter process for the overall aquatic fate of selenium is difficult to determine.

16.3.4 Sorption

Selenium is adsorbed by iron and manganese hydroxides, organic matter, and iron sulfides (Rosenfeld and Beath 1964, Kharkar et al. 1967). Kharkar et al. (1967) used a 1 µg/l solution of selenium that contained radioactive ^{75}Se to study the sorption of selenium by various materials. The hydrous iron and manganese oxides have the greatest affinity for selenium on a mass basis, but these materials usually comprise a smaller

proportion of the suspended solids than do the clays. Thus, most of the selenium in aquatic systems is probably transported as the dissolved species. Subsequent to determining the adsorption of selenium by various sorbents in distilled water, Kharkar et al. (1967) tested the amount desorbed on contact with sea water. Freshly precipitated ferric hydroxide released the smallest percentage, indicating that selenium is probably co-precipitated and incorporated into the structure of the ferric hydroxide. Selenium, thus bound, would be less likely to be desorbed. Based on the composition of the suspended solids load of typical rivers and the sorption of common materials normally comprising the solids load, Kharkar et al. (1967) estimated that selenium is supplied to the oceans predominately as dissolved species with desorption from solids making up only about 10% of the total.

Although no other systematic study of selenium sorption was found in the reviewed literature, a recent study by Frost and Griffin (1977) on the effect of pH on adsorption of selenium by clay minerals from a landfill leachate may have aquatic relevance. They found a pronounced effect of pH on the amount of selenium adsorbed by clay minerals. This strong pH dependency of adsorption results from the effect of pH on the distribution of selenium species present in solution and the inactivation of anion adsorption sites on clay minerals. Their results indicate that selenium would be quite mobile in clays, especially under alkaline conditions. It appears, however, that only in areas of high hydrous iron oxide concentrations, will selenium be sorbed into the bed sediments.

16.3.5 Bioaccumulation

Selenium is bioaccumulated by a number of aquatic organisms (Chau and Riley 1965; Fowler and Benayoun 1976b; Sandholm et al. 1973), and in some instances, it is strongly correlated with the concentration of mercury and other heavy metals in the organism (Koeman et al. 1973; MacKay et al. 1975). The concentration factors for aquatic organisms have been summarized in Table 16-1. Very little quantitative data are available on the bioaccumulation and excretion kinetics of selenium in aquatic biota, and, consequently, very little is known about the parameters that control the biological cycling of selenium in the aquatic environment.

Sandholm et al. (1973) studied selenium uptake in a laboratory food-chain consisting of water, phytoplankton, zooplankton and fish; both selenite and selenomethionine were used. In these experiments, food was determined to be the most important source of selenium to fish, and very little selenium accumulated from the water. In a saltwater study, Fowler and Benayoun (1976a) measured selenium uptake in a marine shrimp (Lysinata seticandata) exposed to ^{75}Se in food and water and in a mussel (Mytilus galloprovincialis) exposed to ^{75}Se in water. Shrimp exoskeleton contained 60 to 90 percent of the selenium accumulated when selenium was taken up via food. Only 10 percent of the selenium present in the exoskeleton

Table 16-1

Bioconcentration Factors for Selenium

Taxon	Bioconcentration Factor[a]	Reference
Freshwater Plants	800	Chapman et al. 1968
Freshwater Invertebrates	400	Chapman et al. 1968
Freshwater Fish	400	Chapman et al. 1968
Marine Plants	800	Chapman et al. 1968
Marine Invertebrates	400	Chapman et al. 1968
Marine Fish	400	Chapman et al. 1968

a. Bioaccumulation factors are the ratio derived from the concentration of the element in the aquatic organism (in ppm wet weight) divided by the concentration of the element in water (in ppm).

was lost during molting. Mussels accumulated the highest concentration of selenium in viscera. Fowler and Benayoun (1976c) found similar results with euphacids (Meganyctiphanes norvegica). Dietary selenium was retained at an efficiency of 66 percent. The biological half-life of selenium was 37 days, and whole body concentration factors were estimated at 11,500 to 7,500 for this species.

Selenium has often been described as the "Dr. Jekyll and Mr. Hyde" element because of living organisms' need for selenium at low concentrations and selenium's extreme toxicity at high concentrations (Stadtman 1974). It is also noteworthy that selenium in the diet is known to exert a protective influence against mercury poisoning (Ganther et al. 1972). Kim et al. (1977) found that creek chubs (Semotilus atromaculatus), immersed in water containing 3.0 mg Se/l for 48 hours, were less susceptible to mercuric chloride in water than untreated individuals. Furthermore, at mercury concentrations below 0.07 mg Hg/l, selenium treatment increased mercury accumulation, but at mercury levels above 0.10 mg Hg/l, selenium inhibited mercury accumulation. No speculation was offered on the mechanism of this interaction. Koeman et al. (1973) showed that mercury and selenium are present in the livers of marine mammals in a 1:1 molar ratio whereas marine fishes usually contain upwards of 40 times more selenium than mercury. This result suggests that selenium and mercury may occur together in marine mammals, perhaps resulting in some degree of protection against mercury.

The small amount of available data suggest that while dietary selenium is the most important source of selenium to many marine and freshwater organisms, little biomagnification takes place. In fact, in some instances, the accumulation of selenium by organisms may be beneficial due to the protective action which selenium provides against mercury. Because of selenium's high toxicity, however, the relationship between selenium toxicity to aquatic organisms and selenium accumulation is uncertain.

16.3.6 Biotransformation

The biochemistry of selenium compounds has been well studied in terrestrial plants and animals (Stadtman 1974; National Research Council 1976). Such studies, however, have not been been carried out in the aquatic environment. Selenium biotransformations have been studied in terrestrial environments because of the agricultural problems encountered in the high selenium soils of the Rocky Mountain states. Selenite and selenate are both taken up by plants and, within the plant, these forms of selenium are reduced to the -2 oxidation state. The Se^{-2} ion is then incorporated into soluble amino acids and/or protein-bound amino acids. This reduction of selenium, especially the selenates, within the plant may not be quantitative. Monogastric animals may reduce selenate and selenite, but they apparently do not incorporate the reduced selenium into amino acids. The

"selenocrisulfides," formed by the reaction of selenite with sulfhydryl groups of amino acids, peptides, and proteins, are a probable first product of the reduction of physiologic doses of selenite in monogastric animals (Ganther 1971). Major excretory products of selenium metabolism in animals are trimethyl selenonium ion in the urine and elemental selenium or metal selenides in the feces.

Some of the chemical changes possibly involved in the movement of selenium from soils through plants and animals are diagramed in Figure 16-2. When the metabolic pathways of selenium in plants and animals are considered along with the reactions of selenium in soils, it appears that the conversion of the element to inert and insoluble forms may occur in aquatic systems. It should be kept in mind that although extrapolation of biochemical mechanisms from the terrestrial to the aquatic environment might be valid, only further study can truly determine the biotransformations of selenium compounds in the aquatic environment. Nonetheless, production of hydrogen selenide or biomethylation by sedimentary mircoflora could remobilize the selenium and result in significant recycling.

16.4 Data Summary

Most of the selenium introduced into the aquatic environment is probably transported in solution to the oceans. Sorption/coprecipitation reactions with hydrous iron and manganese oxides, and to a lesser extent, clays and organic materials, control the mobility of selenium in oxidizing conditions. In reducing conditions, insoluble metal selenides can form, thereby decreasing mobility, or H_2Se can form, increasing mobility. Biologically mediated methylation of selenium results in production of volatile compounds, another mode by which sediment-bound selenium can be remobilized. Table 16-2 summarizes the aquatic fate described above.

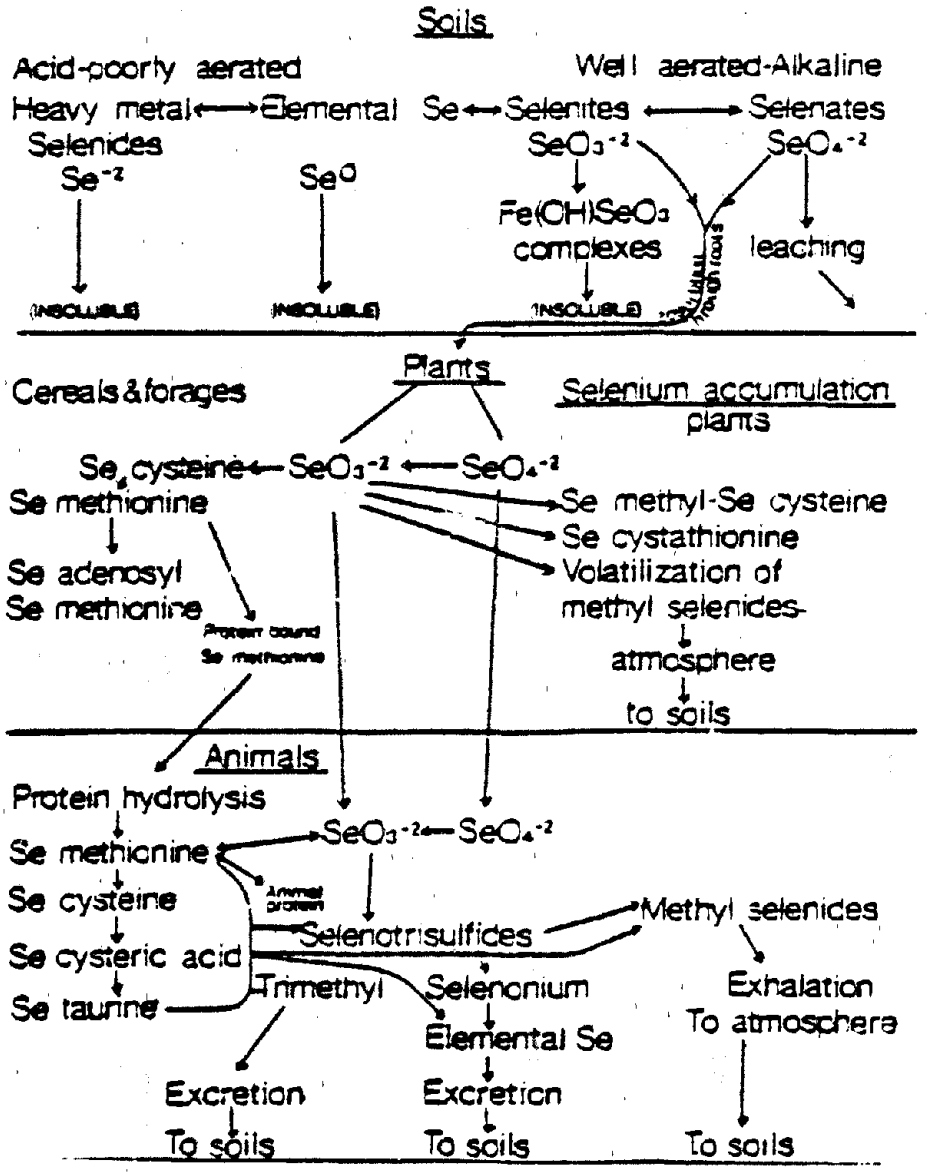


Figure 16-2 The cycling of selenium in the terrestrial biologic system. Modified from National Research Council (1976).

Table 16-2

Summary of Aquatic Fate of Selenium

Environmental Process	Summary Statement	Confidence of Data
Photolysis	Not an important process.	Low
Chemical Speciation[a]	Controls solubility. Under anaerobic conditions and/or low pH, insoluble elemental selenium is formed. Under other conditions, soluble complexes are formed.	Medium
Volatilization[a]	May occur via biomethylation or formation of H_2Se.	Medium
Sorption[a]	Hydrous metal oxides sorb selenium strongly. Clays and organic materials have a lesser affinity.	Medium
Bioaccumulation[a]	Concentration ratios depend on chemical form in soils and organism.	Medium
Biotransformation[a]	Metabolism may result in methylation with subsequent volatilization.	Medium

a. All of the noted environmental processes are important; however, their relative importance with respect to each other is uncertain for determining final fate.

16.5 Literature Cited

Chapman, W.H., H.L. Fisher, and M.W. Pratt. 1968. Concentration factors of chemical elements in edible aquatic organisms. Lawrence Radiation Laboratory, Livermore, Calif. 46p.

Chau, Y.K. and J.P. Riley. 1965. The determination of selenium in sea water, silicates, and marine organisms. Anal. Chem. Acta 33:36-49.

Chau, Y.K., P.T.S. Wong, B.A. Silverberg, P.L. Luxon, and C.A. Bengert. 1976. Methylation of selenium in the aquatic environment. Science 192:1130-1131.

Coleman, R.A. and M. Delevaux. 1957. Occurrence of selenium in sulfides from some sedimentary rocks of Western United States. Econ. Geol. 52(5):499-527.

Cotton, F.A. and G. Wilkinson. 1972. Advanced inorganic chemistry. pp.519-558. Interscience Publishers, Inc. New York. 1145p.

Davidson, D.F. 1960. Selenium in some epithermal deposits of antimony, mercury, silver, and gold. U.S. Geological Survey Bull. 1112-A. Washington, D.C. 15p.

Fowler, S.W. and A. Benayoun. 1976a. Accumulation and distribution of selenium in mussel and shrimp tissues. Bull. Environ. Contam. Toxicol. 16(3):339-346.

Fowler, S.W. and A. Benayoun. 1976b. Influence of environmental factors on selenium flux in two marine invertebrates. Marine Biol. 37:59-68.

Fowler, S.W. and A. Benayoun. 1976c. Selenium kinetics in marine zooplankton. Mar. Sci. Commun. 2(1):43-67.

Frost, R.R. and R.A. Griffin. 1977. Effect of pH on adsorption of arsenic and selenium from landfill leachate by clay minerals. Soil Sci. Soc. Amer. Journ. 41:53-57.

Ganther, H.E. 1971. Selenium: the biological effects of a highly active trace substance. pp.211-221. in Trace substances in environmental health. Vol. IV. D.D. Hemphill (ed.). Univ. of Missouri Press., Columbia, Missouri. 547p.

Ganther, H.E., C. Goudie, M.L. Sunde, M.J. Kopecky, P. Wagner, S-H. Oh, and W.G. Hoekstra. 1972. Selenium: relation to decreased toxicity of methylmercury added to diets containing tuna. Science 175:1122-1124.

Geering, H.R., E.E. Cary, L.H.P. Jones, and W.H. Allaway. 1968. Solubility and redox criteria for the possible forms of selenium in soils. Soil Sci. Soc. Amer. Proc. 32:35-40.

Kharkar, D.P., K.K. Tarekian, and K.K. Bentine. 1967. Stream supply of dissolved silver, molybdenum, antimony, selenium, chromium, cobalt, rubidium and cesium to the oceans. Geochim. Cosmochim. Acta. 32(3):285-298.

Kim, J.H., E. Birks, and J.F. Heisinger. 1977. Protective action of selenium against mercury in northern creek chubs. Bull. Environ. Contam. Toxicol. 17:132-136.

Klayman, D.L. and W.H.H. Gunther. (eds.). 1973. Organic selenium compounds: their chemistry and biology. Wiley-Interscience Publishers, New York. 1188p.

Koeman, J.H., W.H.M. Peeters, C.H.M. Koudstaad-Hol, P.S. Tjioe and J.J.M. DeGoeij. 1973. Mercury-selenium correlations in marine mammals. Nature 245:385-386.

Lakin, H.W. 1973. Selenium in our environment. pp.96-111. in Trace elements in the environment. E.L. Kothny (ed.). Advances in Chemistry Series 123. American Chemical Society, Washington, D.C. 245 p.

MacKay, N.J., M.N. Kazacos, R.J. Williams, and M.I. Leedow. 1975. Selenium and heavy metals in black marlin. Mar. Pollut. Bull. 6:57-61.

National Research Council. 1976. Selenium. pp.1-42, 59-72. National Academy of Sciences. NTIS Springfield, Va. PB-251 318. 310 p.

Rosenfeld, I. and O.A. Beath. 1964. Selenium: geobotany, biochemistry, toxicity and nutrition. pp.9-61. Academic Press, New York. 411p.

Sandholm, M., H.E. Oksanen, and L. Pesonen. 1973. Uptake of selenium by aquatic organisms. Limnol. Oceanogr. 18:496-499.

Stadtman, T.C. 1974. Selenium biochemistry. Science 183:915-922.

Weast, R.C. ed. 1977. CRC handbook of chemistry and physics. 58th ed. CRC Press, Cleveland, Ohio. 2398 p.

17. SILVER

17.1 Statement of Probable Fate

Sorption and precipitation processes are effective in reducing the concentration of dissolved silver and result in higher concentrations in the bed sediments than in the overlying waters. Sorption by manganese dioxide and precipitation with halides are probably the dominant controls on the mobility of silver in the aquatic environment. Some silver is also bioaccumulated, and the remainder is transported in solution to the oceans.

17.2 Identification - Geochemistry of Silver

Silver is a rare element occurring in concentrations of about 0.1 ppm in the earth's crust (Weast 1977). Silver is toxic to aquatic bacteria, invertebrates and fish. Its toxicity ranks second only to mercury among the heavy metals (Freeman 1977).

Silver occurs primarily in the form of the sulfide (argentite Ag_2S) or intimately associated with other metal sulfides, especially those of lead and copper. Other common silver minerals include cerargyrite (AgCl), proustite ($3AgS \cdot As_2S_3$), pyragyrite ($3Ag_2S \cdot Sb_2S_3$), stephanite ($5Ag_2S \cdot Sb_2S_3$) and native metallic silver. Most lead and copper ores are argentiferous though there are important exceptions. Recovery of silver and gold from these ores constitutes an important part of their metallurgical treatment.

Silver is also commonly associated in nature with gold. Not only does gold occur with silver in copper and lead ores, but native metallic gold usually contains silver. Gold and silver are mutually soluble in each other in all proportions in the metallic state.

Silver is usually found in extremely low concentrations in the aquatic environment due both to its low crustal abundance and the effectiveness of controls on its mobility in water. In a study of ten U.S. rivers, Kharkar et al. (1968) detected silver in concentrations ranging from 0.092 to 0.55 µg/l. Hem (1970) cites studies of public drinking water supplies and river waters which report median concentrations of 0.23 and 0.09 µg/l, respectively. The geochemistry of silver has been extensively reviewed by Boyle (1968).

Silver is a transition metal, atomic number 47, atomic weight 107.9 (Weast 1977). Other than in complex ions, silver's only stable cationic state is Ag^+ (Cotton and Wilkinson 1972).

The CAS number of silver is 7440-22-4, and its TSL number is B573-2742.

17.3 Summary of Fate Data

17.3.1 Photolysis

Although the photochemical properties of some silver compounds (notably the bromides and thiosulfates) are well known and form the basis of photographic chemistry, no data was found to indicate that these processes are important in determining the aquatic fate of silver.

17.3.2 Chemical Speciation

In natural waters, silver can be found in several chemical forms, for example, aquated cations, metal-inorganic complexes, and metal-organic complexes. An understanding of the chemical speciation of silver in any given situation is based upon theoretical calculations of hydrolysis, oxidation/reduction and organic complexation.

Ionic silver is found in aqueous systems as the univalent species, although it can form compounds in the Ag(II) or Ag(III) states (Cotton and Wilkinson 1972). Metallic silver is stable over much of the Eh-pH range for water, and formation of the metal (which has very low solublity) may exert a control on its mobility.

Redox potential has an indirect effect on silver speciation in that it dictates the behavior of sulfur and manganese species, which are important controls on silver. Manganese dioxide apparently has more affinity for silver than most of the other sorbents in aqueous systems. If silver-containing manganese dioxide is deposited in bed sediments, which often exhibit reducing conditions, the Mn(IV) in MnO_2 may be reduced to Mn(II), causing dissolution and release of the silver. Under such conditions, however, Ag(I) would probably be reduced to insoluble metallic silver, or it could combine with reduced sulfur to form the sulfide. This compound has the lowest aqueous solubility of any of the silver compounds ($K_{sp}.10^{-50}$) (Cotton and Wilkinson 1972).

Solutions of silver salts may undergo alkaline hydrolysis to form the insoluble oxide via the following reaction (Cotton and Wilkinson 1972):

$$Ag^+ + OH^- \rightleftharpoons 1/2Ag_2O(s) + 1/2H_2O$$
$$\log K = -7.42 \ (25°C, 3M, NaClO_4)$$

In strongly alkaline media, argentious oxide may be hydrolyzed to $Ag(OH)_2^-$, which is soluble. Dissolved carbon dioxide reacts with Ag_2O to form argentious carbonate (Cotton and Wilkinson 1972). The solubility of the oxide and carbonate are sufficient to suggest that neither of these compounds is an efficient control on dissolved silver, except possibly at high pH.

Silver halides are quite insoluble. Hem (1970) speculates that silver chloride may exert a major control on silver where chloride concentration exceeds 10^{-3} M (35 mg/l). In aquatic environments it has been suggested that the silver complexes with chloride, bromide and iodide ions control the amount of free silver present, subject to the effects of physical parameters and other anions and cations.

Jenne et al. (1978) developed a computerized chemical model which allows the prediction of chemical species at equilibrium in abiotic riverine and estuarine environments. This model indicates that at normal silver concentrations, AgHS is an important species (Figure 17-1). In the river end-member, the activity of AgHS exceeds that of Ag^+ and AgCl by as much as 10 fold. In the marine end-member, only the activity of $AgCl_2^-$ exceeds that of AgHS, and Ag^+ is a trivial quantity. AgBr, $Ag(HS)_2^-$, AgF, AgOH, AgI, $AgNO_3$, $Ag(NO_2)_2^-$ and $AgSO_4^-$ are all of minor importance. The low activity of silver in natural waters would seem to preclude any solubility control on silver. Krauskopf (1956) noted that silver levels in marine waters were below saturation with probable solid forms such as AgCl.

No information was found in the reviewed literature on silver-organic interactions. Although much is known about trace metal-organic interaction, it would not be valid to attempt direct extrapolation of that data to silver behavior in aquatic environments. It can be inferred, however, that only a minor fraction of aquatic silver will be in the hydrated, cationic form; and chemical speciation will have great effect on the transport, toxicity and bioavailability of silver in the aquatic environment.

17.3.3 Volatilization

Volatilization of silver compounds is probably not an important process in determining aquatic fate. Formation of volatile biogenic alkylated compounds of silver probably does not occur, inasmuch as these compounds are unstable in environmental conditions (Cotton and Wilkinson 1972).

17.3.4 Sorption

Sorption appears to be the dominant process leading to partitioning of silver into the sediments. Although there is little data on

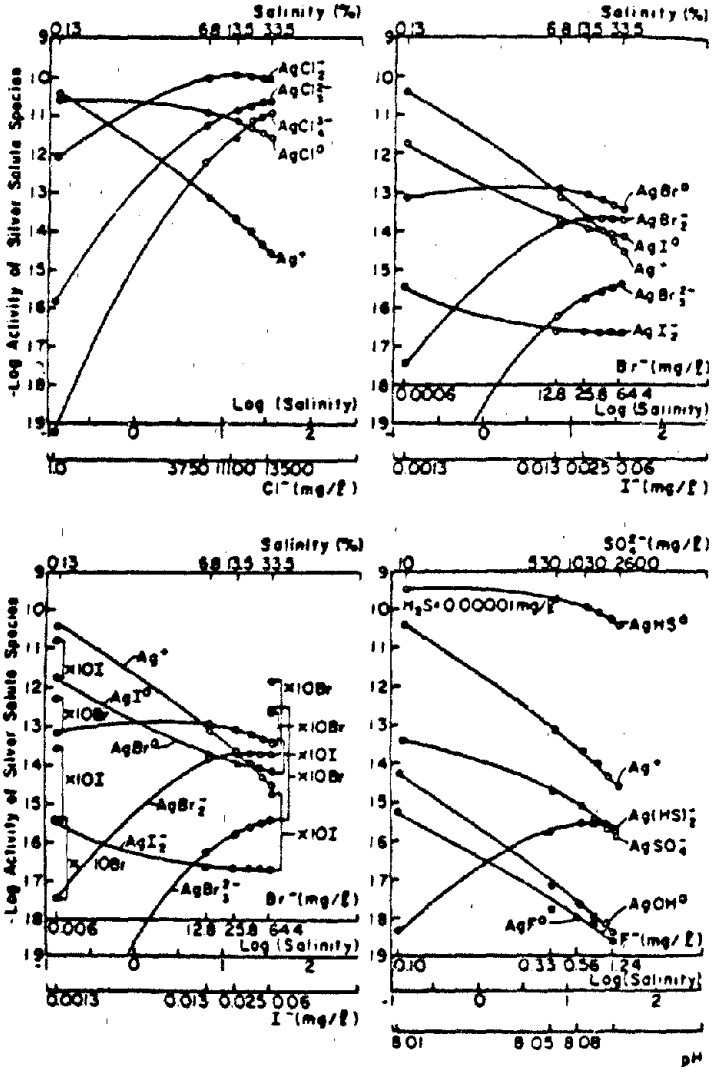


Figure 17-1 Variation in activity of silver solute species with salinity gradient from low conductivity river water to typical marine water. From Jenne et al. (1978).

sorption of silver, it appears that manganese dioxide has a strong affinity for the metal, followed by ferric hydroxide and clay minerals. Kharkar et al. (1968) studied the sorption of several metals on three clays (montmorillonite, illite, and kaolinite) and three hydrous metal oxides (Fe_2O_3, MnO_2, and freshly precipitated $Fe(OH)_3$). Various quantities of these solids were added to a solution of silver (1 µg/l). The affinity of the solids (at 1,000 mg/l) for silver decreased in the order MnO_2 > $Fe(OH)_3$ > montmorillonite > illite > kaolinite > Fe_2O_3. Additionally, the experiments were designed to determine the extent to which adsorbed metals would be desorbed on contact with sea water. Almost all of the silver sorbed to MnO_2 was released on contact with sea water, and significant amounts were released by the other solids as well. Thus, much of the silver transported in the particulate phase of the water column may be desorbed in the estuarine or marine environment. The importance of precipitation of silver chloride under these conditions is uncertain. The fact that silver did not have a strong affinity for the more common solids (the clays), led Kharkar et al. (1968) to estimate that 90 percent of the stream supply of silver to the oceans is in the dissolved form, with desorption from suspended solids making up the remaining 10 percent.

The importance of MnO_2 as a control on silver mobility was confirmed by Chao and Anderson (1974). Sediments from Colorado streams showed a very high correlation ($r = 0.913$) between silver and manganese content. Although sorption by the much more common iron oxides also controls mobility, iron plays a secondary role to manganese. This work confirmed the earlier laboratory study by Anderson et al. (1973) who found that all solid forms of manganese oxide sorbed significant quantities of silver. This sorption was adequately described by the Langmuir equation and showed a direct relationship to pH values.

Dyck (1968) observed, in his study of silver adsorption on hydrous ferric oxide, that this sorption of silver fit Freundlich adsorption isotherms and was explainable in terms of hydrogen-site ion exchange. Adsorption was essentially complete in less than 5 minutes and was strongly dependent on pH. These results would suggest that whenever manganese and/or iron oxides are present, silver will be almost immediately adsorbed and will be relatively immobile in the water column.

Organic materials also adsorb silver. Freeman (1977) found that silver concentration in sediments of an alpine lake and nearby soils was highly correlated with organic content. High silver content also was associated with the finer fractions of sediment rather than coarse fractions. The silver concentrations in sediments were about 1000 times the concentration of overlying waters.

The relationship between silver complexation by humic substances and adsorption is not clearly understood. If silver is complexed by these substances, as are several of the other metals, its complexes would probably have a greater affinity for mineral surfaces than the free Ag^+ ion. Further study is required on sorption of silver before these phenomena can be adequately assessed.

17.3.5 Bioaccumulation

Several studies have shown that silver is accumulated by aquatic organisms. Coleman and Cearley (1974) demonstrated bioaccumulation of silver by largemouth bass and bluegill. Concentration in bass was highest in the internal organs, followed by the gills and remainder of the body. Bioconcentation ratios calculated from these data range from 10-100 (Table 17-1). Cearley (1971) found that juvenile largemouth bass and bluegill, exposed to 0.01 or 0.0001 mg Ag/l for six months accumulated silver for two months after which the pollutant levels appeared to become static. Internal organs contained more silver than did edible muscle tissue.

Activated sludge organisms also bioaccumulate silver. Chiu (1973) found that a suspension of 3 mg/ml of microbes acclimated to heavy metals could extract almost 20 percent of dissolved silver present at 100 mg/l. Expressed as a concentration factor, the microbes had a silver concentration about 100 times that of the solution. In the much more dilute silver concentrations normally found in the environment, activated sludge organisms may exhibit concentration factors on the order of 10^3-10^4.

Freeman (1977) studied the ecological kinetics of silver in an alpine lake, and found that most silver is partitioned to the sediments, with the biota serving as a minor reservoir. Plankton components of the ecosystem showed fluctuations in silver concentrations closely correlated to changes in lake water concentration, while benthic species showed fluctuations more closely correlated to concentrations in the sediments.

Terhaar *et al.* (1972) reported that silver complexes, as they occur in photographic processing effluent, are at most only slightly toxic to fish. Algae, daphina, freshwater mussels and fathead minnows are all capable of accumulating silver from water; but the food chain was not an important route of silver accumulation for animals at the higher trophic levels (Terhaar *et al.* 1977). Luoma and Jenne (1977) found that the accumulation of silver by a deposit-feeding clam was dependent upon the physicochemical nature of the silver-sediment association. Silver bioaccumulation from both biogenic carbonates and synthetic calcites was greater than silver uptake from iron oxides or detrital organic compounds.

Table 17-1

Bioconcentration Factors for Silver

Taxon	Bioconcentration Factor[a]	Reference
Freshwater plants	200	Chapman et al. 1968
Freshwater invertebrates	3,080	Chapman et al. 1968
Freshwater fish	3,080	Chapman et al. 1968
Marine plants	200	Chapman et al. 1968
Marine invertebrates	3,330	Chapman et al. 1968
Marine fish	3,330	Chapman et al. 1968

a. Bioconcentration factors are the ratio derived from the concentration of the element in the aquatic organism (in ppm wet weight) divided by the concentration of the element in water (in ppm).

It would appear, therefore, that silver bioaccumulation is primarily a function of sorption/desorption from sediments. Silver is not present in aquatic animals at very high concentrations because most of its compounds are sparingly soluble in water. Although silver is one of the metals most toxic to aquatic life, there seems to be little food-chain magnification, and silver appears to accumulate mainly in the internal organs. Moreover, silver has a very short biological half-life.

17.3.6 Biotransformation

No data indicating that biota affect the fate of silver were found. Biotransformation of silver in sediments to methylated forms is extremely unlikely due to the instability of alkyl silver compounds. Methyl silver (CH_3Ag) is not stable at temperatures above -30°C (Cotton and Wilkinson 1972).

17.4 Data Summary

Although little data were found in the reviewed literature, it appears that the main control on silver mobility is sorption by manganese dioxide, clays, ferric hydroxide, and organic materials. The available data have been reviewed by Smith and Carson (1977). Bioaccumulation removes some of silver from solution and is apparently strongly related to habitat (water column, benthos) and distribution of biota. Table 17-2 summarizes the aquatic fate described above.

Table 17-2

Summary of Aquatic Fate of Silver

Environmental Process	Summary Statement	Confidence of Data
Photolysis	Probably not important in determining fate.	Low
Chemical Speciation[a]	Chloride, bromide and iodide ions control the levels of hydrated silver cations. Crystalline, metallic silver and silver sulfides may precipitate under reducing conditions.	Medium
Volatilization	Not an important fate.	Medium
Sorption[a]	Silver is strongly sorbed by hydrous manganese and iron oxides, clay minerals and organics. A major controlling mechanism in determining the fate of silver in the aquatic environment.	High
Bioaccumulation[a]	Numerous plants and primary consumer organisms accumulate silver. Little evidence to suggest biomagnification.	High
Biotransformation	Probably not an important fate.	Medium

a. All of the noted environmental processes are important; however, their relative importance with respect to each other is uncertain for determining final fate.

17.5 Literature Cited

Anderson, B.J., E.A. Jenne, and T.T. Chao. 1973. The sorption of silver by poorly crystallized manganese oxides. Geochim. Cosmochim. Acta. 37:611-622.

Boyle, R.W. 1968. The geochemistry of silver and its deposits. Geological Survey of Canada, Bull. 160, Ottawa, Canada. 264p.

Cearley, J.E. 1971. Toxicity and bioconcentration of cadmium, chromium, and silver in Micropteris salmoides and Lepomuis macrocluiers. Ph.D. Thesis, University of Oklahoma, Norman, Okla. 84 p. (Abstract only) Diss. Abstr. 32B:5281(1972).

Chao, T.T. and B.J. Anderson, 1974. The scavenging of silver by manganese and iron oxides in stream sediments collected from two drainage areas of Colorado. Chem. Geol. 14:159-166.

Chapman, W.H., H.L. Fisher, and M.W. Pratt. 1968. Concentration factors of chemical elements in edible aquatic organisms. Lawrence Radiation Laboratory, Livermore, Calif. UCRL-50564. 46p.

Chiu, Y. 1973. Recovery of heavy metals by microbes. pp.18-20. Ph.D. Thesis, School of Engineering, University of Western Ontario, London, Ontario. 136p.

Coleman, R.L. and J.E. Cearley. 1974. Silver toxicity and accumulation in largemouth bass and bluegill. Bull. Environ. Contam. Toxicol. 12(1):53-61.

Cotton, F.A. and G. Wilkinson. 1972. Advanced inorganic chemistry. pp.1044-1052. Interscience Publishers, N.Y. 1145p.

Dyck, W. 1968. Adsorption and coprecipitation of silver on hydrous ferric oxides. Can. J. Chem. 46:1441-1444.

Freeman, R.A. 1977. The ecological kinetics of silver in an alpine lake ecosystem. Second ASTM Symposium on aquatic toxicology, Oct. 31 to Nov. 1,1977. Cleveland, Ohio. (Preprint only).

Hem, J.D. 1970. Study and interpretation of the chemical characteristics of natural waters. pp.202-203. U.S Geological Survey Water-Supply Paper 1473. Washington, D.C. 363p.

Jenne, E.A., D.C. Girvin, J.W. Ball, and J.M. Birchard. 1978. Inorganic speciation of silver in natural water - fresh to marine. pp.41-63. in Environmental impacts of artificial ice nucleating agent. D.A. Klein (ed.). Dowden, Hutchinson, and Ross, Inc. Stroudsburg, Penn. 256p.

Kharkar, D.P., K.K. Turekian, and K.K. Bertine. 1968. Stream supply of dissolved silver, molybdenum, antimony, selenium, chromium, cobalt, rubidium, and cesium to the oceans. Geochim. Cosmochim. Acta. 32:285-298.

Krauskopf, K.B. 1956. Factors controlling the concentration of thirteen rare metals in sea water. Geochim. Cosmochim. Acta. 9:1-32.

Luoma, S.N. and E.A Jenne. 1977. The availability of sediment bound cobalt, silver, and zinc to a deposit-feeding clam. pp. 213-230. in Biological implications of metals in the environment. H. Drucher and R.E. Wildung (eds.). Hanford Life Sciences Symposium, Richland, Wash. NTIS CONF 750929. 682p.

Smith, I.C. and B.L. Carson. 1977. Trace metals in the environment. Vol. II. Silver. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan. 490p.

Terhaar, C.J., W.S. Ewell, S.P. Dziuba, and D.W. Fassett. 1972. Toxicity of photographic processing chemicals to fish. Photograph. Sci. Eng. 16(5):370-377.

Terhaar, C.J., W.S. Ewell, S.P. Dziuba, W.W. White and P.J. Murphy. 1977. A laboratory model for evaluating the behavior of heavy metals in an aquatic environment. Water Res. 11(1):101-110.

Weast, R.C. (ed.). 1977. CRC handbook of chemistry and physics. 58th ed. CRC Press, Cleveland, Ohio. 2398p.

18. THALLIUM

18.1 Statement of Probable Fate

The behavior of thallium in natural waters is not well described in the literature. Thallium can be removed from solution by adsorption onto clay minerals, bioaccumulation, or (in reducing environments) precipitation of the sulfide. Most of the ligands common to aerobic waters form soluble salts with thallium, so that precipitation is not important under oxic conditions.

18.2 Identification - Geochemistry of Thallium

Thallium, a heavy metal, is a member of the Group III elements. It is not used extensively by industry and is introduced into the environment primarily as waste from production of other metals (Zitko 1975). Thallium exhibits the properties of both a lithophylic and chalcophylic element. As a lithophylic element, it is concentrated late during the magmatic crystallization of potassium minerals such as feldspars and micas. As a chalcophylic element, it is found as a component of independent minerals and as a substitute element in minerals such as galena. The average concentration of thallium in the earth's crust is about 1 ppm (Zitko 1975; Magorian et al. 1974). The following minerals of thallium, although rare, have been found to occur in nature: crookesite $(Cu,Tl,Ag)_2Se$; hutchinsonite $PbS(Tl,Ag)_2S \cdot 2As_2S_3$; verbrite $Tl_3S \cdot 3(As,Sb)_2S_3$; lorandrite $Tl_2S \cdot As_2S_3$ and avicennite $7Tl_2O_3 \cdot Fe_2O_3$.

Thallium, atomic number 82, atomic weight 204.87, exists in the elemental form as a bluish white metal (Weast 1977). In compounds, it has a valence of +1 or +3. The +3 state is much less stable in water than is the +1 state (Cotton and Wilkinson 1972). Thallium (III) forms some organometallic compounds; however, Tl(I) forms relatively few complexes with the exception of those with halogen, oxygen, and sulfur ligands (Cotton and Wilkinson 1972). In this and several other respects, Tl(I) has chemical properties similar to those of the alkali metal cations.

The behavior of thallium in the environment can be somewhat explained by a comparison of the ionic and atomic radii of thallium with the radii of some associated elements in Table 18-1. (Numerical values are from Weast 1977.) The similarity of the univalent ionic radius of thallium to those of univalent potassium and rubidium explains the presence of thallium in late state potash and plagioclase feldspars as well as its accompaniment with rubidium with which it is concentrated during the late states of crystallization in igneous rocks. Likewise, the similarity of the metallic and covalent radii of thallium and lead suggests that the behavior of thallium in the aquatic environment will be similar to that of lead.

The CAS number of thallium is 7440-28-0, and its TSL number is B690-2221.

Table 18-1

Radii of Thallium and Some Associated Elements

Ionic radii			Metallic radii			Covalent radii		
Tl(I)	1.49	Å	Tl	1.71	Å	Tl	1.47	Å
Rb (I)	1.49	Å	Pb	1.75	Å	Pb	1.46	Å
K(I)	1.33	Å	In	1.57	Å	In	1.44	Å
			Zn	1.37	Å	Zn	1.31	Å
Tl(III)	1.05	Å						
Y(III)	1.05	Å						
In(III)	0.92	Å						

18.3 Summary of Fate Data

18.3.1 Photolysis

Although some thallium compounds such as TlCl are photosensitive (Cotton and Wilkinson 1972), there is no evidence that the photochemistry of thallium plays a significant role in determining aquatic fate.

18.3.2 Chemical Speciation

In reducing environments, thallium may be precipitated as the metal or, in the presence of sulfur, as the sulfide (Lee 1971; Magorian *et al.* 1974.) In very oxidizing waters, the most oxidized form of thallium, Tl(III), may be present. In other Eh ranges, thallium(I) has a very high solubility compared to the other environmentally important heavy metals.

O'Shea and Mancy (1978), in their study of trace metal ions and complexing agents at different pH values, found that increasing pH decreased thallium-inorganic interactions. Increases in pH, however, produced extensive thallium-humic acid interaction. It appears, therefore, that thallium-organic interactions may be important in most natural water systems. Most commercial uses of thallium are in the form of organometallic compounds (pesticides, poisons, etc.). Further research, however, is required to determine the importance of these interactions on the aquatic fate of thallium.

The thallic ion (Tl^{+3}) is hydrolyzed to form the colloidal oxide over the pH range of natural waters (Cotton and Wilkinson 1972). Depending on the relative kinetics of reduction compared to hydrolysis, however, precipitation as $Tl(OH)_3$ may be an effective mechanism for removing thallium from solution via the following scenario: thallium (III) precipitates as the oxide or hydroxide and settles to the bed sediments; in the sediments, the reducing conditions cause reduction to Tl(I), which reacts with sulfide to form the insoluble compound Tl_2S (Lee 1971).

18.3.3 Volatilization

No evidence was found for formation of volatile thallium compounds in the environment.

18.3.4 Sorption

Thallium is strongly adsorbed by montmorillonitic clays. Magorian *et al.* (1974) demonstrated that a 1 gm/l suspension of the clay hectorite could remove 97% of a 100 µg/l concentration of thallium within 24 hours. Similarly, a 1 mg/l concentration of thallium was reduced to 115 µg/l, and a 10 µg/l solution was reduced to below 1 µg/l. The above values are for

pH 8.1; adsorption is not as effective at pH 4.0. Experiments with copper and zinc ions showed that thallium is not adsorbed as strongly as these metals. Thallium probably has an affinity for hydrous metal oxides. Zitko et al. (1975) observed a 28% decrease in thallium concentration after precipitation of heavy metal hydroxides at pH 9.6 and subsequent centrifugation.

Mathis and Kevern (1975), in a study of heavy metal cycling in a lake in southwestern Michigan, were able to detect thallium only in the sediments. They suggested that their inability to detect thallium in the water, plankton, and fish may have been due to the sensitivity of their analytical methods; however, the levels of thallium in the sediment were an order of magnitude higher than the minimum sensitivity of the atomic adsorption spectrophotometer that was used suggesting that the sediment is an active sink for thallium. This observation, combined with the high solubility of most thallium compounds, implies that thallium is actively being sorbed into the sediments in the aquatic environment.

18.3.5 Bioaccumulation

Since thallium is soluble in most aquatic systems, it is readily available to aquatic organisms. Thus, it is not surprising to find that thallium is quickly bioaccumulated. Goldfish have a higher rate of uptake for thallium than for the five most common alkali metals (Zitko 1975). The alga, Ulothrix sp., was able to concentrate thallium by a factor of 127 to 220 within one hour; in comparison, the concentration factors for 2.7 hours exposure were 114 for lead, 30 for cadmium, 80 for zinc, and 313 for copper (Magorian et al. 1974). Other bioconcentration factors are summarized in Table 18-2.

Overnell (1975), in a study of the effect of thallium and other heavy metals on photosynthesis in freshwater algae, found that thallium decreased photosynthesis by 40 percent. Unfortunately, he did not measure thallium accumulation by the alga. He did report, however, that the inhibition of photosynthesis by thallium could not be relieved by washing of the alga, suggesting that the thallium may have been irreversibly bound and, therefore, was available not only for bioaccumulation but food chain magnification as well.

18.3.6 Biotransformation

Although the toxic effects of thallium are well known (Zitko 1975), no evidence was found that biotransformation of thallium compounds plays an important role in determining aquatic fate. There has been some speculation that thallium could be methylated under aerobic conditions by electrophilic attack (Anon. 1977), but this process has not been demonstrated in the aquatic environment.

Table 18-2

Bioconcentration Factors for Thallium

Taxon	Bioconcentration Factor[a]	Reference
Freshwater Plants	100,000	Chapman *et al.* 1968
Freshwater Invertebrates	150,000	Chapman *et al.* 1968
Freshwater Fish	100,000	Chapman *et al.* 1968
Marine Plants	100,000	Chapman *et al.* 1968
Marine Invertebrates	150,000	Chapman *et al.* 1968
Marine Fish	100,000	Chapman *et al.* 1968
Clam (*Mya arenia*)	17.6-18.6	Zitko *et al.* 1975
Mussel (*Mytilus edulis*)	10.9-12.4	Zitko and Carson 1975
Atlantic salmon	27-1430	Zitko *et al.* 1975

a. Bioconcentration factors are the ratio derived from the concentration of the element in the aquatic organism (in ppm wet weight) divided by the concentration of the element in water (in ppm).

18.4 Data Summary

In aerobic waters, adsorption and bioaccumulation are the primary mechanisms for removal of thallium from solution. In anaerobic environments, precipitation as the sulfide may be important. Much of the thallium introduced into freshwater systems probably remains in solution and is transported to the oceans. The aquatic fate information for thallium is summarized in Table 18-3.

Table 18-3

Summary of Aquatic Fate of Thallium

Environmental Process	Summary Statement	Confidence of Data
Photolysis	Not an important mechanism.	Medium
Chemical Speciation[a]	In reducing environments, Tl(I) may precipitate as a sulfide; otherwise, it will remain in solution.	Medium
Volatilization	Not an important mechanism.	Low
Sorption[a]	Thallium is adsorbed to clay minerals and hydrous metal oxides. Probably a very important process.	Medium
Bioaccumulation[a]	Thallium is accumulated by aquatic organisms. Probably an important process.	Low
Biotransformation	Not an important process.	Low

a. All of the noted environmental processes are important; however, their relative importance with respect to each other is uncertain for determining final fate.

18.5 Literature Cited

Anon. 1977. Tracking trace metals in the biosphere. Chem. Eng. News 55(16):23.

Chapman, W.H., H.L. Fisher, and M.W. Pratt. 1968. Concentration factors of chemical elements in edible aquatic organisms. Lawrence Radiation Laboratory, Livermore, Calif. UCRL-50564. 46p.

Cotton, F.A. and G. Wilkinson. 1972. Advanced inorganic chemistry pp.453-455. Interscience Publishers, New York. 1145p.

Lee, A.G. 1971. The chemistry of thallium. pp.1-18, 295-318. Elsevier Publishing Company, Amsterdam. 336p.

Magorian, T.R., K.G. Wood, J.G. Michalovic, S.L. Pek, and M.M. Van Lier. 1974. Water pollution by thallium and related metals pp.145-160. NTIS PB 253 333. Springfield, Va. 182p.

Mathis, B.J. and N.R. Kevern. 1975. Distribution of mercury, cadmium, lead, and thallium in an eutrophic lake. Hydrobiologia 46(2-3):207-222.

O'Shea, T.A. and K.H. Mancy. 1978. The effect of pH and hardness metal ions in the competitive interaction between trace metal ions and inorganic and organic complexing agents found in natural waters. Water Res. 12:703-711.

Overnell, J. 1975. The effect of some heavy metal ions of photosynthesis in a freshwater alga. Pestic. Biochem. Physiol. 5:19-26.

Weast, R.C. (ed.) 1977. Handbook of chemistry and physics, 58th Ed. CRC Press, Cleveland, Ohio 2398p.

Zitko, V. 1975. Toxicity and pollution potential of thallium. Sci. Total Environ. 4:185-192.

Zitko, V. and W.V. Carson. 1975. Accumulation of thallium in clams and mussels. Bull. Environ. Contam. Toxicol. 14:530-534.

Zitko, V., W.V. Carson, and W.G. Carson. 1975. Thallium: occurrence in the environment and toxicity to fish. Bull. Environ. Contam. Toxicol. 13(1):23-30.

19. ZINC

19.1 Statement of Probable Fate

Most of the zinc introduced into the aquatic environment is partitioned into the sediments by sorption onto hydrous iron and manganese oxides, clay minerals, and organic materials. Precipitation of the sulfide is an important control on the mobility of zinc in reducing environments, and precipitation of the hydroxide, carbonate, or basic sulfate can occur where zinc is present in high concentrations. An essential trace element in nutrition, zinc is bioaccumulated in all organisms. Formation of complexes with organic and inorganic ligands can increase the solubility of zinc and probably increases the tendency for zinc to be adsorbed.

19.2 Identification - Geochemistry of Zinc

Zinc is a naturally occuring element found in the earth's crust at an average concentration of 123 ppm (Weast 1977). Zinc is found chiefly as the minerals sphalerite (ZnS), smithsonite ($ZnCO_3$), willemite (Zn_2SiO_4) and zincite (ZnO); it also substitutes to some extent for magnesium in silicate minerals and is found in most igneous rocks (Cotton and Wilkinson 1972).

Zinc (Zn) is a metallic element, atomic number 30, atomic weight 65.38 (Weast 1977). The chemistry of zinc is similar to that of cadmium, which is directly below it in the periodic table (Cotton and Wilkinson 1972). In aqueous solution, zinc always has a valence of +2, and it exhibits amphoteric properties, dissolving in acids to form hydrated Zn(II) cations and in strong bases to form zincate anions (probably $Zn(OH)_4^{-2}$). Compounds of zinc with the common ligands of surface waters are soluble in neutral and acidic solutions, so that zinc is readily transported in most natural waters and is one of the most mobile of the heavy metals. The geochemistry of zinc in surface water has been extensively reviewed by Hem (1972). Since the divalent zinc ion does substitute to some extent for magnesium in the silicate minerals of igneous rocks, weathering of this zinc-containing bedrock gives rise to Zn^{+2} in solution whereupon the hydrated cation remains dominant to pH values of about 9. Zinc forms complexes with a variety of organic and inorganic ligands, but these compounds are sufficiently soluble to prevent their becoming a limiting factor for the solubility of the small concentrations of zinc found in most aquatic environments. Adsorption on clay minerals, hydrous oxides, and organic matter is a more probable limiting mechanism.

The CAS number for zinc is 7440-66-6; its TSL number is B823-4379.

19.3 Summary of Fate Data

19.3.1 Photolysis

No evidence was found that photolysis of zinc compounds in the aquatic environment significantly affects its fate.

19.3.2 Chemical Speciation

In natural waters, zinc can be found in several chemical forms, for example, as simple hydrated ions, as metal-inorganic complexes, or as metal-organic complexes. An understanding of the chemical speciation of zinc in any given situation is based upon theoretical calculations of hydrolysis, oxidation/reduction and organic complexation. A short presentation of this material will be given after which the chemical speciation of zinc in various aquatic environments will be discussed.

Zinc always has an oxidation state of +2 in aqueous systems (Cotton and Wilkinson 1972). Unlike the transition metals adjacent to it in the periodic table, zinc is not directly affected by changes in Eh (redox potential); however, the valences and reactivity of ligands reacting with zinc are affected by Eh. Figure 19-1 shows the equilibrium solubility and stable solid species of zinc at pH 5 as a function of pE (Huang et al. 1977). At pH levels more characteristic of natural waters, the solubility of the oxide and carbonate are considerably lower. Although the graph shows a very low solubility for Zn^{+2} in oxidizing conditions, measured zinc concentrations are usually much higher, indicating that formation of the basic sulfate ($Zn_4(OH)_6SO_4$) is not normally an effective control on the mobility of zinc.

Precipitation of zinc compounds appears to be important only in reducing or highly polluted environments. Holmes et al. (1974) concluded that formation of zinc sulfide controls the mobility of zinc in Corpus Christi Harbor (an estuarine system). Seasonal fluctuations in dissolved zinc levels were attributed to variations in redox potential: in the summer, reducing conditions prevail in the hypolimnion due to combined effects of lower O_2 solubility, greater biological oxygen demand, and thermal stratification; and zinc, consequently, is incorporated into the sediments via formation of ZnS. In the winter, Eh increases, and zinc is released to the water column; it is then adsorbed by suspended solids and is transported to Corpus Christi Bay, where the solids settle out and zinc is again partitioned into the sediments.

Hydrated zinc cations may be hydrolyzed to form $Zn(OH)_2(s)$ or ZnO(s) (Stumm and Morgan 1970). Patterson et al. (1977) studied the precipitation of $Zn(OH)_2$ and $ZnCO_3$ and found that $Zn(OH)_2$ precipitation

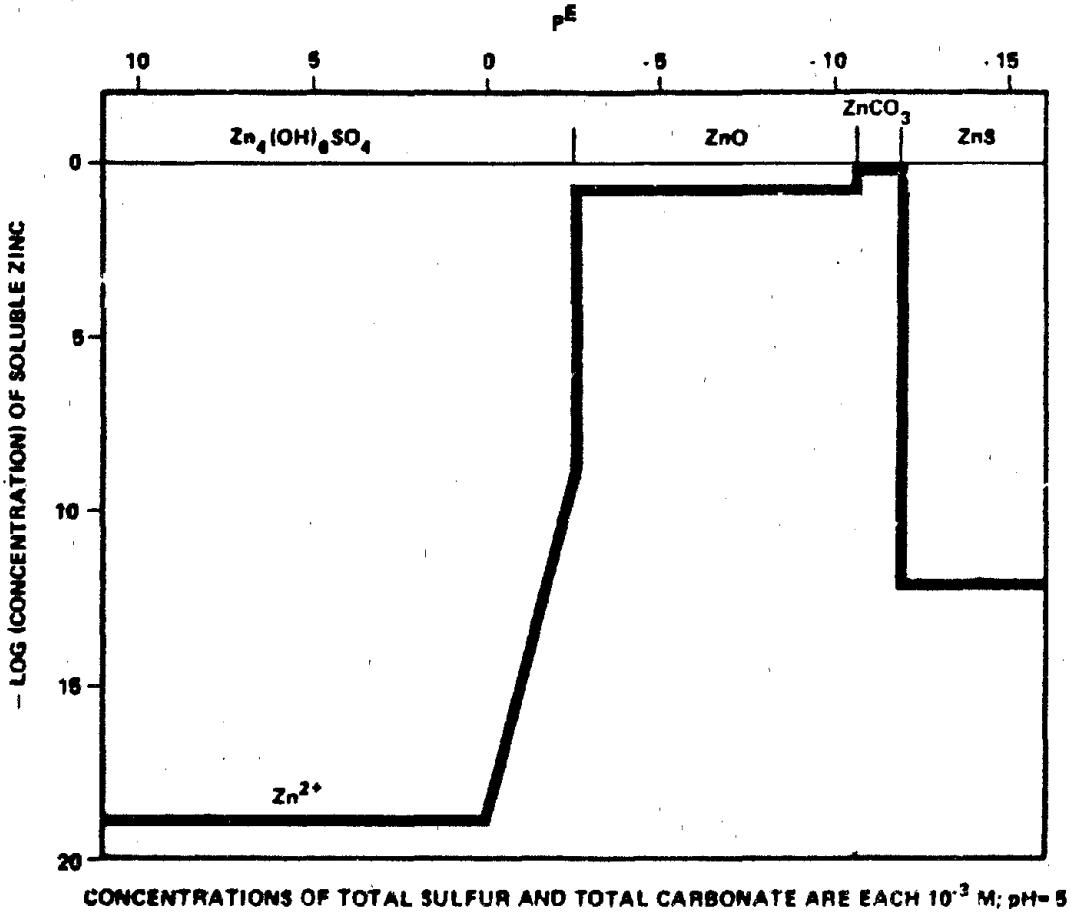


Figure 19-1 Solubility of zinc as a function of pE (pE = - log Eh). (From Huang et al. 1977).

is kinetically favored over $ZnCO_3$ precipitation. Figure 19-2 shows the computed equilibrium solubility of $Zn(OH)_2$ as a function of pH; and Figure 19-3 shows the stability of $Zn(OH)_2$ and $ZnCO_3$ in a $10^{-1.1}$ M carbonate system as a function of pH. When Patterson et al. (1977) added zinc to systems with and without carbonate, they found that the resulting solubilities conformed to those expected if zinc hydroxide alone were controlling solubility (Figure 19-4). Apparently, the zinc hydroxide and carbonate species did not reach thermodynamic equilibrium over the time-span of that study. An interesting observation made by the authors was that precipitation was essentially complete within four hours, with little further reduction in soluble zinc even after 264 hours (Figure 19-5).

In an impoundment polluted with zinc (400 µg/l) introduced by dumping of mine wastes, Weatherley and Dawson (1973) found that zinc was precipitated as an amorphous colloidal deposit of basic carbonates and sulfates. Under oxidizing conditions, precipitation of these zinc compounds is probably important only where high concentrations of zinc exist.

Long and Angino (1977) developed a theoretical model to study the chemical speciation of zinc in aqueous solutions and the response of zinc to variations in ionic strength and complexation. Association of zinc with the ligands OH^-, Cl^-, CO_3^{-2}, SO_4^{-2}, and HCO_3^- were considered at pH values from 3.5 to 11.0 at 25°C in differing seawater-freshwater mixtures. The results are summarized in Figure 19-6. In general, the relative importance of the various ligand-zinc complexes can be predicted from a comparison of their stability constants. This model, however, does not take into account metal-organic complexes, and it is, therefore, useful only in unpolluted relatively organic-free waters.

Guy and Chakrabarti (1976), in their study of metal-organic interactions in natural waters, found that humic acids in solution and other natural complexing agents can maintain zinc ions in a bound form at a pH as low as 3. The release of zinc from sediments is, therefore, apparently controlled by a combination of ion exchange and complex formation whereby the stability of the metal-organic complex determines the amount of metal solubilized.

In summation, the transport of zinc in the aquatic environment is controlled by the speciation of the ion. Although it appears that in most unpolluted waters, zinc will exist mainly as a divalent cation and be easily adsorbed, organic material will have an overwhelming effect on the chemical form in which zinc will be present in polluted areas. Unfortunately, there is at present insufficient information to construct a comprehensive model for the transport and sorption of zinc based upon chemical speciation.

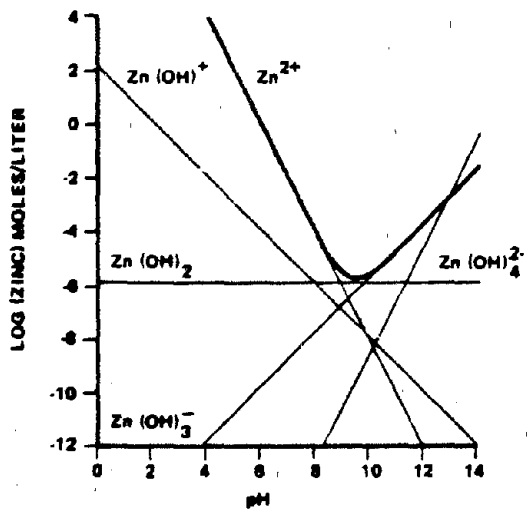


Figure 19-2 Theoretical zinc hydroxide solubility curve. From Patterson et al. (1977).

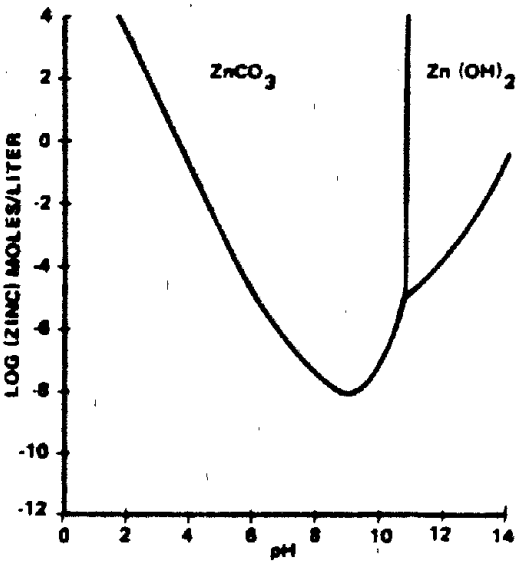


Figure 19-3 Theoretical zinc carbonate-zinc hydroxide phase diagram ($C_T = 10^{-1.1}$ mol/l). From Patterson et al. (1977).

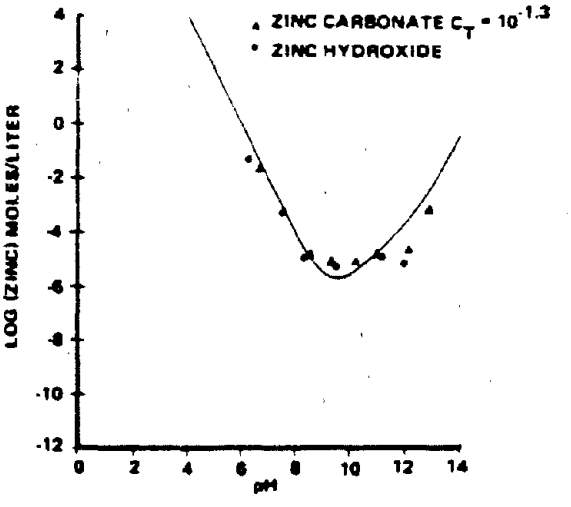


Figure 19-4 Comparison of zinc hydroxide and zinc carbonate data with theoretical hydroxide solubility curve. From Patterson et al. (1977).

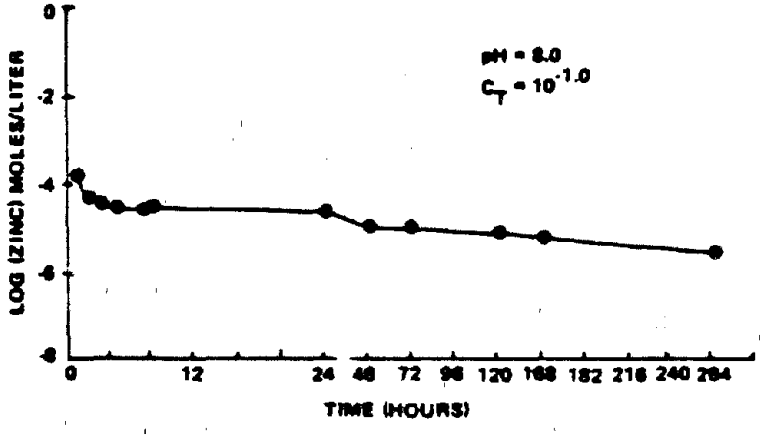


Figure 19-5 Kinetics of zinc precipitation. From Patterson et al. (1977).

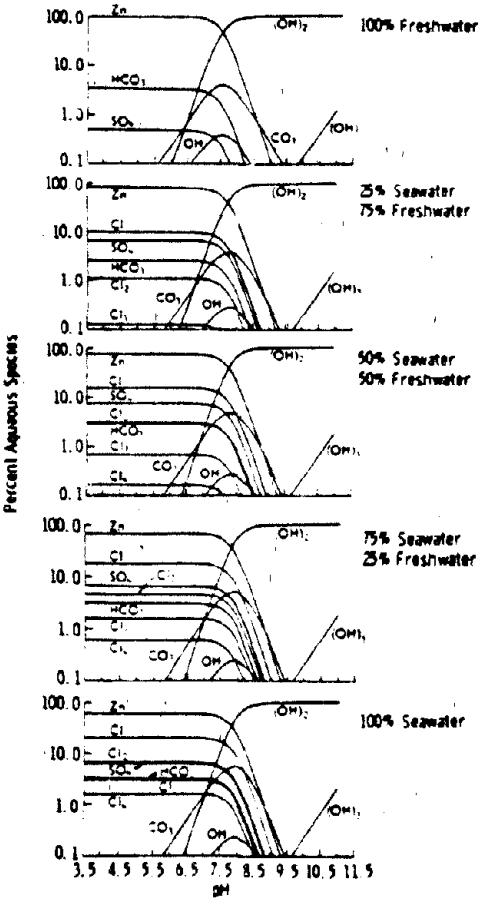


Figure 19-6 Chemical speciation of zinc in seawater-freshwater mixtures. From Long and Angino (1977).

19.3.3 Volatilization

No evidence was found that volatilization of zinc is an important aquatic fate. Alkyl zinc compounds are unstable to oxygen and water (Cotton and Wilkinson 1972), and, therefore, volatile methylated forms analogous to those of mercury, arsenic, antimony, lead, and selenium are probably not formed in aquatic environments.

19.3.4 Sorption

Sorption of zinc by hydrous metal oxides, clay minerals, and organic materials is probably the dominant fate of zinc in the aquatic environment. Concentrations of zinc in suspended and bed sediments always exceed concentrations in ambient waters (Nelson and Hauschild 1970; Hem 1972; Angino et al. 1974; Kubota et al. 1974; Perhac 1974a, 1974b; Rehwoldt et al. 1975, Carpenter et al. 1975; Helz et al. 1975; Pita and Hyne, 1975; Steele and Wagner 1975; Namminga and Wilhm 1977) and there is an inverse correlation between zinc concentration and sediment grain size (Nelson and Hauschild 1970; Perhac 1974b; Pita and Hyne 1975; Steele and Wagner 1975; Namminga and Wilhm 1977). Since smaller grained particles have a higher surface-to-mass ratio, the fact that higher zinc concentrations are associated with such particles implies that sorption is responsible for this phenomenon rather than precipitation. James and MacNaughton (1977) presented theoretical models which show that the removal of zinc from aqueous solutions can be explained by colloidal and surface chemical controls, wherein the presence of insoluble phases, often with high surface areas, provide sites for adsorption or interfacial reactions. Their calculations, based on electrical double-layer and ion-exchange models, developed adsorption isotherms for various pH values, metal ion concentrations, ionic strengths and mineral substrates. These models have provided a valid theoretical background from which to approach the adsorption of zinc on inorganic minerals, but the models have not been extended at present to adsorption on organic materials.

Guy et al. (1975) developed a chemical model to investigate the mechanisms controlling the distribution of zinc between soluble and particulate fractions in natural waters. Using clays, hydrous manganese oxides, and organic material, they found that zinc sorption onto clays followed a Freundlich isotherm but a Langmuir isotherm was required for the other materials. Guy et al. (1975) interpreted these results as indicating that these zinc distributional ratios can be explained in terms of coordination chemistry. While the model presented was in qualitative agreement with reported phenomena in natural waters, further studies are needed to provide more definitive conclusions regarding the predictive possibilities of these models for the aquatic fate of zinc.

The composition of the dissolved and suspended solids load has an important effect on the mode of transport of zinc. Where the solids are primarily dissolved, most of the zinc is transported in solution as the hydrated cation or complex species (Perhac 1972, 1974a; DeGroot and Allersma 1975). Where suspended solids make up a high proportion of the total solids load, most of the zinc transported will be sorbed to the suspended and colloidal particles (Kubota et al. 1974; Steele and Wagner 1975). A common observation is that residence in impoundments reduces the concentration of dissolved zinc, apparently due to scavenging by suspended solids and subsequent deposition (Pita and Hyne 1975; Perhac 1974b; Nelson and Hauschild 1970; Kubota et al. 1974).

Coprecipitation and sorption of dissolved zinc by hydrous oxides of iron and manganese are important controls on the mobility of zinc, especially where high concentrations of reduced iron and manganese are introduced into aerobic surface waters (Lee 1975). As reduced iron and manganese are oxidized, their hydrous oxides precipitate as coatings or discrete particles. The negative zeta-potential usually exhibited by these materials attracts zinc and other cations, and the sorbed cations are incorporated into the crystal lattice structure of the hydrous iron or manganese oxide (Lee 1975). The black encrustation often found on submerged rocks is usually composed of these oxides. Suspended solids can be coated with these oxides as well, and Angino et al. (1974) found a significant correlation between zinc concentration and manganese and iron concentration of suspended solids in Kansas streams. On a mass-per-mass basis, zinc is partitioned more strongly in hydrous Fe-Mn oxides than in other components of the sediment. This has led Carpenter et al. (1975) to suggest that analysis of zinc and other metals in oxide coatings may be a useful tool in geochemical prospecting.

Colloidal and suspended organic matter also adsorbs zinc. Rashid (1974) reported that about 26.1 mg of zinc was sorbed per gram of sedimentary organic matter added to a solution of zinc. Zinc was sorbed more strongly than Ni, Co, and Mn, but less strongly than copper. Jackson and Skippen (1978) found that the presence of organic ligands increased the solubility of zinc in the presence of clays. The organic acids proved capable of remobilizing zinc from solid phases although the reaction is kinetically hindered, especially at basic pH values.

The tendency of zinc to be sorbed is affected not only by the nature and concentration of the sorbent but by pH and salinity as well. In a study of heavy metal adsorption by two oxides and two soils, zinc was completely removed from solution when pH exceeded 7; below pH 6, little or no zinc was adsorbed, as shown in Figure 19-7 (Huang et al. 1977). Addition of inorganic complexing ligands enhanced the affinity for adsorption (Huang et al. 1977).

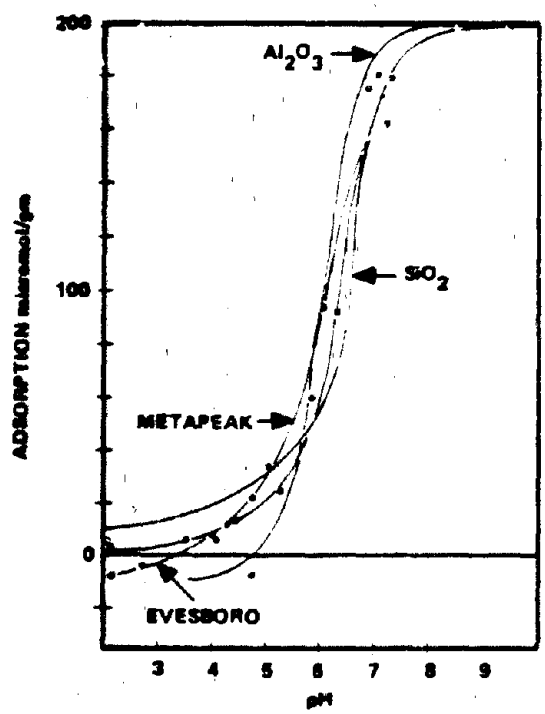


Figure 19-7 Adsorption of zinc on various solids after 24 hours. Ionic Strength = 0.1 M; solid suspension = 5 gm/l; Original $[Zn^{2+}] = 10^{-3}$M; therefore, 200 micromol/gm corresponds to 100% adsorption; from Huang et al. (1977).

Helz et al. (1975) found that zinc is desorbed from sediments as salinity increases. This phenomenon, which is exhibited by many of the other metals as well, is apparently due to displacement of the adsorbed zinc ions by alkali and alkaline earth cations which are abundant in brackish and saline waters. In summary, sorption is the dominant fate process affecting zinc, and it results in enrichment of suspended and bed sediments relative to the water column. Variables affecting the mobility of zinc include the concentration and composition of suspended and bed sediments, dissolved and particulate iron and manganese concentrations, pH, Eh, salinity, concentration of complexing ligands, and the concentration of zinc.

19.3.5 Bioaccumulation

Zinc is bioaccumulated by all organisms. One noteworthy aspect of bioaccumulation is that it occurs even in the absence of abnormally high zinc concentrations since it is an essential nutrient. Bioconcentration factors are listed in Table 19-1.

Zinc has been extensively studied in the freshwater environment. Zinc-65 was accumulated much more readily than ^{60}Co, ^{137}Cs or ^{85}Sr by soft tissues of carp, snails, tadpoles and clams during experiments utilizing isotopic measurements conducted in ponds (Brungs 1967). In laboratory experiments, the brown bullhead (Ictalurus) accumulated ^{65}Zn rapidly for the first seven hours of exposure followed thereafter by a reduced accumulation rate (Joyner 1961). Gill and viscera attained the highest zinc concentration of the tissues analyzed. In one set of experiments, the esophagus was plugged on some fish to determine the fraction of accumulated zinc attributable to swallowed water; this route of uptake was found to have a negligible contribution under the experimental conditions. Zinc-exposed fish that were then transferred to fresh water lost half of their accumulated zinc after six days followed thereafter by a much reduced rate of zinc elimination.

The importance of bioaccumulation, or at least biologically mediated removal of zinc from solution, was shown by Adams et al. (1975), who demonstrated that when dissolved zinc was added to the influent of a wastewater treatment plant at levels of 2.5 to 20 mg/l, primary treatment removed only about 8-14 percent of the zinc. After activated sludge treatment, however, 74-96 percent of the zinc was removed. It is uncertain whether the zinc was bioaccumulated by the microorganisms, or if further removal of solids by sludge formation was responsible for the dramatic reduction in zinc concentration. Nevertheless, it is clear that in the biodensity ranges found in sewage treatment plants, zinc is effectively removed from solution, and bioaccumulation probably plays an important role in such removal.

Table 19-1

Bioconcentration Factors for Zinc

Taxon	Bioconcentration[a] Factor	Reference
Freshwater Plants	4,000	Chapman et al. 1968
Freshwater invertebrates	40,000	Chapman et al. 1968
Chironomid larvae	30,000	Namminga and Wilhm 1977
Freshwater Fish	1,000	Chapman et al. 1968
Marine Plants	1,000	Chapman et al. 1968
Algae - Nitzshia sp.	50,000	Chipman et al. 1958
Seaweeds	900	Stumm and Morgan 1970
Marine invertebrates	100,000	Chapman et al. 1968
American oyster- Crasseotrea virginica	24,000	Chipman et al. 1958
Marine fish	2,000	Chapman et al. 1968
Anchovetta	400	Stumm and Morgan 1970
Yellow fish tuna	700	Stumm and Morgan 1970
Skipjack tuna	500	Stumm and Morgan 1970

a. Bioconcentration factors are the ratio derived from the concentration of the element in the aquatic organism (in ppm of wet weight) divided by the concentration of the element in water (in ppm).

Microcosm studies generally indicate that zinc is not biomagnified. Patrick and Loutit (1975) exposed bacteria to elevated levels of zinc. When the bacteria were fed to tubificid worms, the worms concentrated zinc, but the levels in the worms were lower than levels in the bacteria.

The chemical form in which zinc occurs has a profound effect on its availability for bioaccumulation. The bottom-feeding clam Macoma balthica accumulated zinc much more readily from biogenic carbonates (crushed clamshells) than from other sediment-bound sources (Luoma and Jenne 1977). Zinc was readily accumulated from detrital organic materials as well, but little uptake was observed when zinc was coprecipitated with hydrous iron or manganese oxides. The sinks from which bioaccumulation was greatest also exhibited the greatest rate of sediment to water desorption.

Duke (1967) studied the distribution of ^{65}Zn in an estuarine environment. He found that one day after addition of ^{65}Zn to a model ecosystem, 36 percent was in the sediments, 5 percent was in biota, and 59 percent was in the water column. After 100 days, 99.4 percent was in the sediments, 0.6 percent was in biota, and none was in the water. Maximum ^{65}Zn levels in biota were attained within 2 days; after 100 days, scallops contained 30 percent of their maximum level, oysters 60 percent, and clams 25 percent. Zinc-65 concentration was smaller in fish, crabs and marsh grass than in the molluscs.

Zinc is readily accumulated by both marine and freshwater fish from both food and water, but internal organs and bones accumulate much higher zinc levels than edible muscle tissue (Phillips and Russo 1978). The time required for fish to reach threshold levels of zinc appears to be dependent upon species and the chemical nature of the environment. Upon entering fish, some zinc associates with cadmium-binding protein, and evidence suggests that a zinc-binding protein may exist. The toxicity of zinc to aquatic organisms has been shown to decrease with increasing calcuim concentration even though calcium appears to stimulate zinc uptake. In marine fishes, cadmium reportedly decreases zinc accumulation (Phillips and Russo 1978). In summary, it seems evident that while zinc is actively bioaccumulated, the biota appear to represent a relatively minor sink when compared to the sediments.

19.3.6 Biotransformation

Zinc is one of the most important metals in biological systems, probably second only to iron among the heavy metals (Cotton and Wilkinson 1972); over 25 zinc-containing enzymes have been identified.

A discussion of the metabolic role of zinc can be found in a number of sources (e.g., Prasad (1967)). Since alkyl-zinc compounds are unstable to water and oxygen, biomethylation of zinc in aquatic ecosystems probably does not occur. Nevertheless, the presence of biogenic ligands, such as humic acids, affects the precipitation and adsorption behavior of zinc. Biologically generated microenvironments can also alter the mobility of zinc. Since zinc is actively bioaccumulated, it would not be surprising to find that it exhibits seasonal fluctuations in concentration such as those documented for copper (Kimball 1973; Grimshaw et al. 1976; Namminga and Wilhm 1977), in which degradation of organic material in the fall and winter results in elevated aqueous concentrations relative to the spring and summer months when the metal is actively bioaccumulated.

19.4 Data Summary

The dominant fate of zinc in aerobic waters is sorption by hydrous iron and manganese oxides, clay minerals, and organic material. The efficiency of these materials in removing zinc from solution varies according to their concentrations, pH, Eh, concentrations of ligands, and the concentration of zinc. Precipitation of the sulfide is an important control on the mobility of zinc in reducing environments. Under aerobic conditions, precipitation of zinc compounds is probably important only where zinc is present in high concentrations. Zinc is bioaccumulated, which is to be expected in view of the fact that it is an essential nutrient. Although the biota appear to be a minor reservoir of zinc relative to the sediments, biological activity can affect the mobility of zinc in the aquatic environment. The aquatic fate of zinc is summarized in Table 19-2.

Table 19-2

Summary of Aquatic Fate of Zinc

Environmental Process	Summary Statement	Confidence of Data
Photolysis	Not an important mechanism	Medium
Chemical Speciation[a]	In most unpolluted waters, the majority of zinc will exist as the hydrated divalent cation. In polluted waters, complexation will predominate.	Medium
Volatilization	Not an important mechanism.	Medium
Sorption[a]	Zinc has a strong affinity for hydrous metal oxides, clays, and organic matter. Adsorption increases with pH.	High
Bioaccumulation[a]	Zinc is strongly bioaccumulated. Bioconcentration factors range from 10^2 to 10^5.	High
Biotransformation	No biomethylation in evidence. Organic ligands of biological origin may affect solubility and adsorption.	Medium

a. All of the noted environmental processes are important; however, their relative importance with respect to each other is uncertain for determining final fate.

19.5 Literature Cited

Adams, C.E. Jr., W.W. Eckenfelder, Jr. and B.L. Goodman. 1975. The effects and removal of heavy metals in biological treatment. pp.277-292. in Heavy metals in the aquatic environment. P.A. Koenkel (ed.). Pergamon Press, Oxford, England. 352p.

Angino, E.E., L.M. Magnuson, and T.C. Waugh. 1974. Mineralogy of suspended sediment and concentration of Fe, Mn, Ni, Zn, Cu, and Pb in water and Fe, Mn, and Pb in suspended load of selected Kansas streams. Water Res. 10(6):1187-1191.

Brungs, W.A. 1967. Distribution of cobalt-60, zinc-65, strontium-85, and cesium-137 in a freshwater pond. Publ. No. 999-RH-24, U.S. Public Health Service, Washington, D.C. 52p.

Carpenter, R.H., T.A. Pope, and R.L. Smith. 1975. Fe-Mn oxide coatings in stream sediment geochemical surveys. J. Geochem. Explor. 4:349-363.

Chapman, W.H., H.L. Fisher, and M.W. Pratt. 1968. Concentration factors of chemical elements in edible aquatic organisms. Lawrence Radiation Laboratory, Livermore, Calif. UCRL-50564. 46p.

Chipman, W.A., T.R. Rice, and T.J. Price. 1958. Uptake and accumulation of radioactive zinc by marine plankton, fish, and shellfish. pp.279-291. U.S. Fish and Wildlife Service Fishing Bulletin 135, Vol. 58. Washington, D.C. 459p.

Cotton, F.A. and A. Wilkinson. 1972. Advanced inorganic chemistry. pp.600-610. Interscience Publishers. New York. 1145p.

DeGroot, A.J. and E. Allersma. 1975. Field observations on the transport of heavy metals in sediments. pp. 85-95. in Heavy metals in the aquatic environment. P.A. Krenkel (ed.). Pergamon Press, Oxford, England. 352p.

Duke, T.W. 1967. Possible routes of zinc-65 from an experimental estuarine environment to man. J. Water Pollut. Control Fed. 39(4):536-541.

Grimshaw, D.L., J. Lewin, and R. Fuge. 1976. Seasonal and short-term variations in the concentration and supply of dissolved zinc to polluted aquatic environments. Environ. Pollut. 11:1-7.

Guy, R.D., C.L. Chakrabarti, and L.L. Schramm. 1975. The application of a simple chemical model of natural waters to metal fixation in particulate matter. Can. J. Chem. 53:661-669.

Guy, R.D. and C.L. Chakrabarti. 1976. Studies of metal-organic interactions in model systems pertaining to natural waters. Can. J. Chem. 54:2600-2611.

Helz, G.R., R.J. Huggett, and J.M. Hill. 1975. Behavior of Mn, Fe, Cu, Zn, Cd and Pb discharged from a wastewater treatment plant into an estuarine environment. Water Res. 9:631-636.

Hem, J.D. 1972. Chemistry and occurrence of cadmium and zinc in surface water and groundwater. Water Resource Res. 8(3):661-679.

Holmes, C.W., E.A. Slade, and C.J. McLerran. 1974. Migration and redistribution of zinc and cadmium in a marine-estuarine system. Environ. Sci. Technol. 8(3):255-259.

Huang, C.P., H.A. Elliott, and R.M. Ashmead. 1977. Interfacial reaction and the fate of heavy metals in soil-water systems. J. Water Pollut. Control Fed. 49(5):745-756.

Jackson, K.S. and G.B. Skippen. 1978. Geochemical dispersion of heavy metals via organic complexing: a laboratory study of copper, lead, zinc and nickel behavior at a simulated sediment-water boundary. J. Geochem. Explor. 10:117-138.

James, R.O. and M.A. MacNaughton. 1977. The adsorption of aqueous heavy metals on inorganic minerals. Geochim. Cosmochim. Acta. 41:1549-1555.

Joyner, T. 1961. Exchange of zinc with environmental solutions by the brown bullhead. Trans. Am. Fish. Soc. 90:444-448.

Kimball, K.D. 1973. Seasonal fluctuations in ionic copper in Knight's Pond, Massachusetts. Limmol. Oceanogr. 18(1):169-172.

Kubota, J., E.L. Mills, and R.T. Oglesby. 1974. Lead, Cd, Zn, Cu and Co in streams and lake waters of Cayuga Lake Basin, New York. Environ. Sci. Technol. 8(3):243-248.

Lee, G.F. 1975. Role of hydrous metal oxides in the transport of heavy metals in the environment. pp.137-147. in Heavy metals in the aquatic environment. P.A. Krenkel (ed.). Pergamon Press, Oxford, England. 352p.

Long, D.T. and E.E. Angino. 1977. Chemical speciation of Cd, Cu, Pb, and Zn in mixed freshwater, seawater and brine solutions. Geochim. Cosmochim. Acta. 41:1183-1191.

Luoma, S.N. and E.A. Jenne. 1977. Availability of sediment-bound cobalt, silver, and zinc to a deposit-feeding clam. pp.213-231. in Biological implications of metals in the environment. H. Ducker and R.E. Wildung (eds.). NTIS CONF-750929. Springfield, Va. 682p.

Namminga, H. and J. Wilhm. 1977. Heavy metals in water, sediments, and chironomids. J. Water Pollut. Control Fed. 49(7):1725-1731.

Nelson, J.L. and W.L. Hauschild. 1970. Accumulation of radionuclides in bed sediments of the Columbia River between the Hanford reactors and McNary Dam. Water Resources Res. 6(1):130-137.

Patrick, F.M. and M. Loutit. 1975. Passage of metals in effluents through bacteria to higher organisms. Water Res. 10:333-339.

Patterson, J.W., H.E. Allen, and J.J. Scala. 1977. Carbonate precipitation for heavy metal pollutants. J. Water Pollut. Control Fed. 49(12):2397-2410.

Perhac, R.M. 1972. Distribution of Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn in dissolved and particulate solids from two streams in Tennessee. J. Hydrol. 15:177-186.

Perhac, R.M. 1974a. Water transport of heavy metals in solution and by different sizes of particulate solids. Univ. of Tenn. Water Resource Res. Ctr., Project No. 023. Knoxville, Tenn. 41p.

Perhac, R.M. 1974b. Heavy metal distribution in bottom sediments and water in the Tennessee River-Loudon Lake reservoir system. Univ. of Tenn. Water Resources Res., Ctr. Report No. 40, Knoxville, Tenn. 22p.

Phillips, A.R. and R.C. Russo. 1978. Metal bioaccumulation in fishes and aquatic invertebrates pp.60-67. U.S. Environmental Protection Agency, (ERL), Duluth, Minn. 115p. (EPA-600/3-78-103).

Pita, F.W. and N.J. Hyne. 1975. The depositional environment of zinc, lead, and cadmium in reservoir sediments. Water Res. 9:701-707.

Prasad, A.S. 1967. Nutritional metabolic role of zinc. Fed. Am. Soc. Exp. Biol. Proc. 26(1):172-185.

Rashid, M.A. 1974. Adsorption of metals on sedimentary and peat humic acids. Chem. Geol. 13:115-123.

Rehwoldt, R., D. Karimian-Teherami, and H. Altmann. 1975. Measurement and distribution of various heavy metals in the Danube River and Danube Canal aquatic communities in the vicinity of Vienna, Austria. Sci. Total Environ. 3:341-348.

Steele, K. F. and A. H. Wagner. 1975. Trace metal relationships in bottom sediments of a freshwater stream - the Buffalo River, Arkansas. J. Sediment. Petrol. 45(1):310-319.

Stumm, W. and J.J. Morgan. 1970. Aquatic chemistry. Wiley-Interscience, New York. 583p.

Weast, R.C. (ed.). 1977. CRC handbook of chemistry and physics, 58th edition. CRC Press, Cleveland, Ohio. 2398p.

Weatherley, A.H. and P. Dawson. 1973. Zinc pollution in a freshwater system: analysis and proposal solution. Search. 4(11-12):471-476.

SECTION III: PESTICIDES

Chapters 20-35

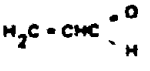
20. ACROLEIN

20.1 Statement of Probable Fate

Literature information indicates that acrolein will be removed from aqueous environments, with half-lives usually on the order of less than a day. The primary loss process appears to be an initial hydration (and possibly some biotransformation) to 3-hydroxypropionaldehyde, which is then biotransformed. Photolysis, oxidation, and volatilization may also be important processes, but no data were available to assess whether these processes will be faster than the hydration-biotransformation sequence.

20.2 Identification

This discussion considers only the fate of the molecular species of acrolein, and not commercial acrolein preparations. Literature information indicates that high concentrations of acrolein in aqueous solution may be "polymerized" by oxidation or hydration processes (see Section 20.4.8). The structure, alternate names, CAS and TSL numbers are as follows:



Alternate Names

1-Propanal
Acraldehyde
Acrylic aldehyde
Allylaldehyde
Acrylaldehyde

Acrolein

CAS No. 107-02-8
TSL No. AS 10500

20.3 Physical Properties

The general physical properties of acrolein are as follows.

Molecular weight	56.06
Melting point (Verschueren 1977)	-87.7°C

Boiling point at 760 torr (Verschueren 1977)	52.5°C
Vapor pressure (Verschueren 1977)	220 torr at 20°C 330 torr at 30°C
(Smith 1962)	215 torr at 20°C 269 torr at 25°C
Solubility in water at 20°C (Martin 1972)	given as 20.8% soluble in water
Log octanol/water partition coefficient (Radding et al. 1977)	-0.090

20.4 Summary of Fate Data

20.4.1 Photolysis

No information on the photolysis of acrolein in aquatic systems was found.

Acrolein has a moderate uv absorption in the solar spectral region, with the following data reported for acrolein in hexane (uv Atlas 1966).

λ max (nm)	$\varepsilon(M^{-1}cm^{-1})$
303	9.7
328	18.5
336	21.0
360	13.5
386	5.0

Buswell et al. (1940) reported that freshly prepared acrolein solutions showed a moderate extinction coefficient in water at 320 nm; this coefficient decreased after the solution was allowed to stand for several weeks. Concommitant with this loss of uv absorption at 320 nm was the significant growth of a new band at 267 nm. No conclusion was made as to the process(es) occurring, but the authors suggested that oxidation or polycondensation of acrolein in the presence of water gave a polymeric material without the α,β-unsaturated carbonyl chromophore (see also Sections 20.4.8). Oxidation was suggested as the causative process since

the presence of hydroquinone slightly retarded the disappearance of the 320-nm absorption in aqueous solution; the formation of the acrolein hydration product, 3-hydroxproprionaldehyde, was not discussed.

Studies of the gas phase photolysis of acrolein suggest that it may be photoreactive in the solar spectral region (> 300 nm) but no information on the aqueous solution phase chemistry is available. Coomber and Pitts (1969) studied the gas-phase photolysis of acrolein at 313 nm; the product quantum yields measured for the major products, carbon monoxide and ethylene, were ~ 5×10^{-3} and ~ 3×10^{-3}, respectively. The low quantum yield and moderate absorption spectrum of acrolein indicate that direct photolysis of acrolein in the atmosphere should not be rapid.

20.4.2 Oxidation

No information on the oxidation of acrolein in aqueous systems was found. The importance of acrolein loss due to polymerization via oxidation (free radical) mechanisms is unlikely at the highly dilute acrolein concentrations in the aquatic environment.

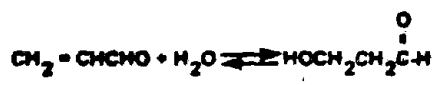
Carmier and Deglise (1973) reported a rate constant of 1.6×10^{3} M^{-1} sec^{-1} for reaction of singlet oxygen at the double bond of acrolein at -10°C in methanol solvent; Zepp et al (1978) have reported a maximum concentration of 2×10^{-12}M singlet oxygen when several natural water samples were irradiated in sunlight in the presence of a chemical model compound known to undergo singlet oxygen reactions. Using this concentration of singlet oxygen, and assuming that the rate constant is temperature independent between -10°C and an environmental temperature of about 20°C, a half-life of about 6 years is calculated. Using a rate constant of 0.1 $M^{-1}sec^{-1}$ for reaction of alkylperoxyl radical with the hydrogen atom on the aldehyde carbonyl group and an ambient alkylperoxyl radical concentration of about 10^{-9}M, the half-life for this oxidation process is calculated to be over 20 years (Mill 1979). It should be noted that hydration of either the double bond or carbonyl groups of acrolein will change the reactivity of the respective oxidation processes, making these oxidations even less important.

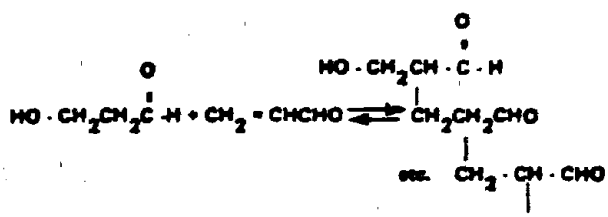
The half-life for oxidation of acrolein in the atmosphere by hydroxyl radical is about 2 days; this half-life is based on a hydroxyl radical-acrolein rate constant of 9×10^{9} M^{-1} sec^{-1} (Radding et al. 1977) and an ambient atmospheric radical concentration of 10^{-15} M.

20.4.3 Hydrolysis

Acrolein contains no hydrolyzable groups that lead to environmental transformations. The hydration of acrolein to form 2-hydroxypropanal is not a hydrolysis process since the reaction is reversible.

Similarly, the polycondensation of acrolein in the presence of water is not a hydrolysis process since it is also potentially reversible.





20.4.4 Volatilization

No specific studies on the volatilization of acrolein from aquatic systems have been reported. Bowmer and coworkers (see Section 20.4.8) have implicated volatilization as a possible process in explaining a ten-fold greater loss of acrolein in field studies compared to a prediction by modelling studies. Another study (Battelle 1970), however, discounts the importance of volatilization in a similar field study. Neither study presents any data to substantiate the significance of volatilization. The application of the equations of Mackay and Leinonen (1975) to predict volatilization are not appropriate since acrolein is very soluble in water.

20.4.5 Sorption

No data are available to assess the importance of acrolein sorption on sediments or onto biota in aquatic systems. Bowmer and Higgins (1976) implicate sorption along with volatilization as possible important processes to explain the discrepancy between modelling and field studies, but no data were given to support such processes (see Section 20.4.4). The high water solubility and low partition coefficient of acrolein suggest that sorption is not an important process in aquatic systems.

20.4.6 Bioaccumulation

No information on bioaccumulation of acrolein was found. The small partition coefficients (octanol/water) indicates that bioaccumulation of acrolein will not be significant in aquatic systems.

20.4.7 Biotransformation and Biodegradation

No data were found regarding biotransformation of acrolein in aquatic systems.

Brink (1975) found that the presence of up to 3 mg/liter acrolein in sewage sludge did not effect the sludge unit efficiencies or the BOD, COD, TDC, pH, and dissolved oxygen compared to a control system with acrolein. Wierzbicki and Wojcik (1965) have found that activated sludge effectively transforms acrolein at less than 2300 ppm, but no other information was provided. Larson (1967) has also stated that acrolein can be biologically oxidized in refinery systems.

Experiments of Bowmer and Higgins (1976) (see Section 20.4.8) suggest that biotransformation may occur in aquatic systems since the rate constant for loss of acrolein in supply water samples from an irrigation area was reduced from 2.37×10^{-2} hr^{-1} to 1.59×10^{-2} hr^{-1} when thymol was added to suppress biological activity ($t_{1/2}$ of 29 hr and 43 hr, respectively); the latter half-life was the same as that observed for acrolein in buffered distilled water at the same pH. However, acrolein in irrigation drainage water samples containing thymol had a half-life of three times longer that in buffered sterile solutions; hence biotransformations occurring in these systems are probably variable. The authors also indicate they believe that unknown catalysts in the natural waters are responsible for a more rapid loss of acrolein, but no evidence other than the first-order kinetic data was provided. Bowmer and Higgins also noted that the pH dropped more markedly in experiments where higher initial concentrations of acrolein were used (range was 6.0 to 50.5 ppm), and they suggested that carboxylic acids were formed as products.

20.4.8 Other Reactions

Burczyk et al. (1968) studied the kinetics of reversible hydration of acrolein in distilled water to form β-hydroxypropionaldehyde, as shown below. Using an equilibrium constant K of 21.2 (Smith et al. 1962), these

$$CH_2=CHCHO + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} HOCH_2CH_2CHO \qquad K = \frac{k_1}{k_2}$$

authors calculated a pseudo-first order rate constant [$k_1[H_2O]$] of 0.032 day^{-1} for hydration of acrolein in water; the calculated half-life for hydration of acrolein is then 21 days. The equilibrium constant of 21.2 further indicates that the acrolein will be ~ 95% in the hydrated form once equilibrium is established.

Bowmer and Higgins (1976) studied the loss of acrolein in buffered water in the pH region 5 to ~ 8.5, where acrolein half-lives of 69 and 34 hours, respectivelv, were measured; presumably the losses were due to hydration* (see also Section 20.4.9). In distilled water Bowmer and Higgins obtained a rate constant for "acrolein decay" of 2.7×10^{-3} hr^{-1}, or a half-life of about 11 days (no pH reported).

There is no clear explanation to rationalize the two-fold difference in hydration rates in distilled water between the data of Burczyk et al. and the data of Bowmer and Higgins. The more rapid loss of acrolein from the experiments in buffered water and one experiment in natural water do suggest that hydration may be catalyzed by other agents, but more definitive experiments are necessary. The hydration of acrolein has been shown to be catalyzed at high acid concentrations (Hall and Stern 1950; Pressman and Lucas 1942) with polycondensation catalyzed at high base concentrations (Gilbert and Donleavy 1938).

It is of interest that while all studies on the hydration of acrolein have focused on the addition of water to the double bond of acrolein, aldehydes are also known to hydrate at the carbonyl group to give gem-diols (two hydroxyl groups on the same carbon). Data of Bell (1966) show that acetaldehyde is 60 percent hydrated in aqueous solution, and that electron withdrawing groups (such as the acrolein double bond) favor more extensive

---

*In all papers by Bowmer and coworkers, the aldehyde in solution was determined by colorimetric procedure using 2,4-dinitrophenylhydrazine (DNPH); the procedure was developed by Shell Chemical Company. Acrolein concentration was determined by the difference in total aldehyde measurement between two solutions, one of which had been purged with air. The acrolein was considered to have been removed by purging, leaving a non-volatile "degraded acrolein" product. The authors did not characterize this product, but is presumably as the hydrated or polycondensed acrolein (or both), which does maintain all the aldehydic groups intact and susceptible to the DNPH procedure (see Section 20.4.3).

hydration. There is no information to assess the relative rates or extent of hydration of acrolein at the two possible hydration positions. Hydration will, however, change the reactivity of acrolein toward oxidation (see 20.4.2), destroy the carbonyl chromophore responsible for any photolysis, and possibly change the ease of biotransformation. Hydration will also change the physical properties of acrolein in water from those expected based on the structure and properties of acrolein itself.

20.4.9 Microcosm Studies, Field Studies, and Modelling

Bartley and Gangstad (1974) monitored the dissipation of acrolein in a canal as a function of distance. Initial acrolein concentrations of 100 ppb were reduced to 90 ppb, 50 ppb, and 30 ppb at 5, 10, and 20 miles downstream. No data for specific transformation, transport or dilution processes in the canal were given, and the authors state only that "very low levels" of acrolein persist downstream of the application site.

Bowmer and coworkers reported laboratory and field studies on acrolein (Bowmer and Higgins 1976; O'Loughlin and Bowmer 1975; Bowmer et al. 1974). In the 1974 paper they reported that acrolein in bottles and in a large tank of water (sterility or quality of water was not described) disappeared much faster when determined by bioassay or gas-purging methods than when the water was analyzed directly by colorimetric methods using the dinitrophenyl hydrazine [DNPH] procedure (see Section 20.4.8). The authors concluded that acrolein was "degraded" to a nonvolatile, nonphytotoxic (less than 0.1 times as toxic as acrolein) product that gave a positive DNPH test. They also reported that acrolein disappearance in their experiments had a first-order rate constant of 0.83 day^{-1} ($t_{1/2}$ = 0.83 day). This loss rate was much faster than that predicted due to hydration alone (see Section 20.4.8); furthermore, no equilibrium concentration of acrolein with hydrated acrolein was found. No specific loss processes other than hydration were discussed, except that volatilization was determined to be much less important than "degradation" in these experiments. The 1975 paper extended the acrolein studies to evaluations using a one-dimensional model, with field studies used to measure "decay rate constants" for acrolein of 0.14 to 0.21 hr^{-1} ($t_{1/2}$ of 5 to 3.3 hours, respectively). The subsequent 1976 paper reported studies of acrolein loss in buffered and natural waters in the laboratory and in field studies. Although an equilibrium concentration of acrolein was found in the buffered waters (see Section 20.4.8) no equilibrium acrolein concentrations were found in the natural waters where all acrolein was eventually lost. The rate of loss of acrolein in these natural waters was 1.5 to 3 times faster than that in buffered water. Addition of thymol to suppress biological activity did decrease the rate of loss of acrolein in the natural waters so that it was similar to the rate in sterile buffered water in one experiment; another natural water experiment containing thymol, however, showed an acrolein

loss rate that was still three times faster than that in buffered water. Thus, hydration and biodegradation seem to be important removal processes for acrolein. Bowmer and Higgins further suggest that substances in natural waters may be catalyzing the "decay" process (presumably referring to hydration) so that it is faster than the reaction in distilled water. The papers by Bowmer and coworkers do not, however, attempt to identify acrolein products other than by the 2,4-DNPH test which is useful only for analyzing for total carbonyl.

Bowmer and Higgins (1976) also monitored the kinetics of the loss of the acrolein "degradation product," and found that although it was stable in buffered waters, the loss in supply waters was consistent with the "lag phase" character of microbiological processes, with a lag phase time of ~ 100 hours from addition of acrolein to the water.

20.5 Data Summary

Table 20-1 summarizes the data on the aquatic fate of acrolein.

Table 20-1

Summary of Aquatic Fate of Acrolein

Environmental Process [a]	Summary Statement	Rate	Half-Life $t_{\frac{1}{2}}$	Confidence of Data
Photolysis	May be important process.	-	-	Medium
Oxidation	Oxidation is slow.	-	> 6 yrs.	High
Hydrolysis	Not an important process.	-	-	High
Volatilization	May be important process.	-	-	Medium
Sorption	Not an important process.	-	-	Medium
Bioaccumulation	Not an important process.	-	-	Medium
Biotransformation/ Biodegradation	Is an important process. [b]	-	< 4 days	Medium

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Literature data suggest that acrolein may undergo reversible hydration of acrolein to a product which is readily biotransformed. Some experiments show a half-life of about 3-5 hours for acrolein.

20.6 Literature Cited

Bartley, T., and E.O. Gangstad. 1974. Environmental aspects of aquatic plant control. J. of the Irrigation and Drainage Division-ASCE. 100:231-244.

Battelle 1970. Information supplied by EPA.

Bell, R.P. 1966. The reversible hydration of carbonyl compounds. Adv. Phys. Org. Chem. 4:1-29.

Bowmer, K.H., and M.L. Higgins. 1976. Some aspects of the persistence and fate of acrolein herbicide in water. Arch. Environ. Contam. Tox. 5:87-96.

Bowmer, K.H., A.R.G. Lang, M.L. Higgins, A.R. Pillay, and Y.T. Tchan. 1974. Loss of acrolein from water by volatilization and degradation. Weed Research 14:325-328.

Brink, R. H., Jr. 1975. Studies with chlorophenols, acrolein, dithiocarbamates and dibromonitrilopropionamide in bench-scale biodegradation units. Proc. Int. Biodegradation Symp., 3rd. 1975 (Pub. 1976) 785-91. CA87:90236.

Burczyk, L., K. Walczyk, and R. Burczyk. 1968. Kinetics of reaction of water addition to the acrolein double-bond in dilute aqueous solution. Przem. Chem. 47(10):625-627.

Buswell, A.M., E.C. Dunlop, W.H. Rodebush, and J.B. Swartz. 1940. Change of the ultraviolet absorption spectrum of acrolein with time. J. Amer. Chem. Soc. 62(2):325-8.

Carmier, J.C., and X. Deglise. 1973. Kinetic study of the photosensitized oxidation of α,β-unsaturated aldehydes in the liquid phase at -10°C. C.R. Acad. Sci., Ser. C 277(22):1187-1189.

Coomber, J.W., and J.N. Pitts, Jr. 1969. Molecular structure and photochemical rectivity. XII. The vapor-phase photochemistry of acrolein at 3130 Å. J. Amer. Chem. Soc. 91(3):547-550.

Gilbert, E. E., and J.J. Donleavy. 1938. The polycondensation of acrolein. J. Amer. Chem. Soc. 60:1911-1914.

Hall, R.H., and E.S. Stern. 1950. Acid-catalyzed hydration of acraldehyde. Kinetics of the reaction and isolation of β-hydroxypropaldehyde. J. Chem. Soc.:490-498.

Larson, R.G. 1967. Biological treatment in water conservation. Amer. Chem. Soc., Div. Petrol. Chem., Preprints 12(4):A63-A70.

Mabey, W.R., and T. Mill. 1976. Kinetics of hydrolysis and oxidation of organic pollutants in the aquatic environment. Symp. on nonbiological transport and transformation of pollutants on land and water: Processes and critical data required for predictive description. May 11-13, 1976.

Mackay, D., and P.J. Leinonen. 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Tech. 9(13):1178-1180.

Martin, H. (ed.). 1972. Pesticide manual, 3rd edition. British Crop Protection Council, Worcester, Engl.

Mill, T. 1979. Structure reactivity correlations for environmental reactions. EPA Final Report EPA 560/11-79-012.

O'Loughlin, E.M., and K.H. Bowmer. 1975. Dilution and decay of aquatic herbicides in flowing channels. J. Hydrol. 26(3-4):217-35.

Pressman, D., and H.J. Lucas. 1942. Hydration of unsaturated compounds. XI. Acrolein and acrylic acid. J. Amer. Chem. Soc. 64:1953-1957.

Radding, S.B., D.H. Liu, H.L. Johnson, and T. Mill. 1977. Review of the environmental fate of selected chemicals. U.S. Environmental Protection Agency Report No. EPA-560/5-77-003.

Smith, C.W. (ed.). 1962. Acrolein. John Wiley and Sons, Inc., New York.

UV Atlas. 1966. Plenum Press.

Verschueren, K. 1977. Handbook of environmental data on organic chemicals. Van Nostrand Reinhold Company. 659 pp.

Wierzbicki, T., and O. Wojcik. 1965. Preliminary trials on the decomposition of acrolein, allyl alcohol, and glycerol by activated sludge. Zesz. Nauk. Politech. Slaska, Inz. Sanit. (8):173-85, via Chemical Abstracts 68:1589z (1968).

Zepp, R. G., N. L. Wolfe, G. L. Baughman, and R. C. Hollis. 1978. Singlet oxygen in natural water. Nature 278:421.

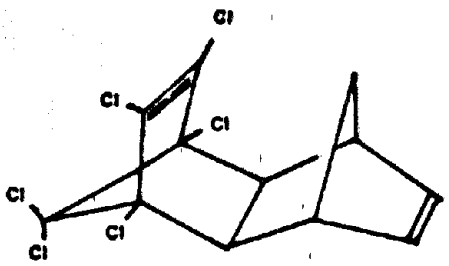
21. ALDRIN

21.1 Statement of Probable Fate

Biotransformation, volatilization, bioaccumulation, and indirect photolysis all may be important fate processes for aldrin introduced into aquatic environments. Volatilization half-lives of less than a few days are likely in aquatic systems when sorption to biota and subsequent biotransformation to dieldrin do not occur rapidly. Photosensitized and photooxidation processes may also be important fates for aldrin, but insufficient information is available to assess how general and reliable these processes are for environmental assessments.

21.2 Identification

This chapter considers aldrin as the pure chemical. The structure, alternate names, CAS and TSL numbers for aldrin are given below:



Alternate Names

Aldrin
1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-dimethanonaphthalene
HHDN
Compound 118
Octalene

Aldrin

CAS No. 309002
TSL No. IO 21000

21.3 Physical Properties

The general physical properties of aldrin are given as follows.

Molecular weight	365
Melting point (Martin 1972)	104-104.5°C

Boiling point at 760 torr	No data found
Vapor pressure	
(Martin 1972)	2.31×10^{-5} torr at 20°C
(Gunther and Gunther 1971)	6×10^{-6} torr at 25°C
Solubility in water	
(Park and Bruce 1968)	27 ppb at 25-29°C
(Weil 1974)	17 ppb at 25°C
(Biggar and Riggs 1974)*	180 ppb at 25°C
Log octanol/water partition coefficient	No data found

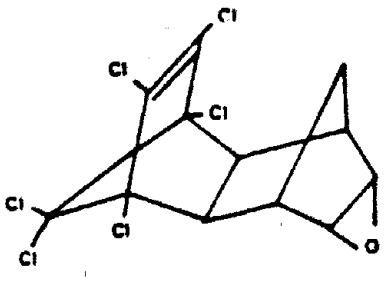
*Particle size < 5.0 μm.

21.4 Summary of Fate Data

21.4.1 Photolysis

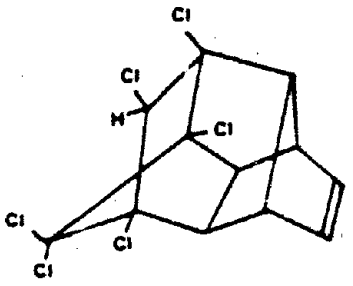
No data are available to estimate the direct photolysis rate constant for aldrin in aquatic systems, although two experiments suggest direct photolysis may be slow compared to indirect photolysis in aquatic environments.

Ross and Crosby (1975) examined the photolysis of aldrin in aqueous solutions containing acetone or acetaldehyde and in a sterile paddy water example. Although photolyses were performed with a sunlamp with wavelengths > 300 nm and in sunlight, the information and data presented in the paper do not specify which irradiation source was used. Therefore, no quantitative estimate of aldrin photolyses in aquatic environments can be made. The authors reported that irradiation of aldrin in demineralized water for 10 hours produced no loss of aldrin. Photolyses of aldrin for 1 hour in water containing 0.1 percent acetone or acetaldehyde gave 22 percent and 24 percent yields, respectively, of dieldrin (I); in the paddy water, a 25 percent yield of dieldrin was obtained after 36 hours irradiation. Unlike other photolyses of aldrin (see below), these photolyses did not give photoaldrin (II), a cage-type product. The authors concluded that photochemically generated oxidants were responsible for aldrin conversion to dieldrin.



I

Dieldrin



II

Photoaldrin

Singmaster (1975) reported that the photolysis of 0.33 ppb of aldrin in a sample of San Francisco Bay water gave a half-life of 1.1 day in sunlight. In contrast to the products observed by Ross and Crosby (1975), the photolysis product in Singmaster's study was determined not to be dieldrin; the product corresponded to the retention time of photoaldrin in the glpc analysis.

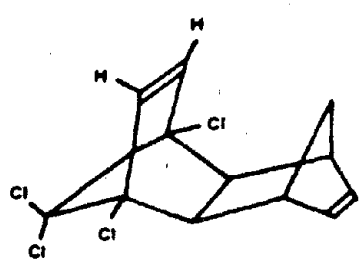
Other studies of the photolysis of aldrin have been reported, but the reaction conditions used are not relevant to aquatic systems. A brief discussion of these experiments is useful, however, to describe the products of the reactions and to further demonstrate the possible importance of photosensitized processes in aldrin reactions.

Ivie and Casida (1971a) examined the sunlight photolysis of aldrin on silica gel plates in the presence of a number of photosensitizers. Although no clear correlation between loss of aldrin and the triplet energies of the sensitizers was found, most sensitizers with energies above ~ 50 kcal/mole did show some sensitization in aldrin conversion; the product of the reactions apparently was photoaldrin. A subsequent paper (Ivie and Casida 1971b) reported that rotenone codeposited with aldrin on bean leaves and exposed to sunlight was also effective in sensitizing photolysis of aldrin; both photoaldrin and photodieldrin were found as products.

Rosen and Carey (1968) reported that photoaldrin was formed in a 77 percent yield when aldrin was photolyzed at 268-356 nm in benzene solution in the presence of the sensitizer benzophenone. Rosen and Sutherland (1967) reported the sunlight photolysis of an aldrin film in a glass dish. At the end of one month's photolysis (mid-June to mid-July) the reaction mixture contained 2.6 percent aldrin, 4.1 percent dieldrin, 24.1 percent

photodieldrin, 9.6 percent photoaldrin, and 59.7 percent polymeric material. Analysis of a film of aldrin exposed to 3 days of sunlight in early June showed approximately 13 percent aldrin remaining, with 31 percent dieldrin, 7 percent photodieldrin, 1 percent photoaldrin, and 40 percent polymeric material formed (see Chapter 26 on dieldrin for discussions on photodieldrin).

Henderson and Crosby (1967) found that the dechlorinated aldrin isomer III was the major photolysis product of aldrin in hexane solvent



III

irradiated at 254 nm; the same product was also obtained in methanol and cyclohexane solvents. Rosen (1967) found a 24 percent yield of II and 13 percent yield of III when solid aldrin was photolyzed at 254 nm, with 9 percent aldrin recovered; the remainder of the material was described as a polymer. Gäb et al. (1974) photolyzed aldrin in the solid phase using a high pressure Hg lamp with pyrex filter (> 300 nm) and found small amounts of photoaldrin, dieldrin, HCl, and CO_2; most of the material recovered was identified as a polymer. Roburn (1963) found that a film of aldrin irradiated at 254 nm gave dieldrin as the major product.

Since volatilization of aldrin from water bodies appears to be an important process, Crosby and Moilanen (1974) studied the vapor phase photolyses of aldrin. Photolysis of aldrin at concentrations below saturation in the vapor phase for 168 hours with a sunlamp resulted in a 40 percent recovery of aldrin and a 63 percent yield of dieldrin, with about 2 percent yields each of photoaldrin and photodieldrin; in a dark control experiment 84 percent of the aldrin was recovered and a yield of 14 percent dieldrin was measured. The authors attributed the presence of dieldrin in the dark control as being due to contamination problems. Other photolysis experiments with aldrin at saturation in the vapor phase also gave photoaldrin and dieldrin as products. Although these studies indicate that aldrin pho-

tolysis may occur in the atmosphere, no data are available to predict how fast the photoreactions will occur.

21.4.2 Oxidation

Although photooxidation processes are important in the formation of dieldrin from aldrin, no data are available to assess the half-lives for oxidation processes in aquatic environments (see Section 21.4.1).

In studies on the photooxidation of aldrin to dieldrin, Ross and Crosby (1975) found that aldrin was not oxidized by singlet oxygen. They did find that peracetic acid oxidized aldrin to dieldrin in the dark, but no information is available to predict how fast such peroxide oxidations might be in aquatic environments.

Hoffman and Eichelsdoerfer (1971) found that some ozone readily oxidized aldrin to dieldrin in hexane and in 10 percent acetone in water solvents. Saravanja-Bozanic et al. (1977) reported that oxygen atoms oxidize aldrin to dieldrin, but no data are available to predict the rates at which this oxidation process may occur in the atmosphere.

21.4.3 Hydrolysis

No information is available on the hydrolysis of aldrin in aquatic systems; hydrolysis of aldrin is not expected to be important, however, since the chlorine groups are located at bridgehead and vinylic positionson the aldrin structure, and these positions are not readily hydrolyzable. Hydrolysis half-lives of many years are probable. Eichelberger and Lichtenberg (1971) found that aldrin was 80 percent converted to dieldrin in a sample of raw river water in 8 weeks; these results suggest that biotransformation is probably more rapid than hydrolysis in aquatic environments.

21.4.4 Volatilization

Volatilization of aldrin from aquatic systems is an important process, with half-lives on the order of a few hours to a few days.

Singmaster (1975) described studies designed to measure relative rates of volatilization of chlorinated pesticide from pure water and several natural waters. In these experiments approximately 1 pptr concentrations of pesticides in 900 ml of water in a 5-liter flask were gently agitated on a shaker while air was drawn through the flask (but not bubbled through solution) at a rate of 4.5 l/min. The half-lives for volatilization of aldrin from pure water and waters from San Francisco Bay, the American River, and Sacramento River (all in California) were 0.38 hour, 0.59

hour, 0.60 hour, and 0.60 hour, respectively; the water loss in these experiments averaged 3.6 ± 0.2 g/hr. Singmaster concluded that volatilization of aldrin in natural waters would not be more than two times slower than in pure water. Although the total experiment is difficult to relate to conditions in aquatic environments (e.g., temperature, agitation), the author noted that the air exchange in the flask corresponded to a wind velocity of about 10 m/hr, which is much lower than the velocity usually found in the environment. Based on the wind velocity factor alone and assuming removal of aldrin from the vapor space is the dominant force in volatilization of aldrin, the half-lives for volatilization of aldrin in aquatic environments could be on the order of a few hours.

Mackay and Wolkoff (1973) and subsequently Mackay and Leinonen (1975) described equations for calculating volatilization rates of chemicals based on mass transfer data; the calculated half-life for volatilization of aldrin was 7.7 days. In their calculation, Mackay and coworkers used 200 ppb as the water solubility of aldrin, and as seen in Section 21.3, this value is about an order of magnitude higher than two other measured values. If the lower values of aldrin solubility are used, the calculated volatilization half-life would be approximately an order of magnitude shorter than the value calculated by Mackay and coworkers, or about 1 day.

Additional evidence for the rapid volatilization of aldrin has also been obtained in volatilization studies performed by Ernst (1977) preparatory to conducting bioaccumulation measurements. In aerated aquaria containing seawater and various pesticides, Ernst observed a 97 percent loss of aldrin, compared to losses of 11 percent for dieldrin and 67 percent for DDT.

21.4.5 Sorption

Very few data are available to evaluate the importance of sorption of aldrin to sediments in aquatic environments. Kenaga and Goring (1978) cite a K_{OC} value for aldrin of 410, which suggests that sorption of aldrin to sediments will not be extensive in aquatic systems. Sorption will eventually remove aldrin from aquatic systems if biological processes do not occur, however.

Leshniowsky et al. (1970) studied sorption of aldrin by bacterial floc and by a lake sediment. The authors found that aldrin equilibrium between water and floc was attained in about 20 minutes, with a concentration factor of 625; it was not stated whether the concentration factor was based on a wet- or dry-weight basis. Equilibrium of aldrin between sediment (silt) and water was attained in 10 minutes, but no partition coefficient was given.

Yaron et al. (1967) studied the adsorption of aldrin on soils, clays, and sands. Less aldrin was adsorbed in sand than on clays; more aldrin was sorbed by a soil with 6 percent organic matter than the same soil with the organic matter removed by oxidation. Unfortunately, the authors did not analyze and present their data in a manner that is useful for estimating sorption coefficients for environmental assessment applications.

21.4.6 Bioaccumulation

The results of terrestrial-aquatic microcosm experiments indicate that bioconcentration factors for aldrin in aquatic systems will be approximately 10^3 - 10^4. Although biouptake may then be an important process for aldrin in short time periods, significant bioaccumulation of aldrin through the food chain will probably not occur because it is quite rapidly converted in dieldrin.

In terrestrial-aquatic microcosm experiments, Metcalf et al. (1973) measured bioconcentration factors of 3.9×10^4, 4.5×10^4, and 3.1×10^3 for alga, snail, and fish, respectively. Given the presence of large amounts of dieldrin in these species (see Section 26.4.6), these factors may be low, because metabolism of aldrin to dieldrin may also be a process competing with uptake/depuration in the species studies.

Metcalf et al. (1973) conducted separate experiments in which Daphnia, mosquito larvae, and fish were exposed to aldrin by water contact only (no food chain). Bioconcentration factors for the fish ranged from 260 to 460 between the first and third days of exposures. Values for the Daphnia ranged from 1800 to 9100, and for the larvae from 970 to 1100.

Schauberger and Wildman (1977) reported aldrin concentrations in two species of blue-green algae that were 1×10^3 and 1.3×10^3 times the initial aldrin concentrations of the solutions in which they were grown; a third algae failed to accumulate aldrin, but rather effected epoxidation to give dieldrin.

21.4.7 Biotransformation and Biodegradation

Although biotransformation of aldrin to dieldrin is probably the dominant transformation process in aquatic systems, there are no useful data for predicting the rate at which aldrin epoxidation may occur in the environment.

The rapid transformation of aldrin to dieldrin in vivo has been shown by Bowman et al. (1964), who introduced aldrin into solutions containing mosquito larvae. Some aldrin, but no dieldrin, was recovered from

the solution phase after 20 hours at 27°C; however, in the larvae dieldrin predominated over aldrin by factors of 10:1 and 1.6:1 for initial aldrin concentrations of 24 and 270 ppb, respectively.

Eichelberger and Lichtenberg (1971) examined the persistence of aldrin in raw water from the Little Miami River for 8 weeks; at the end of 1, 2, 4, and 8 weeks, the percentages of aldrin remaining were 100, 80, 40, and 20 percent, respectively. Since dieldrin was the product of the reaction, biotransformation was probably occurring.

Metcalf et al. (1973) also found extensive conversion of aldrin to dieldrin in terrestrial-aquatic microcosm experiments, where ^{14}C-aldrin was introduced into microcosm in the terrestrial compartment and the aldrin or aldrin metabolites were subsequently transported to the aqueous phase by several pathways. Of the ^{14}C material recovered from alga, snail, mosquito larvae, and fish, dieldrin was the major compound found, and was present as 86 percent, 92 percent, 97 percent, and 96 percent, respectively, of the total ^{14}C label. The largest percentage of ^{14}C-aldrin in any of the four organisms was 10 percent in the alga. Other metabolites were also present in the four organisms at less than 4 percent of the total ^{14}C; these metabolites were tentatively identified by the retention times as 9-hydroxydieldrin, 9-ketodieldrin, and trans-dihydroxydihydroaldrin. Although it was not determined whether the metabolism of aldrin to dieldrin occurred in the terrestrial or aqueous compartments of the microcosm, it is clear that epoxidation of aldrin to dieldrin is a dominant fate process.

Many papers and reviews report that biological epoxidation of aldrin to give dieldrin is a common fate (see reviews by Sanborn et al. 1977, and Rosenblatt et al. 1975). This conversion probably can be accomplished by most organisms. It has been reported to occur in microbes, crustaceans, insects, fish, mammals, and birds (see citations to other literature by Carlson 1974; Sanborn et al. 1977; Rosenblatt et al. 1975). Tu et al. (1968) screened 92 soil cultures for their ability to convert aldrin to dieldrin, and found that most of the microbes could effect the epoxidation reaction.

21.4.8 Other Reactions

No processes other than those listed are considered important processes for the fate of aldrin in aquatic systems.

21.4.9 Microcosm Studies, Field Studies, and Modelling

Microcosm experiments have demonstrated bioaccumulation of aldrin in several aquatic species as well as the rapid epoxidation to give diel-

drin in the microcosm system. The discussion and data for these experiments are presented in Sections 21.4.6 and 21.4.7.

21.5 Data Summary

Table 21-1 summarizes the data on the aquatic fate of aldrin.

Table 21-1

Summary of Aquatic Fate of Aldrin

Environmental Process[a]	Summary Statement	Rate	Half-Life $t_{\frac{1}{2}}$	Confidence of Data
Photolysis	Direct photolysis is slow.	-	-	High
	Indirect photolysis may be important.	-	One expt, $t_{\frac{1}{2}}$=1 day	Low
Oxidation	No quantitative information available.	-	-	-
Hydrolysis	Not an important process.	-	> 4 years	High
Volatilization	Probably an important process.	-	Few hours to few days	Medium
Sorption	Can be an important process.	-	-	Medium
Bioaccumulation	Possibly an important process.	-	-	Medium
Biotransformation/ Biodegradation	Is a dominant process in some systems.	-	-	Medium

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

21.6 Literature Cited

Biggar, J.W., and L.R. Riggs. 1974. Apparent solubility of organochlorine insecticides in water at various temperatures. Hilgardia. 42(10):383-391.

Bowman, M.C., F. Acree, Jr., C.S. Lofgren, and M. Beroza. 1964. Chlorinated insecticides: fate in aqueous suspensions containing mosquito larvae. Science. 146(3650):1480-1481.

Carlson, G.P. 1974. Epoxidation of aldrin to dieldrin by lobsters. Bull. of Environ. Contam. Toxicol. 11(6):577-582.

Crosby, D.G., and K.W. Moilanen. 1974. Vapor-phase photodecomposition of aldrin and dieldrin. Arch. Environ. Contam. Toxicol. 2(1):62-74.

Eichelberger, J.W., asnd J.J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5(6):541-544.

Ernst, W. 1977. Determination of the bioconcentration potential of marine organisms. - a steady state approach. Chemosphere. 6(11):731-740.

Gäb, S., H. Parlar, S. Nitz, K. Hustert, and F. Korte. 1974. Beitrage zur okologischen chemie. LXXXI. Photochemischer abbau von aldrin, dieldrin and photodieldrin als festkorper im sauerstoffstrom. Chemosphere. 3(5):183-186.

Gunther, F.A., and J.D. Gunther. 1971. Residues of pesticides and other foreign chemicals in foods and feeds. Residue Rev. 36:69-77.

Henderson, G.L., and D.G. Crosby. 1967. Photodecomposition of dieldrin and aldrin. J. Agric. Food Chem. 15:888-893.

Hoffmann, J., and D. Eichelsdoerfer. 1971. Effect of ozone on chlorinated-hydrocarbon-group pesticides in water. Vom Wasser 38:197-206.

Ivie, G.W., and J.E. Casida. 1971(a). Sensitized photodecomposition and photosensitizer activity of pesticide chemicals exposed to sunlight of silica gel chromatoplates. J. Agric. Food Chem. 19:405-409.

Ivie, G.W., and J.E. Casida. 1971(b). Photosensitizers for the accelerated degradation of chlorinated cyclodienes and other insecticide chemicals exposed to sunlight on bean leaves. J. Agric. Food Chem. 19(3):410-416.

Kenaga, E.E., and C.A.I. Goring. 1978. Relationship between water solubility, soil-sorption, octanol-water partitioning, and bioconcentration of chemicals in biota. Amer. Soc. Test. Mat. Third Aquatic Tox. Symp., New Orleans, LA, 63 pp.

Leshniowsky, W.O., P.R. Dugan, R.M. Pfister, J.I. Frea, and C.I. Randles. 1970. Adsorption of chlorinated hydrocarbon pesticides by microbial floc and lake sediment and its ecological implications. Proc., Conf. Gt. Lakes Res., 13th. 2:611-618.

Mackay, D., and P.J. Leinonen. 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Tech. 9(13):1178-1180.

Mackay, D., and A.W. Wolkoff. 1973. Rate of evaporation of low solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 7(7):611-614.

Martin, H., ed. 1972. Pesticide Manual, 3rd Ed. British Crop Protection Council, Worcester, Engl.

Metcalf, R.L., I.P. Kapoor, P.-Y. Lu, C.K. Schuth, and P. Sherman. 1973. Model ecosystem studies of the environmental fate of six organo-chlorine pesticides. Environ. Health Perspect. 4:35-44.

Park, K.S., and W.N. Bruce. 1968. The determination of the water solubility of aldrin, dieldrin, heptachlor and heptachlor expoxide. J. Econ. Entomol. 61(3):770-774.

Roburn, J. 1963. Effect of sunlight and ultraviolet radiation on chlorinated pesticide residues. Chem. Ind. (1963):1555-1556.

Rosen, J.D. 1967. The photolysis of aldrin. Chem. Commun. (4):189-190.

Rosen, J.D., and W.F. Carey. 1968. Preparation of the photoisomers of aldrin and dieldrin. J. Agric. Food Chem. 16(3):536-537.

Rosen, J.D., and D.J. Sutherland. 1967. The nature and toxicity of the photoconversion products of aldrin. Bull. Environ. Contam. Toxicol. 2(1):1-9.

Rosenblatt, D.H., T.A. Miller, J.C. Dacre, I. Muul, and D.R. Cogley. 1975. Appendix K - Aldrin/Dieldrin. Preliminary assessment of ecological hazards and toxicology of environmental pollutants at Rocky Mountain Arsenal.

Ross, R.D., and D.G. Crosby. 1975. The photooxidation of aldrin in water. Chemosphere 4(5):277-282.

Sanborn, J.R., B.M. Francis, and R.L. Metcalf. 1977. The degradation of selected pesticides in soil: A review of the published literature. U.S. NTIS, PB Rep., PB-272353, 633pp.

Saravanja-Bozanic, V., S. Gab. K. Hustert, and F. Korte. 1977. Reacktionen von aldrin, chlorden und 2,2;-dichlorobiphenyl mit $O(^3P)$. Chemosphere. 6(1):21-26.

Schauberger, C.W., and R.B. Wildman. 1977. Accumulation of aldrin and dieldrin by blue-green algae and related effects of photosynthetic pigments. Bull. Environ. Contam. Toxicol. 17(5):534-541.

Singmaster, J.A., III. 1975. Environmental behavior of hydrophobic pollutants in aqueous solutions. Ph.D. Thesis. Univ. California, Davis, Calif. 143pp. University Microfilms, Ann Arbor, Mich., Order No. 76-14,237. (Diss. Abstr. Int. B 1976, 36(12, Pt.1):6206-6207).

Tu, C.M., J.R.W. Miles, and C.R. Harris. 1968. Soil microbial degradation of aldrin. Life Sci. 7(6):311-322.

Weil, L., G. Dure, and K.E. Quentin. 1974. Solubility in water of insecticide chlorinated hydrocarbons and polychlorinated biphenyls in view of water pollution. Z. Wasser Abwasser Forsch. 7(6):169-175.

Yaron, B., A.R. Swoboda, and G.W. Thomas. 1967. Aldrin adsorption by soils and clays. J. Agric. Food Chem. 15(4):671-675.

22. CHLORDANE

22.1 Statement of Probable Fate

Volatilization, sorption to sediments, and bioaccumulation are important fates for the chlordane isomers in aqueous environments. The chlordane isomers also undergo photosensitized isomerizations, but no information is available to determine whether such reactions may occur in aquatic systems. Although biotransformations of chlordane may be important for the ultimate transformation of chlordane, these processes are likely to be very slow in the environment.

22.2 Identification

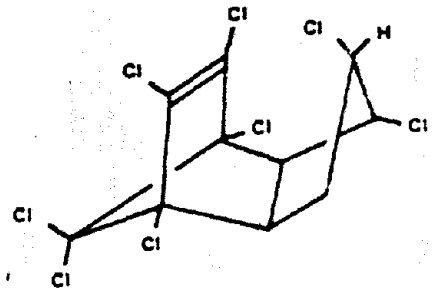
This chapter considers only the two major components of the mixture known as technical chlordane. An approximate composition of technical chlordane is given below (Brooks 1974, from data of Velsicol Chemical Corporation):

Fraction	Percentage Present
Diels-Alder adduct of cyclopentadiene pentachlorocyclopentadiene ($C_{10}H_7Cl_5$)	2 ± 1
Chlordene ($C_{10}H_6Cl_6$); isomer 1	1 ± 1
Chlordene isomers 2, 3, and 4 together	7.5 ± 2 13 ± 2
Heptachlor ($C_{10}H_5Cl_7$)	10 ± 3
Cis-chlordane ($C_{10}H_6Cl_8$) (β-isomer)	19 ± 3
Trans-chlordane ($C_{10}H_6Cl_8$) (γ-isomer)	24 ± 2
Nonachlor ($C_{10}H_5Cl_9$)	7 ± 3
Hexachlorocyclopentadiene (C_5Cl_6)	> 1
Octachlorocyclopentene (C_5Cl_8)	1 ± 1
$C_{10}H_{7-8}Cl_{6-7}$	8.5 ± 2
Constituents with shorter GC retention time than C_5Cl_8 (includes hexachloro cyclopentadiene)	2 ± 2
Constituents with longer GC retention times than nonachlor	4 ± 3

Sovocool et al. (1977) analyzed a technical chlordane sample by gas chromatography/mass spectrometry and partially or completely identified 45 constituents of the mixture.

Morley et al. (1974) reviewed information on technical chlordane and its components, and provided an excellent discussion on the history of the nomenclature of the chlordane isomers. The γ-chlordane designation has been used for both the vicinal dichloro sructure and for a geminal dichloro structure. Cis- and trans-chlordane have been called α- and γ-chlordane, respectively, by one group of researchers, and β- and α-chlordane, respectively, by another group. This report uses the cis-and trans designations to avoid confusion, and any references in literature to the Greek nomenclature are converted to the corresponding cis/trans notation.

The structures, alternate names, and CAS and TSL numbers of the two chlordane isomers are given below:

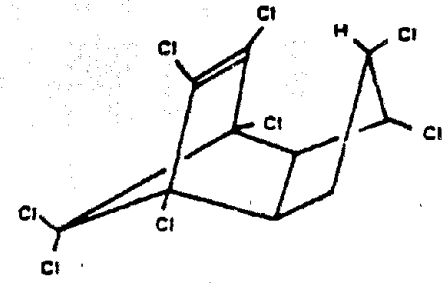


Trans-chlordane

CAS No. 5103-71-9
TSL No. PB 98000

Alternate Names

Trans-chlordane
γ-Chlordane
4,7-Methanoindan, 1,2,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro
α-Chlordane



Cis-chlordane

CAS No. 5103-74-2
TSL No. PC 01750

Cis-chlordane

β-Chlordane
4,7-Methanoindan, alpha-1,2,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro
α-Chlordane

22.3 Physical Properties

The general physical properties of the chlordane isomers are given below, with the data for individual isomers noted when available.

Molecular weight	406
Melting Point	107.0-108.8°C (*cis*) 103.0-105.0°C (*trans*)
Boiling point (Roark 1951)	175°C at 2 torr
Vapor pressure at 25°C (Martin 1972)	1×10^{-5} torr*
Solubility in water at 25°C	
(Weil *et al.* 197)	1.85 ppm
(Sanborn *et al.* 1976)	0.056 ppm
Log octanol/water partition coefficient (Sanborn *et al.* 1976)	2.78

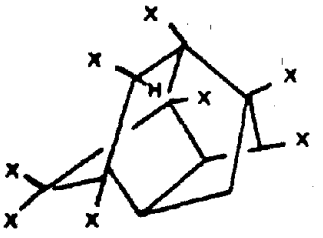
*For "refined product", which was not further defined.

22.4 Summary of Fate Data

22.4.1 Photolysis

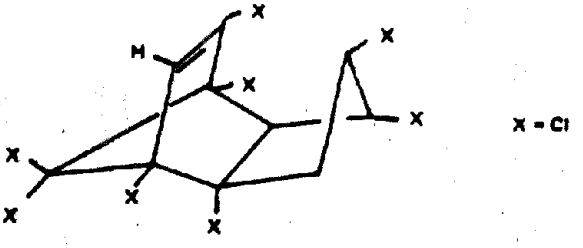
There are no data useful for estimating the half-life for photolysis of either of the two chlordane isomers in aquatic environments. Although no information is available for assessing how the processes may be relevant to photosensitized reactions in aquatic environments, the chlordane isomers have been shown to undergo photosensitized reactions with acetone as sensitizer, with the *cis* isomer being more susceptible to photolysis than the *trans* isomer.

Several studies on the photolysis of chlordane isomers in acetone solvent have been reported. Fischler and Korte (1969) reported that cis-chlordane photolyzed at 254 nm gave the cage product I; trans-chlordane



I

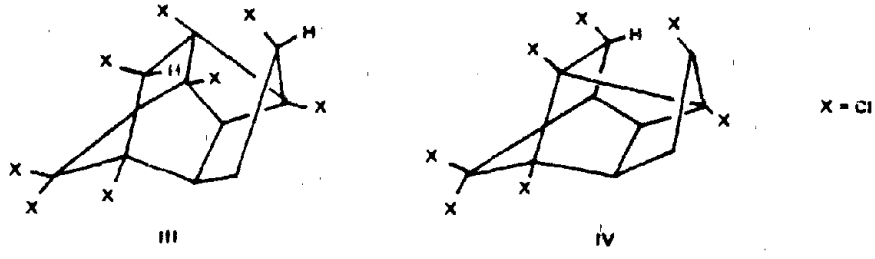
did not undergo photoisomerization. A subsequent paper by Parlar and Korte (1973) reported that at wavelengths above 300 nm cis-chlordane photolyzed to give I, and also gave product II in which a chlorine atom migrated to the tertiary carbon. Benson et al. (1971) also found that I was a product from cis-chlordane photolysis at > 300 nm. Trans-chlordane also photo-



II

reacted under these conditions, but no photoisomer was found; the authors reported that only 60% of trans-chlordane was reacted in 50 hours, whereas cis-chlordane was 99% reacted in 27 hours using the same light source.

Onuska and Comba (1975) reported that cis-chlordane photolyzed at > 300 nm gave I, and that trans-chlordane gave the two products, III and IV. The same products were also reported by Ivie et al. (1972) and Knox et al. (1973).



III IV

Ivie et al. (1972) also studied the photolysis of cis- and trans-chlordane in sunlight on the surface of bean leaves that had been treated with rotenone (a photochemical sensitizer). In the bean leaf study exposure of the chlordane isomers to sunlight for 4 hours resulted in a 70 to 80% loss of cis-chlordane and a 15 to 20% loss of trans-chlordane; no loss of chlordane from the bean leaves exposed to sunlight occurred in the absence of rotenone. The same photoisomerization products were found in the leaf study and in the acetone solvent experiments.

Vollner et al. (1971) reported that photolysis of cis- or trans-chlordane at 254 nm in dioxane-water solvent gave mainly photoreduction at the vinylic group of the chlordane structure. This result indicates that formations of products I through IV are probably due to acetone-photosensitized processes. There is no information available to determine whether such photosensitized processes may occur with natural substances present in aquatic environments.

Benson et al. (1971) reported that exposure of a thin film of cis-chlordane to sunlight for 460 hours resulted in a 10% loss, with a 1% yield of I. Baker and Applegate (1974) also found that chlordane films subjected to irradiation from a lamp with a maximum output at 350 nm showed extensive loss of chlordane; neither the chlordane isomer(s) studied nor any products were reported. Ginsburg (1953) also reported that a chlordane emulsion lost toxicity to mosquitos after 6 days exposure to sunlight; no further information was given.

22.4.2 Oxidation

No information is available to assess the oxidation half-life of chlordane in aquatic environments.

22.4.3 Hydrolysis

Eichelberger and Lichtenberg (1971) reported that both isomers of chlordane were 100 percent recovered from samples of Little Miami River (Ohio) water after 8 weeks at room temperature; since the recoveries were rounded off to the nearest 5 percent, the loss must have been less than 2.5 percent, which corresponds to a half-life of at least 4 years for hydrolysis. Bevenue and Yeo (1969) also reported that both chlordane isomers were stable in water for 60 days.

22.4.4 Volatilization

Laboratory experiments by several researchers suggest that volatilization may be an important loss process for the chlordane isomers in aquatic environments, although the information available is not useful for estimating volatilization half-lives in aquatic systems.

Oloffs et al. (1972; 1973) and Oloffs and Albright (1974) reported experiments in which cis- and trans-chlordane were incubated in flasks containing natural waters and sediments. Chlordane in water without sediments was readily volatilized, with some of the chlordane found in the glass wool plugs in the neck of the incubation flasks. Losses of chlordane isomers were approximately 40 to 50% in 6 weeks and about 60% in 12 weeks, presumably because of volatilization and possibly biotransformation; no chlordane metabolites were detected in the aqueous phase, however, when ^{14}C-labeled chlordane was used. Other experiments with an initial concentration of 25 ppb trans-chlordane in natural water at 9°C for 3 days resulted in 34% of the chlordane being recovered from the glass wool plug and 70% of the chlordane recovered from the water. In a similar experiment with cis-chlordane, about 24% and 76% of the chlordane was found in the glass wool and water, respectively. Flasks sealed with glass stoppers showed no loss of chlordane from water. Other experiments where surfactants or sediments were added to the flasks showed less chlordane loss, apparently because volatilization was suppressed.

Bowman et al. (1964) found that volatilization of trans-chlordane was apparently a significant loss process. In their experiments, 51 µg of trans-chlordane was placed in a 250 ml solution of water-chlordane containing mosquito larvae; at the end of 20 hours, only 30% of the chlordane was

recovered from water and larvae. The authors suggested that volatilization was responsible for the poor recovery of chlordane.

22.4.5 Sorption

No useful data are available for evaluating the sorption of chlordane to sediments in aquatic environments. Oloffs et al. (1972; 1973) and Oloffs and Albright (1974) reported experiments in which cis- and trans-chlordane were placed in flasks containing natural water and sediments. Volatilization was an important loss process in the experiment without sediment (see Section 22.4.4). When sediment was present, more than 80% of the chlordane initially at 25 ppb in solution was recovered from the sediment after 12 weeks. The authors stated that these experiments showed the competition between sediment sorption and volatilization in the fate of chlordane.

22.4.6 Bioaccumulation

Bioaccumulation in bacteria, daphnids, and fish is an important fate for the chlordane isomers in aquatic environments. Bioconcentration factors for these species are on the order of 10^3 to 10^4.

Grimes and Morrison (1975) reported bioconcentration factors for cis- and trans-chlordane in bacterial species. The concentration factors for the individual isomers in each species did not vary by more than 10% from the average of the concentration factors, as may be expected of such similar structures. The bioconcentration factors for cis-chlordane varied from 2.0×10^2 to 5.6×10^4; four factors were between 200 and 900, and four factors were between 10^3 and 10^4, with three factors at 1.6×10^4, 2.3×10^4, and 5.6×10^4, specifically.

Moore et al. (1977) reported chlordane bioconcentration factors of 5.6×10^3 and 2.4×10^4 for algae and daphnids, respectively. The daphnids were found to readily eliminate chlordane, with 75% lost in 48 hours after the daphnids were placed in clean water. In another experiment, concentration factors in daphnids of 1.6×10^4 and 2.0×10^4 were measured for cis- and trans-chlordane, respectively. The authors also report a bioconcentration factor of 162 for goldfish; since this factor is calculated on a wet weight basis, it is lower than values figured on a dry weight basis. When removed to clean water, the goldfish eliminated 50% of the absorbed chlordane in 3 days.

Schimmel et al. (1976b) reported bioconcentration factors for trans-chlordane in the range of $(3.6\text{-}6.4) \times 10^3$ for the fish, spot, in

72-hour exposure test. Schimmel et al. (1976a) also found trans-chlordane concentration factors of (3.7-14.8) x 10^3 for spot and (9.0-16.8) x 10^3 for sheepshead minnow in 96-hour exposure tests. Parrish et al. (1976) reported that bioconcentration factors for chlordane (no isomers cited) in marine species in 96-hour exposure tests (1.3-1.9) x 10^4 for sheepshead minnow and 3.0-7.5 x 10^3 for pinfish; in a 28-day exposure test, the sheepshead minnow had concentration factors in the range (8.5-12.3) x 10^3.

Roberts et al. (1977) reported a study of the bioaccumulation of chlordane isomers in fish (redhorse and white suckers); a concentration factor for cis-chlordane in fish was estimated to be 5.5 x 10^3. The authors also found that the trans-isomer was eliminated from the fish about 1.8 times faster than the cis-isomer, with half-lives for elimination of cis-and trans-chlordane being 60 and 30 days, respectively.

22.4.7 Biotransformation and Biodegradation

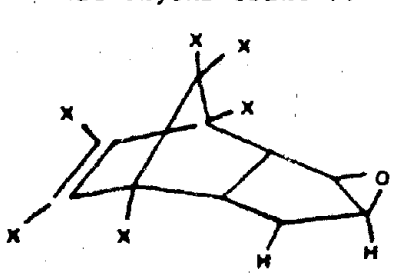
Very little information is available on the biotransformation of chlordane, and no data were found for estimating the biotransformation half-lives of chlordane in aquatic systems.

Castro and Yoshida (1971) and Watanabe (1973) both reported that chlordane is persistent in flooded and nonflooded soils and suggest that chlordane is comparable to dieldrin in its slow biotransformation.

Iyengar and Rao (1973) reported that the fungus, Aspargillus niger, could utilize chlordane in nutrient solutions, with more than 90% loss found in 48 hours for chlordane concentrations initially below 38 ppm. The authors found that chlordane could not serve as a sole carbon source for growth of the fungus, and unadapted organisms could not utilize the pesticide. They did find that the heptachlor-acclimated-fungus could utilize chlordane as a substrate. No metabolites were identified.

In terrestrial-aquatic microcosm exeriments, Sanborn et al. (1976) found some metabolism of chlordane, but they did not identify any of the some 20 products detected by tlc (see Section 22.4.9). Morley et al. (1974) reviewed the metabolites found in rabbit experiments and concluded they were products from hydroxylation at the chlorinated positions of the cyclopentane ring. A dominant metabolite found in a rat experiment by Barnett and Dorough (1974) was oxychlordane V.

V



X = Cl

22.4.8 Other Reactions

No processes other than those described have been found to be important in the fate of chlordane in aquatic environments.

22.4.9 Microcosm Studies, Field Studies, and Modelling

Sanborn *et al.* (1976) reported a terrestrial-aquatic microcosm study that demonstrates the bioaccumulation and slow biotransformation of chlordane in aquatic systems. The ^{14}C chlordane constituted 94.5%, 91.2%, 47.6%, and 77.9% of the total ^{14}C recovered from alga, snail, mosquito larvae, and fish, respectively. The ratios of *cis*:*trans* isomers of chlordane in the organisms were also found to be different from the 3.04 ratio in the original chlordane mixture, with the ratios being 4.02 in water, 3.08 in the alga, 5.39 in the snail, and 6.98 in the fish. The authors note that the increase in the *cis*:*trans* ratio suggests either more facile biotransformation of the *trans*-isomer over the *cis*, or different accumulation tendencies for the isomers in the organisms. No metabolites were identified in the experiment, although some 20 compounds were evident in the tlc analysis. The bioconcentration factors determined were 9.8×10^4 for alga, 1.32×10^5 for snail, 6.1×10^3 for mosquito larvae, and 8.3×10^3 for fish.

22.5 Data Summary

Table 22-1 summarizes the data on the aquatic fate of chlordane.

Table 22-1

Summary of Aquatic Fate of Chlordane

Environmental Process [a]	Summary Statement	Rate	Half-Life $t_{\frac{1}{2}}$	Confidence of Data
Photolysis	Sensitized processes may be important.	-	-	Low
Oxidation	No information available.	-	-	-
Hydrolysis	Not an important process.	-	> 4 years	High
Volatilization	Probably an important process.	-	-	Medium
Sorption	Probably an important process.	-	-	Medium
Bioaccumulation	Is an important process.	-	-	High
Biotransformation/ Biodegradation	Is very slow, may be an important process for ultimate degradation.	-	-	Medium

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

22.6 Literature Cited

Baker, R. D., and H. G. Applegate. 1974. Effect of ultraviolet radiation on the persistence of pesticides. Tex. J. Sci. 25(1-4):53-59.

Barnett, J. R. and H. W. Dorough. 1974. Metabolism of chlordane in rats. J. Agr. Food Chem. 22(4):612-619.

Benson, W. R., P. Lombado, I. J. Egry, R. D. Ross, Jr., R. P. Barron, D. W. Mastbrook, and E. A. Hansen. 1971. Chlordane photoalteration products: Their preparation and identification. J. Agric. Food Chem. 19(5):857-862.

Bevenue, A., and C. Y. Yeo. 1969. Gas chromatographic characteristics of chlordane. II. Observed compositional changes of the pesticide in aqueous and non-aqueous environments. J. Chromatogr. 42:45-52.

Bowman, M. C., F. Acree, Jr., C. S. Lofgren, and M. Beroza. 1964. Chlorinated insecticides: Fate in aqueous suspensions containing mosquito larvae. Science. 146(3650):1480-1481.

Brooks, G. T. 1974. Chlorinated insecticides: Volume I: Technology and applications. CRC Press, Cleveland, OH., 249 pages.

Castro, T. F., and T. Yoshida. 1971. Degradation of organochlorine insecticides in flooded soils in the Philippines. J. Agric. Food Chem. 19(6):1168-1170.

Eichelberger, J. W., and J. J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5(6):541-544.

Fischler, M. H. and F. Korte. 1969. Sensitized and unsensitized photoisomerization of cyclodiene insecticides. Tetrahedron Lett. (32):2793-2796.

Ginsburg, J. M. 1953. Rate of decomposition of the newer insecticides when exposed to direct sunlight. Proc. New Jersey Mosquito Exterm. Assoc. 40:163-168.

Grimes, D. J. and S. M. Morrison, 1975. Bacterial bioconcentration of chlorinated hydrocarbon insecticides from aqueous systems. Microb. Ecol. 2(1):43-59.

Ivie, G. W., J. K. Knox, S. Khalifa, I. Yamamoto, and J. E. Casida. 1972. Novel photoproducts of heptachlor epoxide, trans-chlordane and trans-nonachlor. Bull. Environ. Contam. Toxicol. 7(6):376-382.

Iyengar, L., A. V. S. P. Rao. 1973. Metabolism of chlordane and heptachlor by aspergillus niger. J. Gen. Appl. Microbiol. 19(4):321-324.

Knox, J. R., S. Khalifa, G. W. Ivie, and J. E. Casida. 1973. Characterization of the photoisomers from cis- and trans-chlordanes, trans-nonachlor and heptachlor epoxide. Tetrahedron. 29:3869-3879.

Martin, H., ed. 1972. Pesticide Manual, 3rd Ed. British Crop Protection Council, Worcester, Engl.

Moore, R., E. Toro, M. Stanton, and M. A. Q. Khan. 1977. Absorption and elimination of ^{14}C-alpha- and gamma-chlordane by a fresh-water alga, daphnid, and goldfish. Arch. Environ. Contam. Toxicol. 6:411-420.

Morley, H. V. et al. 1974. Chlordane, its effects on Canadian ecosystems and its chemistry. Natl. Res. Counc. Can., Environ. Secr., NRCC No. 14094, 189 pp.

Oloffs, P. C., and L. J. Albright. 1974. Transport of some organochlorines in British Columbia waters. Proc. Int. Conf. Transp. Persistent Chem. Aquat. Ecosyst. 1:89-92.

Oloffs, P. C., L. J. Albright, and S. Y. Szeto. 1972. Fate and behavior of five chlorinated hydrocarbons in three natural waters. Can. J. Microbiol. 18(9):1393-1398.

Oloffs, P. C., L. J. Albright, S. Y. Szeto, and J. Lau. 1973. Factors affecting the behavior of five chlorinated hydrocarbons in two natural waters and their sediments. J. Fish. Res. Board Can. 30(11):1619-1623.

Onuska, F. I., and M. E. Comba. 1975. Isolation and characterization of the photoalteration products of cis- and trans-chlordane. J. Assoc. Off. Anal. Chem. 58(1):6-9.

Parlar, H., and F. Korte. 1973. Ecological chemistry. LX. Photochemistry of chlordane derivatives. Chemosphere 2(4):169-172.

Parrish, P. R., S. C. Schimmel, D. J. Hanson, J. M. Patrick, Jr., and J. Forester. 1976. Chlordane: Effects on several estaurine organisms. J. Toxic. Environ. Health 1:485-494.

Roark, R. C. 1951. A digest of information on chlordane. U.S. Dept. Agr. Bur. Entomol. and Plant Quarantine E-817, 132pp.

Roberts, J. R., A. S. W. De Frietas, and M. A. J. Bidney. 1977. Influence of lipid pool size on bioaccumulation of the insecticide chlordane by northern redhorse suckers (Moxostoma macrolepidotum). J. Fish. Res. Board Can. 34(1):89-97.

Sanborn, J. R., R. L. Metcalf, W. N. Bruce, and P.-Y. Lu. 1976. The fate of chlordane and toxaphene in a terrestrial-aquatic model ecosystem. Environ. Entomol. 5(3):533-538.

Schimmel, S. C., J. M. Patrick, Jr., and J. Forester. 1976a. Heptachlor: Toxicity to and uptake by several estuarine organisms. J. Toxic. Environ. Health 1:955-965.

Schimmel, S. C., J. M. Patrick, Jr., and J. Forester. 1976b. Heptachlor: Uptake, depuration, retention, and metabolism by spot, (Leiostomus xanthurus). J. Toxicol. Environ. Health 2(1):169-178.

Sovocool, G. W., R. G. Lewis, R. L. Harless, N. K. Wilson, and R. D. Zehr. 1977. Analysis of technical chlordane by gas chromatography/mass spectrometry. Anal. Chem. 49(6):734-740.

Vollner, L., H. Parlar, W. Klein and F. Korte. 1971. Beitrage zur okologischen chemie-XXXI. Photoreaktionen der komponenten des technischen chlordans. Tetrahedron 27:501-509.

Watanabe, I. 1973. Decompostion of pesticides by soil microorganisms-Special emphasis on flooded soil condition. JARQ. 7(1):15-18.

Weil, L., G. Dure and K. E. Quentin. 1974. Solubility in water of insecticide chlorinated hydrocarbons and polychlorinated biphenyls in view of water pollution. Z. Wasser Abwasser Forsch. 7(6):169-175.

23. DDD

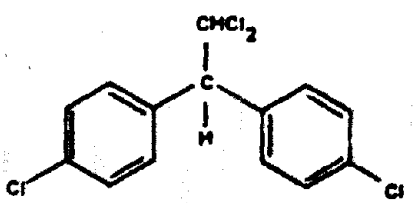
23.1 Statement of Probable Fate

The major fate processes for DDD in aquatic environments are bioaccumulation and sorption to sediments and biota. Volatilization will also be an important process for loss of DDD from aquatic systems, with DDD half-lives on the order of a few days to several weeks. DDD is quite stable to chemical transformations in aquatic environments, and biotransformation is probably the process resulting in the ultimate degradation of DDD in the environment.

23.2 Identification

This chapter considers only the pure DDD; as for technical DDT, the pp'-isomer is the major component in the technical mixture and most DDD studies have focused on this isomer. Martin (1972) described technical DDD as having a melting point of 86°C and containing related compounds in small amounts.

The structure, alternate names, and CAS and TSL numbers of DDD are given below:



pp'-DDD

CAS No. 72548
TSL No. KI 07000

Alternate Names

TDE
1,1-Dichloro-2,2-bis (4-chlorophenyl)ethane
Dichlorodiphenyl dichloroethane
Rhothane

23.3 Physical Properties

The general physical properties of DDD are as follows.

Molecular weight	320
Melting point (Martin 1972)	112°C

Boiling point	No data found
Vapor pressure at 30°C (Spencer 1975)	10.2×10^{-7} torr (pp') 18.9×10^{-7} torr (op')
Solubility in water at 25°C	
(Weil et al. 1974)	20 ppb (pp')
(Biggar and Riggs 1974)*	90 ppb (pp') 100 ppb (op')
Log octanol/water partition coefficient (O'Brien 1974)	5.99 (pp') 6.08 (op')

*Particle size < 5 μm.

23.4 Summary of Fate Data

23.4.1 Photolysis

No data are available for estimating the photolysis rate of DDD in aquatic environments. Several papers indicate that direct photolysis of DDD is slower than that of DDT, and since the half-life for direct photolysis of DDT in water is estimated to be more than 150 years, photolysis of DDD in water should also be very slow. No information is available on the indirect photolysis of DDD.

Mosier et al. (1969) measured a reaction quantum yield of 0.04 for photolysis of DDD in hexane solvent at 254 nm; the quantum yield for DDT photolysis under this condition was 0.16. Only one product peak was found by glpc analysis of the DDD photolysis solution and it was not identified. Roburn (1963) reported that DDD on glass plates irradiated for several hours with a germicidal lamp (wavelength of 254 nm) gave dechlorination of DDD. The loss of DDD in this experiment was less than the losses of DDE or DDT under the same photolysis conditions.

Volatilization of DDD to the atmosphere is probably an important process for DDT and DDD (Sections 23.4.4 and 25.4.4). Crosby and Moilanen (1977) studied the photolysis of DDT in the vapor phase at wavelengths greater than 290 nm and found DDD as a minor product (See Section 25.4.1). The authors stated that under experimental conditions where DDT was about half photoreacted, DDD "... appeared to be stable to light." No other information was given on DDD photolysis.

23.4.2 Oxidation

No information has been found concerning the oxidation of DDD in aquatic environments. Using diphenylmethane as a model for peroxyl radical oxidation of DDD at the benzylic position with a rate constant of 1.0 M^{-1} sec^{-1} at 30°C, Hendry et al. (1974), we can calculate a half-life of 22 years using an assumed radical concentration in the aquatic environment of 10^{-9} M. Oxidation of DDD by peroxyl radical in the aquatic environment is then expected to be slow.

23.4.3 Hydrolysis

In a study of the hydrolysis of DDT, Wolfe et al. (1977) estimated the hydrolysis half-lives for DDD and DDE. From structure-reactivity relationships and literature data, they calculated a second-order rate constant of 1.4×10^{-3} M^{-1} sec^{-1} for hydroxyl-ion-promoted hydrolysis of DDD at 27°C. This value corresponds to a half-life of 570 days at pH 9. They also estimated a 190-year half-life for hydrolysis of DDD at pH 5 and 27°C.

The calculations of Wolfe et al. are in good agreement with the finding of Eichelberger and Lichtenberg (1971), who observed no loss of DDD (i.e., less than 2.5%) after 8 weeks for 10-ppb DDD solutions in distilled water or in raw river water from the Little Miami River in Ohio.

23.4.4 Volatilization

Data available for the relative rates of volatilization of DDT and DDD indicate that DDD is volatilized from aquatic systems at about one-third the rate of DDT. Volatilization of DDT from aquatic systems occurs with half-lives that range from a few hours to several weeks (see Section 25.4.4). Therefore, volatilization of DDD from aquatic environments will probably have half-lives ranging from a day to less than a month.

Singmaster (1975) described studies designed to measure relative rates of volatilization of chlorinated pesticides, including DDD from deionized water (see also Sections 23.4.4 and 24.4.4). In one experiment, about 1 pptr pp'-DDD in 900 ml of water in a 5-liter flask at 25°C was

agitated by bubbling nitrogen through solution at 0.45 l/min while 4.5 l/min of air was drawn through the air space above the solution. The ratio for relative rates of volatilization of DDE, DDT, and DDD was about 10:3:1, respectively. Although the experimental conditions are not directly applicable to volatilization processes in aquatic systems, they do indicate that DDD is less volatile than DDT or DDE. Since there is strong evidence that volatilization is an important process for loss of DDT and DDE from water (see Sections 23.4.4 and 24.4.4), volatilization from water is also probably an important loss process for DDD, with a rate about one-third that of DDT.

Ernst (1977) performed experiments to determine the relative volatility of chlorinated organics preparatory to conducting bioconcentration experiments in marine mussels. In these experiments, aquaria containing 0.5 ppb of chlorinated material were aerated at a rate of 2.5 l/hr for 67 hours. Although the conditions do not simulate any realistic aquatic environment, DDD was 81% recovered, compared with 33% recovery of DDT in similar experiments; thus, DDD is less volatile from water than DDT. The ratio of DDT to DDD lost in this experiment was 3.5:1 (ie., 67% DDT: 19% DDD), and is in excellent agreement with the 3.3:1 ratio measured by Singmaster.

23.4.5 Sorption

Sorption to sediments and biota are important processes for DDD in aquatic systems. Although no specific data are available for DDD sorption to sediment, the importance of sorption processes in the fate of DDT indicates that sorption of DDD to sediment must also be an important fate in aquatic systems. In lieu of available data for DDD, sorption data for DDT will suffice for some environmental assessment purposes.

Hom et al. (1974) examined the DDD content of undisturbed sediments from the Santa Barbara Basin off the California coast. By means of radio dating of the sediment layers they determined that DDD began to appear in the sediments in about 1955 (at 12-ppb concentration) and attained 18-ppb levels by 1976. These data clearly show that significant amounts of DDD in aquatic environments must be associated with sediment.

Although no sediment/water partition coefficients have been reported for DDD, coefficients on the order of 10^5 are probable by analogy to DDT data. This value is based on the correlation between the partition coefficient for octanol/water and for sorption as described by Kenaga and Goring (1978). Since the logarithm of the octanol/water partition coefficients for DDD and DDT are 5.99 and 5.98, respectively (as cited by Kenaga and Goring), the sorption coefficients should also be similar. Sorption of DDT is discussed in Section 25.4.5.

23.4.6 Bioaccumulation

Bioaccumulation is an important fate process for DDD in aquatic systems. As would be expected, based on the structural similarities between DDD, DDT and DDE, bioconcentration factors for DDD range from 10^3 to 10^5, similar to those found for DDE and DDT. The tragic effects of bioaccumulation of DDD have also been demonstrated in the Clear Lake incident described in Section 23.4.9.

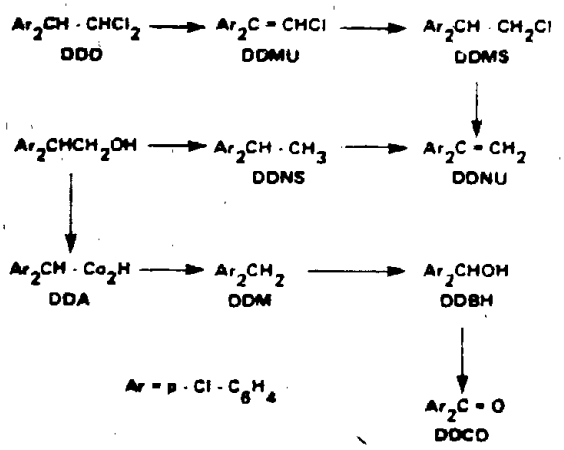
Ernst (1977) measured a concentration factor of 9120 for uptake of DDD in marine mussel, but this value is based on a wet weight of the mussel, and therefore is lower than factors calculated on a dry-weight basis. When mussel containing 456 ppb (wet weight) DDD was placed in clean water, only 150 ppb loss was found in 48 hours, indicating a slow elimination from mussel; other pesticides (i.e., dieldrin, heptachlor epoxide, endrin) in similar depuration experiments had elimination half-lives that were two times faster than DDD.

Bioaccumulation of DDD has also been studied in terrestrial-aquatic microcosm experiments by Metcalf *et al.* (1971; 1973); data from these experiments are presented in Section 23.4.9.

23.4.7 Biotransformation and Biodegradation

No useful data are available for evaluating the biotransformation of DDD in aquatic systems, although several reviewers of DDT literature have stated that DDD is more easily metabolized than DDT or DDE. The persistence of DDD in microcosm studies, and especially in the Clear Lake incident described in Section 23.4.9, does suggest that DDD biotransformations in aquatic systems are slow.

In a thorough review of DDT metabolism in microbial systems, Johnsen (1976) also discusses the biotransformation of DDE and DDD. Whereas DDE appears to be a rather stable product of DDT biotransformation, the formation of DDD from DDT provides for further transformation of the DDT structure. Johnsen cites the biological sequence shown on the following page as a proposed route for DDD conversion to DDCO.



Johnsen notes that this scheme is based on a synthesis of information from a number of papers, and that no one paper demonstrates this pathway. Obviously, for the above sequence, some cycling of the DDT residues through anaerobic and aerobic systems is required, so that transport processes along with the biological variables will determine how fast the transformation sequence occurs.

23.4.8 Other Reactions

No reactions of DDD other than those listed previously are expected to be important fate processes in aquatic environments.

23.4.9 Microcosm Studies, Field Studies, and Modelling

A field study and microcosm experiment have shown that bioaccumulation of DDD is an important fate process in aquatic systems. The microcosm experiment also indicates that DDD is subject to some biotransformation.

The pronounced tendency for accumulation of DDD in fish and the western grebe has been shown dramatically in a case where DDD was applied to a lake to control gnats (Hunt and Bischoff 1960). Clear Lake, a fresh water lake in northern California, was treated with DDD at levels of 14 ppb in 1949, and 20 ppb in 1954 and again in 1957. Deaths of numerous grebes in 1954-1955 and 1957, and the presence of 1600 ppm DDD in the fatty tissue of a grebe, prompted examination of DDD levels in the wildlife of the area. Analysis of nine fish species in the lake showed concentrations of DDD in edible fish flesh ranging from 5.0 to 221 ppm, with DDD levels in visceral

fat exceeding 2000 ppm in some samples. Although no other data on water or sediment concentrations of DDD were reported, this case history alone is sufficient to demonstrate the tendency of DDD to accumulate in wildlife, and to obvious tragic consequences.

The fate of DDD in a terrestrial-aquatic microcosm has been reported by Metcalf et al. (1971). Bioconcentration factors of 933, 967, and 6500 were found for DDD in snail, mosquito larvae, and fish; the concentration in water was 0.4 ppb. Of the total ^{14}C in these species, 59%, 59%, and 85%, respectively, was present as DDD; the authors compared these data to those of microcosm experiments with DDT and DDE and concluded that DDD was the most biodegradable of the DDT-R compounds in their microcosm experiments. Small amounts of 1,1- bis(p-chlorophenyl)ethane (DDNS, in Section 23.4.6) were found as approximately 4% of the total ^{14}C in snail and fish, along with two unknowns and polar metabolites (as detected by tlc.). Bioconcentration factors in snail, mosquito larvae, and fish of 1.3×10^4, 3.3×10^3, and 4.4×10^4, respectively, were also measured for DDD formed in a microcosm experiment that studied the fate of DDT, but the authors did not comment on reasons why these data differed from those in the DDD-microcosm experiments. Metcalf et al. (1973) also reported bioconcentration factors of 8.4×10^4 and 8.2×10^3 for fish and snail, respectively, but the source of these data is unclear.

23.5 Data Summary

Table 23-1 summarizes the data on the aquatic fate of DDD.

Table 23-1

Summary of Aquatic Fate of DDD

Environmental Process [a]	Summary Statement	Rate	Half-Life $t_{\frac{1}{2}}$	Confidence of Data
Photolysis	Not an important process.	-	> 150 years	Medium
Oxidation	Probably not an important process.	-	~ 22 years	Medium
Hydrolysis	Not an important process.	-	570 days at pH 9 190 years at pH 5	High
Volatilization	May be an important process.	-	Few days to about a month	Medium
Sorption	Is an important process.	-	-	High
Bioaccumulation	Is an important process.	-	-	High
Biotransformation / Biodegradation	Is a slow, but important process for ultimate transformation.	-	-	Medium

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

23.6 Literature Cited

Biggar, J. W., and L. R. Riggs. 1974. Apparent solubility of organochlorine insecticides in water at various temperatures. Hilgardia 42(10):383-391.

Crosby, D. G., and K. W. Moilanen. 1977. Vapor-phase photodecomposition of DDT. Chemosphere. 6(4):167-172.

Eichelberger, J. W., and J. J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5(6):541-544.

Ernst, W. 1977. Determination of the bioconcentration potential of marine organisms - a steady-state approach. Chemosphere 6(11):731-740.

Hendry, D. G., T. Mill, L. Piszkiewicz, J. A. Howard, and H. K. Eigenmann. 1974. A critical review of h-atom transfer in the liquid phase: chlorine atom, alkyl, trichloromethyl, alkoxy, and alkylperoxy radical. J. Phys. Chem. Ref. Data. 3(4):937-978.

Hom, W., R. W. Risebrough, A Soutar, and D R. Young. 1974. Deposition of DDE and polychlorinated biphenyls in dated sediments of the Santa Barbara basin. Science. 184:1197-1200.

Hunt, E. G., and A. I. Bischoff. 1960. Inimical effects on wildlife of periodic DDD applications to Clear Lake. Calif. Fish and Game. 46:91-106.

Johnsen, R. E. 1976. DDT metabolism in microbial systems. Residue Rev. 61:1-28.

Kenaga, E. E., and C. A. I. Goring. 1978. Relationship between water solubility, soil-sorption, octanol-water partitioning, and bioconcentration of chemicals in biota. Amer. Soc. Test. Mat. Third Aquatic Tox. Symp., New Orleans, LA. 63 pp.

Martin, H., ed. 1972. Pesticide Manual, 3rd. Ed. British Crop Protection Council, Worcester, Engl.

Metcalf, R., I. P. Kapoor, P.-Y. Lu, C. K. Schuth, and P. Sherman. 1973. Model ecosystem studies of the environmental fate of six organochlorine pesticides. Environ. Health Perspect. 4:35-44.

Metcalf, R. L., G. K. Sangha, and I. P. Kapoor. 1971. Model ecosystem for the evaluation of pesticide biodegradibility and ecological magnification. Environ. Sci. Technol. 5(8):709-713.

Mosier, A. R., W. D. Guenzi, and L. L. Miller. 1969. Photochemical decomposition of DDT by a free-radical mechanism. Science 164:1083-1085.

O'Brien, R. D. 1974. Nonenzymic effects of pesticides on membranes. Pages 331-342 in R. Haque and V. H. Freed, eds. Environmental dynamics of pesticides. Plenum Press, New York, N. Y.

Roburn, J. 1963. Effect of sunlight and ulltraviolet radiation on chlorinated pesticide residues. Chem. Ind. (1963):1555-1556.

Singmaster, J. A., III. 1975. Environmental behavior of hydrophobic pollutants in aqueous solutions. Ph.D. Thesis. Univ. California, Davis, Calif. 143pp. University Microfilms, Ann Arbor, Mich., Order No. 76-14, 237. (Diss. Abstr. Int. B 1976, 36(12, Pt.1):6206-6207).

Spencer, W. F. 1975. Movement of DDT and its derivatives into the atomosphere. Residue Rev. 59:91-117.

Weil, L., G. Dure, and K. E. Quentin. 1974. Solubility in water of insecticide chlorinated hydrocarbons and polychlorinated biphenyls in view of water pollution. Z. Wasser Abwasser Forsch. 7(6):169-175.

Wolfe, N. L., R. G. Zepp, D. F. Paris, G. L. Baughman, and R. C. Hollis. 1977. Methoxychlor and DDT degradation in water: Rates and products. Environ. Sci. Technol. 11(12):1077-1081.

24. DDE

24.1 Statement of Probable Fate

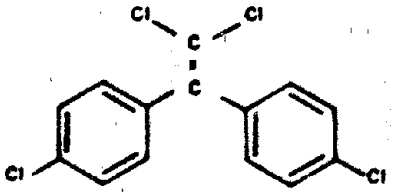
The major fate processes for DDE in aquatic environments are bioaccumulation and sorption to sediments and biota. Laboratory studies suggest that in aquatic environments, DDE may have volatilization half-lives of several hours and photolysis half-lives of several days; the observed persistence of DDE in such environments may be due to the fact that DDE is mainly formed from DDT under biological conditions in which DDE in the sorbed state is then not available for volatilization or photolysis.

The ultimate loss of DDE may be through photolysis in water or in the atmosphere after desorption or release from biota or sediments; biotransformation may also be an ultimate transformation process, although DDE is much less susceptible to such processes than DDT or DDD.

24.2 Identification

DDE is formed as a degradation product of DDT and is not manufactured as a commercial product. Unless otherwise stated, all references to DDE in this chapter will be for the pp'-DDE isomer, since no data specific to the op'-DDE isomer were found.

The structure, alternate names, and CAS and TSL numbers of DDE are as follows:



DDE

CAS No. 72559
TSL No. KV 94500

Alternate names

1,1-Dichloro-2,2-bis
(p-chlorophenyl)-ethylene
2,2-Bis(4-chlorophenyl)
1,1-dichloroethene

24.3 Physical Properties

The general physical properties of DDE are as follows (isomer in parenthesis).

Molecular weight	318.0
Melting point (Leffingwell 1975)	88-90°C
Boiling point	No data found
Vapor pressure at 20°C (Spencer 1975)	6.5×10^{-6} torr (pp') 6.2×10^{-6} torr (op')
Solubility in water at 25°C	
(Weil et al. 1974)	14 ppb (pp')
(Biggar and Riggs 1974)*	120 ppb (pp') 140 ppb (op')
(Zepp et al. 1977)	1.3 ppb
(Chiou et al. 1977)	40 ppb (pp') at 20°C
(Metcalf et al. 1973)	1.2 ppb
Log octanol/water partition coefficient (O'Brian 1974)	5.69 (pp') 5.78 (op')

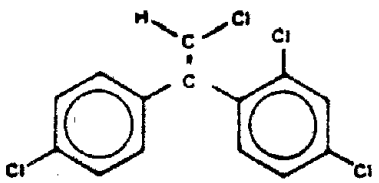
*Particle size < 5 µm.

24.4 Summary of Fate Data

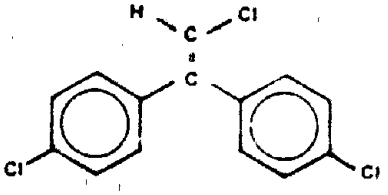
24.4.1 Photolysis

Direct photolysis of DDE in aquatic systems will result in half-lives ranging from about 1 day in summer to 6 days in winter; no information on indirect photolysis of DDE in aquatic environments has been found.

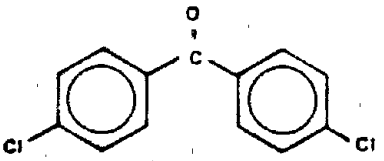
Zepp et al. (1976, 1977) measured a quantum yield of 0.3 for photolysis of DDE at 313 nm in water, and calculated that the direct photolysis half-life of DDE in sunlight at 40° latitude will range from 0.9 days in summer to 6.1 days in winter. The photolysis products identified were 1-(4-chlorophenyl)-1-(2,4-dichlorophenyl)-2-chloroethylene (o-Cl-DDMU), 1,1-(4-chlorophenyl)-2-chloroethylene (DDMU), and dichlorobenzophenone (DDCO); yields of o-Cl-DDMU and DDCO were 2% and 15%, respectively. The authors note that the observed persistence of DDE in the environment is probably due to its being sorbed to sediments or biota where no light for photolysis is available, but that photolysis of DDE is likely to be an important fate in the ultimate transformation of DDE in aquatic systems.



o-Cl-DDMU



DDMU



DDCO

Other studies on DDE photolysis have been reported. Singmaster (1975) measured a sunlight photolysis half-life of 1.1 days for 0.84 ppb DDE in San Francisco Bay water, with only one unidentified product detected. In contrast to the findings of Zepp et al. (1977), Singmaster found only a trace of DDCO and the presence of the other possible products was not determined. Although Singmaster did not discuss whether direct or indirect photolysis of DDE was occurring in the bay water, the half-life of 1.1 day (at an unspecified season) is in good agreement with the direct photolysis half-life calculation of Zepp et al (1977).

Other studies at higher energy wavelengths have also been reported. Mosier et al. (1969) measured a reaction quantum yield of 0.26 for photolysis of DDE in hexane at 254 nm. This resullt is in good agreement with a quantum yield of 0.24 measured by Zepp et al. (1977) for DDE photolysis in hexane solution at 313 nm.

The products reported by Zepp et al. (1977) have also been found by Kerner et al. (1972) for photolysis of DDE at > 250 nm in various solvents and in the solid and gas phase; DDMU and o-Cl-DDMU were each formed in yields of approximately 20-40% when DDE was photolyzed in hexane or dioxane-water solvents; the yield of DDCO was about 5%. Photolysis of solid DDE for 10 days (with 12% DDE remaining) gave yields of 40% DDCO and 45% DDMU with about 1% o-Cl-DDMU; when a solid mixture of DDE and chlorophyll was photolyzed, a 90% yield of o-Cl-DDMU was found. Photolysis of DDE in the gas phase gave yields of 8% DDMU and 12% o-Cl-DDMU at a 20% loss of DDE.

Plimmer et al. (1970) reported that photolysis of DDE at 260 nm in N_2-sparged methanol solvent gave reductive dechlorination by a free radical mechanism, and with oxygen present a complex mixture of products was obtained, including DDCO, DDMU and 3,6-dichlorofluorenone; the latter was obtained in 10% yield. Leffingwell (1975) has also reported studies on the photolysis of 10-ppm suspensions of DDE in air-saturated water at wavelengths below 290 nm and found a complex mixture of products.

Since volatilization of DDE is an important fate, the atmospheric chemistry of DDE may be an important process. Crosby and Moilanen (1977)

studied the sunlamp photolysis of DDT in the vapor state in air and found DDE as the major product. Studies on DDE under the same photolysis conditions found 4% of the DDE was photolyzed in 4 days, which was about eight times slower than the rate for DDT (see Section 25.4.1). This order of reactivity for photolysis of DDT and DDE is opposite of that found and predicted for direct photolysis in solution, and is at present unexplained. The major DDE photolysis products were DDCO and DDMU; some products were tentatively identified as o-Cl-DDMU, and the di-, tri-, and tetrachlorobiphenyls. In an earlier study on the photolysis of DDT in methanol, Plimmer et al. (1970) also found dichlorobiphenyl. As in the case of DDT, the data provided are not useful for estimating the photolysis half-life of DDE in the atmosphere.

24.4.2 Oxidation

No information has been found on the rates of oxidation of DDE in aquatic environments. The products reported by Plimmer et al. (1970) and Leffingwell (1975) do indicate that oxidation of DDE as a result of photolysis processes is extensive.

24.4.3 Hydrolysis

Wolfe et al. (1977) found DDE was the product of hydrolysis of DDT for pH values of 3-11. DDE appears quite stable to hydrolysis under the reaction conditions, with a half-life in excess of 120 years at pH 5 and 27°C.

In good agreement with this expected stability of DDE toward hydrolysis, Eichelberger and Lichtenberg (1971) found no decrease (within 2.5%) in concentration after monitoring a 10-ppb DDE solution in distilled water and in raw river water, respectively, for an eight-week period at ambient temperatures.

24.4.4 Volatilization

Volatilization of DDE is probably an important loss process in aquatic systems. Although only one study of DDE volatilization has been reported, this study found that DDE volatilized from distilled water and natural water solutions five times faster than DDT under identical conditions. Since volatilization of DDT from aquatic systems is established as an important process (see Section 25.4.4), volatilization of DDE may also be an important loss process.

Singmaster (1975) described studies designed to measure relative rates of volatilization of chlorinated pesticide from pure water and several natural waters. In these experiments the pesticide at about ' pptr con-

centrations in 900 ml of water in a 5-liter flask was gently agitated on a shaker while air was drawn through the flask (but not bubbled through solution) at a rate of 4.5 l/min. The half-lives for volatilization of pp'-DDE from pure water and waters from San Francisco Bay, the American River, and Sacramento River were 0.67, 1.2, 1.4, and 1.9 hour, respectively; the water loss in these experiments averaged 3.6 ± 0.2 g/hr. Singmaster concluded that volatilization of DDE in natural waters would not be more than two times slower than in pure water. Although it is difficult to relate the experimental results to conditions in aquatic environments (i.e., temperature, agitation, etc.), the author noted that the air exchange in the flask corresponded to a wind velocity of about 10 m/hr, which is much lower than that usually found in the environment. Based on the wind velocity factor alone, and assuming removal of DDE from the vapor space is the dominant force in volatilization of DDE, the half-lives for volatilization of DDE in aquatic environments could be on the order of a few hours. In any event, since the volatilization half-lives of DDT under identical experimental conditions ranged from 3 to 10 hours, and volatilization of DDT is recognized as an important loss process in aquatic systems (see Section 25.4.4), volatilization of DDE must also be an important loss process.

24.4.5 Sorption

Sorption to sediment and biota are important processes for DDE in aquatic systems. Although no specific data are available for DDE sorption coefficients, information from field studies and, by analogy, to the importance of sorption processes for DDT, suggest that sorption of DDE to sediments will be a significant fate in aquatic systems. In lieu of available data for DDE, sorption data for DDT will suffice for some environmental assessment purposes.

Hamelink and Waybrant (1976) studied the fate of DDE in a flooded rock quarry; this study, which includes the movement of DDE into sediment, is fully described in Section 24.4.9. An important pathway for DDE in this system was sorption to suspended particulates and subsequent deposition into sediment. The authors also found that DDE in the sediment remained in the top 1.5-cm layer and did not move into lower sediment layers.

Hom et al. (1974) examined the DDE content of undisturbed sediments from the Santa Barbara Basin off the California coast. By means of radio dating of the sediment layers, they determined that DDE began to appear in the sediment in about 1955 (at 24-ppb concentration), and rose to 160 ppb by 1967. These data clearly show that significant amounts of DDE in aquatic environments must be associated with sediment.

Although no sediment/water partition coefficients have been reported for DDE, coefficients on the order of 10^5 are indicated by analogy

to DDT data. This value is based on the correlation between partition coefficient for octanol/water and for sorption as described by Kenaga and Goring (1978). Since the logarithms of the octanol/water partition coefficients for DDE and DDT are 5.77 and 5.98, respectively (as cited by Kenaga and Goring), the sorption coefficients should also be similar. Sorption of DDT is discussed in Section 25.4.5.

24.4.6 Bioaccumulation

Bioaccumulation is an important fate process for DDE in aquatic systems; in this respect, DDE is similar to DDT. Bioconcentration factors for aquatic species measured in a field study and in microcosm experiments are in the range 10^4-10^5.

Hamelink et al. (1977) found the concentration (Y) of DDE in zooplankton to be directly related to the DDE concentration (X) in water, and correlated by the equation Y (ppb) = 27.3 + 53.75X (pptr); the data for this correlation were obtained in the flooded quarry experiment described in Section 24.4.9, where other data for DDE bioconcentration are also cited. Data for bioaccumulation of DDE obtained in a microcosm experiment are also presented in Section 24.4.9.

24.4.7 Biotransformation and Biodegradation

There are no data useful for predicting the rate of biotransformation of DDE in aquatic environments. Several reviews of DDT have described DDE as being less susceptible for biotransformation than DDT or DDD. In a summary statement in a review of DDT metabolism in microbial systems, Johnsen (1976) noted that "...despite some evidence to the contrary...", DDE "...appears to be a stable end product incapable of being further degraded." Bohonos and Francis (1975) reached a similar conclusion, stating that formation of DDE from DDT was a "dead end pathway" for DDT biotransformation. Although the terrestrial-aquatic microcosm experiments of Metcalf et al. (see Section 24.4.9) did find small amounts of polar metabolites by thin layer chromatography analysis, it is not clear whether the biotransformation occurred in terrestrial or aqueous phases of the microcosm. Given the rather strong statements of Johnsen and of Bohonos and Francis regarding the lack of reactivity of DDE, it appears that DDE will be very slowly biotransformed in aquatic environments, if at all.

24.4.8 Other Reactions

No processes other than those listed above are considered important in evaluating the fate of DDE in aquatic environments.

24.4.9 Microcosm Studies, Field Studies, and Modelling

Microcosm experiments and a field study have shown that important fate processes for DDE in aquatic systems are bioaccumulation and sorption to sediments. The microcosm experiments also indicate that DDE is quite resistant to biotransformation processes.

Hamelink and Waybrant (1976) reported a field study on the fate of DDE introduced into a flooded quarry where the water, sediment, and biota were monitored for DDE levels for one year. The calculated initial DDE concentration in the epilimnion was 200 pptr, or 50 pptr for the whole water column. The DDE in the water column declined rapidly, with 69% loss occurring in 5 days; the loss was facilitated by sorption to soil after an influx of soil due to runoff from a rainstorm on the second day of the experiment. The concentration of DDE in the water column reached an equilibrium concentration of about 0.5 to 1.0 pptr DDE in four months. DDE in the bottom mud was found to be in the top 1.5 cm, with a maximum of (35 $\pm$ 27) ppb level found in the 1.5-cm top layer after 81 days. The equilibrium of DDE between water and zooplankton reached equilibrium after one day, with concentration factors of (3-6) x 10^4. DDE reached equilibrium between water and a resident quarry fish, bluegill, after 60 days, with a concentration factor of about 1.1 x 10^5; the concentration facto for trout 108 days after the intial DDE application was measured to be 1.8 x 10^5.

Based on this study, the authors concluded that sorption to particulate, which subsequently settled, facilitated distribution of DDE throughout the water column by sorption/desorption processes as well as the disappearance of DDE from the water. Sedimented material collected up to day 21 contained an average of 1.4 ppm DDE, and accounted for 82% of the DDE lost from the water at this time. After 173 days, 94% of the DDE found in their analyses was associated with the bottom mud. It is also interesting to note that at 358 days the DDE concentration in water samples analyzed was roughly twice that at 242 days (i.e., 1.15-2.73 pptr compared to 0.66-0.96 pptr, respectively). The authors attributed this result to DDE release from sediments following decomposition of organic matter during winter and the higher water temperature, which increased DDE solubility.

Metcalf *et al.* (1971, 1975.) studied the fate of DDE in a terrestrial-aquatic microcosm experiment. In the 1971 paper Metcalf *et al.* reported concentration factors for snail, mosquito larvae, and mosquito fish in the aquatic phase to be 2 x 10^4, 3 x 10^4, and 3 x 10^4, respectively; the DDE concentration in water phase was 5.3 ppb. The metabolites found in these species were identified as only polar metabolites (by tlc), in the amounts 14%, 6%, and 3% of the total ^{14}C in the respective species. The microcosm experiment was subsequently repeated and reported in the 1975 paper. The bioconcentration factors found were 3.6 x 10^4, 5.9 x

10^4, and 1.2×10^4 for snail, mosquito larvae, and fish; a concentration factor for algae in this experiment was 1.1×10^4. The concentration of DDE in the water in this latter experiment was 3.8 ppb. DDE was present as 92, 93, 95, and 97% of the total ^{14}C in snail, alga, fish, and mosquito larvae. Although it is impossible to determine how much of the DDE was metabolized in the aquatic phase since the DDE was introduced into the terrestrial phase by several routes (mainly caterpillar excrement and leaf fragments), it is apparent that DDE is not readily biotransformed in the organisms examined. The importance of the food chain in the bioaccumulation of DDE reported above has also been suggested by Metcalf et al. (1973), who found concentration factors of only 110-515 and 300-344 for mosquito larvae and fish exposed to 0.90 ppb DDE through aquatic exposure alone in an aquatic microcosm where the food chain did not exist. An alternative interpretation of these data is that bioaccumulation in a food chain provides a more rapid uptake of DDE in the mosquito larvae and fish, and that in the aquatic exposure experiment sufficient time was not allowed for DDE to reach equilibrium between organism and the aqueous phase.

24.5 Data Summary

Table 24-1 summarizes the data on the aquatic fate of DDE.

Table 24-1

Summary of Aquatic Fate of DDE

Environmental Process[a]	Summary Statement	Rate	Half-Life t½	Confidence of Data
Photolysis	Can be important process for DDE in water.	-	1 day in summer 6 days in winter	High
Oxidation	No information available.	-	-	-
Hydrolysis	Not an important process.	-	> 120 year at pH 5	High
Volatilization	Probably an important process.	-	Few days to few weeks	Medium
Sorption	Is an important process.	-	-	High
Bioaccumulation	Is an important process.	-	-	High
Biotransformation/ Biodegradation	Very slow but may be important for eventual degradation.	-	-	Low

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

24.6 Literature Cited

Biggar, J. W., and L. R. Riggs. 1974. Apparent solubility of organochlorine insecticides in water at various temperatures. Hilgardia 42(10):383-391.

Bohonos, N., and A. J. Francis. 1975. Microbiological degradation of military standard pesticide formulations. Final Report. SRI to the U.S. Army Medical Research Development Command. Contract #DADA17-73-C-3214.

Chiou, C., V. Freed, D. Schmedding, and R. Kohnert. 1977. Partition coefficient and bioaccumulation of selected organic chemicals. Environ. Sci. Technol. 11(5):475-478.

Crosby, D. G., and K. W. Moilanen. 1977. Vapor-phase photodecomposition of DDT. Chemosphere. 6(4):167-172.

Eichelberger, J. W., and J. J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5(6):541-544.

Hamelink, J. L., R. C. Waybrant, and P. R. Yant. 1977. Mechanisms of bioaccumulation of mercury and chlorinated hydrocarbon pesticides by fish in lentic ecosystems. Pages 261-268 in I. M. Suffet, Fate of pollutants in the air and water environment. Part II. John Wiley and Sons, New York, N. Y.

Hamelink, J. L., and R. C. Waybrant. 1976. DDE and lindane in a large-scale model lentic ecosystem. Trans. Am. Fish. Soc. 105(1):124-134.

Hom, W., R. W. Risebrough, A Soutar, and D. R. Young. 1974. Deposition of DDE and polychlorinated biphenyls in dated sediments of the Santa Barbara basin. Science 184:1197-1200.

Johnsen, R. E. 1976. DDT metabolism in microbial systems. Residue Rev. 61:1-28.

Kenaga, E. E., and C. A. I. Goring. 1978. Relationship betwen water solubility, soil-sorption, octanol-water partitioning, and bioconcentration of chemicals in biota. Amer. Soc. Test. Mat. Third Aquatic Tox. Symp., New Orleans, LA. 63 pp.

Kerner, I., W. Klein, and F. Korte. 1972. Beitrage zur okologischen chemie-XXXIII. Photochemische reaktionene von 1,1-dichlor-2(p,p'-dichlorphenyl) athylen (DDE). Tetrahedron 28:1575-1578.

Leffingwell, J. T. 1975. The photolysis of DDT in water. Ph.D. Thesis. University of California, Davis. 124 p. University Microfilms, Ann Arbor, Mich., Order No. 76-14, 218. (Diss. Abstr. Int. B 1976, 37(1):177-178).

Metcalf, R. L., I. P. Kapoor, P.-Y. Lu, C. K. Schuth, and P. Sherman. 1973. Model ecosystem studies of the environmental fate of six organochlorine pesticides. Environ. Health Perspect. 4:35-44.

Metcalf, R. L., G. K. Sangha, and I. P. Kapoor. 1971. Model ecosystem for the evaluation of pesticide biodegradability and ecological magnification. Environ. Sci. Technol. 5(8):709-713.

Metcalf, R. L., J. R. Sanborn, P.-Y. Lu, and D. Nye. 1975. Laboratory model ecosystem studies of the degradaion and fate of radio-labeled tri-, tetra-, and pentachlorobiphenyl compared with DDE. Arch. Environ. Contam. Toxicol. 3(2):151-165.

Mosier, A. R., W. D. Guenzi, and L. L. Miller. 1969. Photochemical decomposition of DDT by a free-radical mechanism. Science 164:1083-1085.

O'Brien, R. D. 1974. Nonenzymic effects of pesticides on membranes. Pages 331-342 in R. Haque and V. H. Freed, eds. Environmental dynamics of pesticides. Plenum Press, New York, N. Y.

Plimmer, J. R., U. I. Klingbiel, and B. E. Hummer. 1970. Photooxidation of DDT and DDE. Science. 167:67-79.

Singmaster, J. A., III. 1975. Environmental behavior of hydrophobic pollutants in aqueous solutions. Ph.D. Thesis. Univ. California, Davis, Calif. 143pp. University Microfilms, Ann Arbor, Mich., Order No. 76-14,237. (Diss. Abstr. Int. B 1976, 36(12, Pt.1):6206-6207.

Spencer, W. F. 1975. Movement of DDT and its derivatives into the atmosphere. Residue Rev. 59:91-117.

Weil, L., G. Dure, and K. E. Quentin. 1974. Solubility in water of insecticide chlorinated hydrocarbons and polychlorinated biphenyls in view of water pollution. Z. Wasser Abwasser Forsch. 7(6):169-175.

Wolfe, N. L., R. G. Zepp, D. F. Paris, G.. L. Baughman, and R. C. Hollis. 1977. Methoxychlor and DDT degradation in water: Rates and products. Environ. Sci. Technol. 11(12):1077-1081.

Zepp, R. G., N. L. Wolfe, L. V. Azarraga, K. H. Coz, and C. W. Pape. 1977. Photochemical transformation of the DDT and methoxychlor degradation products, DDE and DMDE, by sunlight. Arch. Environ. Contam. Toxicol. 6:305-314.

Zepp, R. G., N. L. Wolfe, J. A. Gordon, and R. C. Fincher. 1976. Light-induced transformations of methoxychlor in aquatic systems. J. Agric. Food Chem. 24(4):727-733.

25. DDT

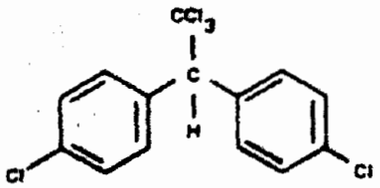
25.1 Statement of Probable Fate

There is ample evidence to demonstrate that DDT is very persistent in the environment. The dominant fate processes in aquatic environments are volatilization and sorption to biota and sediments, with the importance of sorption being determined by the amount of suspended particulate available in the water body. The ultimate transformation of DDT in the aquatic environment is probably by biotransformation, although one study indicates that indirect photolysis may also be a significant loss processs for DDT in a natural water, with a photolysis half-life on the order of a week. Photolysis of DDT in the gas phase has also been reported, but since DDT has been widely found throughout the biosphere, atmospheric transformations appear to be slow. There is also abundant evidence to demonstrate that bioaccumulation of DDT is a significant process in the environment.

The following evaluation of the fate processes for DDT in aquatic systems is based on an abbreviated literature search; in several cases, literature reviews on DDT have been used without a critical review of the original literature, which for some processes is extensive. The rationale for this limited search is that experience has already clearly demonstrated the persistence and bioaccumulation of DDT in the environment, and another review is not needed. Thus, although the literature cited may be incomplete, omitted information is not contradictory to conclusions presented in this chapter.

25.2 Identification

This chapter discusses the fate in the aquatic environment of the individual pp'- and op'-DDT isomers. Technical DDT comprises mainly a mixture of two DDT isomers; one reference gives a range of DDT isomers in three technical mixtures as 70 to 73 percent of the pp'-isomer, 12 to 21 percent of the op'-isomer, and a small amount (0.01%) of the oo'-isomer (Gunther and Gunther 1971). Gunther (1945) described a technical DDT preparation as containing approximately 70% pp', 18% op', and 6% oo'. The structures, alternate names, and TSL and CAS numbers of the two major isomers are as follows.

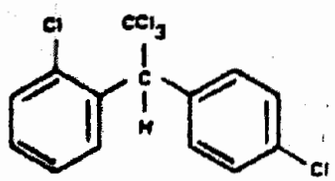


pp'-DDT

CAS No. 50293
TSL NO. KJ 33250

Alternate Names

1,1,1-Trichloro-2,2-bis (4-chlorophenyl)-ethane



op'-DDT

CAS No. 789-02-6
TSL No. None assigned

1,1,1-Trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane

Other Common Names

Dichlorodiphenyltrichloroethane
Chlorophenotane
Dicophane
Chlorophenothane
Gesarol
Guesarol
Neocid

In this chapter, information on a particular isomer will be so noted whenever available; in many instances, however, the isomer is not specified and will only be identified as DDT.

25.3 Physical Properties

The general physical properties of the DDT isomers are given below:

Molecular weight	354.5
Melting point	108.5-109.0°C (pp')
(Gunther and Gunther 1971)	74-74.5°C (op')
Boiling Point	185°C (pp')
(Gunther and Gunther 1971)	
Vapor pressure	
(Martin 1972)	1.9×10^{-7} torr (pp') at 25°C
(Spencer 1975)	7.3×10^{-7} torr (pp') at 30°C
	5.5×10^{-6} torr (op') at 30°C
(Metcalf 1972) at 20°C	1.5×10^{-7} torr (pp') at 20°C
Solubility in water at 25°C	
(Weil et al. 1974)	5.5 ppb (pp')
	26 ppb (op')
(Biggar and Riggs 1974)*	25 ppb (pp')
	85 ppb (op')
(Metcalf 1972)	~ 2 ppb
(Bowman et al. 1960)	< 1.2 ppb (pp')
Log octanol/water partition coefficient	
(O'Brien 1974)	6.19 (pp', calc.)
(Kenaga and Goring 1978)	5.98
(Wolfe et al. 1977)	4.89
(Kapoor et al. 1973)	3.98 (pp', measured)

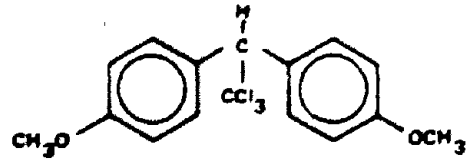
*Particle size <5.0 μm.

25.4 Summary of Fate Data

25.4.1 Photolysis

Direct photolysis of DDT in aqueous solution is very slow, with a half-life of probably greater than 150 years. Natural substances in some aquatic environments may cause indirect photolysis processes to be important for DDT transformation, with half-lives on the order of a few days or possibly even hours for DDT loss. Half-lives for indirect photolysis of DDT are difficult to predict for general environmental assessments because of lack of information on the variability of natural waters to produce such indirect reactions through photosensitized, photo-initiated free radical, or other reactions.

Zepp et al. (1976) calculated that DDT will probably have a direct photolysis half-life of more than 150 years. This estimate was based on a measured uv-absorption spectrum of DDT and assuming a reaction quantum yield of unity, the maximum quantum yield value expected for photolysis of a chemical in dilute solution. This calculation was made in conjunction with extensive studies on the DDT analogue, methoxychlor (I). The reaction



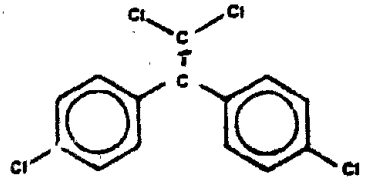
I

quantum yields measured for photolysis of I in hexane and in water solvents were 0.12 and 0.3, respectively. The authors also found that although the sunlight photolysis of methoxychlor in distilled water had a half-life of over 300 hours, methoxychlor photolyzed in three natural waters had half-lives ranging from 2 to 5 hours at midday in May; in two other natural

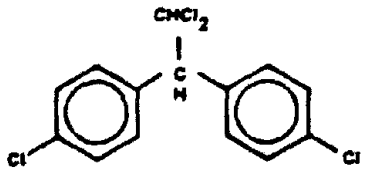
waters no photolysis of I was found after 2 hours exposure to midday sunlight. Sunlight photolysis of I in distilled water containing 20 ppm of a commercial "humic acid" had a half-life of 7.3 hours. Since DDT and methoxychlor have similar structures and apparently analogous photoreactions involving the $CH-CCl_3$ group (see discussion below), indirect photolysis of DDT in natural waters may also be rapid and as variable as that found for methoxychlor.

Singmaster (1975) studied the sunlight photolysis of 0.90 ppb DDT in distilled water and in water from San Francisco Bay. After 7 days exposure to sunlight, the DDT concentration in distilled water was unchanged where as the DDT in the bay water was 50% lost. The authors also determined that no DDE, DDD, or the related photoproducts were formed in the reaction, a finding that conflicts with other literature reports (see below). They suggested that transformation in solution may occur through photodissociation of the $CH-CCl_3$ bond.

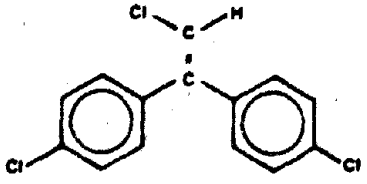
Because indirect photolysis of DDT appears to be a rapid and possibly important fate of DDT in aquatic systems, further discussions on the photochemistry of DDT are useful, especially regarding the formation of the DDE and DDD photoproducts. Since similar products have been reported to be formed by direct and indirect photolysis of DDT, both processes will be reviewed; however, only the latter is important in aquatic environments. Some of the compounds formed by DDT photolysis are given below with their acronyms:



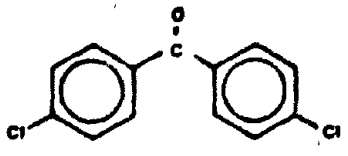
DDE



DDD



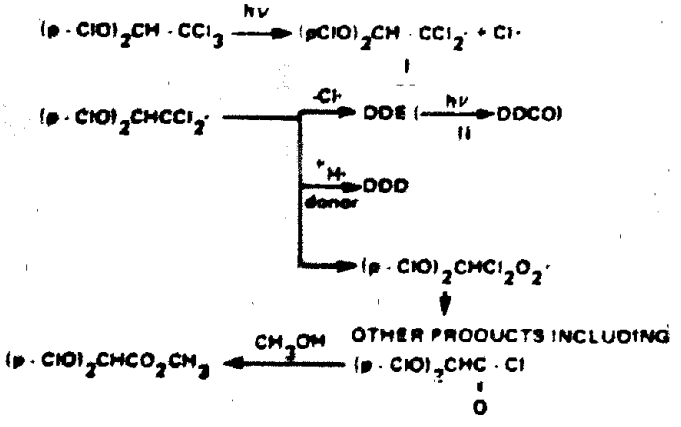
DDMU



DDCO

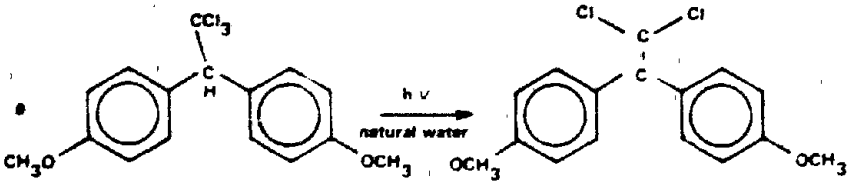
Several studies have provided information on the direct photolysis of DDT at wavelengths less than 290 nm. A reaction quantum yield of 0.16 was measured for photolysis of DDT at 254 nm in hexane solvent (Mosier et al. 1969). DDD and HCl were the only products identified, and the yield of DDD increased from 5% in hexane as the sole solvent to 12% when 1M n-butylmercaptan was present; DDE was found to undergo photolysis more rapidly than DDT under the reaction conditions and, therefore, DDE was not found as a product. The authors did find DDD, DDE, and DDCO when DDT films exposed to air were photolyzed at 254 nm. Plimmer et al. (1970) found DDD and DDMU as the products when DDT in N_2-sparged methanol solvent was photolyzed at 260 nm. The photolysis of DDT at 280 nm in methanol with oxygen present gave a complex product mixture, in which the methyl ester of 2,2-bis(p-chlorophenyl) acetic acid was found. Leffingwell (1975) found 16 products when a 10-ppm suspension of DDT in air-saturated water was photolyzed using a lamp with an output below 290 nm. Other studies of photolysis of DDT on soil and as films have found DDE and DDCO among other products (Baker and Applegate 1970, 1974; Fleck 1949; Roburn 1963).

All these results are in accord with a mechanism of initial photodissociation of a CCl_2-Cl bond to give the radical I, which then may (1) lose a chlorine atom to give DDE, (2) react with a hydrogen atom donor to give DDD, or (3) react with oxygen to give the peroxyl radical II, which may undergo further reactions to give a complex set of products (Plimmer et al. 1970; Mosier et al. 1969). It is interesting to note that Leffingwell



(1975) also found CCl_4 and $CHCl_3$ as DDT photolysis products, although it was not determined whether these products resulted by direct photolysis of the C-CCl_3 bond or by indirect processes.

Several examples of indirect photolysis of DDT are also known; however, except for two studies, the reaction conditions are difficult to relate to environmental aquatic systems. As discussed earlier, Singmaster found no DDE, DDD, or related products when DDT was photolyzed in sunlight in a bay water. In apparent contrast to this observation, Zepp et al. (1976) found the dehydrohalogenated methoxychlor analog of DDE (II) as a product when methoxychlor was photolyzed in several natural freshwaters.



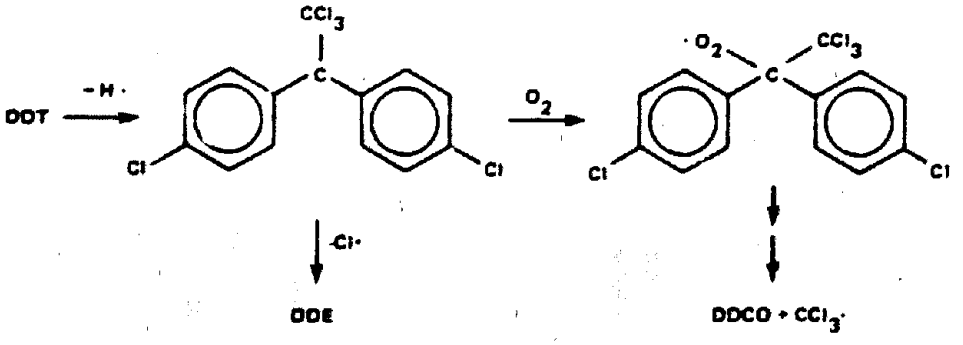
I II

Leffingwell (1975) reported that the photolysis rate of a 10-ppm suspension of DDT in water in sunlight or a Hg lamp was accelerated by the presence of triphenylamine, diphenylanthracene, or a free radical initiator, azo-bis-isobutyronitrile. No detailed product information was reported, but he did comment that the products were the same as those found for direct photolysis (presumably DDE, DDD, DDMU, DDCO, etc.) Miller and Narang (1970) reported earlier that photolysis of DDT in cyclohexane solvent at 310 nm occurred only when triphenylamine or N,N-diethylaniline (NNDA) was present; DDD, DDE and DDCO were formed in 6%, 15%, and 16% yields when NNDA was at initial concentration of 10^{-3}M. The authors also determined that triplet-state-sensitized processes were not responsible for the indirect photolysis of DDT in these systems.

Ivie and Casida (1971a) also found that triplet sensitizer chemicals codeposited with DDT on silica gel plates were generally ineffective in promoting the photolysis of DDT in sunlight. Although carbazole and triphenylamine did promote the photolysis of DDT in these studies, the extent of the DDT photolyses were not correlated with the triplet energies of

the 21 sensitizers used. Ivie and Casida (1971b) also found that triphenylamine catalyzed the sunlight photolysis rate of DDT applied to bean leaves, but only DDE and DDCO were found as the photoproducts. Earlier reports by Linquist et al. (1946) and Ginsburg (1953) indicated that DDT in media such as kerosene, fuel oil, wettable powders, and emulsions was also degraded in sunlight.

Although these examples show that indirect photolysis of DDT does occur, the mechanisms and the relevance of these studies to photolysis of DDT in aquatic systems are generally unclear. Singmaster's finding that no DDE, DDD, or related photoproducts were formed in bay water, compared with the findings of Zepp et al. that the DDE analog was a major photolysis product of methoxychlor in several freshwaters, may only reflect different transformation mechanisms available in the different natural waters. Since both DDD and DDE are persistent pollutants of concern (see Chapters 23 and 24, respectively), further studies on the indirect photolysis of DDT in natural waters seem advisable. In addition to transformations via radicals I and II, photooxidation of DDT at the benzylic position may also provide DDCO and the trichloromethyl radical, the latter leading to $CHCl_3$ or CCl_4 as found by Leffingwell:



Because volatilization of DDT into the atmosphere is an important environmental process (see Section 25.4.4), Crosby and Moilanen (1977) examined the photolysis of DDT in the gas phase using light of wavelengths

greater than 290 nm. After 4 days, 32% of the DDT had been photolyzed to give a 14:1 ratio of DDE:DDD, with a product balance of 96 percent. Thus, although DDE is then expected to be the major product in the gas phase photolysis of DDT, these data are not useful for predicting the photolysis half-life in the gas phase. Since DDT has been found in atmospheric sampling studies, photolysis in the atmosphere is apparently slow.

24.4.2 Oxidation

No information is available on oxidation of DDT under conditions relevant to aquatic environments. Using diphenylmethane as a model for peroxyl radical oxidation of DDT at the benzylic position with a rate constant of 1.0 M^{-1} sec^{-1} at 30°C, (Hendry et al. 1974), we can calculate a half-life of 22 years using an assumed radical concentration in the aquatic environment of 10^{-9}M. Oxidation of DDT by peroxyl radical in the aquatic environment is then expected to be slow. Hoffman and Eichelsdoerfer (1971) found that DDT was 78% removed when a 17 mg/l ozone stream was passed through a solution of DDT in 10% acetone in water for 45 minutes. In similar experiments, 3% DDT was removed in the same solvent system with a 4 mg/l ozone concentration, and 1% DDT was removed when hexane solvent with 240 mg/l ozone concentration was used. No products were identified, and no other information is available to explain the different reactivity of DDT in these systems.

25.4.3 Hydrolysis

Wolfe et al. (1977) studied the hydrolysis of DDT in a solvent of 5% acetonitrile in water and found that the hydrolysis rate was independent of pH in the range pH 3-5; they also found that the hydrolysis was hydroxide ion catalyzed above pH 5. Based on data obtained at higher reaction temperatures, an extrapolated rate constant of 1.9×10^{-9} sec^{-1} at 27°C was calculated for the region pH 3-5; this rate constant corresponds to a half-life of 12 years. The second-order rate constant for hydroxide-promoted hydrolysis was measured as 9.9×10^{-3} $M^{-1}sec^{-1}$ at 27°C, a value that corresponds to a half-life of 81 days at pH 9. The product formed in the hydrolyses was DDE.

The above calculations regarding the slow hydrolysis of DDT are corroborated by an experiment of Eichelberger and Lichtenberg (1971), who found that the concentration of DDT in a sample of raw river water (pH 7-8) was unchanged after 8 weeks at ambient room temperature.

25.4.4 Volatilization

The worldwide atmospheric distribution of DDT clearly indicates that volatilization of DDT from soils or aquatic systems (or both) is an important process. Laboratory studies and field studies have shown that volatilization of DDT from water is a rapid processs, although no useful data are available for quantitatively evaluating the rate of the volatilization process in aquatic systems. Although several authors have suggested that volatilization of DDT will be facilitated if DDT is concentrated in the microlayer of a water body, no sound evidence for this process has been found. The information available does indicate, however, that DDT may be volatilized from water with half-lives of less than a week.

Singmaster (1975) described studies designed to measure relative rates of volatilization of chlorinated pesticides from pure water and several natural waters. In these experiments about 1 pptr concentrations of pesticide in 900 ml of water in a 5 -liter flask were gently agitated on a shaker while air was drawn through the flask (but not bubbled through solution) at a rate of 4.5 l/min. The half-lives for volatilization of pp'-DDT from pure water and waters from San Francisco Bay, the American River, and Sacramento River were 3.9 hour, 6.5 hour, 6.0 hour, and 10 hour, respectively; the water loss in these experiments averaged 3.6 $\pm$ 0.2 g/hour. From these experiments, Singmaster concluded that volatilization of DDT in natural waters would not be more than two times slower than in pure water. Although the experiment is difficult to relate to conditions in aquatic environments (i.e., temperature, agitation, etc.), the author noted that the air exchange in the flask corresponded to a wind velocity of about 10 m/hr which is much lower than that usually found over aquatic systems in the environment. Based on the wind velocity factor alone and assuming removal of DDT from the vapor space is the dominant force in volatilization of DDT, the half-lives for volatilization of DDT in aquatic environments could then be on the order of a few hours. Mackay and Wolkoff (1973) and Mackay and Leinonen (1975) have calculated volatilization half-lives for a series of chemicals based on equations for mass transfer in an idealized aquatic system. A half-life of 3.1 days was calculated for DDT volatilization, and the authors note that for DDT the volatilization rate is determined by the DDT concentration gradient in the vapor phase (Mackay and Leinonen 1975).

Acree et al. (1963) reported studies on volatilization of DDT from aqueous solutions as a follow-up to earlier studies that reported more than a 50% loss of a 10-ppb DDT suspension in water after the solution remained for 24 hours at room temperature. Although the authors described the loss process as "codistillation" of DDT with water, Spencer (1975) pointed out that the "codistillation" term is inappropriate, because it connotes an additive vapor pressure relationship between water and DDT that

is only applicable at the boiling point of a solution and not at environmental temperatures. Water and DDT, in fact, vaporize from solution independent of each other. Acree et al. did find, however, that the weight loss of DDT per weight loss of water was on the order of 3 to 6 percent at 25°-30°C for initial DDT concentrations of 100 to 0.36 ppb. In all experiments, more than 50% of the initial DDT was lost in 24 hours; insufficient experimental information or discussion is available to determine whether the loss of DDT was completely due to volatilization or how the data obtained may be relevant to environmental aquatic systems.

Other studies have also implicated volatilization as an important loss process. Hamelink et al. (1971) studied the fate of DDT applied at concentrations of 5-15 ppb to natural and artificial ponds, and attributed a 90 percent loss of the applied DDT after 30-40 days to volatilization (see Section 25.4.9). Oloffs and Albright (1974) reported that DDT losses from solutions incubated for 12 days in two natural waters were 20 to 50 percent, with some of the DDT recovered from the glass wool plugs stoppering the flasks; no DDT was lost in water samples incubated in glass-stoppered flasks. The authors also found no loss of DDT from volatilization in water containing sediments, although some DDT was converted to DDD. They concluded that these experiments with sediment demonstrated the competition of sorption to sediments versus volatilization that exists in natural waters.

A more general discussion of the movement of DDT and its residues (DDD and DDE) into the atmosphere was given by Spencer (1975); this review covers a few papers on the volatilization of DDT from water and the more extensive literature on volatilization of DDT from soil. In a discussion of DDT in the atmosphere, Bidleman and Olney (1974) sugggest that the atmospheric DDT is in the vapor phase rather than associated with particulate matter, because the difference between the amount of some materials in particulates (e.g., lead) found over Rhode Island and Bermuda was a hundredfold greater than the difference in DDT concentrations in the air samples. Woodwell et al. (1971) estimated that the mean residence time for DDT in the atmosphere is 4 years.

With regard to the preceeding paragraph, it should be noted that if DDT is in the vapor phase in the atmosphere as suggested by Bidleman and Olney, DDT should be rapidly oxidized by hydroxyl radicals in the atmosphere; data of Hendry and Kenley (1979) indicate that the half-life should be on the order of a few days or less. There is no information to determine whether this oxidation half-life is underestimated, whether atmospheric DDT is actually on particulates, or whether the residence time in the atmosphere of 4 years estimated by Woodwell and his associates is too long. Although this discrepancy cannot be resolved at this time, it does show the problems- and usefullness- of approaching fate evaluations using several different methodologies, which in the case of DDT unfortunately do not give the same conclusions.

25.4.5 Sorption

The sorption of DDT to suspended sediments and bottom muds has been well established by analyses of environmental samples; few quantitative studies of DDT sorption onto suspended particulates in water are available. Sorption to sediments is an important process for DDT in aquatic systems, however, with partition coefficients of 10^3 to 10^7 found for some soils suspended in aqueous solutions. Kenaga and Goring (1978) cited a value for K_{OC} of 2.38×10^5.

Weil et al. (1973) measured the sorption of DDT by an aqueous suspension of sodium humate and by a soil containing 1.4% humic substances; the 1/n and K vlues for the Freundlich isotherm plots were 0.7 and 1.1×10^5, respectively, for the suspended sodium humate, and 0.7 and 1×10^7, respectively, for the soil.

Shin et al. (1970) also measured K values for sortion of DDT from aqueous solution to three soils; no data were reported for the 1/n Freundlich parameter. The K values for sandy loam, clay, and muck soils were 1.3×10^3, 1.4×10^4, and 1.1×10^5 respectively. Picer et al. (1977) measured the sorption isotherm for sorption of DDT from seawater onto several oceanic sediments containing 0.84% to 0.51% organic carbon; the values of 1/n and K were 2 and 10^6, respectively.

Huang and Liao (1970) reported Freundlich isotherm data for sorption of DDT on three clays; the 1/n parameters they calculated are given below and the K values have been recalculated to make K unitless (X/m in µg/gm and C in µg/ml):

Sorption System	K	1/n
Montmorillinite (clay)	9.0×10^{12}	6.0
Kaolinite (clay)	1.2×10^{10}	5.1
Illite (clay)	1.9×10^7	3.3

The authors did not comment on the unusually high 1/n values measured for these experiments; the partition coefficient(s) are exceptionally large, probably because of the large 1/n value. The authors did note that the equilibrium between water and clay was reached within several hours. A subsequent paper by Huang (1971) reported that 50 and 300 mg/l concentrations of glucose in solution did not affect the amount of DDT taken up by the montmorillinite clay. The authors also noted that the DDT was not readily desorbed from montmorillinite. The amount of DDT taken up by the clays was greater than the uptake of heptachlor or dieldrin for the respective clays.

25.4.6 Bioaccumulation

The bioaccumulation of DDT in various species in the biosphere is well established. Various studies have found bioconcentration factors for DDT that range up to 10^6 in aquatic systems. DDT in concentrations up to hundreds of ppm have also been found in analyses of numerous environmental samples as a result of direct uptake, sorption to biota, and bioaccumulation in food chains. Bioaccumulation is undoubtedly an important fate of DDT in aquatic systems.

The bioconcentration and distribution of DDT in the environment has been thoroughly reviewed by Bevenue (1976), Kenaga (1972), and Edwards (1970), and need not be extensively reviewed in this report. Bioconcentration factors (BCF) cited by Kenaga range up to 10^6 for species in aquatic systems; some BCFs in literature appear to be low, possibly due to DDT being present in the aqueous phase as a suspension and therefore not available for true equilibrium between water and organisms. Terrestrial-aquatic microcosm experiments have found BCFs for aquatic organisms ranging from 10^3 to 10^5 in various species (see Section 25.4.9). Metcalf *et al.* (1973) found that the amount of DDT in mosquito fish exposed to DDT via water and food chain was 250 times greater in a 33-day microcosm experiment compared with a 3-day aquatic exposure alone, but this difference was probably because the exposure time in the 3-day experiment was too brief for maximum DDT uptake and equilibrium to be established.

25.4.7 Biotransformation and Biodegradation

The biotransformation of DDT, and of its derivatives DDE and DDD, has been extensively studied in a number of biological systems, and is the subject of thorough review by Johnsen (1976). No data are available, however, to reliably assess the rate of DDT transformation in aquatic environments. Any quantitative evaluation of DDT transformation is made more difficult by the finding of Johnsen that no microorganism has been found to utilize DDT as the sole carbon source, and that only cometabolic transformations of DDT are known. Vast literature as well as the widespread environmental occurance of DDT clearly indicates that DDT is not readily metabolized in aquatic environments, although biotransformation is undoubtedly an important process in the ultimate loss of DDT from the environment. Biotransformation of DDT occurs more readily under anaerobic conditions than in aerobic systems; transformation of DDT to DDE is favored in aerobic systems, whereas DDD is the major metabolite in anaerobic environments. In some aerobic experiments, both DDE and DDD have been found as metabolites.

It is difficult to state whether DDE or DDD is the primary DDT metabolite in the environment since the products formed are obviously in part determined by the environment where metabolism or chemical transformation occurs; the issue is also complicated because DDD undergoes further metabolism in the environment more rapidly than DDT itself or DDE. Some papers note that the ultimate transformation of DDT to DDCO via DDD requires cycling through anaerobic and aerobic systems, so that metabolism and transport via sorption/desorption will be required for total DDT degradation. For DDT in aquatic systems, however, sorption of DDT to suspended particulates and subsequent deposition into anaerobic sediment systems appears to be the dominant process.

Johnsen (1976) thoroughly reviewed DDT metabolism in microbial systems. The review covers DDT metabolism in undefined microbial populations in soils, sewage, sediment, silage, water, and digestive systems; transformations in defined microbial populations of bacteria, fungi, and algae and mixed microbial populations were also reviewed. Johnsen concluded that the major route of DDT metabolism is through DDD, which can be subsequently degraded to DDCO or bis-(p-chlorophenyl)-methane. DDD formation is favored by anaerobic conditions, although DDD has also been found to occur along with DDE in aerobic conditions. Johnsen further notes that DDE is very stable to further metabolism; there is not evidence to indicate that DDE is reduced to DDD. He also notes that no microorganism has been found to utilize DDT as the sole carbon source but rather that cometablism of DDT occurs.

25.4.8 Other Reactions

Stotter (1977) reviewed studies of the reaction of DDT to DDD with emphasis on the role of metal ions in the biological transformation of DDTs. His review includes reactions of iron-containing systems, and cobalt systems as well as chromium- and zinc-centered systems. The studies described include in vivo, in vitro, and model studies. Although most of the metal-DDT interactions described for cobalt or iron are part of anaerobic biological systems, the possibility exists that release of the complexes from biological systems may result in abiotic reduction of DDT in the aquatic environments if the reduced metal species are stable in the aquatic environment. No information is available, however, to assess the importance of such abiotic processes in aquatic systems compared with anaerobic biological processes for reduction of DDT.

Castro (1964) and Miskus et al. (1965) showed that porphyrins reduce DDT to DDD under anaerobic conditions. Glass (1972) found that

ferrous ion reduced DDT to DDD and that the reduction of DDT was facilitated in soils with higher organic content where ferric ion could be reduced by easily oxidizable organic matter.

In studies of the reduction of DDT by vitamin B_{12}, Berry and Stotter (1977) showed that hydroxycob(II)alamin is capable of reducing DDT to DDD under anaerobic conditions; the cobalt(II) compound was formed by reduction of the cobalt(III) form with carbon monoxide. The authors do note, however, that while cobalamin can then effect reduction of DDT, cyanocobalamin--the form in which B_{12} is usually available--is not reducible to the Co(II) state.

Ross and Biros (1970) demonstrated that DDT acts as an electron acceptor molecule to form π-complexes with several alkylated aromatic molecules in chloroform and carbon tetrachloride solvents. Although such interactions may also occur with natural materials such as humic acid in aquatic environments, there is no information to indicate whether such processes are important in the environment.

25.4.9 Microcosm Studies, Field Studies, and Modelling

Several field studies and a microcosm experiment have been reported that demonstrate various aspects of the fate of DDT in aquatic systems. Unfortunately, these reports do not provide an integrated study that can be used to evaluate all the dominant processes occurring in these aquatic systems.

Hamelink et al. (1971) studied the fate of DDT introduced into a natural pond and several artificial ponds. DDT concentration in the water dropped from 15 ppb in the natural pond and 5 ppb in the artificial pond to minimum detectable levels of about 0.02 ppb in 30 to 40 days. A material balance at this time found that at least 90% of the initial DDT was not present in components of the ponds (water, sediment, algae, invertebrates, and fish), and the DDT was presumed to have been lost by volatilization. The DDT or DDT residues, designated DDT-R, in the water were present mainly as DDT in the first 30 days, as both DDT and DDD in the second 30 days, and primarily as DDD in the last 30 days. The authors also determined that less than 25% of the DDT applied to the artificial ponds was deposited in or on the sandy bottom of the ponds.

The accumulation of DDT-R in the other components of the ponds was also determined. DDT-R were accumulated by the algae present, and depended on the amount of DDT-R present in the water. The concentration of DDT-R in invertebrates rose rapidly in initial stages of the experiment and reached

equilibrium within 5 days. The DDT-R concentration then declined as the DDT-R content of the water declined. The DDT-R content of fish, on the other hand, rose rapidly and attained levels of about 12 ppm. A somewhat similar study by Bridges et al. (1963) suffered from the uncertainties of the analytical methods at that time, but the results followed the same trend, except that accumulation of DDT-R in fish was not as dramatic as in Hamelink's study. In Bridges' study, DDT-R levels fell below 1 ppb within 2 days after application of 20 ppb DDT to a farm pond, with subsequent DDT-R levels generally exceeding 1 ppm in pond vegetation for 8 weeks and in pond sediments for 3 weeks. DDT-R levels were also monitored in pond fish for 16 months. DDT levels showed a general trend for loss of DDT to trace or undetectable levels after about 9 months; both DDD and DDE were present at levels varying from 2 to 0.4 ppm, and neither compound appeared to be the major DDT metabolite/product in the pond.

The fate of DDT has also been examined in terrestrial-aquatic microcosms. Metcalf et al. (1971) found that DDT in this system after 30 days gave DDE concentrations in water, snail, mosquito larvae, and fish that exceeded the DDT levels; some DDD was also formed in this system. Since the pathway of DDT (or DDT-R) in this system involves application to plants that are ingested, in part, by caterpillar before the DDT-R are transported into the aquatic phase of the microcosm, we cannot make firm conclusions on the transformation of DDT in the aquatic phase alone. From the data obtained in this study, bioconcentration factors of 3.4×10^4, 8.2×10^3, and 8.5×10^4 were calculated for snail, mosquito larvae, and mosquito fish, respectively (Metcalf et al. 1973). In a study in an identical microcosm, Booth (1975) found DDT was still the major DDT-R, with bioconcentration factors of 1.1×10^5 for snail, 930 for mosquito larvae, 2.6×10^4 for fish, 5.9×10^3 for algae, and 6.2×10^3 for daphnia. In Booth's microcosm experiment the amount of DDD relative to DDE in the various organisms was slightly larger than in the experiment by Metcalf et al., and this difference in products as well as the difference in bioconcentration factors is probably due to the difficulty in reproducing such microcosm experiments between laboratories.

25.5 Data Summary

Table 25-1 summarizes the data on the aquatic fate of DDT.

Table 25-1

Summary of Aquatic Fate of DDT

Environmental Process[a]	Summary Statement	Rate	Half-life $t_{\frac{1}{2}}$	Confidence of Data
Photolysis	Direct photolysis is slow. Indirect photolysis may be important.	-	>150 years ~7 days	High Low
Oxidation	Not an important process.	-	~22 years	High
Hydrolysis	May be important under certain conditions.	-	~12 years, pH < 5 81 days pH 9	High
Volatilization	Is an important process.	-	Few hours to several weeks.	Low
Sorption	Is an important process.	-	-	High
Bioaccumulation	Is an important process.	-	-	High
Biotransformation/ Biodegradation	Is an important process in ultimate loss of DDT.	-	-	Medium

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

25.6 Literature Cited

Acree, F. Jr., M. Beroza, and M. C. Bowman. 1963. Codistillation of DDT with water. Agricultural and Food Chem. 11(4):278-80.

Baker, R. D., and H. G. Applegate. 1970. Effect of temperature and ultraviolet radiation on the persistence of methyl parathion and DDT in soils. Agron. J. 62:509-512.

Baker, R. D., and H. G. Applegate. 1974. Effect of ultraviolet radiation on the persistence of pesticides. Tex. J. Sci. 25(1-4):53-59.

Berry, J. D., and D. A Stotter. 1977. Dechlorination of DDT by vitamin B_{12} under mildly reducing conditions. Chemosphere 8(11):783-787.

Bevenue, A. 1976. The bioconcentration aspects of DDT in the environment. Residue Rev. 61:37-112.

Bidleman, T. F., and C. E. Olney. 1974. DDT in the ocean: Is the atmosphere the source? Maritimes, May 74:1-3.

Biggar, J. W. and L. R. Riggs. 1974. Apparent solubility of organochlorine insecticides in water at various temperatures. Hilgardia. 42(10):383-391.

Booth, G. M. 1975. The usefulness of mode ecosystems in insecticide development. Environ. Qual. Saf., Suppl. 3(Pesticides):351-358.

Bowman, M. C., F. Acree, Jr., and M. K. Corbett. 1960. Solubility of carbon-14 DDT in water. J. Agric. Food Chem. 8(5):406-408.

Bridges, W. R., B. J. Kallman, and A. K. Andrews. 1963. Persistence of DDT and its metabolites in a farm pond. Trans. Am. Fish. Soc. 92:421-427.

Castro, C. E. 1964. The rapid oxidation of iron (II) porphyrins by alkylhalides. A possible mode of intoxication of organisms by alkyl halides. J. Amer. Chem. Soc. 86:2310-2311.

Crosby, D. G., and K. W. Moilanen. 1977. Vapor-phase photodecomposition of DDT. Chemosphere 6(4):167-172.

Edwards, C. A. 1970. Persistent pesticides in the environment. CRC Press, Cleveland, Ohio. 78pp.

Eichelberger, J. W., and J. J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5(6):541-544.

Fleck, E. E. 1949. The action of ultraviolet light on DDT. J. Amer. Chem. Soc. 71:1034-1036.

Ginsburg, J. M. 1953. Rate of decomposition of the newer insecticides when exposed to direct sunlight. Proc. New Jersey Mosquito Exterm. Assoc. 40:163-168.

Glass, B. L. 1972. Relation between the degradation of DDT and the iron redox system in soils. J. Agric. Food Chem. 20(2):324-327.

Gunther, F. A. 1945. Aspects of the chemistry of DDT. J. Chem. Ed. 22:238-242.

Gunther, F. A., and J. D. Gunther. 1971. Residues of pesticides and other foreign chemicals in foods and feeds. Residue Rev. 36:69-77.

Hamelink, J. L., R. C. Waybrant, and R. C. Ball. 1971. A proposal: exchange equilibria control the degree chlorinated hydrocarbons are biologically magnified in lentic environments. Trans. Amer. Fish. Soc. 100(2):207-214.

Hendry, D.G., and R. Kenley. 1979. Atmospheric reaction products of organic compounds. EPA Final Report. EPA Contract 560/12-79-001.

Hendry, D. G., T. Mill, L. Piszkiewicz, J. A. Howard, and H. K. Eigenmann. 1974. A critical review of H-atom transfer in the liquid phase: chlorine atom, alkyl, trichloromethyl, alkoxy, an alkylperoxy radicals. J. Phys. Chem. Ref. Data. 3(4):937-978.

Hoffman, J., and D. Eichelsdoerfer. 1971. Effect of ozone on chlorinated-hydrocarbon-group pesticides in water. Vom Wasser 38:197-206.

Huang, J.-C. 1971. Effect of selected factors on pesticide sorption and desorption in the aquatic system. J. Water Pollut. Control Fed. 43(8):1739-1748.

Huang, J.-C., and C.-S. Liao. 1970. Adsorption of pesticides by clay minerals. J. Sanit. Div., Amer. Soc. Civ. Eng. 96(SA5):1057-1078.

Ivie, G.W., and J.E. Casida. 1971(a). Sensitized photodecomposition and photosensitizer activity of pesticide chemicals exposed to sunlight of silica gel chromatoplates. J. Agric. Food Chem. 19(3):405-409.

Ivie, G. W., and J. E. Casida. 1971 (b). Photosensitizers for the accelerated degradation of chlorinatged cyclodienes and other insecticide chemicals exposed to sunlight on bean leaves. J. Aric. Food Chem. 19(3):410-416.

Johnsen, R. E. 1976. DDT metabolism in microbial systems. Residue Rev. 61:1-28.

Kapoor, I. P., R. L. Metcalf, A. S. Hirwe, J. R. Coats, and M. S. Khaisa. 1973. Structure activity correlations of biodegradability of DDT analogs. J. Agric. Food Chem. 21(2):310-315.

Kenaga, E. E. 1972. Factors related to bioconcentration of pesticides. Pages 193-228 in F. Matsumura, G. M. Boush, and T. Misato, eds. Environmental toxicology of pesticides. Academic press, New York and London.

Kenaga, E. E., and C. A. I. Goring. 1978. Relationship between water solubility, soil-sorption, octanol-water partitioning, and bioconcentration of chemicals in biota. Amer. Soc. Test. Mat. Third Aquatic Tox. Symp., New Orleans, LA. 63 pp.

Leffingwell, J. T. 1975. The photsolysis of DDT in waters. Ph.D. Thesis. University of California, Davis. 124 pp. University Microfilms, Ann Arbor, Mich, Order No. 76-14, 218. (Diss. Abstr. Int. B 1976, 37(1):177-178).

Linquist, A. W., H. H. Jones, and A. H. Madden. 1946. DDT residual-type sprays as affected by light. J. Econ. Entomol. 39:55-59.

Mackay, D., and P. J. Leinonen . 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Tech. 9(13):1178-1180.

Mackay, D., and A.W. Wolkoff. 1973. Rate of evaporation of low solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 7(7):611-614.

Martin, H., ed. 1972. Pesticide Manual, 3rd Ed. British Crop Protection Council, Worcester, Engl.

Metcalf, R.L. 1972. DDT substitutes. Crit. Rev. Environ. Control. 3(1):25-59.

Metcalf, R. L., I. P. Kapoor, P.-Y. Lu, C. K. Schuth, and P. Sherman. 1973. Model ecosystem studies of the environmental fate of six organochlorine pesticides. Environ. Health Perspect. 4:35-44.

Metcalf, R. L., G. K. Sangha, and I. P. Kapoor. 1971. Model ecosystem for the evaluation of pesticide biodegradability and ecological magnification. Environ. Sci. Technol. 5(8):709-713.

Miller, L. L., and R. S. Narang. 1970. Induced photolysis of DDT. Science 169:368-370.

Miskus, R. P., D. P. Blair, and J. E. Casida. 1965. Conversion of DDT to DDD by bovine rumen fluid, lake water, and reduced porphyrins. J. Agric. Food Chem. 13(5):481-83.

Mosier, A. R., W. D. Guenzi, and L. L. Miller. 1969. Photochemical decomposition of DDT by a free-radical mechanism. Science 164:1083-1085.

O'Brien, R. D. 1974. Nonenzymic effects of pesticides on membranes. Pages 331-342 in R. Haque and V. H. Freed, eds. Environmental dynamics of pesticides. Plenum Press, New York, N.Y.

Oloffs, P. C., and L. J. Albright. 1974. Transport of some organochlorines in British Columbia waters. Proc. Int. Conf. Transp. Persistent Chem. Aquat. Ecosyst. 1:89-92.

Picer, N., M. Picer, and P. Strohal. 1977. The interaction of DDT with suspended particles in seawter. Water, Air, and Soil Pollut. 8:429-440.

Plimmer, J. R., U. I. Klingbiel, and B. E. Hummer. 1970. Photooxidation of DDT and DDE. Science. 167:67-69.

Roburn, J. 1963. Effect of sunlight and ultraviolet radiation on chlorinated pesticide residues. Chem. Ind. (1963):1555-1556.

Ross, R. T., and F. J. Biros. 1970. Molecular complexes of 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane with aromatic donors. Biochem. Biophys. Commun. 39(4):723-731.

Shin, Y. O., J. J. Chodan, and A. R. Wolcott. 1970. Adsorption of DDT by soils, soil fractions, and biological materials. J. Agric. Food Chem. 18(6):1129-1133.

Singmaster, J. A., III. 1975. Environmental behavior of hydrophobic pollutants in aqueous solutions. Ph.D. Thesis. Univ. California, Davis, Calif. 143pp. University Microfilms, Ann Arbor, Mich., Order No. 76-14,237. (Diss. Abstr. Int. B 1976, 36(12, Pt. 1):6206-6207).

Spencer, W. F. 1975. Movement of DDT and its derivatives into the atmosphere. Residue Rev. 59:91-117.

Stotter, D. A. 1977. Metal centres and DDT. J. Inorg. Nucl. Chem. 39:721-727.

Weil, L., G. Dure, and K. E. Quentin. 1973. Adsorption of chlorinated hydrocarbons to organic particles and soils. Z. Wasser Abwasser Forsch. 6(4):107-112.

Weil, L., G. Dure, and K. E. Quentin. 1974. Solubility in water of insecticide chlorinated hydrocarbons and polychlorinated biphenyls in view of water pollution. Z. Wasser Abwasser Forsch. 7(6):169-175.

Wolfe, N. L., R. G. Zepp, D. F. Paris, G. L. Baughman, and R. C. Hollis. 1977. Methoxychlor and DDT degradation in water: Rates and products. Environ. Sci. Technol. 7(110):1077-1081.

Woodwell, G. M., P. P. Craig, and H. A. Johnson. 1971. DDT in the biosphere: Where does it go? Science 174:1101-1107.

Zepp, R. G., N. L. Wolfe, J. A. Gordon, and R. C. Fincher. 1976. Light-induced transformations of methoxychlor in aquatic systems. J. Agric. Food Chem. 24(4):727-733.

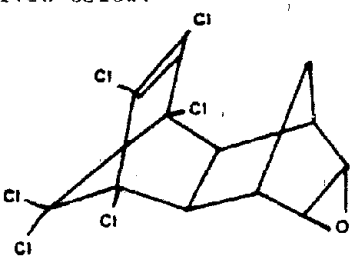
26. DIELDRIN

26.1 Statement of Probable Fate

The literature information as well as analysis of numerous environmental samples indicates that dieldrin is persistent in the environment. The important fate processes in aquatic environments are sorption to sediment, bioaccumulation, and volatilization; the latter process may have half-lives of several hours to several days in some aquatic systems. Although direct photolysis of dieldrin in water is slow ($t_{1/2}$ ~ 2 months), photosensitized processes may result in photolysis if sensitizers are available in aquatic environments. Although dieldrin is quite resistant to biotransformation, this process will probably be an important fate for dieldrin in sediment and biota.

26.2 Identification

This section considers only the fate of the pure chemical dieldrin. The structure, alternate names, and CAS and TSL numbers of dieldrin are given below:



Dieldrin

CAS No. 60-57-1
TSL No. IO 17500

Alternate Names
1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,-8a-octahydroexo-1,4-endo-5,8-dimethano-naphthalene
HEOD
Compound 497
Octalox

26.3 Physical Properties

The general physical properties of dieldrin are as follows:

Molecular weight	381
Melting point (Martin 1972)	175-176 °C
Boiling point	No data found

Vapor pressure at 20°C*	
(Martin 1972)	1.78×10^{-7} torr
(Spencer and Cliath 1969)	2.8×10^{-6} torr
Solubility in water	
(Park and Bruce 1968)	186 ppb at 25-29°C
(Biggar and Riggs 1974)†	195 ppb at 25°C
(Weil et al. 1974)	200 ppb at 25°C
(Bhavnagary and Jayaram 1974)	200 ppb at 26.5°C
Log octanol/water partition coefficient	No data found

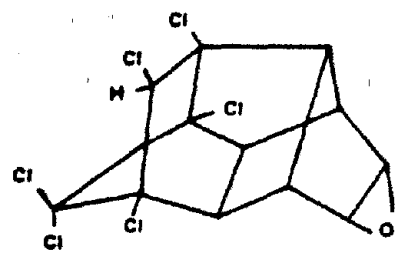
*Reported values range from 1.78×10^{-7} to 2.9×10^{-6} torr at 20°C (Benchmark 1975).
† Particle size < 5 µm.

26.4 Summary of Fate Data

26.4.1 Photolysis

The direct photolysis half-life of dieldrin is about 2 months. Although photosensitized processes are known for dieldrin, insufficient information is available to predict how rapid these processes may be in comparison to direct photolysis in aquatic environments.

Henderson and Crosby (1968) reported an experiment in which a saturated solution of dieldrin in distilled water was photolyzed in sunlight. At the end of 3 months photolysis, 0.14 ppm dieldrin remained and 0.32 ppm of the isomer photodieldrin I (see below) was present. Based on the concentration of dieldrin in a dark control (0.51 ppm) or on the



I

Photodieldrin

material balance in the reaction (0.14 + 0.32 = 0.46 ppm), the half-life for direct photolysis of dieldrin is 2.1 or 1.8 months, respectively. Although some of the initial concentration of 0.51 ppm dieldrin must have exceeded the solubility and have been in suspension, these data are the best available for estimating the direct photolysis half-life of dieldrin in aqueous solution.

Photodieldrin has also been reported to be a product from photolysis of dieldrin in the solid state at wavelengths below 300 nm. (Robinson et al. 1966; Benson 1971; Rosen et al. 1966). Benson et al. also reported that I was formed in yields of 7 percent after 3 weeks and 25 percent after 2 months for solid films of dieldrin exposed to sunlight. Photolysis of dieldrin at < 300 nm in the solid phase under a current of oxygen also gave a small yield of I but most of the residue was unreacted dieldrin or polymer (Gäb et al. 1974). This information, although not relevant to aquatic systems, does demonstrate that photodieldrin is a commonly found product of direct photolysis of dieldrin.

Ivie and Casida (1970, 1971b) also reported that photodieldrin is a product of the rotenone-sensitized photolysis of dieldrin on bean leaves exposed to sunlight. Triplet sensitizers codeposited with dieldrin on silica gel plates and exposed to sunlight also produced I (Ivie and Casida 1971a). Rosen and Carey (1968) prepared I in 75 percent yield by the benzophenone-sensitized photolysis of dieldrin in benzene solvent. Although these studies clearly show that photodieldrin can be formed by photosensitized processes, there is no information on what sensitizers are present in aquatic environments that could also effect such reaction, or what the half-lives of such processes may be.

In several studies of the photolysis of dieldrin at wavelengths below 300 nm, products were reported in which dieldrin was dechlorinated at the vinylic position (Benson 1971; Nagl et al. 1970; Henderson and Crosby 1967.) The latter authors have shown, however, that such dechlorinated products are not likely to be formed at wavelengths above 300 nm in the solar region.

Since volatilization of dieldrin from water and soil is an important process, Crosby and Moilanen (1974) studied the photolysis of dieldrin in the vapor phase. The only product obtained when dieldrin was photolyzed with a sunlamp was photodieldrin, and no data are available to estimate how fast dieldrin will be photolyzed in the atmosphere.

26.4.2 Oxidation

No information is available on the oxidation of dieldrin in aquatic systems. The highly chlorinated dieldrin structure with the bridge-

head positions should, however, be unreactive toward free radical oxidation under environmental conditions. Hoffman and Eichelsdoerfer (1971) found that dieldrin was unreactive toward reaction with ozone in hexane and in water-acetone solvents.

26.4.3 Hydrolysis

A study by Eichelberger and Lichtenberg (1971) indicates that hydrolysis of dieldrin in aquatic environments is probably very slow. They reported that 10 ppb of dieldrin in distilled water and in a sample of raw water from the Little Miami River (Ohio) was 100 percent recovered after 8 weeks at room temperature; since the recoveries were rounded off to the nearest 5%, less than 2.5% loss of dieldrin had occurred. A 2.5 percent loss after 8 weeks corresponds to a half-life of 4 years; hence, the hydrolysis half-life of dieldrin is greater than 4 years in aquatic environments.

26.4.4 Volatilization

Volatilization of dieldrin from aquatic systems into the atmosphere is probably an important process with half-lives on the order of a few hours to a few days.

Singmaster (1975) described studies designed to measure the relative rate of volatilization of chlorinated pesticides from pure water and several natural waters. In these experiments the pesticides at approximately 1 pptr concentrations in 900 ml of water in a 5-liter flask were gently agitated on a shaker while air was drawn through the flask (but not bubbled through solution) at a rate of 4.5 l/min. The half-lives for volatilization of dieldrin from pure water and waters from San Francisco Bay, the American River, and Sacramento River (in California) were 7.7 hr, 6.1 hr, 9.0 hr, and 8.5 hr, respectively; the water loss in these experiments averaged 3.6 $\pm$ 0.2 g/hr. Singmaster concluded that volatilization of dieldrin in natural waters would not be more than two times slower than in pure water. Although the total experiment is difficult to relate to conditions in aquatic environments (e.g., temperature, agitation), the author noted that the air exchange in the flask corresponded to a wind velocity of about 10 m/hr, which is much lower than that usually found in the environment. Based on the wind velocity factor alone and assuming removal of dieldrin from the vapor space is the dominant force in volatilization of dieldrin, the half-lives for volatilization of dieldrin in aquatic environments could be on the order of a few hours to a few days.

Mackay and Wolkoff (1973) and Mackay and Leinonen (1975) derived equations to predict volatilization of low-solubility organic chemicals from aquatic environments. Assuming a reasonable value for evaporation of

water from an aquatic system and using physical-chemical data for dieldrin at 25°C, a half-life of about 1.5 years was calculated. The significant disagreement between this value and that suggested by the data of Singmaster is probably due to the failure of Mackay's calculation to include the contribution of mass transfer in the gas phase for removal of dieldrin.

26.4.5 Sorption

Sorption of dieldrin to sediments containing significant amounts of organic material will probably be an important fate in aquatic systems, especially since transformation processes for dieldrin are slow.

Weil et al. (1973) reported Freundlich isotherm data for sorption of dieldrin to humic acid and a soil at 15°C. The 1/n and K values for the humic acid-dieldrin sorption experiment were 0.79 and 228, respectively; for the sorption to soil, the 1/n and K values were 0.64 and 1.6×10^4, respectively. The latter sorption coefficient suggests that sorption of dieldrin to sediments will be appreciable. Boucher and Lee (1972) studied the uptake of dieldrin from water on aquifer and silica sands at 5°C; equilibrium between water and sand was reached within several hours. A Freundlich isotherm sorption partition coefficient (K) of 2-5 was estimated from isotherm plots presented in the paper. Such low coefficients are not unexpected for particulates low in organic material.

The sorption of dieldrin to several clays was reported by Huang and Liao (1970) and by Huang (1971; 1974). As discussed in the chapters on heptachlor and DDT, the Freundlich isotherm parameters 1/n and K in these studies were unusual in that 1/n exceeded 3 instead of being unity as is usually found. In the 1971 paper the 1/n values for sorption of dieldrin ranged from 8.8 to 11.6; therefore, the corresponding K values are so large as to be meaningless in the normal comparison and use of K values where 1/n = 1.

26.4.6 Bioaccumulation

Bioconcentration factors for dieldrin in various organisms range from 10^2 to 10^4, indicating that dieldrin will show moderate to significant bioaccumulation in various species present in aquatic systems.

Grimes and Morrison (1975) have reported dieldrin concentration factors for 13 bacterial species that ranged from 90 to 2.8×10^4; 6 species had factors between 90 and 700, with the other 7 bacteria having factors of 1.1×10^3, 1.2×10^3, 1.5×10^3, 3.0×10^3, 4.7×10^3, 1.6×10^4, and 2.8×10^4. Neudorf and Khan (1975) found a concentration factor of 3.2×10^4 for a fresh water alga exposed to dieldrin for 3 hours.

Data from microcosm experiments also suggest similar ranges of bioconcentration factors. Metcalf et al. (1973) found bioconcentration factors of 4.57×10^2, 6.2×10^4, and 2.7×10^3 for an alga, snail, and fish, respectively. Sanborn and Yu (1973) found concentration factors of 7.5×10^3, 1.1×10^5, and 6.1×10^3 for the same species in their experiments. Ernst (1977) found a bioconcentration factor of 1.6×10^3 for accumulation of dieldrin by a salt water mussel, with a half-life for dieldrin elimination of about 50 hours when the mussel was transferred to clean water.

26.4.7 Biotransformation and Biodegradation

Several authors cite dieldrin as being one of the more nonbiodegradable chlorinated pesticides, and although several papers have reported biotransformation of dieldrin, no useful data are available for estimating biotransformation rates in aquatic environments.

Bohonos and Francis (1975) and Sanborn et al. (1977) reviewed the literature on biotransformation of dieldrin and stated that dieldrin is one of the more persistent chlorinated pesticides. In studies comparing the rates of biotransformation of chlorinated pesticides (including DDT and metabolites, HCH isomers, endrin, heptachlor, and methoxychlor) in flooded and nonflooded soils, Watanabe (1973) and Castro and Yoshida (1971) found both dieldrin and chlordane to be unique in that they were persistent in both types of soils. Hill and McCarty (1967) stated that dieldrin was more stable than lindane, heptachlor, endrin, DDT, aldrin, or heptachlor epoxide in anaerobic sewage sludge. Matsumura and Boush (1967) found that the majority of 577 microbial isolates from soil incubated in nutrient solutions for 30 days showed no capacity for biological transformation of dieldrin. These qualitative observations are difficult to relate to aquatic environments, but they do indicate that dieldrin biotransformations will be very slow.

The persistence of dieldrin has also been shown in terrestrial-aquatic microcosm experiments. Sanborn and Yu (1973) found that of the ^{14}C applied as dieldrin in the terrestrial compartment of the microcosm an average of 97% of the ^{14}C extracted from algae, clam, crab, daphnia, mosquito larvae, fish, and snail was present as dieldrin. Trace amounts of metabolites were found, among them 9-hydroxydieldrin and 9-ketodieldrin. Metcalf et al. (1973) also studied the fate of dieldrin in a terrestrial-aquatic microcosm, and found dieldrin present as 88, 96, and 95% of the total ^{14}C recovered from alga, snail, and fish, respectively; the small amounts of metabolites found were the same as those found by Sanborn and Yu.

26.4.8 Other Reactions

No reactions other than those described above are considered important fates for dieldrin in aquatic systems.

26.4.9 Microcosm Studies, Field Studies, and Modelling

The microcosm experiments of Metcalf et al. (1973) and Sanborn and Yu (1973) have demonstrated the stability of dieldrin toward biotransformation and its propensity for bioaccumulation in several aquatic species (see Sections 26.4.6 and 26.4.7).

26.5 Data Summary

Table 26-1 summarizes the data on the aquatic fate of dieldrin.

Table 26-1

Summary of Aquatic Fate of Dieldrin

Environmental Process[a]	Summary Statement	Rate	Half-Life $t_{\frac{1}{2}}$	Confidence of Data
Photolysis	Direct photolysis may be important.	-	2 months	Medium
Oxidation	Not an important process.	-	-	High
Hydrolysis	Not an important process.	-	> 4 years	High
Volatilization	Is an important process.	-	few hours to few days	Medium
Sorption	Probably an important process.	-	-	Medium
Bioaccumulation	Is an important process.	-	-	High
Biotransformation / Biodegradation	Is very slow, but may be ultimate loss process in sediment.	-	-	High

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

26.6 Literature Cited

Benchmark. 1975. Draft of Preliminary Summaries of Literature Surveys of Benchmark Pesticides. George Washington University Medical Center. Draft dated October 30, 1975.

Benson, W. R. 1971. Photolysis of solid and dissolved dieldrin. J. Agric. Food Chem. 19(1):66-72.

Bhavnagary, H. M., and M. Jayaram. 1974. Determination of water solubilities of lindane and dieldrin at different temperatures. Bull. Grain Technol. 12(2):95-99.

Biggar, J. W., and L. R. Riggs. 1974. Apparent solubility of organochlorine insecticides in water at various temperatures. Hilgardia 42(10):383-391.

Bohonos, N., and A. J. Francis. 1975. Microbiological degradation of military standard pesticide formulations. Final Report. SRI to the U.S. Army Medical Research Development Command. Contract No. DADA17-73-C-3124.

Boucher, F. R., and G. F. Lee. 1972. Adsorption of lindane and dieldrin pesticides on unconsolidated aquifer sands. Environ. Sci. Technol. 6(6):539-543.

Castro, F., and T. Yoshida. 1971. Degradation of organochlorine insecticides in flooded soils in the Philippines. J. Agric. Food Chem. 19(6):1168-1170.

Crosby, D. G., and K. W. Moilanen. 1974. Vapor-phase photodecomposition of aldrin and dieldrin. Arch. Environ. Contam. Toxicol. 2(1):62-74.

Eichelberger, J. W., and J. J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5(6):541-544.

Ernst, W. 1977. Determination of the bioconcentration potential of marine organisms - a steady state approach. Chemosphere 6(11):731-740.

Gäb, S., H. Parlar, S. Nitz, K. Hustert, and F. Korte. 1974. Beitrage zur ökologischen chemie. LXXXI. Photochemischer abbau von aldrin, dieldrin and photodieldrin als festkorper im sauerstoffstrom. Chemosphere 3(5):183-186.

Grimes, D. J., and S. M. Morrison. 1975. Bacterial bioconcentration of chlorinated hydrocarbon insecticides from aqueous systems. Microb. Ecol. 2:43-59.

Henderson, G. L., and D. G. Crosby. 1968. The photodecomposition of dieldrin residues in water. Bull. Environ. Contam. Toxicol. 3(3):131-134.

Henderson, G. L., and D. G. Crosby. 1967. Photodecomposition of dieldrin and aldrin. J. Agric. Food Chem. 15:888-893.

Hill, D. W., and P. L. McCarty. 1967. Anaerobic degradation of selected chlorinated hydrocarbon pesticides. J. Water Pollut. Control Fed. 39(8):1259-1277.

Hoffmann, J., and D. Eichelsdoerfer. 1971. Effect of ozone on chlorinated-hydrocarbon-group pesticides in water. Vom Wasser 38:197-206.

Huang, J.-C. 1971. Effect of selected factors on pesticide sorption and desorption in the aquatic system. J. Water Pollut. Control Fed. 43(8):1739-1748.

Huang, J.-C. 1974. Water-sediment distribution of chlorinated hydrocarbon pesticides in various environmental conditions. Proc. Int. Conf. Transp. Persistent Chem. Aquat. Ecosyst. II:23-30.

Huang, J.-C., and C.-S. Liao. 1970. Adsorption of pesticides by clay minerals. J. Sanit. Div. Am. Soc. Civ. Eng. 96(SA5):1057-1078.

Ivie, G. W., and J. E. Casida. 1970. Enhancement of photoalteration of cyclodiene insecticide chemical residues by rotenone. Science. 167(329S):1620-1622.

Ivie, G. W., and J. E. Casida. 1971a. Sensitized photodecomposition and photosensitizer activity of pesticide chemicals exposed to sunlight of silica gel chromatoplates. J. Agric. Food Chem. 19:405-409.

Ivie, G. W., and J. E. Casida. 1971b. Photosensitizers for the accelerated degradation of chlorinated cyclodienes and other insecticide chemicals exposed to sunlight on bean leaves. J. Agric. Food Chem. 19(3):410-416.

Mackay, D., and P. J. Leinonen. 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 9(13):1178-1180.

Mackay, D., and A. W. Wolkoff. 1973. Rate of evaporation of low solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 7(7):611-614.

Martin, H., ed. 1972. Pesticide Manual, 3rd Ed. British Crop Protection Council, Worcester, Engl.

Matsumura, F., and G. M. Boush. 1967. Dieldrin: Degradation by soil microorganisms. Science 156(3777):959-961.

Metcalf, R. L., I. P. Kapoor, P.-Y. Lu, C. K. Schuth, and P. Sherman. 1973. Model ecosystem studies of the environmental fate of six organo-chlorine pesticides. Environ. Health Perspect. 4:35-44.

Nagl, H. G., W. Klein, and F. Korte. 1970. Betraige zur okologischen chemie-XXVIII. Uber das peaktionsverhalten von dieldrin in losung und in der gasphase. Tetrahedron 26:5319-25.

Neudorf, S., and M. A. Q. Khan. 1975. Pick-up and metabolism of DDT, dieldrin, and photoaldrin by a freshwater alga (Ankistrodesmus Amalloides) and a microcrustacean (Daphnia Pulex) Bull. Environ. Contam. Tox. 13(4):443-450.

Park, K. S., and W. N. Bruce. 1968. The determination of the water solubility of aldrin, dieldrin, heptachlor and heptachlor epoxide. J. Econ. Entomol. 61(3):770-774.

Robinson, J., A. Richardson, B. Bush, and K. E. Elgar. 1966. A photo-isomerization product of dieldrin. Bull. Environ. Contam. Toxicol. 1(4):127-132.

Rosen, J. D., and W. F. Carey. 1968. Preparation of the photoisomers of aldrin and dieldrin. J. Agric. Food Chem.. 16(3):536-537.

Rosen, J. D., D. J. Sutherland, and G. R. Lipton. 1966. The photochemical isomerization of dieldrin and endrin and effects on toxicity. Bull. Environ. Contam. Toxicol. 1(4):133-140.

Sanborn, J.. R., B. M. Francis, and R. L. Metcalf. 1977. The degradation of selected pesticides in soil: A review of the published literature. U.S. NTIS, PB Rep., PB-272353, 633pp.

Sanborn, J. R. and C. Yu. 1973. The fate of dieldrin in a model ecosystem. Bull. Environ. Contam. Toxicol. 10(6):340-346.

Singmaster, J. A., III. 1975. Environmental behavior of hydrophobic pollutants in aqueous solutions. Ph.D. Thesis. Univ. California, Davis, Calif. 143pp. University Microfilms, Ann Arbor, Mich., Order No. 76-14,237. (Diss. Abstr. Int. B 1976, 36(12, Pt.1):6206-6207).

Spencer, W. F., and M. M. Cliath. 1969. Vapor density of dieldrin. Environ. Sci. Technol. 3(7):670-674.

Watanabe, I. 1973. Decomposition of pesticides by soil microorganisms - Special emphasis on flooded soil condition. JARQ 7(1):15-18.

Weil, L., G. Dure, and K. E. Quentin. 1973. Adsorption of chlorinated hydrocarbons to organic particles and soils. Z. Wasser Abwasser Forsch. 6(4):107-112.

Weil, L., G. Dure, and K. E. Quentin. 1974. Solubility in water of insecticide chlorinated hydrocarbons and polychlorinated biphenyls in view of water pollution. Z. Wasser Abwasser Forsch. 7(6):169-175.

27. ENDOSULFAN AND ENDOSULFAN SULFATE

27.1 Statement of Probable Fate

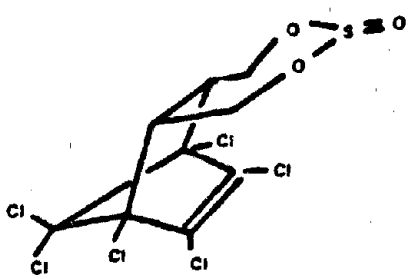
Data are incomplete, regarding the important processes for determining the fate of endosulfan in aquatic systems. The hydrolysis half-life of endosulfan at 20°C is about a month at pH 7 and about 6 months at pH 5.5. Other information suggests that photolysis, oxidation, biodegradation, sorption, and volatilziation may be occuring under some environmental conditions, but data for predicting the rates and relative importance of these processes in aquatic systems are not available.

No data have been found on the transformation or transport of endosulfan sulfate. Hydrolysis could be the most important process for endosulfan sulfate, but no hydrolysis data have been found.

27.2 Identification

Endosulfan and its derivatives exist in two steroisomeric forms, the α- and the β-forms.

The structure, CAS and TSL numbers, and nomenclature for endosulfan and endosulfan sulfate are as follows:



α-Endosulfan

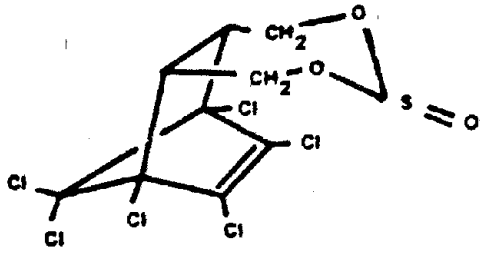
CAS No. 115-29-7
TSL No. RB 92750

Alternate Names (α and β isomers)

5-Norbornene-2,3-dimethanol-1,4,5,6,7,7-hexachloro-, cyclic sulfite
6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9,-methano-2,4,3-benzo[e]di-oxathiepin-3-oxide
α,β-1,2,3,4,7,7-Hexachlorobi-cyclo-(2.2.1)-hepten-2-bi-xymethylene-5,6-sulfate
Thiodan
Cyclodan
Beosit
Malix
Thimul
Thifor

Alternate Names

See page 27-1.

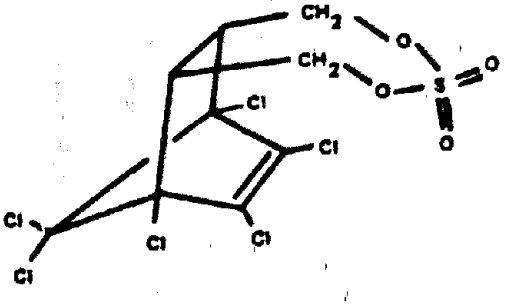


β-Endosulfan

CAS No. 115-29-7
TSL No. RB 92750

Alternate Names

None found.



Endosulfan sulfate

CAS No. 1031-07-8
TSL No. None assigned

27.3 Physical Properties

The general physical properties of endosulfan (α- and β- isomers) and endosulfan sulfate are as follows.

		Endosulfan	Endosulfan Sulfate
Molecular weight		406.9	422.9
Melting point			
(Phillips et al. 1975)	Technical	70-100°C	
(Ali 1978)	α Endosulfan	108-110°C	198-201°C
(Ali 1978)	β Endosulfan	207-209°C	
Boiling point		No data found	No data found
Vapor pressure			
(Phillips et al. 1975)		9×10^{-3} torr at 80°C	
(Martens 1972)		1×10^{-5} torr at 25°C	

Solubility in water	α	β	
(Ali 1978)	0.164 ppm	0.070 ppm	0.117 ppm
(Phillips 1975) at 22°C, pH 7.2	0.15 ppm	0.06 ppm	
(Phillips 1975) at 20°C, pH 5.5	0.26 ppm	0.10 ppm	
(Weil et al. 1974) at 25°C	0.530 ppm	0.280 ppm	
(MRI 1977)	0.6 ppm		0.22 ppm

Log octanol/water partition coefficient - (α) 3.55
(Ali 1978) (β) 3.62
(sulfate) 3.66

27.4 Summary of Fate Data

27.4.1 Photolysis

There are no data useful for evaluating the rate of photolysis of endosulfan or its sulfate in aquatic environments. Endosulfan photolyses in solution and solid state have been reported at wavelengths > 300 nm using laboratory light sources and filters. Since endosulfan sulfate has been reported as a product from photolysis of endosulfan, a review of endosulfan photochemistry is required. The uv spectrum of endosulfan reported in literature (Gore et al. 1971) is insufficient to evaluate the absorption above 290 nm except that the absorption coefficients must be less than 800 M^{-1} cm^{-1}.

Several researchers have reported that β-endosulfan is photoisomerized to α-endosulfan in hexane (Schumacher et al. 1971; Putnam et al. 1975) and in aqueous suspension (MRI 1977). Since no quantitative data were given and laboratory lamps were used in these photolyses, it is impossible to determine how important this isomerization will be in the environment, or whether an equilibrium mixture of the isomers is attained before other photoreactions occur.

Schumacher et al. (1971, 1974) reported that irradiation of endosulfan at > 300 nm in various organic, mixed organic, and water-organic solvents gave different individual or sets of dechlorinated endosulfan products. Gas phase photolysis of β-endosulfan produced endosulfan ether, diol, sulfate, and lactone as well as the dechlorinated ether and α-isomer (See section 27.5 for structures).

Endosulfan diol was reported to be the product when an emulsion of either endosulfan isomer in water was irradiated at 250-580 nm (MRI 1977); dechlorinated diols were also found.

Schuphan and Ballschmiter (1972) found that diol was formed when either endosulfan isomer was irradiated in alkaline aqueous methanol. When irradiated in neutral solution, however, the isomers gave different (unidentified) products. It is significant to note that no solution photolyses of endosulfan have been reported to give endosulfan sulfate as a product.

Harrison et al. (1967) reported endosulfan sulfate as the only product detected from sunlight photolysis of endosulfan on apple leaves. These authors also conducted experiments to test the variables in the sulfate formation and concluded that uv irradiation and a moisture-containing substrate were necessary for sulfate formation.

Archer et al. (1972) studied the photolysis of thin films of both isomers on glass plates; GE germicidal lamps with output > 300 nm were used for irradation. Endosulfan diol was the major photolysis product, with minor amounts of endosulfan ether, lactone, α-hydroxyether, and several other unidentified products formed. Endosulfan sulfate was not formed in these photolyses and was found to be stable to photolyses under these conditions. Subsequently, Archer (1973) studied the fate of endosulfan on alfalfa dried in sunlight, uv light, and air (in the absence of light). The total residue of endosulfan and products decreased rapidly in the first several days and then decreased slowly thereafter. In the air-dried dark control sample, however, endosulfan appeared to be quantitatively converted to endosulfan sulfate after the initial decrease. Koshy (1972) studied the persistence of endosulfan on glass dishes and sweet potato leaves exposed to sunlight and assayed for residues by a 24-mortality test with insects. For the endosulfan exposed on leaves for 2 and 4 days the insect mortality was 15 and 0%, respectively; at 8 and 32 days

the mortality was 43 and 1%, respectively, for the endosulfan exposed on the glass dishes.

In summary, the above information is confusing and incomplete as to what photolysis processes and products may be expected from the environmental photolysis of endosulfan. Because of the different light sources and reaction conditions used, it is difficult to reliably assess endosulfan photolysis. The information does suggest, however, that endosulfan sulfate is more stable to photolysis than endosulfan itself.

27.4.2 Oxidation

Although oxidation of endosulfan to endosulfan sulfate has been frequently reported as occuring in photochemical, biological, and chemical systems, the source or the nature of the oxidants are unclear (see also Sections 27.4.1 and 27.4.6). The only quantitative data on oxidation of endosulfan isomers indicate that in air-saturated water the oxidation of endosulfan (presumably by molecular oxygen) may have a half-life of about 70 days at 20°C, and in the absence of product information this half-life must be used with caution.

Greve and Wit (1971) reported the oxidation rate constants shown below for both endosulfan isomers in water at two pH values and 20°C:

	α Endosulfan	β-Endosulfan
pH 7.0	10.4×10^{-3} days^{-1}	9.7×10^{-3} days^{-1}
pH 5.5	8.3×10^{-3} days^{-1}	9.9×10^{-3} days^{-1}

The rate constants were determined by the difference between first-order rate constants measured in aerobic and anaerobic buffered reaction solutions. The authors concluded that the oxidation rate was independent of pH, but they did not discuss what species were responsible for the supposed oxidation reaction; no products were reported, and it is therefore impossible to verify that oxidation was actually being measured.

In striking contrast to the apparent reactivity of endosulfan toward oxidation reported by Greve and Wit, Hoffman and Eichelsdoerfer (1971) have reported that endosulfan is only slowly oxidized by ozone as follows:

O_3 Concentration in Solvent	Initial Concentration of Pesticide	% Endosulfan Reacted α	β
24 mg/l in hexane	5 mg/l	2	52
17 mg/l O_3 in 9:1 water/acetone	2 mg/l	8	12

The reaction conditions were effected by bubbling the ozone solution through the endosulfan in solution for 45 minutes; heptachlor and aldrin were completely reacted under these conditions.

Thus, although endosulfan may be expected to be oxidized to its sulfate, it is difficult to explain why molecular oxygen should effect oxidation while the powerful oxidant ozone does not give significant oxidation; no conclusion regarding endosulfan oxidation in the environment can therefore be substantiated. Endosulfan sulfate should be more stable than endosulfan towards oxidation.

27.4.3 Hydrolysis

Both isomers of endosulfan will hydrolyze slowly in aquatic environments of pH < 7 and < 20°C with half-lives of greather than 1 month. Although the hydrolysis of endosulfan will be faster above pH 7, literature information provides no direct quantitative data for a half-life estimate at pH > 7. However, analysis of the data of Martens (1976) and Greve and Wit (1971) indicates that at pH 8 and 20°C the half-life will be about 3.5 days.

Greve and Wit (1971) measured the following hydrolysis rate constants for both isomers of endosulfan at 20°C and two pH values:

	α-Endosulfan	β-Endosulfan
pH 7.0	2.0×10^{-2} days^{-1}	1.9×10^{-2} days^{-1}
pH 5.5	4.6×10^{-3} days^{-1}	3.7×10^{-3} days^{-1}

Subsequently, Martens (1976) reported hydrolysis data that were obtained as controls in biotransformation studies at 27°C. Based on one data point taken after 10 days for each pH, the following losses of endosulfan were reported:

pH	4.3	5.5	6.3	7	>8
Endosulfan lost	<1%	2%	8%	28%	>90%

The author also reported that endosulfan diol was the only product formed, and that in some biodegradation studies above pH 8 endosulfan was not hydrolyzed as rapidly as in the control because of sorption by the cell mass and, therefore, was not available for alkaline hydrolysis.

Ali (1978) reported that α- and β-endosulfan were 82% and 87% recovered after 33 days in water used in a microcosm experiment, with no pH or temperature information given; these losses correspond to half-lives of 115 and 164 days for the respective isomers. Eichelberger and Lichtenberg (1971) studied the persistence of endosulfan at 10 µg/l concentration in a

sample of raw river water from the Little Miami River, Ohio. They reported that the peaks of both isomers, as determined by glc, were reduced 70% within one week; at the end of 2 weeks, only 5% endosulfan remained, though identification by glpc was extremely difficult. The hydrolysis product contained no sulfur; infrared spectral data indicated that it was probably endosulfan diol. The pH of the river water was reported to vary from 7.3 to 8.0 during the experiment, so that the rapid hydrolysis of endosulfan found is reasonable. Since in the same river water samples, dieldrin was formed from aldrin, the sterility of the water must be questioned; biotransformation may have therefore contributed to the endosulfan transformation rate found.

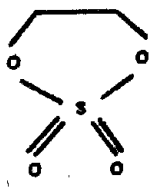
From the above information, the data at 20°C of Greve and Wit (1971) are in moderate agreement (i.e., within a factor of two) with the less precise, one-datum point experiments of Martens (1976) at 27°C; the half-lives (days) calculated from their data are compared below:

	Greve and Wit at 20°C	Martens at 27°C
pH 5.5	150 α, 187 β	343
pH 7.0	34 α, 37 β	21

The more rapid rate of hydrolysis of endosulfan reported by Eichelberger ($t_{1/2} \simeq 4$ days) may be partially explained by the higher reaction pH, but biotransformation is also a possible explanation.

The only information on the hydrolytic stability of endosulfan sulfate is that of Ali (1978), who reported that endosulfan sulfate was 88% recovered after 33 days in water used in a microcosm experiment, with no pH or temperature data given (Section 27.4.9). This loss corresponds to a half-life of 178 days. It is interesting to note that two other cyclic

I



II

sulfates, trimethylene and ethylene sulfate (I and II, respectively) have hydrolysis half-lives of 3.1 and 0.31 hours, respectively, at pH 7 and 20°C (Radding et al. 1977). The slower rate of hydrolysis of endosulfan sulfate may reflect the influence of the seven member ring.

27.4.4 Volatilization

Limited and somewhat contradictory data are available on the volatilization of endosulfan from water. This information suggests that endosulfan will have a volatilization half-life of more than 11 days, and possibly more than a year.

A theoretical volatilization half-life of 11 days is calculated for a quiescent water body using the equations and assumptions of Mackay and Leinonen (1975); the calculated half-life would be less in more turbulent water bodies.

Volatilization of endosulfan was also measured as a control in a bioaccumulation study by Ernst (1977). Aquaria aerated at 2.5 liter-hr^{-1} for 67 hours showed only an 11% loss of endosulfan; in this system the same losses (11%) of dieldrin and heptachlor epoxide were measured. Since Mackay and Leinonen (1975) calculated a half-life of 1.5 years for volatilization of dieldrin using the same equations and assumptions that we used to calculate an endosulfan volatilization half-life of 11 days, there is clearly some discrepancy in these data.

Martens (1976) also studied volatilization as a control in biotransformation studies in which the biodegradation flasks were aerated for one hour per day for the 10 days allowed for incubation. Sorption on biota was found to reduce the amount of endosulfan volatilized, with less than 1% volatilization loss of endosulfan observed in the presence of fungi; volatilization losses were 2 and 20% in the presence of bacteria and actinomycetes, which showed less sorption of endosulfan than the fungi.

Although not directly relevant to aquatic systems, other studies have provided information on volatilization from the solid state (glass plates). Although not discussed in the text of the paper, as much as one half of the endosulfan isomers and endosulfan sulfate applied to the plates was lost by volatilization during a 7-day uv-lamp irradation (Archer et al. 1972).

No information was found regarding the volatilization of endosulfan sulfate from aqueous systems.

27.4.5 Sorption

Sorption is an important fate for endosulfan in aquatic systems and sediments may be a sink for endosulfan.

Greve and Wit (1971) analyzed water from the Rhine River and determined the concentration of endosulfan in the supernatant water, in the

water containing silt that settled on standing, and in the bottom mud. Although the data presented are crude, endosulfan was shown to be > 75% associated with the particulate material (silt or mud), indicating significant sorption of both isomers of endosulfan.

Richardson and Epstein (1971) studied the adsorption of endosulfan on silt loam and found that the greatest retention of endosulfan occurred on the colloidal and 0.08 to 0.5 μm fraction of silt and clay. The authors also stated that treatment of the soil with hydrogen peroxide (to remove oxidizable organic material) reduced the amount of endosulfan retained on the soil; no data were given.

No data were found on the sorption of endosulfan sulfate.

27.4.6 Bioaccumulation

Ernst (1977) reported uptake and elimination of several pesticides, including α-endosulfan, in mussels in seawater. No bioaccumulation studies were found in freshwater aquatic systems. α-Endosulfan was found to have a concentration factor of 600 (ppb wet weight in mussel vs. water at steady state with a 2.05-ppb initial concentration in water). Ernst also gives first-order rate constant data for uptake and elimination of α-endosulfan in the mussels, but the half-lives of 3 minutes and 34 hours for uptake and elimination, respectively, are questionable because the data reported clearly show that more than half of the 84-ppb (wet weight) concentration in the mussel is eliminated after 9 hours. Based on the latter and the concentration factor of 600, it is not likely that bioaccumulation of α-endosulfan (and presumably also β-endosulfan) is a significant process.

No information was obtained on the bioaccumulation of endosulfan sulfate.

27.4.7 Biotransformation and Biodegradation

Greve and Wit (1971) reported that endosulfan can be degraded by microorganisms in waters of at least pH 7 and with high dissolved oxygen. Under these conditions (pH 7, air-saturated water) and at 20°C and in the presence of *Pseudomonas* at 10^5 cells/liter, the half-life of endosulfan was one week (no products reported).

Martens (1976) studied the transformation of endosulfan by soil microorganisms in nutrient solutions. After 6 weeks of incubation, 16 of 28 soil fungi were found to have degraded more than 30% of the applied en-

dosulfan; 13 of the 16 fungi gave endosulfan sulfate as the major product (i.e., an amount at least 10 times greater than that for endosulfan diol). Martens also found that after 10 days of incubation, 15 of 49 soil bacteria had degraded more than 30% of the applied endosulfan with 10 bacteria giving endosulfan diol as the major identified product; endosulfan sulfate was the major product of the other 5 bacteria. In similar experiments, 3 of 10 actinomycetes metabolized more than 30% of the applied endosulfan after incubation for 10 days.

No information was found regarding biotransformation of endosulfan sulfate in aquatic systems, although the formation and presence of the sulfate in the fungi experiments suggest some stability toward biological hydrolysis. In cases where the diol was the major product in biotransformation there is no information to indicate whether the diol arose directly from endosulfan or did indeed proceed via hydrolysis of the endosulfate intermediate.

27.4.8 Other Reactions

No reactions other than those cited above have been reported to occur with endosulfan or endosulfan sulfate.

27.4.9 Microcosm Studies, Field Studies, and Modelling

Ali (1978) reported results of terrestrial-aquatic microcosm experiments in which the α and β-endosulfan isomers and endosulfan sulfate were each studied in separate experiments; a mixture of endosulfan isomers was studied in another microcosm experiment. In the latter study, the β-isomer was reported to be rapidly lost, with none detected in the aqueous phase 26 days after introduction of the mixture into the micrososm. At the end of the 33 days, the α-isomer comprised 16% of the total endosulfan material recovered from water, with the remainder beng endosulfan sulfate. In all experiments, endosulfan sulfate was the only metabolite and also the major compound found in water or in the organisms (algae, snail, mosquito, and fish). Based on the microcosm experiments, Ali concluded that the β-isomer was not oxidized metabolically to endosulfan sulfate, but was first isomerized to the α-isomer, which was then oxidized; in studies on each isomer, some small conversion to the other isomer was also found. Data for bioconcentration factors were also found to depend on the starting

material and on the organism used. The upper and lower concentration factor reported for each orgarism and compound are given below:

	Bioconcentration factor for:		
	α-endosulfan	β-endosulfan	endosulfan sulfate
Algae	17-999	44-3863	223-1654
Snail	1336-5763	8174-39457	5457-29430
Mosquito	218-831	1245, 1508*	210-763
Fish	30-304	90,388*	935-1741

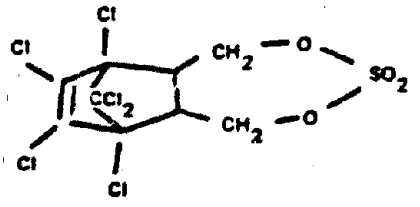
* Only two values reported; three factors were reported for other endosulfan measurements, with four factors for endosulfan sulfate.

Ali described a combination of processes involving isomerization, oxidation, uptake by organisms, and sorption to sediment to explain some of the results obtained in his experiments; because of the terrestrial processes, which in part determined the fate of endosulfan and the sulfate in the experiment, no detailed conclusions on the fate of these compounds in aquatic systems can be made. From the information presented it appears however that endosulfan sulfate is generally more persistent and bioaccumulates more than the endosulfan isomers. It is of interest to note that when the three compounds were dissolved in water from the microcosm and exposed to the artificial light used in the experiments, the α-isomer, β-isomer, and endosulfan sulfate were 82%, 87% and 88% recovered, respectively after 33 days, indicating that, at least for endosulfan, hydrolysis and photolysis are not important relative to biological processes.

Greve and Wit (1971) calculated an endosulfan half-life of about two days in a pond, based on data supposedly obtained from a paper by "Bears and Ware" (actually Beard and Ware 1969), but the reference cited contains no data from such an experiment.

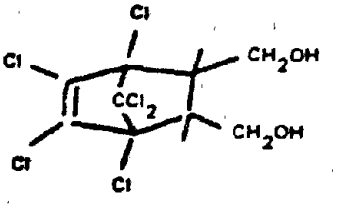
27.5 Reaction Products

The following products have been reported for endosulfan in various studies, with the associated processes as listed:



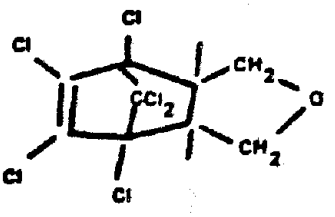
Endosulfan sulfate

- Photolysis of solid or gas phase
- Biotransformation
- Oxidation(?)



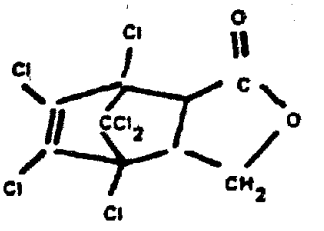
Endosulfan diol

- Photolysis in solid, liquid, and gas phase
- Hydrolysis
- Biotransformation



Endosulfan ether

- Photolysis



Endosulfan lactone

- Biotransformation

27.6 Data Summary

Tables 27-1 and 27-2 summarize the data on the aquatic fate of endosulfan isomers and endosulfan sulfate, respectively.

Table 27-2

Summary of Aquatic Fate of Endosulfan Sulfate

Environmental Process[a]	Summary Statement	Rate	Half-Life $t_{\frac{1}{2}}$	Confidence of Data
Photolysis	No information available.	-	-	-
Oxidation	Probably not important.	-	-	Low
Hydrolysis	Probably an important process.	-	178 days	Medium
Volatilization	No information available.	-	-	-
Sorption	No information available.	-	-	-
Bioaccumulation	No information available.	-	-	-
Biotransformation/ Biodegradation	Could be important via hydrolysis processes.	-	-	Low

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

27.7 Literature Cited

Ali, S. 1978. Degradation and environmental fate of endosulfan isomers and endosulfan sulfate in mouse, insect and laboratory model ecosystem. Ph. D. Thesis. Univ. Illinois. 101 pp. Univ. Microfilms, Ann Arbor, Mich., Order No. 7820891. (Diss. Abstr. Int. B 1978, 39(5):2117).

Archer, T.E. 1973. Endosulfan residues on alfalfa hay exposed to drying by sunlight, ultraviolet light and air. Pestic. Sci. 4:59-68.

Archer, T.E., I.K. Nazer, and D.G. Crosby. 1972. Photodecomposition of endosulfan and related products in thin films by ultraviolet light irradiation. J. Agric. Food Chem. 20(5):954-956.

Beard, J. E., and G.W. Ware. 1969. Fate of endosulfan on plants and glass. J. Agric. Food Chem. 17(2):216-220.

Eichelberger, J.W., and J.J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5(6):541-544.

Ernst, W. 1977. Determination of the bioconcentration potential of marine organisms. - a steady state approach. Chemosphere 6(11):731-740.

Gore, C., R.W. Hannah, S.C. Pattacini, and T.J. Porro. 1971. Infrared and ultraviolet spectra of seventy-six pesticides. J. Assoc. Off. Anal. Chem. 54(5):1040-1082.

Greve, P.A., and S.L. Wit. 1971. Endosulfan in the Rhine River. J. Water Pollut. Control Fed. 43(12):2338-2348.

Harrison, R.B., D.C. Holmes, J. Roburn and J. O'G. Tatton. 1967. The fate of some organochlorine pesticides on leaves. J. Sci. Food Agric. 18:10-15.

Hoffmann, J., and D. Eichelsdoerfer. 1971. Effect of ozone on chlorinated-hydrocarbon-group pesticides in water. Vom Wasser 38:197-206.

Koshy, C., N.M. Das, and M.R. G.K. Nair. 1972. Deterioration of insecticides on glass and on leaf surface. Agric. Res. J. Kerala. 10(2):128-132.

Mackay, D., and P.J. Leinonen. 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Tech. 9(13):1178-1180.

Martens, R. 19[illegible]. Decomposition of endosulfan by soil microorganisms. Schrifter. Ver. Wasser-, Boden-,Lufthg., Berlin-Dahlem, (37):157-173.

Martens, R. 1976. Degradation of [8,9-^{14}C] endosulfan by soil microorganisms. Appl. Environ. Microbiol. 31(6):853-858.

Midwest Research Institute. 1977. Initial scientific review of endosulfan. MRI Report Nov. 1977.

Phillips, W.E.J. 1975. [Publ.] Endosulfan. Its effects on environmental quality. Nat. Res. Counc. Can., Environ. Secr., 14098, 100pp.

Putnam, T.B., D.D. Bills, and L.M. Libbey. 1975. Identification of endosulfan based on the products of laboratory photolysis. Bull. Environ. Contam. Toxicol. 13(6):662-665.

Radding, S.B., D.H. Liu, H.L. Johnson, and T. Mill. 1977. Review of the environmental fate of selected chemcials. U.S. Environmental Protection Agency Report No. EPA-560/5-77-003.

Richardson, E.M. and E. Epstein. 1971. Retention of three insecticides on different size soil particles suspended in water. Soil Sci. Soc. Am. Proc. 35(6):884-887.

Schumacher, G., W. Klein, and F. Korte. 1971. Photochemical breakdown of endosulfans in solution. Tetrahedron Lett. No. 24:2229-2232.

Schumacher, H. G., H. Parlar, W. Klein and F. Korte. 1974. Beitrage zur okologischen chemie. LV. Photochemische reaktion von endosulfan. Chemosphere 3(2):65-70.

Schuphan, I., and K. Ballschmiter. 1972. Persistence of hexachlorobicyclo [2.2.1]heptene derivatives. Fresenius' Z. Anal. Chem. 259(1):25-28.

Weil, L., G. Dure, and K.E. Quentin. 1974. Solubility in water of insectiide chlorinated hydrocarbons and polychlorinated biphenyls in view of water pollution. Z. Wasser Abwasser Forsch. 7(o):169-175.

28. ENDRIN AND ENDRIN ALDEHYDE

28.1 Statement of Probable Fate

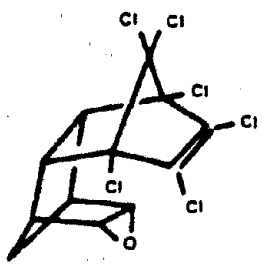
Little information is available for evaluating the fate of endrin in aquatic systems. Photolysis and biotransformation of endrin occur under environmental conditions, but no data are available to assess the rates of these processes in aquatic environments; biotransformation will also be affected by the microbial types and populations available to utilize endrin. No information on the sorption or volatilization of endrin from aquatic systems is available, although bioaccumulation does appear to be significant with concentration factors on the order of 10^3 - 10^4.

No information whatsoever has been found to evaluate the fate of endrin aldehyde in aquatic systems. Information available on the photolysis, biotransformation, and thermolysis of endrin suggests that endrin aldehyde will be only a minor product of these processes.

28.2 Identification

This section discusses only the pure chemicals endrin and endrin aldehyde. A typical technical endrin sample contains 96.6% pure endrin and at least eight impurities, with each usually at less than 1% concentration; the impurities include dieldrin, isodrin, aldrin, heptachloronorbornadiene, heptachloronorbornene, endrin aldehyde and 3-keto endrin (Brooks 1974).

The structure, alternate names, and CAS and TSL numbers for endrin are given below.



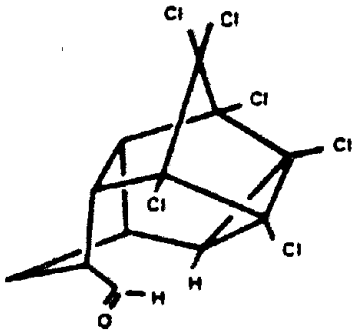
Endrin

CAS No. 72-20-8
TSL No. IO 15750

Alternate Names

Hexachloroepoxy-octahydro-endo-endo-dimethanonaphthalene
Nendrin
1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydroexo-1,4-exo-5,8-dimethanonaphthalene
Isodrin epoxide

Endrin aldehyde is a transformation product of endrin. The structure of endrin aldehyde cited by Burton and Pollard (1974) is given below.



Endrin aldehyde

Alternate Names

1,2,4-Methenocyclopenta(c,d) pentalene-r-carboxaldehyde, 2,2a,3,3,4,7 hexachlorodecahydro

CAS No. 7421-93-4
TSL No. None assigned

28.3 Physical Properties

The general physical properties of endrin are as follows.

Molecular weight	381.0
Melting point	235°C, with decomposition
Boiling point	No data found
Vapor pressure at 25°C (Martin 1972)	2 x 10^{-7} torr
Solubility in Water at 25°C	
(Weil et al. 1974)	0.26 ppm
(Bigger and Riggs 1974)*	0.25 ppm
Log octanol/water partition coefficient (Neely et al. 1974)	5.6 calc.

* Particle size <5.0µm

No physical property data were found for endrin aldehyde except for a melting point of 145°C - 149°C (Phillips et al. 1962); the molecular formula and weight of endrin aldehyde are the same as those of endrin.

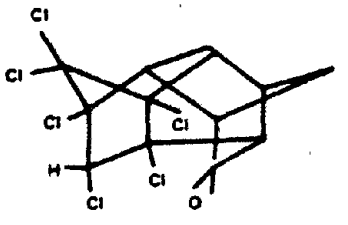
28.4 Summary of Fate Data

28.4.1 Photolysis

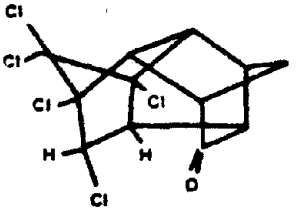
Although the photolysis of endrin in the solid state and in hexane solution has been shown to occur in sunlight, there are no data to evaluate the photolysis rates of endrin in aquatic systems. The studies reported do suggest that endrin aldehyde is not a major photolysis product in sunlight.

No information was found on the photolysis of endrin aldehyde.

Fujita et al. (1969) found that II (below) was a product of the sunlight photolysis of endrin in hexane solution; they presumed II was a photolysis product of I. No information regarding the product yield or photolysis rate of endrin was given. Zabik et al. (1971) also found II to be the major photoproduct when endrin was photolyzed in hexane or cyclohexane solvents at wavelengths above and below 290 nm and in sunlight, with II obtained in yields as large as 80% in some experiments. The authors also reported that irradiation of I at 254 nm for 26 hours did not give II; the photoproducts of I were not determined, however.

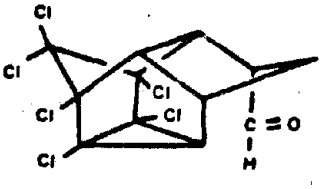


I. (δ-Keto endrin)



II.

Burton and Pollard (1974) studied the sunlight photolysis of endrin as thin solid layers of glass planchets. The major product was the endrin photoisomer I, which is also called δ-keto endrin. The authors state that only minor amounts of other compounds, such as endrin aldehyde III, were formed. After 5 and 12 days of exposure to sunlight in June,



III. Endrin aldehyde

5-keto endrin was found in yields of 46 and 65%, respectively, it is not clear whether the percentages were based on the initial amount of endrin or the amount reacted. Burton and Pollard also reported that "endrin was 50% isomerized to I in 7 ± 2 days in intense summer sun with complete conversion of endrin in 17 ± 2 days," and noted that the thicker films were photolyzed more rapidly than thinner films. Applications of their data to reactions in aqueous solution must therefore be made with caution. They also reported that I was stable to sunlight; thus endrin aldehyde is not a product of further photolysis of I, and may be a direct photoproduct of endrin.

Roburn (1963) and Rosen et al. (1966) reported other studies of the photolysis of endrin under various conditions. Although their studies do not provide any data useful in evaluating the photolysis rates of endrin in aquatic systems, they do provide more information on the photolysis of endrin and the products formed. Roburn (1963) found that solid films of endrin irradiated at 254 nm for several hours gave one main product and several minor products. Rosen et al. subsequently identified two of these photolysis products as δ-keto endrin I and endrin aldehyde III in yields of 37% and 9%, respectively.

Bulla and Edgerly (1968) reported that the photolysis rate of endrin in dilute aqueous solution at 254 nm was independent of reaction temperature (20° to 40°C). Baker and Applegate (1974) studied the photolysis of solid endrin films using a lamp with a maximum output at 350 nm; the loss of the endrin was found to be due to both photolysis and volatilization from glass surfaces.

Ivie and Casida (1971) reported studies of the sunlight photolysis of endrin on bean leaves in the presence of rotenone as a photosensitizer. After one hour exposure to sunlight, the endrin photoproducts (as determined by ^{14}C label) were found in yields of 2%, 15%, and 42% at rotenone levels of 1, 10 and 100 ppm, respectively. Although these data indicate that endrin photolysis can be sensitized by rotenone, the relevance of these solid state, sensitized processes to aquatic systems is unknown.

From the above information, it is concluded that although photolysis of endrin in sunlight does occur, the nature of the products is uncertain. Endrin aldehyde does appear to be a minor photolysis product of endrin. It is unlikely that the dechlorinated 5-keto endrin product II would be formed in aquatic systems unless suitable hydrogen-atom donating substrates are available in aquatic systems. If photolysis of endrin is determined to be an important fate of endrin, more relevant product studies are required.

28.4.2 Oxidation

No information on the oxidation of endrin or endrin aldehyde that is relevant to aquatic systems was obtained. Leigh (1969) studied the oxidation of endrin with chlorine, permanganate, and persulfate and concluded that endrin was unaffected by these oxidants at 50°C.

28.4.3 Hydrolysis

Eichelberger and Lichtenberg (1971) examined the persistence of endrin in a sample of raw water from the Little Miami River in Ohio. After 8 weeks at room temperature, all of the endrin was recovered, indicating that endrin has a half-life of at least 4 years; this calculation was made assuming that a 2.5% conversion in the 8 week period could have been detected.

There is no evidence to suggest that hydrolysis of endrin aldehyde will occur in aquatic systems; by analogy to endrin, a hydrolysis half-life of at least 4 years is probable for endrin aldehyde.

28.4.4 Volatilization

No data were obtained on the volatilization of endrin or endrin aldehyde from aquatic systems.

28.4.5 Sorption

No information was found on sorption of endrin or endrin aldehyde to sediments or biota.

28.4.6 Bioaccumulation

Bioaccumulation appears to be an important process for endrin in aquatic systems, with concentration factors ranging from 10^3 to 10^4 for species in microcosm experiments.

Ernst (1977) has measured a concentation factor of 1.9×10^3 for uptake of endrin by mussels. When the mussel was placed in clean water the time required for elimination of about 50% of the endrin was about 24 hours.

Metcalf et al. (1973) measured the concentrations of endrin in several elements of a microcosm; 11.56 ppm, 125 ppm, and 3.40 ppm concentrations of endrin were found in an algae, snail, and fish, respectively,

compared to 0.00254 ppm in the water. The ratios of endrin concentrations in the organisms to the concentration of endrin in solution were 1300 for fish, 49000 for snails, and 4600 for the alga. When exposed to endrin only in the aquatic medium (i.e., no dietary routes), the ratios were 680 for the fish, 310 for mosquitoes, and 330 for Daphnia after three days. The difference in the ratios for the fish may result from several factors, including insufficient time for equilibration in conjunction with the different routes for uptake of the pesticide by the fish.

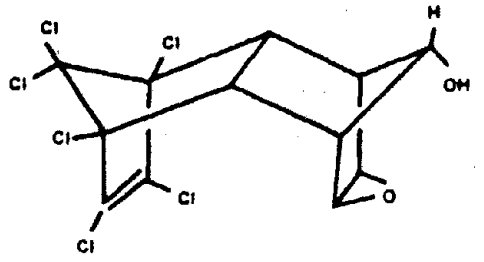
28.4.7 Biotransformation and Biodegradation

Although endrin has been found to undergo biotransformation in a microcosm and in studies with microbial isolates, there are no data useful for predicting biotransformation rates in aquatic systems. It is interesting that the metabolites reported in the two types of experiments appear to be different, with isomerization/dechlorination occurring in the microbial isolates and (possibly) hydroxylation occurring in the microcosm experiment. No information has been found on the biotransformation of endrin aldehyde.

Several studies on the biotransformation of endrin have been reported by Matsumura's group (Patil et al. 1970; Matsumura et al. 1971; Patil et al. 1972). In the 1970 paper, it was reported that 20 microbia isolates from soil that were previously found capable of degrading dieldri in solution were also found to degrade endrin. Of the several metabolites detected by tlc, only δ-keta endrin was identified. Matsumura et al. (1971) subsequently reported that 25 of 150 microbial isolates from soil showed activity in transforming endrin in solution in 30 day experiments. Three major and four minor metabolites were generally found in these studies, with δ-keto endrin being obtained in yields ranging from 5% to 95% in the various cultures. Other metabolites were not specifically identified although the authors did conclude on the basis of mass spectral and infrared spectral evidence that the other metabolites were ketones and aldehydes with five or six chlorine atoms per molecule; two metabolites had infrared spectra that were identical to that of endrin aldehyde (III) reported by Phillips et al. (1962). Patil et al. (1972) also studied the transformation of several chlorinated insecticides, including endrin, in water and algae from a marine fish pond. An unknown metabolite of endrin was obtained in a 36% yield in the water, whereas a 24% yield of δ-keto endrin was obtained from the algae collected from a stagnant fish pond.

Microcosm experiments by Metcalf et al. (1973) also revealed biotransformation of endrin; 23% of the endrin ingested by a caterpillar in

the terrestrial phase of the microcosm was metabolized to unknown products, and it was not determined whether any transformation also occurred in the aquatic phase of the microcosm (see Section 28.4.9). Of the products detected by tlc, δ-keto endrin was determined not to be a product. The authors suggested one metabolite was 9-hydroxyendrin IV, which was a metabolite found in rat feces (Baldwin et al. 1970). Baldwin found another hydroxylated endrin in the rat feces as well as 9-keto endrin in the fat of the rat; the 9-keto endrin is the oxidation product of 9-hydrogen endrin. There is no information other than Metcalf's study to indicate whether hydroxylated endrin metabolites will be formed in aquatic systems. It is also found that about 80% of the ^{14}C labelled material recovered from the alga, snail, and fish was in the form of the original endrin applied in the terrestrial phase of the microcosm, this suggests that endrin is moderately stable toward transformation in vivo (see Section 28.4.9).



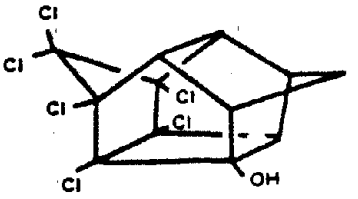
IV

Hill and McCarty (1967) reported that endrin was about 50% reacted in thick anaerobic sewage sludge in 5-14 days, and they observed four unidentified products; no other information was given.

24.4.8 Other Reactions

Phillips et al. (1962) reported that endrin is thermally isomerized at 230°C during gas chromatographic analysis. The two products identified - - the aldehyde III and ketone I -- gave peaks of approximately equal size in the glpc trace. A thermal decomposition of endrin was found to be an exothermic reaction; the total residue contained approximately 15 to 20% aldehyde III, 55 to 60% ketone I, 5% of a "bird-cage" alcohol V, and 15 to 20% volatile, carbonaceous and unidentified decomposition products. Barlow (1966) also reported that a sample of pure endrin stored in the dark

for four years underwent spontaneous isomerization to give a 70% yield of I. No information is available to determine whether such reactions may be catalyzed and occur in aquatic systems.



V

28.4.9 Microcosm Studies, Field Studies, and Modelling

Metcalf et al. (1973) investigated the fate of ^{14}C-labeled endrin in a terrestrial-aquatic microcosm. Of the total ^{14}C-labeled material recovered from the alga, snail, and fish, the endrin component constituted 85%, 53%, and 76% of the label, respectively. The bioconcentration factors for the above organisms were 4.5×10^3, 4.9×10^4, and 1.3×10^3, respectively. None of the major metabolites co-chromatographed (tlc) with δ-keto endrin. The authors suggested one unknown could be 9-hydroxyendrin IV, which was a metabolite found in rat feces (Baldwin et al. 1970).

28.5 Data Summary

Table 28-1 summarizes the data on the aquatic fate of endrin and endrin aldehyde.

Table 28-1

Summary of Aquatic Fate of Endrin and Endrin Aldehyde[a]

Environmental Process[b]	Summary Statement	Rate	Half-Life $t_{\frac{1}{2}}$	Confidence of Data
Photolysis	May be an important process.	-	-	Low
Oxidation	No information available.	-	-	
Hydrolysis	Not an important process.	-	> 4 years	High
Volatilization	No information available.	-	-	
Sorption	No information available.	-	-	
Bioaccumulation	Is an important process.	-	-	Medium
Biotransformation/ Biodegradation	May be an important process.	-	-	Medium

a. No information was available for any process for endrin aldehyde.

b. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

28.6 Literature Cited

Baker, R. D., and H. G. Applegate. 1974. Effect of ultraviolet radiation on the persistence of pesticides. Tex. J. Sci. 25(1-4):53-59.

Baldwin, M. K., J. Robinson, and D. V. Parke. 1970. Metabolism of endrin in the rat. J. Agric. Food Chem. 18(6):1117-1123.

Barlow, F. 1966. Spontaneous decomposition of a sample of pure endrin. Nature 212:505.

Biggar, J. W., and I. R. Riggs. 1974. Apparent solubility of organochlorine insecticides in water at various temperatures. Hilgardia 42(10):383-391.

Brooks, G. T. 1974. Chlorinated insecticides: Volume I:Technology and applications. CRC Press, Cleveland, OH., 249 pages.

Bulla, C. D., III, and E. Edgerley. 1968. Photochemical degradation of refractory organic compounds. J. Water Pollut. Control. Fed. 40:546-556.

Burton, W. B., and G. E. Pollard. 1974. Rate of photochemical isomerization of endrin in sunlight. Bull. Environ. Contam. Toxicol. 12(1):113-116.

Eichelberger, J. W., and J. J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5(6):541-544.

Ernst, W. 1977. Determination of the bioconcentration potential of marine organisms. - a steady state approach. Chemosphere 6(11):731-740.

Fujita, M., A. Ishii, and Y. Sakagami. 1969. Photodecomposition of endrin. J. Hyg. Chem. 15:9-12.

Hill, D. W., and P. L. McCarty. 1967. Anaerobic degradation of selected chlorinated hydrocarbon pesticides. J. Water Pollut. Control Fed. 39(8):1259-1277.

Ivie, G. W., and J. E. Casida. 1971. Sensitized photodecomposition and photosensitizer activity of pesticide chemicals exposed to sunlight of silica gel chromatoplates. J. Agric. Food Chem. 19:405-409.

Leigh, G. M. 1969. Degradation of selected chlorinated hydrocarbon insecticides. J. water Pollut. Control Fed. 41(11)(Pt. 2):R450-R460.

Martin, H., ed. 1972. Pesticide Manual, 3rd Ed. British Crop Protection Council, Worcester, Engl.

Matsumura, F., V. G. Khanvilkar, K. C. Patil, and G. M. Boush. 1971. Metabolism of endrin by certain soil microorganisms. J. Agric. Food Chem. 19(1):27-31.

Metcalf, R. L., I. P. Kapoor, P.-Y. Lu, C. K. Schuth, and P. Sherman. 1973. Model ecosystem studies of the environmental fate of six organochlorine pesticides. Environ. Health Perspect. 4:35-44.

Neely, W. B., D. R. Branson, and G. E. Blau. 1974. Partition coefficient to measure bioconcentration potential of organic chemicals in fish. Environ. Sci. Technol. 8(13):1113-1115.

Patil, K. C., F. Matsumura, and G. M. Boush. 1970. Degradation of endrin, aldrin, and DDT by soil microorganisms. Appl. Microbiol. 19(5):879-881.

Patil, K. C., F. Matsumura, and G. M. Boush. 1972. Metabolic transformation of DDT, dieldrin, aldrin, and endrin by marine microorganisms. Environ. Sci. Tech. 6(7):629-632.

Phillips, D. D., G. E. Pollard, and S. B. Soloway. 1962. Thermal isomerization of endrin and its behavior in gas chromatography. J. Agric. Food Chem. 10(3):217-221.

Roburn, J. 1963. Effect of sunlight and ultraviolet radiation on chlorinated pesticide residues. Chem. Ind. (1963):1555-1556.

Rosen, J. D., D. J. Sutherland, and G. R. Lipton. 1966. The photochemical isomerization of dieldrin and endrin and effects on toxicity. Bull. Environ. Contam. Toxicol. 1(4):133-140.

Rosenblatt, D. H., T. A. Miller, J. C. Dacre, I. Maul, and D. R. Cogley. 1975. Appendix M- Endrin. Preliminary Assessment of Ecological Hazards and Toxicology of Environmental Pollutants at Rocky Mountain Arsenal.

Weil, L., G. Dure and K. L. Quentin. 1974. Solubility in water of insecticide chlorinated hydrocarbons and polychlorinated biphenyls in view of water pollution. Z. Wasser Abwasser Forsch. 7(6):169-175.

Zabik, M. J., R. D. Schuetz, W. L. Burton, and B. E. Pape. 1971. Photochemistry of bioactive compounds. Studies of a major photolytic product of endrin. J. Agric. Food Chem. 19(2):308-313.

29. HEPTACHLOR

29.1 Statement of Probable Fate

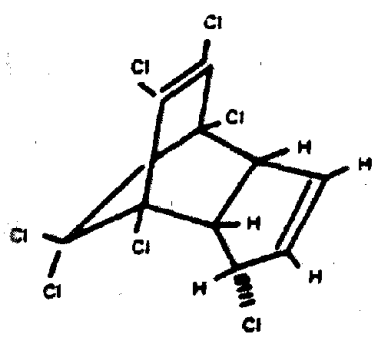
The major fate of heptachlor in the solution phase of aquatic systems will be hydrolysis to give 1-hydroxychlordene (1-HC) with a half-life of about 1-3 days; 1-HC will then be biotransformed to give 1-hydroxy-2,3-chlordene epoxide (1-HCE). Although literature information also indicates that heptachlor photolysis, volatilization, and sorption to sediments may also occur in aquatic environments, no data are available to compare these processes with the hydrolysis transformation rate.

The toxic metabolite, heptachlor epoxide (HE), appears to be a minor product of heptachlor transformations in aquatic systems; the amount of HE formed is dependent on uptake by organisms capable of effecting the epoxidation of heptachlor.

29.2 Identification

This chapter considers only the heptachlor component of the technical heptachlor product. The technical product contains 72% heptachlor and 28% related compounds, and has a melting range of 46 to 74°C (Martin 1972).

The structure, alternate names, and CAS and TSL numbers for heptachlor are given below.



Heptachlor

CAS No. 76-44-8
TSL No. PC 07000

Alternate Names

4,7-Methanoindene-1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro
E 3314
Velsicol 104
Heptachlorodicyclopentadiene

29.3 Physical Properties

The general physical properties of pure heptachlor are given below.

Molecular weight	373.3
Melting point (Martin 1972)	95-96°C
Boiling point	No data found
Vapor pressure at 25°C (Martin 1972)	3×10^{-4} torr
Solubility in water (Biggar and Riggs 1974)*	0.180 ppm at 25°C
(Park and Bruce 1968)	0.056 ppm at 25-29°C
Log octanol/water partition coefficient	No data found

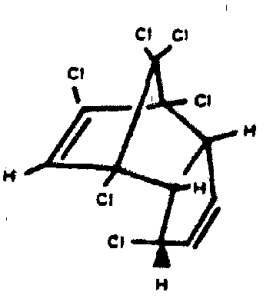
*particle size < 5.0 µm

29.4 Summary of Fate Data

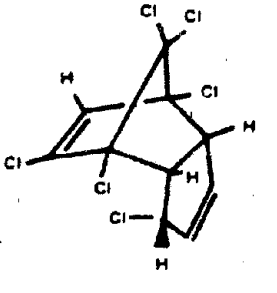
29.4.1 Photolysis

Although literature information indicates that heptachlor may undergo direct photolysis in sunlight and is also susceptible to photosensitized reactions, insufficient data are available to predict half-lives for photolysis in sunlight.

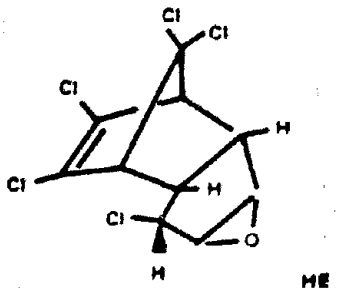
Ehmann (1976) reported that the dechlorinated heptachlor isomers I and II and heptachlor epoxide (HE) were products of heptachlor films photolyzed at > 290 nm. The same author reported that photolysis of heptachlor film in sunlight (June through September) gave the sage product III in 10% yield.



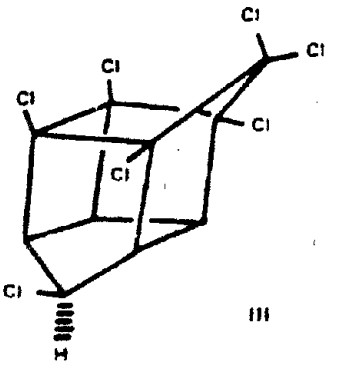
I



II



HE



III

The photoisomer III has also been reported as the product of benzophenone-sensitized photolysis of heptachlor in benzene solution (Rosen et al. 1969; Rosen and Siewierski 1970). The same product was found in the acetone-solvent sensitized photolysis of heptachlor (Onuska and Comba 1975b; McGuire et al. 1970; Fischler and Korte 1969); III was also reported to be the product from the photolysis at > 290 nm of heptachlor in the solid phase, as a film, in water-methanol solution and in the gas-phase (Vollner et al. 1971). In an earlier paper Vollner et al. (1969) reported that photolysis of heptachlor film at 254 nm gave yields of 48% and 43% for III and an unidentified product, respectively. Photolysis of heptachlor in methanol-water solution with a Pyrex-filtered Hg lamp (> 290 nm) gave a 38:52 ratio of these products and in dioxane-water solvent the product ratio was 7:61.

McGuire et al. (1972) have measured photolysis product quantum yields for heptachlor photolysis. Photolysis of heptachlor at 254 nm in cyclohexane solvent gave the dechlorinated products I and II with a product quantum yield of 0.025. Photolysis of heptachlor in acetone solvent gave photoisomer III with a product quantum yield of 9.4×10^{-3} based on total light absorption by the photosensitizer (acetone). The authors also report that in cyclohexane solvent, III is photolyzed at 290 nm to regenerate heptachlor with a quantum yield of 0.195. The authors suggest that the dechlorination products (I and II) and cage product (III) are formed via singlet and triplet state photochemical processes, respectively.

The above information suggests that heptachlor will photolyze in sunlight (i.e., > 290 nm) by direct photolysis and possibly by indirect photolysis if effective naturally occurring tiplet sensitizers are available in aquatic systems. The uv spectrum for heptachlor given by Gore et al. (1971) does show a tailing absorbance above 290 nm, indicating that direct photolysis in sunlight can occur. If the quantum yield of 0.025 for formation of products I and II is independent of wavelength and solvent and represents the photodissociation of the vinylic C-Cl bond, the product quantum yield of 0.025 may represent some fraction of a larger reaction quantum yield (that is, products other than I and II may have been formed but not detected., Unfortunately, sufficient uv absorption spectral data

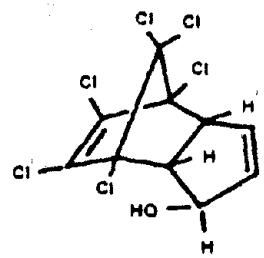
are not available to calculate possible direct photolysis rate constants using the quantum yield data. In aquatic systems the products I and II should not be formed unless suitable hydrogen atom donors are present, but the cage compound III may be formed.

29.4.2 Oxidation

Singh (1969) reported that heptachlor is oxidized by CrO_3 in acetic acid to give a heptachlor epoxide (HE) with a melting point of 158-160°C; this isomer is the toxic component that is formed by metabolic processes. Cochrane and Forbes (1974) found HE as well as other products resulting from oxidative cleavage of the allylic double bond when heptachlor was oxidized with CrO_3. Neither study provides information useful in evaluating chemical oxidation of heptachlor in aquatic environments.

29.4.3 Hydrolysis

Several studies have shown that abiotic hydrolysis of heptachlor occurs rapidly, with half-lives of 1-3 days under environmentally relevant conditions. The hydrolysis product is 1-hydroxychlordene (1-HC).



1-HC

Demayo (1972) has measured the first-order rate constant for hydrolysis of heptachlor at 29.88 ± 0.03°C in unbuffered distilled water; the rate constant was (3.00 ± 0.08) x 10^{-2} hr^{-1}, which corresponds to a half-life of 23.1 hours. Eichelberger and Lichtenberg (1971) have reported that of the heptachlor added to a sample of an Ohio river water maintained at ambient room temperature, only 25% remained after one week, and no heptachlor remained after 2 weeks; the product formed was identified as 1-hydroxychlordene (1-HC). The authors also found a second product evident in the glpc trace after 2 weeks; this product, which was tentatively identified as heptachlor epoxide (HE), was present after 4 weeks in 40% yield based on initial heptachlor. In parallel studies in water from the same source it was found that dieldrin was formed from aldrin; thus, for heptachlor, biological or other transformations may also have been occurring, although the formation of HE from 1-hydroxychlordene via any biological or chemical process appears to be without precedent. Nevertheless, the 75% loss of heptachlor after one week, when only 1-HC was present, corresponds

to a half-life of 3.5 days. Given the variable and unspecified, but probably lower, temperatures of the latter experiment, this 3.5 day half-life is in good agreement with the 23 hour half-life for hydrolysis of heptachlor at 30°C reported by Demayo. This information is also in agreement with the observation of Bevenue and Yeo (1969a) that heptachlor in aqueous solution at 22-25°C was markedly decreased in 24 hours and had almost disappeared after 14 days. Other studies have also reported rapid abiotic hydrolysis (see Section 29.4.6).

Although the pH dependence of the hydrolysis rate of heptachlor has not been reported, it is reasonable to expect that the rate will be pH independent by analogy to other allylic halides, specifically allyl chloride (Mabey and Mill 1978) and hexachlorocyclopentadiene (Zepp et al. 1979).

29.4.4 Volatilization

No studies that quantitatively define the volatilization of heptachlor from aquatic systems have been found, although several reports on biotransformation studies of heptachlor have sited volatilization as a probable loss process (Bourquin et al. 1972; Miles et al. 1969; Leigh 1969).

29.4.5 Sorption

Only one set of papers on the sorption of heptachlor to particulate material has been found, and although the data do fit Freundlich isotherm plots, the large deviation from unity of the Freundlich 1/n term makes the partition coefficients unreasonably large for a simple quantitative assessment of the sorption process. Sorption does appear to be an important process for heptachlor in aquatic systems, however.

Huang and Liao (1970), Huang (1971, 1974) studied the adsorption of heptachlor to three types of clay and on humic substances. The adsorption of heptachlor onto the clays reached equilibrium concentrations within two hours, whereas the humic materials required more than five hours for equilibrium to be attained. The parameters 1/n and K for the Freundlich isotherm equation ($x/m = KC^{1/n}$) are given below; the parameters have been calculated from data in Huang (1974) using units where the sediment concentration is in µg heptachlor per gram absorbent and C is the equilibrium solution concentration in µg heptachlor per ml solution:

Sorption System	K	1/n
Montmorillinite (clay)	5.0×10^6	3.51
Illite (clay)	1.5×10^9	6.05
Kaolinite (clay)	1.5×10^8	4.49
Leonardite	4.1×10^5	1.69
Humic acids (colloidal)	1.8×10^8	2.42

The humic acids used were obtained by alkaline extraction of Leonardite, which was described as a coal-like, humus rich substance; the humic acids were oven dried, pulverized, and then dispersed in colloidal solution for sorption experiments. The authors did not comment on the unusually high 1/n values measured for the clay sorption experiments; the partition coefficient (K) values are exceptionally large for sorption of an organic substrate to particulate and may be considered an artifact of the calculation owing to the use of large 1/n values. Although the 1/n parameters for sorption onto the humic substances are not close to unity as would normally be expected for Freundlich isotherm data, the experiment for Leonardite where $1/n = 1.69$ and $K = 4.1 \times 10^5$, does indicate that sorption to sediments may be a significant process.

29.4.6 Bioaccumulation

Heptachlor shows strong tendencies for bioaccumulation, with bioconcentration factors on the order of 10^4 for several organisms. Uptake and bioaccumulation in biota of heptachlor may then be an important process for heptachlor. Low levels of heptachlor found in environmental samples may result from sorption and accumulation in biota where solution hydrolysis cannot occur.

Data obtained from a terrestrial-aquatic microcosm experiment of Lu et al. (1975) indicate heptachlor has bioconcentration factors of 2.1×10^4 for an alga, 3.7×10^4 for a snail, 3.1×10^4 for mosquito larvae, and 3.8×10^3 for mosquito fish; the experiment was complicated, however, by the toxicity of heptachlor to the organisms studied. In this paper, the authors also report that in a 3-day, aquatic microcosm experiment, heptachlor had bioconcentration factors of 1.8×10^3 and 1.1×10^3 for snail and fish, respectively. The authors did not comment on the smaller bioconcentration values obtained in the latter experiment compared with the terrestrial-aquatic microcosm experiment, however because the experiments were run for 3 and 71 days, respectively, the difference may be due to the exposure time and related transport/food chain differences in the experiments. Lack of sufficient exposure time to reach equilibrium is also a reason Bowman et al. (1964) did not find extensive uptake of heptachlor by mosquito larvae, finding bioconcentration factors of ~ 35 for 20 hour exposures.

Schimmel et al. (1976) reported bioconcentration factors of 3.6×10^3 in a 72-hour test and 7.4×10^3 in a 96 hour test with spot, an estuarine fish species. They also cite prior studies showing concentration factors ranging from 2800 to 21,300 for finfish and shellfish. When the fish containing 3 ppm heptachlor were transferred to clean water, about 50%

of the heptachlor was lost in 14 days. It was not stated whether the loss was due to excretion or metabolism, or both; the heptachlor metabolite, heptachlor epoxide, was found in all fish, however.

Voerman (1969) has measured the distribution ratio $K = C_o/C_w$, where C_o and C_w are the concentrations of heptachlor in hexane and water, respectively (units are µg/ml). K was determined to be 1.11 x 10^5, with data from five experiments giving C_o^1 (concentration of heptachlor in hexane extract of water phase) = 0.009 ± 0.001 µl, indicating good precision of data. The K value for heptachlor was greater than that for lindane, aldrin, dieldrin, heptachlor epoxide or DDT.

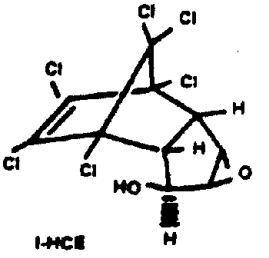
Since 1-hydroxychlordene (1-HC) is formed in significant amounts by hydrolysis of heptachlor, and 1-HC is subsequently metabolized to 1-hydroxy chlordene epoxide (1-HCE), data on bioconcentration factors for these products are of interest here. Lu et al. (1975) reported concentrations of 1-HC and 1-HCE in water and the various organisms in their terrestrial-aquatic microcosm experiments using chlordene and heptachlor. Except for one value where the BCF for snail was 690, the 1-HC BCF values ranged from 197 to 57. Bioconcentration factors for 1-HCE ranged from 119 to 5.7. These data indicate that bioaccumulation of 1-HC and 1-HCE will not be appreciable in aquatic environments. Bonderman and Slach (1972) reported 1-HC was present in soil, fish and crops in a farming area, but found no 1-HC in tissue and fluids from human subjects in the area.

29.4.7 Biotransformation and Biodegradation

Several studies have shown that heptachlor can be biotransformed by oxidation to heptachlor epoxide (HE) or by reduction to chlordene. The consensus of several biotransformatin studies is, however, that abiotic hydrolysis of heptachlor in solution is more rapid than biotransformation, with the hydrolysis product itself then epoxidized biologically. Significantly, the toxic heptachlor metabolite, heptachlor epoxide, does not appear to be a major product in aquatic systems studied.

Lu et al. (1975) have conducted microcosm studies to determine the fate of heptachlor; bioconcentration data from these experiments are reported in Section 29.4.7. In an aquatic microcosm experiment where data for products (or metabolites) were determined as the percentage of total ^{14}C label in the organic fraction of the water sample, heptachlor was found to decrease from 100% to 10% of total ^{14}C material within one day. After one day, 1-hydroxy-2,3,-chlordene epoxide (1-HCE) was present as 50% of the total ^{14}C, rose to 70% at the second day, and then remained constant for the duration of the 13 day experient. The heptachlor hydrolysis

product, 1-HC, reached a maximum of 10% of the total ^{14}C at one day and decreased thereafter. Heptachlor epoxide was never found to be greater than 5% of total ^{14}C; unidentified polar products/metabolites as detected by tlc analysis reached a constant value of about 10% of the total ^{14}C for days 5 through 13. The authors concluded that the major pathway of heptachlor in aquatic systems is rapid, abiotic hydrolysis of heptachlor to 1-HC followed by metabolism to 1-HCE.



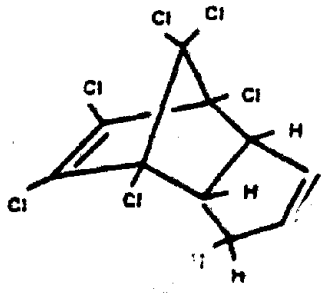
1-HCE

Although this experiment of Lu et al. gives information on the products and metabolites found in the aqueous phase of the microcosm, a complete material balance cannot be made with these data because the product information is only based on ^{14}C in the water sample, and does not include losses due to soprtion or volatilization.

Lu et al. (1975) have reported several studies on the metabolic products of heptachlor in conjunction with terrestrial-aquatic microcosm studies. Heptachlor epoxide (HE) was the major metabolite found in the whole body homogenate of a salt marsh caterpillar after ingestion of heptachlor-coated leaves; 1-HCE was the major metabolite in the caterpillar excretions. The authors also reported that HE was the major metabolite identified in a sheep liver microsomal preparation to which heptachlor was added.

Lu et al. (1975) also studied heptachlor in a 71-day terrestrial-aquatic microcosm experiment. Since the heptachlor was introduced into the microcosm by application to terrestrial plants which were then consumed by a salt marsh caterpillar, the heptachlor probably entered the aquatic phase of the microcosm by several routes (e.g., leaf fragments, fecal matter). As in the aquatic microcosm system, 1-HCE concentrations were higher than 1-HC concentrations in the aqueous phase as well as in alga, snail, mosquito larvae, and fish. The heptachlor metabolite in highest concentration was HE, with levels of 1-1.6 ppm found in snail, fish, and mosquito larvae; concentrations of 1-HC and 1-HCE ranged from 0.05-0.08 ppm and 0.27-0.12 ppm, respectively, in these species. The larger amount of HE than 1-HCE

found in this experiment, compared with the aquatic microcosm data, was probably due to metabolism of heptachlor to HE in the terrestrial segment of the microcosm before the compound entered the aquatic phase, followed by accumulation of HE in the various species.

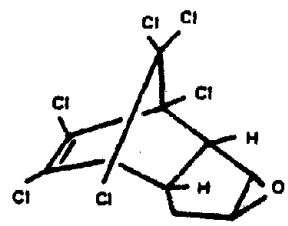


CHLORDENE

Miles et al. (1971) studied the transformation of heptachlor in aqueous solution containing a mixed culture of organisms extracted from a soil; the experiments described appear to have favored anaerobic conditions. The only products found were ~ 7-14% chlordene and 1-7% 1-HCE, with less than 0.04% HE. The reduction of HE to 1-HC was also observed in this system. Although this latter pathway may be a source of 1-HC and eventually 1-HCE, the sequence (heptachlor → HE → 1-HCE) is probably less important in aerobic systems than to the abiotic hydrolysis of heptachlor to 1-HC and then transformation to 1-HCE.

An earlier paper by Miles et al. (1969) reports studies on the aerobic transformations of heptachlor in solution by various organisms isolated from soil. Thirty-five of 47 fungi and 26 of 45 bacteria and actinomycetes were found to produce HE. Besides HE, other products found were 1-HC, chlordene, chlordene epoxide, 1-HCE and one unknown compound. The highest yield of HE from heptachlor was 6% formed in 6 weeks. The chlordene was obtained in variable but small yields by bacterial dechlorination of heptachlor. The authors also established that 1-HCE was formed by epoxidation of 1-HC rather than by hydrolysis of HE; of the 45 bacteria

and actinomycetes, 4 were found to epoxidize 1-HC to 1-HCE, whereas 43 of the 47 fungi were able to effect this transformation.



CHLORDENE EPOXIDE

Bourquin et al. (1972) studied the transformations of heptachlor in mixed cultures of Pseudomonas sp and individual isolates. Chlordene, 1-HCE and HE were identified as metabolites, nine unknown products were also detected. Although no yield data were given for metabolites, the authors stated that the major pathway for loss of heptachlor was abiotic hydrolysis to 1-HC followed by biotransformation to 1-HCE.

Leigh (1969) attempted to study the biotransformation of heptachlor in a solution of settled primary wastewater with added yeast extract. The average removal of heptachlor found in these experiments after 4 weeks was 95.3% compared with 99.5% loss in control solutions (containing no wastewater or yeast extract). The authors concluded that no statement could be made regarding the biodegradability of heptachlor; in fact, the data may show that sorption by biota may make some heptachlor unavailable for hydrolysis in solution.

Sethunathan and Yoshida (1973) have reported that under anaerobic conditions a Clostridium sp isolated from a flooded soil previously treated with lindane was able to effect a 36% transformation of heptachlor (initial concentration 12.8 ppm) in 24 hours. Iyengar and Rao (1973) found that the fungus Aspergillus niger was able to transform 12.5 ppm heptachlor to undetectable levels in 48 hours under aerobic conditions, but they noted that the pesticide could not serve as the sole carbon source for the fungus. The authors also state that unadapted organisms could not utilize heptachlor, but that chlordane-adapted A. niger could. Neither of these 1973 publications discussed the possibility of the competing hydrolysis process or identified any metabolites.

Hill and McCarty (1967) found that heptachlor was completely transformed to an unidentified product within one day in thick, biologically active wastewater sludge at 35°C. The authors further reported that this product persisted for at least 42 days but was completely removed after 266 days.

In summary, the studies by Lu et al. (1975), Miles et al. (1969, 1971), Leigh (1969), and Bourquin et al. (1972) concluded that abiotic hydrolysis of heptachlor to 1-HC will be more rapid than biological transformations, and that in aerobic systems, 1-HCE will be formed from 1-HC by biotransformation. HE does not appear to be a major transformation product of heptachlor introduced into aquatic systems. The amount of HE formed will depend on the amount of biota present and the capability of the organisms to effect epoxidation to give HE.

29.4.8 Other Reactions

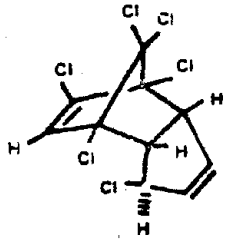
No environmental processes other than those previously discussed have been reported to be significant in influencing the fate of heptachlor in aquatic systems.

29.4.9 Microcosm Studies, Field Studies, and Modelling

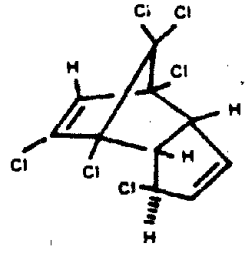
Lu et al. (1975) studied the fate of heptachlor in aquatic and aquatic-terrestrial microcosm experiments. Information from these studies on the bioaccumulation and transformation of heptachlor is presented in Sections 29.4.6 and 29.4.7, respectively.

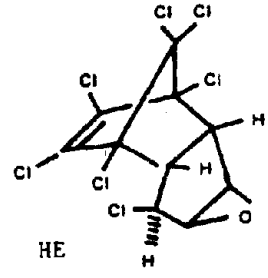
29.5 Reaction Products

The following products or metabolites have been reported for heptachlor in various studies.



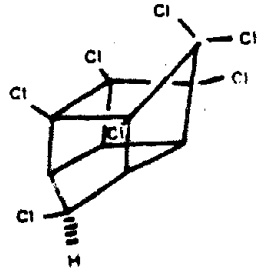
. Photolysis (reduction)



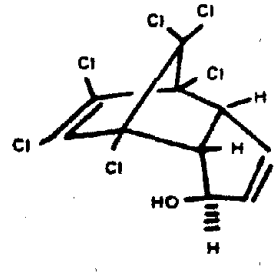


HE

. Photolysis
. Biotransformation
. Oxidation

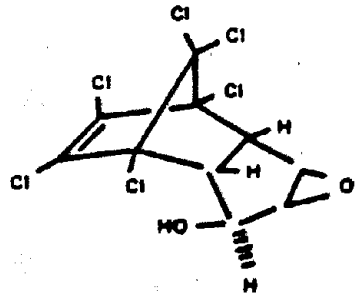


. Photolysis

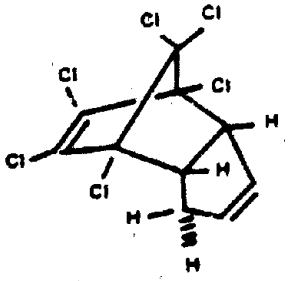


1-HC

. Hydrolysis



1-HCE



- Biotransformation (of 1-HC)
- Biotransformation

29.6 Data Summary

Table 29-1 summarizes the data on the aquatic fate of heptachlor.

Table 29-1

Summary of Aquatic Fate of Heptachlor

Environmental Process	Summary Statement	Rate	Half-Life $t_{\frac{1}{2}}$	Confidence of Data
Photolysis	Will photolyze in sunlight at undetermined rate(s).	-	-	Low
Oxidation	No information available.	-	-	-
Hydrolysis[a]	Rapid process for heptachlor in solution.	3×10^{-2} hr^{-1} at 30°C	1-3 days in environment	High
Volatilization	May be an important process.	-	-	Low
Sorption	Probably an important process, but no reliable data available.	-	-	Medium
Bioaccumulation	Will bioaccumulate if not hydrolyzed.	-	-	High
Biotransformation/ Biodegradation	Slow compared to hydrolysis.	-	-	High

a. The predominant environmental process which is thought to determine the fate of the compound.

29.7 Literature Cited

Bevenue, A., and C.Y. Yeo. 1969(a). Gas chromatographic characteristics of chlordane. I. Effect of an aqueous environment on the heptachlor component. Bull. Environ. Contam. Toxicol. 4(2):68-76.

Bevenue, A., and C.Y. Yeo. 1969(b). Gas chromatographic characteristics of chlordane. II. Observed compositional changes of the pesticide in aqueous and non-aqueous environments. J. Chromatogr. 42:45-52.

Biggar, J.W., and I.R. Riggs. 1974. Apparent solubility of organochlorine insecticides in water at various temperatures. Hilgardia 42(10):383-391.

Bonderman, D.P. and E. Slach. 1972. Appearance of 1-hydroxychlordene in soil, crops, and fish. J. Agric. Food Chem. 20(2):328-331.

Bourquin, A.W., S.K. Alexander, H.K. Speidel, J.E. Mann, and J.F. Fair. 1972. Microbial interactions with cyclodiene pesticides. Dev. Ind. Microbiol. 13:264-270.

Bowman, M.C., F. Acree, Jr., C.S. Lofgren, and M. Beroza. 1964. Chlorinated insecticides: fate in aqueous suspensions containing mosquito larvae. Science. 146(3650):1480-1481.

Cochrane, W.P., and M.A. Forbes. 1974. Oxidation products of heptachlor and its metabolites-A chemical study. Chemosphere 3(1):41-46.

Demayo, A. 1972. Gas chromatographic determination of the rate constant for the hydrolysis of heptachlor. Bull. Environ. Contam. Toxicol. 8(4):234-237.

Ehmann, J.L. 1976. A model system: the photochemical interaction of heptachlor and selected epicuticular wax components of the tomatoe fruit and pear leaf. Ph.D. Thesis. Michigan State University. 302 pp. University Microfilms, Ann Arbor, Mich., Order No. 76-18, 015. (Diss. Abstr. Int. B 1976, 37(2):597-598).

Eichelberger, J.W., and J.J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5(6):541-544.

Fischler, H.-M. and Korte, F. 1969. Sensibilizierte und unsensibilisierte photoisomeririerung von cyclodien-insektiziden. Tetrahedron Lett. 1969. (32):2793-2796.

Gore, R. C., W. Hannah, S.C. Pattacini, and T.J. Porro. 1971. Infrared and ultraviolet spectra of seventy-six pesticides. J. Assoc. Anal. Chem. 54(5):1040-1082.

Hill, D.W., and P.L. McCarty. 1967. Anaerobic degradation of selected chlorinated hydrocarbon pesticides. J. Water Pollut. Control Fed. 39(8):1259-1277.

Huang, J.-C. 1971. Effect of selected factors on pesticide sorption and desorption in the aquatic system. J. Water Pollut. Control Fed. 43(8):1739-1748.

Huang, J.-C. 1974. Water-sediment distribution of chlorinated hydrocarbon pesticides in various environmental conditions. Proc. Int. Conf. Transp. Persistent Chem. Aquat. Ecosyst. II:23-30.

Huang, J.-C., and C.-S. Liao. 1970. Adsorption of pesticides by clay minerals. J. Sanit. Eng. Div., Am. Soc. Civ. Eng. 96(SAS):1057-1078.

Iyengar, L. and A.V.S. P. Rao. 1973. Metabolism of chlordane and heptachlor by Aspergillus niger. J. Gen. Appl. Microbiol. 194:321-324.

Leigh, G.M. 1969. Degradation of selected chlorinated hydrocarbon insecticides. J. Water Pollut. Control Fed. 41(11)(Pt. 2):R450-R460.

Lu, P.-Y., R.L. Metcalf, A.S. Hirwe, and J.W. Williams. 1975. Evaluation of environmental distribution and fate of hexachlorocyclopentadiene, chlordene, heptachlor, and heptachlor epoxide in a laboratory model ecosystem. J. Agric. Food Chem. 23(5):967-973.

Mabey, W.R., and T. Mill. 1978. Critical review of hydrolysis of organic compounds in water under environmental conditions. J. Phys. Chem. Ref. Data 7:383.

Martin, H., ed. 1972. Pesticide Manual, 3rd Edition. British Crop Protection Council, Worcester, Engl.

McGuire, R.R., M.J. Zabik, R.D. Schuetz, and R.D. Flotard. 1970. Photochemistry of bioactive compounds. J. Agric. Food Chem. 18(2):319-321.

McGuire, R.R., M.J. Zabik, R.D. Schuetz, and R.D. Flotard. 1972. Photochemistry of bioactive compounds. Photochemical reactions of heptachlor. Kinetics and mechanisms. J. Agric. Food Chem. 20(4):856-861.

Miles, J.R.W., C.M.Tu, and C.R. Harris. 1969. Metabolism of heptachlor and its degradation products by soil microorganisms. J. Econ. Entomol. 62(6):1334-1338.

Miles, J.R.W., C.M. Tu, and C.R. Harris. 1971. Degradation of heptachlor epoxide and heptachlor by a mixed culture of soil microorganisms. J. Econ. Entomol. 64(4):839-841.

Onuska, F.I., and M.E. Comba. 1975(a). Isolation and characterization of the photoalteration products of cis- and transchlordane. J. Assoc. Off. Anal. Chem. 58(1):6-9.

Onuska, F.I., and M.E. Comba. 1975(b). Isolation and characterization of some methanoindene photoproducts. Biomed. Mass Spectrom. 2(4):176-182.

Park, K.S., and W.N. Bruce. 1968. The determination of the water solubility of aldrin, dieldrin, heptachlor, and heptachlor epoxide. J. Econ. Entomol. 61(3):770-774.

Rosen, J.D., D.J. Sutherland, and M.A.Q. Khan. 1969. Properties of photoisomers of heptachlor and isodrin. J. Agric. Food Chem. 17(2):404-405.

Rosen, J.D., and M. Siewierski. 1979. Sensitized photolysis of heptachlor. J. Agric. Food Chem. 18:943.

Schimmel, S.C., J.M. Patrick, Jr., and J. Forester. 1976. Hepatachlor: Uptake, depuration, retention and metabolism by spot, (Leisotomus santhurus). J. Toxicol. Environ. Health 2(1):169-178.

Sethunathan, N. and T. Yoshida. 1973. Short communication: Degradation of chlorinated hydrocarbons by clostridium sp. isolated from lindane-amended, flooded soil. Plant Soil. 38(3):663-666.

Singh, J. 1969. Conversion of heptachlor to its epoxide. Bul. Environ. Contam. Toxicol. 4(2):77-79.

Voerman, S. 1969. Distribution of ratio of some chlorinated hydrocarbon insecticides between hexane and water. Bull. Environ. Contam. Toxicol. 4(2):64-67.

Vollner, L., W. Klein and F. Korte. 1969. Ecological chemistry. XVIII. Photo rearrangement of the components of technical chlordans. Tetrahedron Lett. (34):2967-2970.

Vollner, L., H. Parlar, W. Klein and F. Korte. 1971. Beitrage zur okologischen-XXXI. Photoreaktionen derr komponenten des technischen chlordans. Tetrahedron 27:501-509.

Zepp, R.G., N.L. Wolfe, G.L. Baughman, P.F. Schlotzhaver, and J.N. MacAllister. 1979. Dynamics of processes influencing the behavior of hexachlorocyclopentadiene in the aquatic environment. U.S. Environmental Protection Agency (ERL), Athens, Ga. (Paper presented before the Division of Environmental Chemistry, American Chemical Society, Washington, D.C. September 9-14, 1979.)

30. HEPTACHLOR EPOXIDE

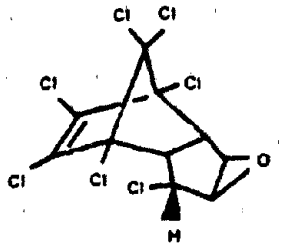
30.1 Statement of Probable Fate

Heptachlor epoxide is resistant to chemical and biological transformations in aquatic environments, and half-lives of over several years are probable. Although sediment sorption and bioaccumulation are not appreciable, they may ultimately be relatively important processes in view of the stability of heptachlor epoxide in the environment. Photosensitized reactions and biotransformation in anaerobic sediments are possibly important processes for eventual transformation of heptachlor epoxide in aquatic environment.

30.2 Identification

Heptachlor epoxide (HE) is known to exist in two isomeric forms (Singh 1969); a metabolic product of heptachlor melting at 157-159°C and a product formed in halohydrin reactions, melting at 86-89°C. The 157-158°C isomer, shown below, is the toxic chemical and is assumed to be the dominant isomer and of concern in this fate assessment. In most literature the possibility of two isomers have not been recognized.

The structure, alternate names, and CAS and TSL names of HE are given below:



Heptachlor epoxide

CAS No. 1024-57-3
TSL No. PB 94500

Alternate Names

Heptachlor epoxide
4,7-Methanoindan-1,4,5,6,7,8,
8-heptachlor-2,3-epoxy-3a4,
7,7a-tetrahydro
Velsicol 53-CS-17

30.3 Physical Properties

The general physical properties of HE are as follows:

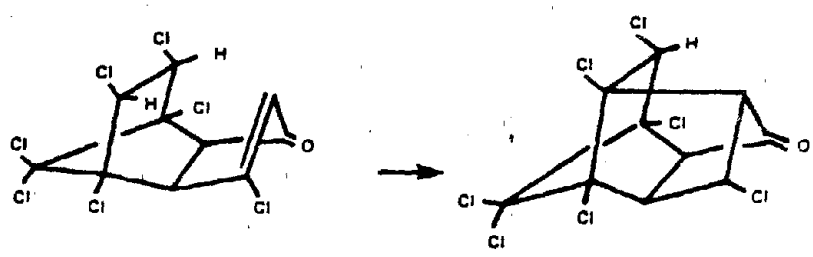
Molecular weight	389.2
Melting point (Singh 1969)	157-160°C
Boiling point	No data found
Vapor pressure	No data found
Solubility in water at 25°C	
(Park and Bruce 1968)	0.350 ppm
(Weil et al. 1974)	0.350 ppm
(Biggar and Riggs 1974)	0.200 ppm
	0.110 ppm at 15°C
Log octanol/water partition coefficient	No data found

30.4 Summary of Fate Data

30.4.1 Photolysis

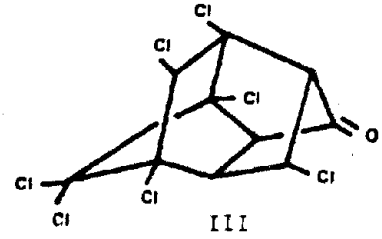
No data are available for estimating the photolysis half-life of HE in aqueous systems. Information on the photolysis of HE in the solid phase suggests that photolysis of HE can occur in sunlight. Other information indicates that the direct and sensitized photolysis of HE can give the same products.

Fischler and Korte (1969) reported that HE in acetone solvent was photoisomerized to a bridged chlorinated ketone structure; the reaction was attributed to acetone acting as a photosensitizer. Ivie et al. (1972) and Knox et al. (1973) repeated the photolysis of HE in acetone solvent using light of wavelengths above 280 nm and determined the photoproduct as structure II, which was formed through the intermediacy of photoproduct I. A 50-60% yield of I was formed when HE on bean leaves treated with the sensitizer rotenone was photolyzed in sunlight for 4 hours. In this experiment only 1% II was formed, and more II was formed only after prolonged exposure to sunlight. No photoproducts were formed in the absence of rotenone. The authors further noted that direct photolysis of I on plant foilage gave "slow" conversion to II, with a small (unspecified) amount of I remaining after 7 days time.



I II

Graham et al. (1973) studied the photolysis of HE as a solid (pressed) desk, as a powder, and as 0.5% HE in a KBr disk. After 121 hours of exposure to sunlight in July (in Texas), 93%, 98% and 0% HE remained in the solid disk, powder, and KBr disk, respectively. Powdered HE exposed to sunlight from January to mid-September was 39% photoisomerized. The products isolated were the same as those identified by Ivie et al. (1972) and Knox et al. (1973), but Graham and coworkers also identified a photoisomer, III, which is the same product originally suggested by Fischler and Korte (1969).



III

30.4.2 Oxidation

Singh (1969) reported that heptachlor is oxidized to the toxic HE isomer by CrO_3 in acetic acid in 60% yield; the fairly high yield of HE suggests that it is not easily further oxidized under these rather drastic conditions. Hoffmann and Eichelsdoerfer (1971) found that when ozone at concentrations of 17 and 4 mg/liter was bubbled through solutions of HE in 10% acetone in water for 45 minutes, losses of HE were 26% and 6%, respectively. Under the same conditions aldrin and heptachlor were completely oxidized. Although the latter paper suggests some susceptibility of HE to oxidation by ozone, neither paper provides any information useful for evaluating the rate of HE oxidation in the aquatic environment.

30.4.3 Hydrolysis

In a study of the hydrolysis of HE, Eichelberger and Lichtenberg (1971) reported that HE was unchanged after 3 weeks at room temperatures in a sample of river water (pH 7.3 to 8.0) and in distilled water. Assuming an analytical error at ± 2.5% (100% recovery cited was rounded off to the nearest 5%), a half-life of at least 4 years is calculated.

30.4.4 Volatilization

No information on the volatilization of HE from aquatic systems is available.

30.4.5 Sorption

Information on sorption of HE on soil and clay indicate that sorption is not an extensive process in aquatic environments, with partition coefficients on the order of a few hundred. However, the lack of HE transformation by chemical and biological processes does indicate that sorbed HE may ultimately be transported to sediments where anaerobic transformation may slowly occur.

Weil et al. (1973) measured the Freundlich isotherm parameters for sorption of HE by a humic acid at 15°C and found $1/n = 0.83$ and $K = 209$. Sorption of HE on a soil (pH 6.7, 1.4% humic material) gave Freundlich parameters of $1/n = .71$ and $K = 400$. From the isotherm graph reported by Hill and McCarty (1967) for sorption of HE on bentonite clay, Freundlich parameters of $1/n = 1.4$ and $K = 650$ are calculated. These authors also noted that for the chlorinated pesticides they studied, sorption on algae was usually one to two orders of magnitude higher than on the clay; no specific data for sorption of HE on algae were given.

30.4.6 Bioaccumulation

Grimes and Morrison (1975) have reported HE bioconcentration factors for 10 bacterial species; eight factors were between 60 and 900, with the other two factors being 1,900 and 15,200. The authors also reported that HE uptake was rapid, with near maximum concentrations achieved in 15 minutes. Lu et al. (1975) have found concentration factors of roughly 2×10^3, 8×10^4, and 6×10^3 for alga, snail, and mosquito fish in microcosm experiments. In the microcosm, the HE concentrations killed daphnia and mosquito larvae throughout the 43 day experiment; hence the food chain system was perturbed and this disturbance may have affected

the uptake and depuration of HE in the system. Ernst (1977) also measured a concentration factor of 1700 for mussel and found a half-life of about 2 days for HE elimination when the mussel was transferred to clean water.

The above data show that HE may be moderately accumulated in some biological systems.

30.4.7 Biotransformation and Biodegradation

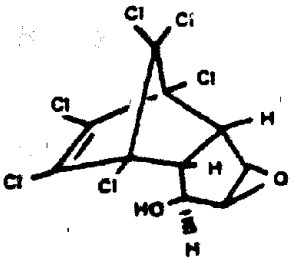
HE is very slowly transformed by biological processes and is likely to have half-lives of several years in many aquatic systems. Although biotransformations are slow, such processes may be important fates for HE since other transformation processes are also slow, and HE may ultimately be transported to aquatic sediments where anaerobic transformation occurs.

Lu *et al.* (1975) reported studies related to biotransformation of HE showing that HE is quite resistant to biotransformations in aquatic microcosms. Thus, HE was present as 91%, 92%, and 70% of the total ^{14}C extracted from alga, snail and fish, respectively, after a 43 day microcosm experiment. The product 1-hydroxyl-2,3-epoxychlordene (IV) was also found as 3.5%, 8.7%, and 19% of the extractable ^{14}C in alga, snail, and fish, respectively; this product was probably due to *in vivo* biotransformation since chemical hydrolysis of HE has been found to be slow (see Section 30.4.3). Lu *et al.* (1975) also found that HE was 96% recovered after ingestion by a caterpillar and 98% recovered when subjected to microsomal oxidation.

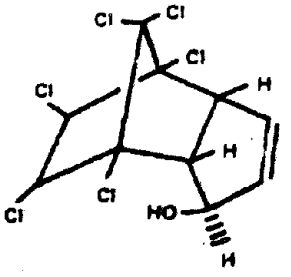
Hill and McCarty (1967) studied the degradation of several chlorinated pesticides, including HE, in sewage sludges and found no HE loss in aerobic dilute sludge and only slight HE loss in anaerobic dilute sludge. About a 50% loss of HE was found in thick sludge after approximately 60 days. The authors concluded that HE was similar to dieldrin in its resistance to anaerobic transformation, with both epoxides more stable than the other chlorinated pesticides, including aldrin, DDD, DDT, endrin, and heptachlor.

Miles *et al.* (1971) examined the degradation of HE in aqueous solution containing a mixed culture of soil microorganisms and found that HE

was lost at the rate of about 1% per week for a 12 week experiment. The hydroxychlordane product V was isolated in this experiment.



IV



V

30.4.8 Other Reactions

No reactions other than those discussed above have been considered for HE in aquatic environments. In view of the lack of reactivity of HE toward biological and chemical transformation processes, anaerobic reduction of HE may be an important fate, but no studies on this subject have been reported.

30.4.9 Microcosm Studies, Field Studies, and Modelling

Lu et al. (1975) reported on the fate of HE in a terrestrial-aquatic microcosm and in an aquatic microcosm. These experiments were made difficult by the toxicity of HE to organisms in the microcosm because the food chain was interrupted. Information from this paper on bioaccumulation and biotransformation is given in Sections 30.4.6 and 30.4.7.

30.5 Data Summary

Table 30-1 summarizes the data on the aquatic fate of heptachlor epoxide.

Table 30-1

Summary of Aquatic Fate of Heptachlor Epoxide

Environmental Process[a]	Summary Statement	Rate	Half-Life $t_{\frac{1}{2}}$	Confidence of Data
Photolysis	No quantitative information available.	-	-	-
Oxidation	Not an important process.	-	-	Medium
Hydrolysis	Not an important process.	-	-	High
Volatilization	No information available.	-	-	-
Sorption	Occurs to a moderate degree.	-	-	High
Bioaccumulation	Occurs to a moderate degree.	-	-	High
Biotransformation/ Biodegradation	Very slow, but could be important.	-	-	Medium

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

30.6 Literature Cited

Biggar, J.W., and I.R. Riggs. 1974. Apparent solubility of organochlorine insecticides in water at various temperatures. Hilgardia 42(10):383-391.

Eichelberger, J.W., and J.J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5(6):541-544.

Ernst, W. 1977. Determination of the bioconcentration potential of marine organisms - a steady state approach. Chemosphere 6(11):731-740.

Fischler, H.-M. and Korte, F. 1969. Sensibilisierte and unsensibilisierte photoisomeririerung von cyclodien-insektiziden. Tetrahedron Lett. 1969. (32):2793-2796.

Graham, R.E., K.R. Burson, C.F. Hammer, L.B. Hansen, and C.T. Kenner. 1973. Photochemical decomposition of heptachlor epoxide. J. Agric. Food Chem. 21:824-834.

Grimes, D.J. and S.M. Morrison. 1975. Bacterial bioconcentration of chlorinated hydrocarbon insecticides from aqueous sytems. Microb. Ecol. 2(1):43-59.

Hill, D.W., and P.L. McCarty. 1967. Anaerobic degradation of selected chlorinated hydrocarbon pesticides. J. Water Pollut. Control Fed. 39(8):1259-1277.

Hoffmann J., and D. Eichelsdoerfer. 1971. Effect of ozone on chlorinated-hydrocarbon-group pesticides in water. Vom Wasser 38:197-206.

Ivie, G.W., J.R. Knox, S. Khalifa, I. Yamamoto and J.E. Casida. 1972. Novel photoproducts of heptachlor epoxide, trans-chlordane and trans-nonachlor. Bull. Environ. Contam. Toxicol. 7(6):376-382.

Knox, J.R., S. Khalifa, G.W. Ivie, and J.E. Casida. 1973. Characterization of the photoisomers from cis- and trans-chlordanes, trans-nonachlor and heptachlor epoxide. Tetrahedron. 29:3869-3879.

Lu, P.-Y., R.L. Metcalf, A.S. Hirwe, and J.W. Williams. 1975. Evaluation of environmental distribution and fate of hexachlorocyclopentadiene, chlordene, heptachlor, and heptachlor epoxide in a laboratory model ecosystem. J. Agric. Food Chem. 23(5):967-973.

Miles, J.R.W., C.M. Tu, and C.R. Harris. 1971. Degradation of heptachlor epoxide and heptachlor by a mixed culture of soil microorganisms. J. Econ. Entomol. 64(4):839-841.

Park, K.S., and W.N. Bruce. 1968. The determination of the water solubility of aldrin, dieldrin, heptachlor, and heptachlor epoxide. J. Econ. Entomol. 61(3):770-774.

Singh, J. 1969. Conversion of heptachlor to its epoxide. Bull. Environ. Contam. Toxicol. 4(2):77-7°.

Weil, L., G. Dure, and K.E. Quentin. 1973. Adsorption of chlorinated hydrocarbons to organic particles and soils. Z. Wasser Abwasser Forsch. 6(4):107-112.

Weil, L., G. Dure, and K.E. Quentin. 1974. Solubility in water of insecticide chlorinated hydrocarbons and polychlorinated biphenyls in view of water pollution. Z. Wasser Abwasser Forsch. 7(6):169-175.

31. HEXACHLOROCYCLOHEXANE (α-, β-, and δ-BHC isomers)

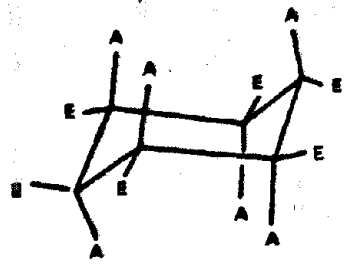
31.1 Statement of Probable Fate

The fate of the α-, β-, and δ-BHC isomers in aquatic systems is determined by their availability to biotransformation processes. Although sorption to suspended sediment and biota is not extensive, sorption is probably an important process for ultimately transporting BHC to anaerobic sediments where transformations occur. As for lindane (see Chapter 32), hydrolysis, oxidation, and photolysis are not important processes for the BHC isomers in aquatic environments.

31.2 Identification

Brooks (1974) and Gunther (1971) provided excellent summaries on the preparation, separation, structure, and characteristics of the 1,2,3,4,5,6-hexachlorocyclohexane isomers. According to Demozay and Marechal (1972), BHC has 17 optical or stereoisomeric forms, but only 9 of these are energetically feasible. Five of these isomers are given below along with the approximate percentage ranges found in technical BHC preparations. Because of its acute toxicity, most studies on BHC have focused on the γ-BHC isomer, also called lindane; lindane is the subject of chapter 32. Lindane isomerizes to the α-, β-, and δ-BHC isomers by biological proceses and to β-BHC by photochemical reaction (see Chapter 32).

The structure and orientations of α, β, and δ-BHC are given below, and the CAS and TSL number, and alternate names for the isomers are given on the following page.



Orientation of Cl atoms on ring	Isomer	Percent of Isomer in Technical BHC
AAEEEE	α	60 - 70
EEEEEE	β	5 - 12
AAAEEE	γ(lindane)	10 - 15
AEEEEE	δ	6 - 10
AEEAEE	ε	3 - 4

Isomer	α	β	δ
CAS No.	319-84-6	319-85-7	319-86-8
TSL No.	GV 35000	GV 43750	GV 45500

Alternate Names

Benzene hexachloride
HCH
BHC

31.3 Physical Properties

The physical properties of α-, β-, and δ-BHC are shown below.

Molecular weight 291

	α	β	δ
Melting point			
(Gunther 1971)	157-158°C	309°C	138-139°C
(Metcalf 1955)	159-160°C	309-310°C	138-139°C
Boiling point	No data found		
Vapor Pressure (in torr) at 20°C			
(Balson 1947)*	2.5×10^{-5}	2.8×10^{-7}	1.7×10^{-5}
(Slade 1945)	2×10^{-2}	5×10^{-3}	2×10^{-2}
Solubility in water (in ppm) at 25°C			
(Kurihara et al. 1973)†	1.21-2.03	0.13-0.20	8.64-15.7
(Weil et al. 1974)	2.00	0.240	31.4
(Brooks 1974)	1.63	0.70	21.3
Log octanol/water partition coefficient at 25°C (Kurihara et al. 1973)	3.81	3.80	4.14

*Preferred values, based on agreement of data of Balson with data of other researchers for lindane; see Section 32.3.
†This reference reported solubility values at 28°C.

31.4 Summary of Fate Data

31.4.1 Photolysis

Kawahara (1972) reported that the rates of disappearance of the BHC isomers were in the order $\alpha > \gamma > \beta > \delta$ when dissolved in water at concentrations 0.01 to 5.0 ppm and exposed to sunlight; half-lives ranging from 4 to 6 days for α-BHC to 10-22 days for δ-BHC were reported. These data are highly suspect, however, because experimental details were lacking (no controls described) and the graphical presentation of data which shows a rapid decrease in BHC concentrations within 10 days followed by a slower loss out to 48 days. Ginsburg (1953) reported that the toxicity of a BHC emulsion was lost after 12 days exposure to sunlight (the toxicity was attributed to lindane); as described for lindane (see Section 32.4.1), the BHC isomers are not expected to photolyze rapidly in sunlight because of the slight, if any, light absorption coefficients above 290 nm. Roburn (1963) reported that the four isomers of BHC gave no reaction products after photolysis with a 254 nm light source for 2-3 hours. Roburn's experiments and the expected low absorbance of the BHC isomers suggest that photolysis will not be an important process in the environment; the reported photolyses of BHC are likely due to adventitious processes such as volatilization, sorption on glass, or photoreaction caused by impurities in the BHC used.

31.4.2 Oxidation

No information was obtained concerning oxidation of any BHC isomer in the aquatic environment. By analogy to limited studies on the oxidation of lindane, the other BHC isomers should be quite stable to oxidation.

31.4.3 Hydrolysis

No data are available on hydrolysis rates of the individual BHC isomers although information from one paper does indicate that the BHC (all isomers together) has a half-life for hydrolysis of more than two years.

Eichelberger and Lichtenberg (1971) examined the persistence of BHC for 8 weeks in water samples from the Little Miami River and in distilled water; the pH of the river water varied from 7.3 to 8.0 during the 8 week period. No change in BHC concentration was found during this time. Assuming a maximum analytical error of 2.5% (recoveries reported were rounded off to nearest 5%), the half-life for BHC under these conditions must be at least 4 years, indicating that the BHC isomers are quite stable to hydrolysis.

Cristol (1947) has studied the hydroxide promoted hydrolysis (elimination of HCl) of the α-, β-, γ-, and δ-BHC isomers at 20.1°C in a solvent of 76% ethanol in water. The second order rate constants for the elimination of HCl from the α-, β- and γ-isomers (latter is lindane) were 1.7×10^{-1}, 3×10^{-6}, and $4.4 \times 10^{-2} M^{-1} sec^{-1}$, respectively; HCl elimination from δ-BHC was too fast to be measured under the experimental conditions. Although the data do show the relative reactivities of the individual BHC isomers, these data are not applicable to an environmental assessment because of the unknown effect of the high concentration of ethanol in the reaction solvent.

31.4.4 Volatilization

There are no reliable data with which to estimate a half-life for volatilization of BHC isomers from aquatic environments. Although loss of BHC through volatilization has been addressed by several research groups investigating biotransformation or bioaccumulation of BHC isomers, the information obtained cannot be directly compared or even used to decide whether volatilization of BHC can be an important process in aquatic environments.

Tsukano (1973) has reported on the loss of BHC isomers from aqueous solution at 25°C (see Section 31.4.5). Data presented (in graphical form) showed that 0, 25, 75, and 75% of the α-, γ (lindane)-, β-, and δ-BHC isomers, respectively, remained after 2 weeks. No experimental details were reported for these experiments, although the graph did also show that about 80% of the water had evaporated after the two week experiment. The author suggested volatilization as the process responsible for the loss, but no data or information useful for actually demonstrating volatilization or estimating volatilization rates in aquatic environments were reported. Although lacking any specific data, Newland et al. (1969) also implicated volatilization of α-BHC from aquatic systems as the reason why significant amounts of δ-BHC are not formed biologically in the sequence γ-BHC (lindane) → α-BHC → α-BHC (see Section 32.4.6).

Ernst (1977) reported data seemingly contradictory to this information that suggests the facile volatilization of α-BHC. He aerated aquaria containing several chlorinated pesticides, including α-BHC and lindane, and quantitatively recovered both BHC isomers from water after 67 hours. The experiments were conducted as controls in bioaccumulation studies. This information, as well as that cited in the discussion of lindane volatilization (see Section 32.4.4), would suggest that volatilization of BHC (at least the α and γ-isomers) is not a facile process. Since chemical and biological processes appear to be rather slow to transform BHC in aquatic environments, the question of volatilization rates of BHC isomers is important and should be pursued.

31.4.5 Sorption

Only one paper on the sorption of the individual BHC isomers to sediments was found and in agreement with data on the γ-BHC isomer (lindane see Section 32.4.5), this information indicates that BHC should not be sorbed extensively onto biota and sediments. Because of the lack of chemical and biological transformation in aerobic systems, however, sorption onto particulates with subsequent deposition and transformation in anaerobic systems may be the most important fate for BHC.

Tsukano (1973) reported experiments on the translocation of BHC isomers from standing water to a sediment-soil layer and the partition of BHC isomers between soil and water. Insufficient experimental information was provided in the translocation experiments for use in a quantitative environmental assessment except to show that equilibrium between soil and water was attained in about 7 days, and that the amount of BHC isomer sorbed in the soil layer compared with the amount in water was in the order $\delta \approx \beta > \alpha$; information on the γ-BHC isomer (lindane) was complicated by biotransformation. Tsukano also presented Freundlich isotherm plots for sorbtion of BHC isomers from water to two soils. For the soil containing 1.9% carbon, values of 1/n were approximately 0.91 and K was between 10 and 30 for the α, β, and δ-BHC. For a soil with 5.2% carbon, 1/n was approximately 0.71 to 0.83 and K ranged from 30 to 120 for the four BHC isomers. These rough data, which were calculated from the isotherm plots given in the paper, indicate that the BHC isomers will not be extensively sorbed onto sediments in aquatic environments.

31.4.6 Bioaccumulation

Information available on the bioaccumulation of α-, β-, and δ-BHC is similar to that for γ-BHC and indicates that BHC isomers are not extensively bioaccumulated in organisms (see also Section 32.4.7). Concentration factors vary among the four BHC isomers in the range of about 10 to 500, depending on the isomer and organism.

Schimmel et al. (1977b) reported that pink shrimp, pinfish, and oysters accumulated BHC to concentrations that were 80, 480, and 130 times the concentrations of BHC in water. Ernst (1977) reported concentration factors in mussels of 106 and 100 for α-BHC and lindane, respectively. This paper also presented data showing that both BHC isomers are eliminated from the mussels when placed in clean water, although the first-order rate constants and approximately 20-hour half-lives given by the author are clearly not correct when compared to the actual data showing the loss of the pesticides from the mussels as a function of time. Only 43 ppb of

α-BHC of the initial 94 ppb remained in the mussel after 2 hours in clean water, with 12 ppb remaining after 48 hours. For lindane initially at 124 ppb in the mussel, 54 ppb and 18 ppb remained after 2 and 48 hours, respectively.

Sugiura et al. (1976) studied the effects of β-BHC concentration in an aquatic microcosm. The relationship between the concentration of β-BHC (in ppm) in the microorganism (bacteria and algae) and the concentration of β-BHC (in ppm) in the medium was given by the following equation:

$$\log(C_{organisms}) = (0.85)\bullet\log(C_{medium}) + 2.54.$$

This expression can be restated as

$$C_{organisms} = 350\bullet(C_{medium})^{(0.85)}$$

Although slightly dependent on the exponential factor of C_{medium}, the factor of 350 is in good agreement (i.e., an order of magnitude) with the concentration factors found by Schimmel et al. (1977b) and Ernst (1977) for the higher organisms.

Szokolay et al. (1977) reported an extensive study on the cumulation of BHC and of the separate isomers it comprises. The dynamics of the transfer of the isomers in a food chain using chickens (fodder, flesh, and eggs) were studied. The authors concluded that the beta isomer showed a greater tendency to accumulate than the alpha, gamma, or delta isomers; more rapid degradation of the other isomers and isomerization to the beta form were suggested as the reason for β- isomer predominance. The BHC content was also observed to decrease after feeding of the pesticide was stopped. The amounts of alpha, gamma, and delta isomers decreased 90-96% in 2 weeks, but the beta isomer decreased only 40% in the same period. These experimental data with chickens are paralleled by survey data of the same authors (Szokolay et al. 1977) showing ratios of BHC concentrations in human milk relative to BHC concentrations in soil to be 16, 250, and 61 for the alpha, beta, and delta isomers, respectively.

31.4.7 Biotransformation and Biodegradation

Very little information is available to assess biotransformation of α-, β-, or δ-BHC. However, biotransformation of lindane may be a significant source of α-BHC in the environment as discussed in Section 32.4.6. β-BHC and δ-BHC have also been reported as biotransformation products of lindane.

Tsukano (1973) reported that BHC isomers incubated in a soil-water mixture were degraded in the order $\gamma > \alpha > \beta > \delta$; the amounts remaining after 56 days were approximately 5%, 10%, 30%, and 50%, respectively. Since the added presence of sodium azide in the soil-water medium resulted in very little loss of BHC, microbial processes were assumed responsible for the observed losses of BHC. Tsukano also stated that in another study in his laboratory, a flooded soil experiment tentatively identified δ-3,4,5,6-tetrachloro-1-cyclohexane as a degradation product of α-BHC.

Heritage and MacRae (1977a) reported that washed cell suspension of Clostridium sphenoides degraded α-BHC and lindane. These authors did not give any kinetic information for the transformation except to mention that no α-BHC was recovered after incubation for 4 hours; in an identical experiment, no lindane was recovered after 2 hours of incubation. The product from the transformation of α-BHC was δ-3,4,5,6-tetrachloro-1-cyclohexane, the same product reported by Tsukano (1973). Although not immediately relevant to aquatic systems, it is of interest to note that Steinwandter and Schluter (1978) have reported that β-BHC is a product of γ-BHC (lindane) metabolism in grass via the intermediacy of α-BHC. Interconversion of BHC isomers may also be occurring in aquatic environments and may complicate conclusions on the fate of individual BHC isomers in such systems.

31.4.8 Other Reactions

No processes other than those listed above have been implicated as important in the fate of BHC in aquatic environments. No information was found to indicate that isomerization of BHC isomers occur spontaneously in the aquatic environment, other than the biotransformation discussed in Sections 31.4.6 and 32.4.6.

31.4.9 Microcosm Studies, Field Studies, and Modelling

No microcosm or field studies on the α-, β-, or δ-BHC isomers have been reported. The chemical and physical properties of the BHC isomers are similar enough, however, so that the information in Section 32.4.9 also roughly applies to α-, β- and δ-BHC.

31.5 Data Summary

Table 31-1 summarizes the data on the aquatic fate of the BHC isomers.

Table 31-1

Summary of Aquatic Fate of Hexachlorocyclohexane

Environmental Process[a]	Summary Statement	Rate	Half-Life $t_{\frac{1}{2}}$	Confidence of Data
Photolysis	Not an important process.	-	-	Medium
Oxidation	Not an important process.	-	-	Medium
Hydrolysis	Not an important process.	-	-	Medium
Volatilization	Information contradictory as to how important process is.	-	-	-
Sorption	Important for transport to anaerobic sediments.	-	-	Low
Bioaccumulation	Not an important process.	-	-	Low
Biotransformation/ Biodegradation	Important process that varies with environment.	-	-	Low

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

31.6 Literature Cited

Balson, E. W. 1947. Studies in vapour pressure measurement, Part III. - An effusion manometer sensitive to $5x10^{-6}$ millimetres of mercury: Vapour pressure of DDT and other slightly volatile substances. Trans. Faraday Soc. 43:54-60.

Brooks, G. T. 1974. Chlorinated Insecticides: Volume I:Technology and applications. CRC Press, Cleveland, OH., 249 pages.

Cristol, S. J. 1947. The kinetics of the alkaline dehydrochlorination of benzene hexachloride isomers. The mechanism of second-order elimination reactions. J. Amer. Chem. Soc. 69:338-342.

Demozay, D., and G. Marechal. 1972. Physical and chemical properties, in lindane: Monograph of an insecticide, E. Ulmann, pp.15-21, K. Schiller, Freiburg in Breisgau.

Zichelberger, J. W., and J. J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5(6):541-544.

Ernst, W. 1977. Determination of bioconcentration potential of marine organisms. - a steady state approach. Chemosphere 6(11):731-740.

Ginsburg, J. M. 1953. Rate of decomposition of the newer insecticides when exposed to direct sunlight. Proc. New Jersey Mosquito Exterm. Assoc. 40:163-168.

Gunther, F.A. 1971. Halogen derivatives of aliphatic hydrocarbons. Residue Rev. 36:34-77.

Heritage, A. D., and I. C. MacRae. 1977(a). Identification of intermediates formed during the degradation of hexachlorocyclohexanes by Clostridium sphenoides. Appl. Environ. Microbiol. 33(6):1295-1297.

Heritage, A. D., and I. C. MacRae. 1977(b). Degradation of lindane by cell-free preparations of Clostridium sphenoides. Appl. Environ. Microbiol. 34(2):222-224.

Kawahara, T. 1972. Studies of organochlorine compound residues in crops and soil. Part 20. Disappearance of BHC isomers in water. Bull. Agr. Chem. Inspect. Stn. No. 12:49-51.

Kurihara, N., M. Uchida, T. Fujita, and M. Nakajima. 1973. Studies on BHC isomers and related compounds V. Some physicochemical properties of BHC isomers. Pestic. Biochem. Physiol. 2(4):383-390.

Metcalf, R. L. 1955. Organic Insecticides. Interscience Publishers Inc., New York, N.Y.

Newland, L. W., G. Chesters, and G. B. Lee. 1969 Degradation of γ-BHC in simulated lake impoundments as affected by aeration. J. Water Poll. Control Fed. 41(5)Pt.11:R174-R188.

Roburn, J. 1963. Effect of sunlight and ultraviolet radiation on chlorinated pesticide residues. Chem. Ind. (1963):1555-1556.

Schimmel, S. C., J. M. Patrick, Jr., and J. Forester. 1977(a). Uptake and toxicity of toxaphene in several estuarine organisms. Arch. Environ. Contam. Tox. 5:353-367.

Schimmel, S. C., J. M. Patrick, Jr., and J. Forester. 1977(b). Toxicity and bioconcentration of BHC and lindane in selected estuarine animals. Arch. Environ. Contam. Tox. 6:355-363.

Slade, R. E. 1945. The γ-isomer of hexachlorocyclohexane (Gammexane). An insecticide with outstanding properties. Chem. Ind. 40:314-319.

Steinwandter, H., and H. Schluter. 1978. Experiments on lindane metabolism in plants. IV. A kinetic investigation. Bull. Environ. Contam. Toxicol. 20:174-179.

Sugiura, K., S. Sato, M. Goto, and Y. Kurihara. 1976. Effects of β-BHC on aquatic microcosm. Chemosphere 5(1):39-44.

Szokolay, A., A. Madaric, and J. Uhnak. 1977. Relative cumulation of β-BHC in ecological and biological system. J. Environ. Sci. Health Part B B12(3):193-212.

Tsukano, Y. 1973. Factors affecting disappearance of BHC isomers from field rice soil. JARQ. 7(2):93-97.

Weil, L., G. Dure and K. E. Quentin. 1974. Solubility in water of insecticide chlorinated hydrocarbons and polychlorinated biphenyls in view of water pollution. Z. Wasser Abwasser Forsch. 7(6):169-175.

32. γ- HEXACHLOROCYCLOHEXANE (LINDANE)*

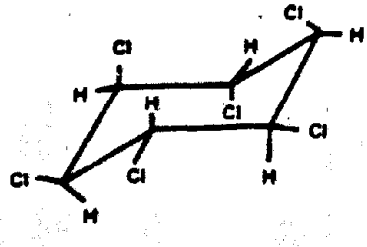
32.1 Statement of Probable Fate

The fate of lindane in aquatic systems will be controlled by the availability of and to biotransformation processes. Lindane transformation will be favored in biologically rich, anaerobic environments. Although sorption to suspended sediment and biota is not extensive, sorption is an important process for ultimately transporting lindane to anaerobic sediments where transformation occurs. Hydrolysis and oxidation do not appear to be important fate processes for lindane; data on the photolysis of lindane are contradictory and confusing. Lindane is only slightly bioaccumulated in organisms.

32.2 Identification

Lindane is the gamma (γ) isomer of 1,2,3,4,5,6-hexachlorocyclohexane and can be isolated from other BHC isomers by solvent extractions and recrystallization (see also Chapter 31). The commercial lindane product is required to contain not less than 99% of the γ-isomer and to have a melting point of at least 112°C.

The structure, nomenclature, and CAS and TSL numbers for lindane are given below.



Lindane

CAS No. 58-89-9
TSL No. GV 49000

Alternate Names

Gamma-BHC
1,2,3,4,5,6-Hexachlorocyclohexane
Gammexane
Benzenehexachloride
BHC, HCCH, HCH, TBH
Jacutin

*The name lindane will be used in this chapter instead of the γ-isomer nomenclature to minimize confusion with other isomers.

32.3 Physical Properties

The general physical properties of lindane are given below.

Molecular weight	291
Boiling point	No data found
Melting point (Martin 1972)	112.9°C
Vapor pressure at 20°C*	
(Benchmark 1975)	$(3.3\text{-}2.1) \times 10^{-4}$ torr
(Martin 1972)	9.4×10^{-6} torr
(Demozay and Marechal 1972)	1.6×10^{-4} torr
Solubility in water	
(Masterton & Lee 1972)	7.52 ± 0.04 ppm at 25°C
(Kurihara et al. 1973)	5.75 to 7.40 ppm at 28°C**
(Biggar and Riggs 1974)	2.15 ppm at 15°C†
	6.80 ppm at 25°C
	11.4 ppm at 35°C
(Weil et al. 1974)	7.8 ppm at 25°C
(Bhavnagary and Jayaram 1974)	12 ppm at 26.5°C
Log octanol/water partition coefficient at 25°C	3.72
(Kurihara et al. 1973)	

*Slade (1945) reported vapor pressures that are several orders of magnitude higher than recently measured data.
**Measured by several procedures.
†After centrifugation, particle size is <5μm.

32.4 Summary of Fate Data

32.4.1 Photolysis

Lindane is a saturated, chlorinated cyclic hydrocarbon structure and should have little, if any, uv absorption above the solar spectral re-

gion cutoff at ~290 nm. In spite of this limited light absorption, several papers have reported that lindane is photolyzed in sunlight. Lack of sufficient experimental information in these papers makes any conclusion on the importance of lindane photolysis in the environment very tenuous.

Steinwandter (1976b) reported that photolysis of lindane at >230 nm in petroleum ether, acetone, or water gave small amounts of α-BHC, and prolonged photolysis of lindane in aqueous solution gave products that could not be extracted with petroleum ether. The authors suggested that such photoisomerization was responsible for finding α-BHC on grass that had been coated with lindane and then dried in the sun. Subsequently, however, Steinwandter (1976a) and Steinwandter and Schluter (1978) reported that α-BHC was a metabolic product in grass (see Section 32.4.6). Thus the photoisomerization of lindane to α-BHC under environmental conditions is not certain.

Zabik and Leavitt (1976) report that a Japanese researcher has found that BHC isomers photoreact in sunlight in the order of α > β > lindane > δ. Ginsburg (1953) reported that a lindane emulsion lost 50% of its toxicity to mosquito larvae after 6 days of sunlight exposure and was nontoxic after 11 days of exposure. Roburn (1963), however, found that BHC isomers did not give any reaction products on exposure to 254 nm light. Thus, the photolysis of lindane in the aquatic environment is still in question, and available information is insufficient to decide whether photolysis is an important environmental process. Especially perplexing is the almost certainly small uv absorptin of lindane in the solar region which should result in low photochemical transformation rates.

32.4.2 Oxidation

No information was obtained concerning the oxidation of lindane in aquatic systems. Hoffmann and Eichelsdoerfer (1971) report that ozone bubbled through solutions of lindane in hexane or water-acetone solvent gave very little loss of lindane under conditions where heptachlor and aldrin were completely consumed.

Leigh (1969) reported attempts to oxidize lindane using the chemical oxidants chlorine, potassium permanganate, and potassium persulfate at pH values of about 2 and 6. Chlorine or permanaganate solutions at 50 mg $liter^{-1}$ produced no reaction with lindane after 48 hours at 20°C; the same concentration of persulfate removed only 1% lindane at pH 2.2 and about 10% lindane at pH 6.0. No products were reported from the persulfate oxidations.

32.4.3 Hydrolysis

No kinetic data have been found with which to estimate the hydrolysis half-life of lindane in aquatic environments. The available information does indicate that lindane will be reasonably stable in aquatic environments with half-lives at least greater than several months.

Eichelberger and Lichtenberg (1971) monitored technical BHC in samples of raw river water from Little Miami River, Ohio, and in distilled water at a BHC concentration of 10 µg/l over a period of 8 weeks. The pH of the river water varied from pH 7 to pH 8 during the experiments. No decrease in concentration was found. BHC contains about 13% lindane and this amount or a significant change in it could have been detected; assuming a 2.5% change in BHC concentration could have been detected, a half-life of over 4 years is calculated.

Gunther (1971) stated that lindane produced only 0.13% HCl when heated in steam at 102°C for one hour. Cristol (1947) studied the alkaline hydrolysis of BHC isomers in alkaline solutions of 76% ethanol in water at 20.11°C; the second order, base-promoted, hydrolysis rate constant reported for lindane under these conditions was 4.4×10^{-2} M^{-1} sec^{-1}. Assuming no solvent effect on the reaction, a hydrolysis half-life at pH 8 is calculated as 180 days. Application of this half-life to aquatic systems is very tenuous because of the different solvent used.

32.4.4 Volatilization

Mackay and Leinonen (1975) have calculated a half-life for volatilization of lindane from water of about 200 days using theoretical equations and assuming mass transfer coefficients in literature for the ocean. Spacie *et al.* (1977) reported that volatilization was not an important loss process in a flooded quarry treated with lindane since the observed lindane half-life was about 120 days (based on total water column analysis) compared to the 8 year volatilization half-life calculated for the water body using Mackay and Leinonen's procedure. Oloffs and Albright (1974) and bioaccumulation studies of Ernst (1977) also indicate that volatilization of lindane from solution is slow and is not an important loss process.

Several papers have also discussed lindane volatilization from soil as a function of water content of the soil (including flooded soils), but they do not contain data useful for evaluating volatilization from natural aquatic systems (Spencer and Cliath 1973; Harper *et al.* 1976; Siddaramappa and Sethunathan 1975).

32.4.5 Sorption

King et al. (1969) studied the sorption of lindane on two species of algae and three soils of different characteristics; data were presented as sorption isotherms without calculation of the parameters of the Freundlich equation, $S_s = K S_w^{1/n}$, where S_s is the weight of lindane sorbed per unit weight of sorbent, S_w is the weight of lindane in solution at equilibrium per unit weight of solvent (water), and n and K are constants. From the graphs presented in the paper, a calculated value of 1/n is about 0.4, and values of K for the three soils range from 500 to 80. The authors note that lindane equilibrium between soil and solution was attained in an hour and that greater sorption was found on soils with higher organic content as clay content. Sorption on algae required 3 days for equilibrium to be attained with values of K of about 30 and 50 for two algae and 1/n equal to about 1.25.

Weil et al. (1973) measured the Freundlich isotherm parameters for sorption of lindane by humic acid at 15°C and found 1/n = 0.8 with K = 45. Boucher and Lee (1972) studied the adsorption of lindane onto a sand aquifer, and found that sorption was rapid during the first four hours, with slight additional adsorption of lindane over the next 95 hours. They also found that less sorption occurred at 40°C than at 5°C and that neither pH (4.8 to 8.9) nor dissolved organic material in the water affected lindane uptake by the sand. From the graphs presented in the paper, a sorption isotherm K value of 0.35 is calculated. Newland et al. (1969) studied the sorption and biotransformation of 5 ppm lindane in water over a lake sediment (10 gm sediment in 3 liters of water) and found 44-57% adsorption of lindane in 18 hours, with slightly more lindane sorbed over longer contact times. More quantitative analysis of the sorption process was not possible due to losses from biotransformation and volatilization occurring during the experiment.

Hamelink et al. (1976), studied the fate of lindane and DDE in a flooded quarry and found that although lindane was rapidly distributed throughout the water column, it was only slightly adsorbed by the bottom mud of this artificial lake; 95% of the lindane accounted for after 6 months was in the water layer. Although the analyses for lindane in mud layers are uncertain, the amount in the mud layer was definitely low. In the same quarry 94% of DDE accounted for was in the mud layer. (See Section 32.4.9 for further information on this lindane experiment.)

32.4.6 Bioaccumulation

Grimes and Morrison (1975) reported lindane concentrations in bacteria that were $\leq$ 10 to 300 times the concentations in the supernatant culture media; 5 of the concentration factors were 20 or less, 5 factors were

between 20 and 100, and 3 factors were greater than 100. Ernst (1977) computed concentration factors of 130 to 170 for mussels raised in seawater.

The fate of ^{14}C-radiolabelled lindane in a terrestrial-aquatic microcosm has been reported by Metcalf et al. (1973). After 33 days 92% of the ^{14}C accounted for in mosquito fish was present as lindane. Of the ^{14}C recovered from snail, only 20% was lindane, with 70% present as γ-pentachlorocyclohexane. A polar metabolite (i.e., nonmobile in the tlc analysis) was found in snail, fish, and alga and which the authors suggested to be trichlorophenol(s). In an extension of this microcosm experiment, Sanborn (1974) found that added Aroclor 5460 caused lindane concentration ratios to be slightly higher; 2,4,6- and 2,4,5-trichlorophenol were identified as lindane metabolites in this study. These authors also reported concentration factors of as much as 810 for daphnia, 125 for mosquito larvae, and 233 for mosquito fish exposed to lindane in small microcosms.

Hamelink et al. (1976; 1977) reported that organisms in a flooded quarry accumulated lindane, but to a lesser extent than DDE (see Section 32.4.9). The zooplankton rapidly accumulated lindane, seeming to reach equilibrium after five days. The lindane content then declined as the concentration in the water declined. The lindane concentrations in fish also appeared to be in equilibrium with the water after five days; the concentration factor was $(7.68 \pm 4.41) \times 10^2$. The concentration factor for lindane in zooplankton ranged from 170 to 448.

Gakstatter and Wiess (1967) found that fish exposed to lindane reached equilibrium within a few hours, and the lindane was eliminated in less than 2 days after the fish were transferred to clean water. Based on this information and their work, Hamelink et al. (1977) suggest that lindane may undergo exchange between fish and water with half-lives of 3 to 6 hours.

32.4.7 Biotransformation and Biodegradation

The results of numerous diverse studies on the biological transformations of lindane suggest that lindane may be transformed with half-lives on the order of several days to more than a year when introduced into biologically rich, aquatic environments. Some papers that demonstrate the varying ease of transformation and products formed from lindane biotransformation are summarized below. It should be noted, however, that the diverse approaches to lindane studies as well as the source of the microorganisms make comparison of the experiments difficult and that the products reported are more likely a function of what products were sought, the organisms present, and when the sample was analyzed.

Tu (1976) reported that 71 of 147 microorganisms isolated from a loamy sand soil were able to utilize lindane in solution as the sole carbon source after 6 weeks incubation as evidenced by cell growth and chloride ion production. Thirteen microorganisms were chosen for further studies. Of these, four bacterial strains showed adaptation times of less than a day whereas another 3 bacterial strains required 5-7 days adaptation. Among the metabolites identified by tlc were:

γ - 2,3,4,5,6-pentachloro-1-cyclohexane (γ-PCCH)

γ - 3,4,5,6-tetrachloro-1-cyclohexane (γ-TCCH)

β - 3,4,5,6-tetrachloro-1-cyclohexane (β-TCCH)

pentachlorobenzene (PCB)

1,2,4,5-tetrachlorobenzene (1,2,4,5-TCB)

1,2,3,5-tetrachlorobenzene (1,2,3,5-TCB)

Oxidation of lindane by a Pseudomonas sp. was suggested since oxygen consumption was found during lindane metabolism. This experiment also found that the Pseudomonas sp. appreciably oxidized γ-PCCH, β-TCCH, γ-TCCH, and 1,2,3,5-TCB but slowly oxidized γ-TCCH, PCB, and 1,2,4,5-TCB. It should be noted, however, that oxygen uptake during lindane metabolism does not necessarily indicate that lindane is being oxidized, but may be due entirely to the normal metabolism of nutrients other than lindane in the system.

Benezet and Matsumura (1973) showed that lindane is transformed to γ-TCCH, γ-PCCH, and the α-BHC isomer in the laboratory by a Pseudomonas culture. α-BHC was also formed in an oceanic sediment treated with lindane. Matsumura et al. (1976) also reported that of 354 bacterial and fungal isolates, 53 aerobes, and 18 anaerobes metabolized lindane. In the 1976 paper, the Matsumura group further elucidated the work reported in their 1973 paper by identifying two metabolic pathways of Pseudomnonas putida, the first gave γ-PCCH as a major product and the second, more complex, NAD dependent metabolic pathway gave γ-TCCH and γ-BHC as the products.

The degradation of lindane by Escherichia coli has been reported to give γ-PCCH (Francis et al. 1975). Lindane degradation by Clostridium

sphenoides has been reported to produce Y-TCCH (Heritage and MacRae 1977a; 1977b; MacRae et al. 1969) the latter species was reported to give greater than 90% degradation of lindane in 2 hours under anaerobic conditions (Sethunathan and Yoshida 1973).

Hill and McCarty (1967) found that 1 ppm and 10 ppm lindane in a thick anaerobic sewage sludge at 35°C was more than 95% transformed after several days and that anaerobic processes were more effective than aerobic processes; the rate of lindane loss was very sensitive to temperature variations.

Oloffs and Albright (1974) and Oloffs et al. (1973) reported that lindane incubated for 3 weeks in samples of river water and sediments was about 80% degraded. When this system was sterilized, more than 95% of the lindane was recovered after 12 weeks. Data reported for the unsterile system showed that 2% of the recovered lindane was in the water and approximately 20% was in the sediment. The sterile system had about 14% of the recovered lindane in the water and approximately 80% was in the sediment.* An earlier paper by Oloffs et al. (1972) reported that lindane incubated in three different river waters (no sediment) for 12 weeks gave no loss of lindane in two waters and only about a 20% loss in the other water. The authors state that these experiments show the importance of sediments in the fate of organochlorine chemicals in natural waters.

Newland et al. (1969) studied the sorption and biotransformation of lindane in water over lake sedment. The experiments were carried out under both aerobic and anaerobic conditions. Although biotransformation of lindane was complicated by adsorption and volatilization in these experiments, the anaerobic conditions clearly degraded lindane more rapidly than the aerobic conditions. The authors estimated that in 87 days, 15 and 90% degradation of lindane had occurred in the aerobic and anaerobic experiments, respectively. The authors also report that α-BHC was a product in both aerobic and anaerobic experiments, with δ-BHC also found in the anaerobic system.

Mathur and Saha (1975) reported that lindane was only 10% degraded after 6 weeks incubation in an anaerobic flooded sandy loam soil and that the major product was γ-3,4,5,6-tetrachlorocyclohexane (γ-BTC) in 5% yield (based on initial lindane added) along with about 1% Y-PCCH and smaller amounts of trichloro- and tetrachlorobenzenes. The authors also noted that chlorophenolic metabolites found in plant, insect, and mammal lindane metabolism studies reported by other researchers were not found in the flooded soil work. In microcosm experiments, Metcalf et al. (1973) and Sanborn (1974) did find chlorophenols, however.

*Experiments used 100 _ sediment and 150 ml water.

Beland et al. (1976) found benzene as a metabolic product of lindane in anaerobic clay loam soil and in sewage sludge; a maximum of 5% yield of γ-TCCH product was obtained (based on lindane added). The authors suggest that this is due to γ-TCCH being metabolized to benzene. In the anaerobic soil system about 50% of the lindane was transformed in approximately 8 weeks. Haider and Jagnow (1975) found up to 90% of lindane was degraded within 4 to 5 days when it was applied to an anaerobic mixed bacterial flora enriched from an arable soil. As would be expected from the results of other researchers, chloride ion was liberated from the lindane structure more rapidly than hydrogen or carbon atom fragments. No γ-PCCH was detected, and increasing the oxygen content in the gas phase decreased the rate of lindane metabolism.

Steinwandter and Schluter (1978) and Steinwandter (1976a) have reported that lindane is metabolically isomerized in grass in two parallel processes. One process gives α-BHC, which then is isomerized to β-BHC. The other process gives hexachlorobenzene (HCB) directly from lindane. In a control experiment, no HCB was formed from α-BHC under the reaction conditions.

32.4.8 Other Reactions

Siddaramappa and Sethunathan (1975) studied the transformation of lindane and β-BHC in five flooded soils and found that the BHC isomers were rapidly reduced, if the redox potentials of the fooded soils were lowered to a range of -40 to -100 mv. No discussion of biotransformation was presented.

Several papers were found that discussed electrochemical reduction of lindane as applied to anaerobic environment (Beland et al. 1976; Block et al. 1977). Beland et al. (1976) found γ-TCCH and benzene as products in both reduction processes.

34.4.9 Microcosm Studies, Field Studies, and Modelling

An excellent study of the fate of lindane in a very oligotrophic, lentic lake aquatic system has been extensively reported (Hamelink et al. 1977; Hamelink and Waybrant 1976; 1973; Waybrant 1973). In this study, equal concentrations of lindane and DDE were added in late May to a flooded limestone quarry and the pesticide concentrations in the water, sediment, and biota were subsequently monitored for a year's time. The lake was thermally stratified during the summer, was intermittently covered with ice in winter, and received a large influx of sediment because of a rainstorm that occurred one day after the pesticides were introduced into the system. Some significant points of lindane fate (in some cases relative to DDE) are listed on the following page.

1. Most of the lindane in the system was retained in the epilimnion until the fall turnover, 123-144 days after application.

2. Lindane decreased 32% in 102 days and 50% in 123 days (the percentage was averaged over entire water column). On day 81, 70% of the lindane accounted for was in the epilmnion, with 15% each in the metalimnion and hypolimnion. The lindane in the latter region was assumed to have been transporred by the sediment-runoff since tne concentration was the same from day 5 until the turnover.

3. After the fall turnover, lindane was fairly homogeneously distributed throughout the water column.

4. Suspended sediment, collected in traps, contained essentially no lindane compared to a high DDE concentration, indicating that sorption to suspended sediment and sedimentation was not a significant process.

5. Lindane in the bottom mud attained a maximum concentration of about 2 ppb compared to the maximum for DDE of 35 ppb. Additionally, the DDE was contained in the top few centimeters of mud, whereas lindane rapidly diffused to the lower mud layers presumably because of lindane's solubility in the interstitial water in mud.

6. Pesticide concentrations in zooplankton were at a maximum at 5 days and decreased thereafter as the pesticide concentration in water declined. Concentration factors for lindane in zooplankton ranged from 170-488. The lindane in fish (bluegill) reached equilibrium with the water in 5 days and showed concentration factors from $(1.47\text{-}0.42) \times 10^3$.

32.5 Data Summary

Table 32-1 summarizes the data on the aquatic fate of lindane.

Table 32-1

Summary of Aquatic Fate of γ - Hexachlorocyclohexane (Lindane)

Environmental Process [a]	Summary Statement	Rate	Half-Life $t_{\frac{1}{2}}$	Confidence of Data
Photolysis	Probably not an important process.	-	-	Medium
Oxidation	Probably not an important process.	-	-	Medium
Hydrolysis	Probably not an important process.	-	-	Medium
Volatilization	Probably not an important process.	-	> 200 days	Medium
Sorption	Important for transport to anaerobic sediments.	-	-	Low
Bioaccumulation	Not a significant process.	-	-	Low
Biotransformation/ Biodegradation	The most important process, and the most rapid in anaerobic environments.	-	-	Low

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

32.6 Literature Cited

Beland, F. A., S. O. Farwell, A. E. Robocker, and R. D. Geer. 1976. Electrochemical reduction and anaerobic degradation of lindane. J. Agri. Food Chem. 24(4):753-756.

Benchmark, 1975. Draft of Preliminary Summaries of Literature Surveys of Benchmark Pesticides. George Washington University Medical Center. Draft dated October 30, 1975.

Benezet, H. I. and F. Matsumura. 1973. Isomerization of γ-BHC to a α-BHC in the environment. Nature 243:480-481.

Bhavnagary, H. M., and M. Jayaram. 1974. Determination of water solubilities of lindane and dieldrin at different temperatures. Bull. Grain Technol. 12(2):95-99.

Biggar, W. J., and R. L. Riggs. 1974. Apparent solubility of organochlorine insecticides in water at various temperatures. Hilgardia 42(10):383-391.

Block, A.M., W. R. Bhajan, J. Estevez, and L. W. Newland. 1977. The electrochemical reduction model of anaerobic degradation of the gamma isomer of 1,2,3,4,5,6-hexachlorocyclohexane (γ-BHC). J. Water Pollut. Control Fed. 49(5):857-859.

Boucher, F. R., and G. F. Lee. 1972. Adsorption of lindane and dieldrin pesticides on unconsolidated aquifer sands. Environ. Sci. Tech. 6(6):539-543.

Cristol, S. J. 1947. The kinetics of the alkaline dehydrochlorination of benzene hexachloride isomers. The mechanism of second-order elimination reactions. J. Amer. Chem. Soc. 69:338-342.

Demozay, D., and G. Marechal. 1972. Physical and chemical properties in lindane: Monograph of an insecticide, E. Ulmann, pp. 15-21, K. Schiller, Freiburg im Breisgau.

Eichelberger, J. W. and J. J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5(6):541-544.

Ernst, W. 1977. Determination of the bioconcentration potential of marine organisms. - a steady state approach. Chemosphere 6(11):731-740.

Francis, A. J., R. J. Spanggord, and G. I. Ouchi. 1975. Degradation of lindane by Escherichia coli. Appl. Microbiol. 29(4):567-568.

Gakstatter, J. H., and C. M. Weiss. 1967. The elimination of DDT-^{14}C, dieldrin-^{14}C, and lindane-^{14}C from fish following a single sublethal exposure in aquaria. Trans. Amer. Fish. Soc. 96(3):301-307.

Ginsburg, J. M. 1953. Rate of decomposition of the newer insecticides when exposed to direct sunlight. Proc. New Jersey Mosquito Exterm. Assoc. 40:163-168.

Grimes, D. J., and S. M. Morrison. 1975. Bacterial bioconcentration of hydrocarbon insecticides from aqueous systems. Microb. Ecol. 2(1):43-59.

Gunther, F. A. 1971. Halogen derivatives of aliphatic hydrocarbons. Residue Rev. 36:34-77.

Haider, K., and G. Jagnow. 1975. Degradation of carbon-14-,tritium-, and chlorine-36-labeled of-hexachlorocyclohecane by anaerobic soil microorganisms. Arch. Microbiol. 104(2):113-121.

Hamelink, J. L., and R. C. Waybrant. 1973. Factors controlling the dynamics of non-ionic synthetic organic chemicals in aquatic environments. Tech. Rep.-Purdue Univ. Water Resour. Res. Cent. 44, 68 pp.

Hamelink, J. L., and R. C. Waybrant. 1976. DDE and lindane in a large-scale model lentic ecosystem. Trans. Am. Fish. Soc. 105(1):124-134.

Hamelink, J. L., R. C. Waybrant, and P. R. Yant. 1977. Mechanisms of bioaccumulation of mercury and chlorinated hydrocarbon pesticides by fish in lentic ecosystems. Pages 261-268 in I. M. Suffet, Fate of pollutants in the air and water environment. Part II. John Wiley and Sons, New York, N.Y.

Harper, L. A., A. W. White, Jr., R. R. Bruce, A. W. Thomas, and R. A. Leonard. 1976. Soil and microclimate effects on trifluralin volatilization. J. Environ. Qual. 5(3):236-242.

Heritage, A. D., and I. C. MacRae. 1977 (a) Identification of intermediates formed during the degradation of hexachlorocyclohexanes by Clostridium sphenoides. Appl. Environ. Microbiol. 33(6):1295-1297.

Heritage, A. D., and I. C. MacRae. 1977 (b) Degradation of lindane by cell-free preparations of Clostridium sphenoides. Appl. Environ. Microbiol. 34(2):222-224.

Hill, D. W., and P. L. McCarty. 1967. Anaerobic degradation of selected chlorinated hydrocarbon pesticides. J. Water Pollut. Control Fed. 39(8):1259-1277.

Hoffmann, J., and D. Eichelsdoerfer. 1971. Effect of ozone on chlorinated-hydrocarbon-group pesticides in water. Vom Wasser 38:197-206.

King, P. H., H. H. Yeh, P. S. Warren, and C. W. Randall. 1969. Distribution of pesticides in surface waters. J. Amer. Water Works Assoc. 61(9):483-486.

Kurihara, N., M. Uchida, T. Fujita, and M. Nakajima. 1973. Studies on BHC isomers and related compounds. V. Some physicochemical properties of BHC isomers. Pestic. Biochem. Physiol. 2(4):383-390.

Leigh, G. M. 1969. Degradation of selected chlorinated hydrocarbon insecticides. J. Water Pollut. Control Fed. 41(11)(Pt. 2):R450-R460.

Mackay, D., and P. J. Leinonen. 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Tech. 9(13):1178-1180.

MacRae, I. C., K. Raghu, and E. M. Bautista. 1969. Anaerobic degradation of the insecticide lindane by Clostridium sp. Nature 221:859-860.

Martin, H., ed. 1972. Pesticide Manual, 3rd Ed. British Crop Protection Council, Worcester, Engl.

Masterton, W. L., and T. P. Lee. 1972. Effect of dissolved salts on water solubility of lindane. Environ. Sci. Technol. 6(10):919-921.

Mathur, S. P., and J. G. Saha. 1975. Microbial degradation of carbon-14-labeled lindane in a flooded sandy loam soil. Soil Sci. 120(4):301-307.

Matsumura, F., H. J. Benezet, and K. C. Patil. 1976. Factors affecting microbial metabolism of γ-BHC. Nippon Noyaku Gakkaishi 1(1):3-8.

Metcalf, R. L., I. P. Kapoor, P.-Y. Lu, C. K. Schuth, and P. Sherman. 1973. Model ecosystem studies of the environmental fate of six organo-chlorine pesticides. Environ. Health Perspect. 4:35-44.

Newland, L. W., G. Chesters, and G. B. Lee. 1969. Degradation of γ-BHC in simulated lake impoundments as affected by aeration. J. Water Pollut. Control Fed. 41(5 Pt.II):R174-R188.

Oloffs, P. C., L. J. Albright, and S. Y. Szeto. 1972. Fate and behavior of five chlorinated hydrocarbons in three natural waters. Can. J. Microbiol. 18(9):1393-1398.

Oloffs, P. C., L. J. Albright, S. Y. Szeto, and J. Iau. 1973. Factors affecting the behavior of five chlorinated hydrocarbons in two natural waters and their sediments. J. Fish. Res. Board of Can. 30(11):1619-1623.

Oloffs, P.C., and L.J. Albright. 1974. Transport of some organochlorines in B. C. waters. Proc. Int. Conf. Transp. Persistent Chem. Aquat. Ecosyst., I:89-92.

Roburn, J. 1963. Effect of sunlight and ultraviolet radiation on chlorinated pesticide residues. Chem. Ind. (1963):1555-1556.

Sanborn, J. R. 1974. The fate of select pesticides in the aquatic environment. U. S. Environ. Prot. Agency, Off. Res. Dev., [Rep.] EPA, EPA-660/3-74-025, 83 pp.

Sethunathan, N. and T. Yoshida. 1973. Short communication: Degradation of chlorinated hydrocarbons by Clostridium sp. isolated from lindane-amended flooded soil. Plant Soil 38(3):663-666.

Siddaramappa, R., and N. Sethunanthan. 1975. Persistence of gamma-BHC and beta-BHC in Indian rice soils under flooded conditions. Pestic. Sci. 6(4):395-403.

Slade, R. E. 1945. The γ-isomer of hexachlorocyclohexane (Gammexane). An insecticide with outstanding properties. Chem. Ind. 40:314-319.

Spacie, A., J. Hamelink, and R. Waybrant. 1977. Application of an evaporative loss model to estimate the persistence of contaminants in lentic environments. Fate of Pollutants in the Air and Water Environment, ASTM, STP 634. Part 2:214-227.

Spencer, W. F. 1975. Movement of DDT and its derivatives into the atmosphere. Residue Rev. 59:91-117.

Spencer, W. F., and M. M. Cliath. 1973. Pesticide volatilization as related to water loss from soil. J. Environ. Qual. 2(2):284-289.

Steinwandter, H. 1976(a). Zum lindanmetabolismus an pflanzen. Chemosphere 5(2):119-125.

Steinwandter, H. 1976(b). Beitrage zur umwandlung der HCH-isomere durch einwirkung von uv-strahlen. I. Isomerisierung des lindans in α-HCH. Chemosphere 5(4):245-248.

Steinwandter, H., and H. Schluter. 1978. Experiments on lindane metabolism in plants. IV. A kinetic investigation. Bull. Environ. Contam. Toxicol. 20:174-179.

Tu, C. M. 1976. Utilization and degradation of lindane by soil microorganisms. Arch. Microbiol. 108(3):259-263.

Waybrant, R. C. 1973. Factors controlling the distribution and persistence of lindane and DDE in lentic environments. Ph.D Thesis, Purdue University, 190 pp. University Microfilms, Ann Arbor, Mich. Order No. 74-15, 256. (Diss. Abstr. Int. B 1974, 35(1):367-368).

Weil, L., G. Dure, and K. E. Quentin. 1973. Adsorption of chlorinated hydrocarbons to organic particles and soils. Z. Wasser Abwasser Forsch. 6(4):107-112.

Weil, L., G. Dure, and K. E. Quentin. 1974. Solubility in water of insecticide chlorinated hydrocarbons and polychlorinated biphenyls in view of water pollution. Z. Wasser Abwasser Forsch. 7(6):169-175.

Zabik, M., and R. Leavitt. 1976. Photochemistry of bioactive compounds, a review of pesticide photochemistry. Annu. Rev. Entomol. 21:61-79.

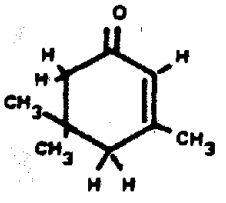
33. ISOPHORONE

33.1 Statement of Probable Fate

No quantitative information is available to assess the environmental fate of isophorone. The moderate water solubility of isophorone indicates that it should remain in the water column until transformation reaction(s) occur. Biological and photochemical reactions could be important in removing isophorone from aquatic systems.

33.2 Identification

The structure, alternate names, and CAS and TSL numbers for isophorone are as follows:



Isophorone

CAS No. 78591
TSL No. GW 77000

Alternate Names

Isooctaphenone
3,5,5-Trimethyl-2-cyclohexene-1-one
Isoacetophorone
Isoforone
Isophoron

33.3 Physical Properties

The general physical properties of isophorone are as follows:

Melting point (Verschueren 1977)	-8°C
Boiling point at 760 torr (Verschueren 1977)	215°C
Vapor pressure at 20°C (Verschueren 1977)	0.38 torr

Solubility in water at unspecified temperature (Verschueren 1977)	12000 ppm
Log octanol/water partition coefficient (Johnson 1978)	1.7

33.4 Summary of Fate Data

33.4.1 Photolysis

Isophorone has a moderate ultraviolet absorption out to approximately 350 nm, with a λ_{max} at 312 nm (ε = 45 M^{-1} cm^{-1}) in the solar spectral region (uv Atlas). However, no information is available to quantitatively assess the photolysis rate of isophorone in the environment.

Several papers indicate that isophorone is photochemically reactive. Jennings (1965) reported that photolysis of isophorone in water at wavelengths > 200 nm gave dimerization products; Chapman et al. (1967) also found dimerization products when isophorone was irradiated at > 300 nm in organic solvents. Such dimerization products are unlikely in the aquatic environment under the highly dilute environmental conditions. Mettee (1967) reported that photolysis of isophorone at > 300 nm in air-saturated, carbon tetrachloride solution resulted in loss of isophorone; phosgene ($COCl_2$) was the only product reported and is probably due to oxidation of CCl_4 involving a trichloromethyl radical intermediate. The above information indicates that loss of isophorone could occur via interactions of an isophorone photo-excited state with naturally occurring organic substances in aquatic systems.

33.4.2 Oxidation

No information is available for assessment of the oxidation of isophorone in aquatic environments. The hydrogens on the allylic carbons of isophorone are the most susceptible to free radical abstraction; oxidation may also occur at the unsaturated bond position. Lack of reliable data on radical concentrations of oxidants present in natural waters prevent any oxidation half-life estimates.

33.4.3 Hydrolysis

Isophorone has no hydrolyzable functional groups that would undergo transformation in aquatic environments.

33.4.4 Volatilization

The high water solubility and moderate vapor pressure of isophorone indicate that volatilization from water is not a significant transport process for isophorone.

33.4.5 Sorption

No information is available on sorption of isophorone to biota or sediments. The high water solubility and moderate partition coefficient of isophorone indicate that sorption is not an important process, and that isophorone will probably remain in solution in aquatic systems.

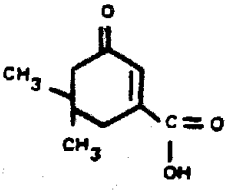
33.4.6 Bioaccumulation

For the reasons cited in Section 33.4.5, bioaccumulation is not likely to be an important process for isophorone.

33.4.7 Biotransformation and Biodegradation

No information was found on biotransformation of isophorone in aquatic systems. Truhaut et al. (1970) reported that the allylic methyl group of isophorone was oxidized to a carboxylic acid group when industrial isophorone was administered orally to rabbits; the product (see I, below)

I.



was detected in urine, and no other products were identified nor were mass balances obtained. This metabolism of isophorone indicates that biological oxidation of isophorone may occur in aerobic environments, but no information was found to substantiate this possibility.

33.4.8 Other Reactions

No processes other than those listed above are important in determining the fate of isophorone in aquatic systems.

33.5 Data Summary

Table 33-1 summarizes the data on the aquatic fate of isophorone.

Table 33-1

Summary of Aquatic Fate of Isophorone

Environmental Process[a]	Summary Statement	Rate	Half-Life $t_{\frac{1}{2}}$	Confidence of Data
Photolysis	Possibly important.	-	-	Low
Oxidation	No information available.	-	-	-
Hydrolysis	Does not occur.	-	-	High
Volatilization	Not important process.	-	-	Medium
Sorption	Not important process.	-	-	Medium
Bioaccumulation	Not important process.	-	-	Medium
Biotransformation/ Biodegradation	No information available.	-	-	-

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

33.6 Literature Cited

Chapman, O.L., P.J. Nelson, R.W. King, D.J. Trecker, and A.A. Griswold. 1967. The mechanism of isophorone photodimerization. Rec. Chem. Progr. 28(3):167-178.

Jennings, P. 1965. Photochemistry of isophorone. Ph.D. Thesis. University of Utah. 94pp. University Microfilms, Ann Arbor, Mich., Order No. 65-4898. (Diss. Abstr. Int. B 1965, 26(2):698).

Johnson, H. 1978. Calculation of the estimated partition coefficient for isophorone. Chemist, Biorganic Chemistry Lab. SRI-International.

Mettee, H. D. 1967. Photochemical studies of α,β-unsaturated ketones in carbon tetrachloride solution. Can. J. Chem. 45(4):339-343.

Truhaut, R., H. Dutertre-Catella, and N.-P. Lich. 1970. Metabolic study of an industrial solvent, isophorone, in the rabbit. C.R. Acad. Sci., Ser. D 271(15):1333-1336.

Verschueren, K. 1977. Handbook of environmental data on organic chemicals. Van Nostrand Reinhold Company. 659pp.

34. TCDD

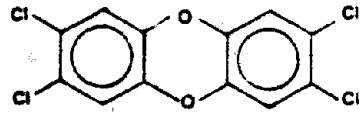
34.1 Statement of Probable Fate

A conclusion as to the fate of TCDD in aquatic systems cannot be provided at this time because of incomplete information. Photolysis of TCDD in sunlight may occur in less than a day if reactive organic substrates are available, but no information is available on the reactions of TCDD with possible substrates in natural waters; other chemical transformation processes do not appear to be important for TCDD. Sorption to sediments and biota and possibly bioaccumulation appear to be important fates for TCDD, with biotransformations having half-lives of more than 1 year in lake water and sediments.

34.2 Identification

TCDD is formed as a by-product under the conditions of synthesis of polychlorinated phenols and products formed from them. Kearney et al. (1973) noted that the amount of TCDD in the herbicide 2,4,5-T varies with each batch and with each manufacturer. Several investigations of the possible formation of TCDD from photolysis or biodegradation of polychlorinated phenols suggest that the latter are not converted to TCDD under environmental conditions (Plimmer and Klingbiel 1971; Kearney et al. 1972; Helling et al. 1973; Crosby et al. 1973). Both Plimmer and Klingbiel (1971) and Crosby et al. (1973) have pointed out, however, that in organic media, TCDD formed during photolysis of the polychlorinated phenols may actually be rapidly photolyzed and therefore not detected. Recent literature has also cited combustion of fuels and wastes as sources of TCDD; while this literature does suggest that combustion may produce polychlorinated dibenzodioxins (PCDDs), the TCDD isomers are usually found in very small porportions of the total PCDD. A thorough material balance on the sources of PCDDs and TCDDs is clearly needed to determine the important sources of these pollutants.

The structure, alternate names and CAS and TSL number for TCDD are as follows:



TCDD

CAS No. 1746-01-6
TSL No. HP 35000

Alternate Names

2,3,7,8-Tetrachloro-
dibenzo-p-dioxin

34.3 Physical Properties

The physical properties of TCDD are as follows.

Molecular weight	322
Melting point (Crummett and Stehl 1973)	303-305° C
Boiling point	No data found
Vapor pressure	No data found
Solubility in water* (Crummett and Stehl 1973)	0.2 ppb
Log octanol/water partition coefficient	No data found

*No temperature given, presumably about 20-25°C.

34.4 Summary of Fate Data

34.4.1 Photolysis

TCDD has a uv absorption maximum at 307 nm, however, no absorption coefficients were reported (Crosby and Wong 1977). Although photochemical transformations of TCDD have been studied in several laboratories, no quantitative information is available to estimate a sunlight photolysis half-life for TCDD in aquatic systems. TCDD in a pure state is photochemically stable, but it will photolyze in sunlight with half-lives of less than a few hours if dissolved in an organic film or solution while in the presence of a hydrogen atom donating substrate (Crosby and Wong 1977). Although these conditions may be met in some environmental situations, insufficient information is available on such interactions in aquatic systems for use in predicting a reliable TCDD photolysis half-life for an environmental assessment.

Plimmer et al. (1973) reported that a TCDD suspension in distilled water was unchanged when irradiated with a sunlamp, however, when TCDD in benzene was added to the water and the solution was stabilized by the surfactant, Tween-80, irradiation with the sunlamp then resulted in loss of TCDD. A similar pattern of reactivity was reported in other studies. For example, a thin dry film of TCDD on a glass plate was quantitatively recovered after exposure to sunlight for 14 days (Crosby et al. 1971). TCDD on dry and wet soils showed negligible loss after irradiation by sunlamps for 96 hours (Crosby et al. 1971). In contrast, TCDD in methanol solution

has a half-life of about three hours in sunlight (Plimmer et al. 1973). Thin films of TCDD on glass plates in Esteron (a commercial brushkiller) and in the herbicide Agent Orange showed 50% transformations at about 4 and 5.5 hours, respectively (Crosby and Wong 1977). Botré et al. (1978) described a method for detoxification of TCDD by solubilization with surfactants and subsequent photolysis by uv light (254-356 nm); Gebefugi et al. (1977) reported that TCDD on silica gel exposed to a Pyrex-filtered mercury lamp (> 290 nm) was 92% decomposed in seven days. Liberti et al. (1978) have reported on the photochemical transformations of TCDD, and again demonstrated the requirement for hydrogen-atom donors in the photolysis of TCDD. These papers do not provide any information relevant to aquatic systems useful in an environmental assessment.

34.4.2 Oxidation

No information has been obtained on the oxidation of TCDD. The electropositive nature of the molecule as calculated by Miller et al. (1977) suggests that TCDD will be more resistant to oxidation than non-chlorinated or less chlorinated aromatic compounds.

34.4.3 Hydrolysis

No information has been obtained on the hydrolysis of TCDD. Hydrolysis of TCDD is not likely under environmental conditions, because the halogen and ether groups on the aromatic ring are not susceptible to hydrolysis except under extreme conditions.

34.4.4 Volatilization

No quantitative information is available on the volatilization of TCDD from aquatic environments. Several papers mention volatilization as a possible loss process, but no studies have been reported on the volatilization process itself.

Ward and Matsumura (1977) reported a study designed to evaluate the microbial degradation of TCDD. In an aerobic degradation study using eutrophic lake sediments and water, they found that the recovery of TCDD was directly related to water loss, with gas evolution from the system (consisting of flasks with cotton plugs) presumably responsible for volatilization of water and TCDD. No useful data were reported for estimating volatilization from aquatic environments.

In studies of the photolysis of solid TCDD on glass plates and leaves, Crosby et al. (1971) concluded that volatilization is not an important loss process. As pointed out in the paper of Mackay and Wolkoff 1973), however, the extreme insolubility of some organics in water may enhance the volatility of such chemicals from water bodies.

34.4.5 Sorption

Data from microcosm experiments indicate that TCDD is highly sorbed to sediments and biota. Isensee and Jones (1975) examined the fate of TCDD introduced into an aquatic microcosm on soil and found 85-99% of the TCDD still remaining in the soil after about 30 days; most of the TCDD not in soil was found in the aquatic organisms. The two experiments in which TCDD could be detected in the water required 4 and 15 days for equilibration among soil, water, and organisms, and the concentration in the organisms was always greater by three orders of magnitude than that in the water. Ward and Matsumura (1977) also found that TCDD remained bound to sediments, with usually more than 90% of the radiolabelled TCDD found in the sediment. These authors further argued that most of the TCDD in solution was bound to organic matter and particulates. Matsumura and Benezet (1973) also reported that TCDD was sorbed and bioconcentrated by aquatic organisms (See Section 34.4.7).

34.4.6 Bioaccumulation

Isensee and Jones (1975) reported that concentrations of TCDD in organisms in microcosms, in which TCDD was added in the form of contaminated sediments, were within an order of magnitude of the concentrations in the sediments, although concentrations in the organisms were 4-26,000 times greater than the concentrations in the water. Concentrations (dry weight basis) in snails, mosquito fish, and daphnids were (2-2.6) x 10^4 times the concentration in water. Concentrations in duckweed, algae, and catfish were (4-9) x 10^3 times the concentrations in water. Isensee and Jones (1975) noted that some aquatic species in their microcosm accumulated TCDD to levels which were 100 to 1000 the LD_{50} of mammals and reported that bioaccumulation occured in the presence of sediments containing 0.1 ppb TCDD. Isensee (1978) confirmed conclusions previously reported based on microcosm studies (Isensee and Jones 1975); more recent data from larger, modified microcosms gave bioconcentration factors of 2 to 7000 in the aquatic organisms used in previous studies.

Matsumura and Benezet (1973), using shorter exposure times, found that concentrations (wet weight basis) in brine shrimp and fish (silversides) were 1600 and 54 times, respectively, greater than the concentration in water. Mosquito larvae had concentrations of TCDD that were 2800-9200 times greater than the concentrations in water in various treatments.

Young et al. (1976) examined a number of organisms subjected to long exposure to soils heavily contaminated with TCDD at a large terrestrial test site (used for testing application of herbicides). The authors stated that TCDD may accumulate in the tissues of rodents, reptiles, birds,

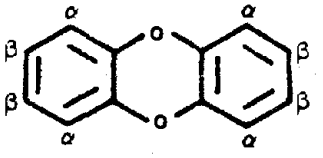
fish, and insects, but that levels of TCDD in the tissues did not exceed the levels found in the environment. The soil (environmental) levels were 10 to 1,500 pptr.

34.4.7 Biotransformation and Biodegradation

Matsumura and Benezet (1973) reported that 5 of 100 microbial strains known to degrade chlorinated pesticides gave transformation of TCDD, but no experimental details or discussion were provided. Ward and Matsumura (1977) reported that in laboratory experiments as much as 6% of the TCDD added to anaerobic sediment-water samples from a eutrophic lake was metabolized and that most of the radioactive label remaining in the aqueous phase after the first day was in the form of metabolites; however, they did not identify the metabolites. No metabolites were observed in aerobic cultures and the major portion of the TCDD was in the sediments. These authors also report that the half-life of TCDD in lake sediment was approximately 550-590 days, and that in lake water alone about 70% of the TCDD remained after 589 days. Isensee and Jones (1975) failed to find evidence of biotransformation of TCDD in aerobic microcosms, despite the use of a wide range of TCDD concentrations with appropriate replication. Young et al. (1976) infer that TCDD may be degraded by soil microorganisms on the basis of the disappearance of TCDD from heavily contaminated soils; no degradation products were mentioned.

34.4.8 Other Reactions

Miller et al. (1977) evaluated the electron acceptor properties of chlorinated dibenzo-p-dioxins using molecular orbital calculation techniques. The calculations indicate that the more extensive the chlorination at the 3 positions (see I, below) the stronger the charge transfer complex, with TCDD being the most susceptible to such complexes. They suggest that strong charge transfer complexation of TCDD may account for a number of environmental fates and effects of TCDD, including binding to soils, mutagenicity, and slow metabolic decomposition. The authors point out that experimental verification is needed regarding the charge transfer complexation of TCDD.

I. 

34.4.9 Microcosm Studies, Field Studies, and Modelling

Microcosm tests, particularly the extensive experiments of Isensee and Jones (1975), demonstrate a marked tendency for TCDD to accumulate in the sediments (85-99% of the TCDD in the microcosm was found in the sediments). They also found that concentrations in organisms were generally within an order of magnitude of the concentrations in the sediments. Similar results were noted by Ward and Matsumura (1977) and Matsumura and Benezet (1973). Ward and Matsumura reported biotransformation of the fraction that remained in the aqueous phase, but Isensee and Jones, in a careful analysis of their own experiments, failed to find any evidence of biotransformation.

34.5 Data Summary

Table 34-1 summarizes the data on the aquatic fate of TCDD.

Table 34-1

Summary of Aquatic Fate of TCDD

Environmental Process[a]	Summary Statement	Rate	Half-Life $t_{\frac{1}{2}}$	Confidence of Data
Photolysis	Will be an important process if reactive substrates are available.	-	-	Low
Oxidation	Not an important process.	-	-	High
Hydrolysis	Does not occur.	-	-	High
Volatilization	Probably not an important process.	-	-	Medium
Sorption	Important process.	-	-	Medium
Bioaccumulation	Probably an important process.	-	-	Medium
Biotransformation/ Biodegradation	Could be an important process over long time periods.	-	> 1 year	Low

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

34.6 Literature Cited

Botré C., A. Memoli, and F. Alhaique. 1978. TCDD solubilization and photodecomposition in aqueous solutions. Environ. Sci. Technol. 12(3):335-336.

Crosby, D.G., K.W. Moilanen, and S.S. Wong. 1973. Environmental generation and degradation of dibenzodioxins and dibenzofurans. Environ. Health Perspect. 5:259-266.

Crosby, D.G., and A.S. Wong. 1977. Environmental degradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Science 195(4284):1337-1338.

Crosby, D.G., A.S. Wong, J.R. Plimmer, and E.A. Woolson. 1971. Photodecomposition of chlorinated dibenzo-p-dioxins. Science 173(3998):748-749.

Crummett, W.B., and R.H. Steni. 1973. Determination of chlorinated dibenzo-p-dioxins and dibenzofurans in various materials. Environ. Health Perspect. 5:15-25.

Gebefugi, I., R. Bamann, and F. Korte. 1977. Photochemischer abbau von 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) unter simulierten umweltbedingungen. Naturwissenschaften 64(9):486.

Helling, C.S., A.R. Isensee, E.A. Woolson, P.D.J. Ensor, G.E. Jones, J.R. Plimmer, and P.C. Kearney. 1973. Chlorodioxins in pesticides, soils, and plants. J. Environ. Quality 2(2):171-178.

Isensee, A.R. 1978. Bioaccumulation of 2,3,7,8-tetrachlorodibenzo-para-dioxin. Conference on chlorinated phenoxy acids and their dioxins. C. Ramel, ed. Ecol. Bull. (Stokholm) (27):250-262.

Isensee, A.R., and G.E. Jones. 1975. Distribution of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in aquatic model ecosystem. Environ. Sci. Technol. 9(7):668-672.

Kearney, P.C., A.R. Isensee, C.S. Helling, E.A. Woolson, and J.R. Plimmer. 1973. Environmental significance of chlorodioxins. Adv. Chem. Ser. 120:105-111.

Kearney, P.C., E.A. Woolson, and C.P. Ellington, Jr. 1972. Persistence and metabolism of chlorodioxins in soils. Environ. Sci. Technol. 6(12):1017-1019.

Liberti, A., D. Brocco, I. Allegrini, A. Cecinato, and M. Possanzini. 1978. Solar and UV photo decomposition of 2,3,7,8-tetrachlorodibenzo-para-dioxin in the environment. Science of the Total Environ. (10):97-104.

Mackay, D., and A.W. Wolkoff. 1973. Rate of evaporation of low solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 7(7):611-614.

Matsumura, F., and H.J. Benezet. 1973. Studies on the bioaccumulation and microbial degradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin. Environ. Health Perspect. 5:253-258.

Miller, G., S. Sontum, and D.G. Crosby. 1977. Electron-acceptor properties of chlorinated dibenzo-p-dioxins. Bull. Environ. Contam. Toxicol. 18(5):611-616.

Plimmer, J.R., and U.I. Klingbiel. 1971. Riboflavin photosensitized oxidation of 2,4-dichlorophenol: Assessment of possible chlorinated dioxin formation. Science 174:407-408.

Plimmer, J.R., U.I. Klingbiel, D.G. Crosby, and A.S. Wong. 1973. Photochemistry of dibenzo-p-dioxins. Adv. Chem. Ser. 120:44-54.

Ward, C., and F. Matsumura. 1977. Fate of 2,4,5-T contaminant, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in aquatic environments. U.S. NTIS, PB Rep., PB-264187, 22 pp.

Young, A.L., C.E. Thalken, E.L. Arnold, J.M. Cupello, and L.G. Cockerham. 1976. Fate of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in the environment: summary and decontamination recommendations. Summary report, department of Chemistry and Biological Sciences, United States Air Force Academy, Colorado. U.S. NTIS, Rep. AD-A033 491, 41 pp.

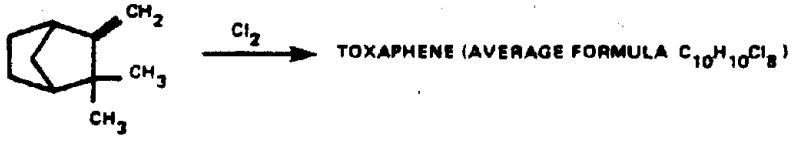
35. TOXAPHENE

35.1 Statement of Probable Fate

An inclusive assessment of the fate of the pesticide toxaphene in aquatic environments is complicated because toxaphene is a complex mixture of polychlorinated camphene derivatives of different physical properties and environmental behavior. Toxaphene is very stable to biological and chemical processes in aerobic environmental systems, but it does undergo partial reduction (loss of chloride content) in anaerobic environments. A dominant process in aquatic environments is direct sorption on sediments or sorption onto particulates followed by deposition into sediment where biological and possibly chemical reduction occurs. The rate of loss of toxaphene from aquatic systems will then be partially determined by particulate loading and quality of the water body; shallow, particulate-laden, eutrophic waters give maximum transformation rates of toxaphene, with half-lives on the order of a few months for some components. The physical properties and chlorinated functionality of the individual toxaphene structures will govern which components will be sorbed and then subsequently reduced. The finding of some toxaphene components in aquatic sediments and species after several years indicates that bioaccumulation in the food chain may occur. Unless clear evidence proves otherwise, the absence of acute toxicity effects of toxaphene should not be interpreted as indicating that all toxaphene has been degraded and chronic toxic effects are absent.

35.2 Identification

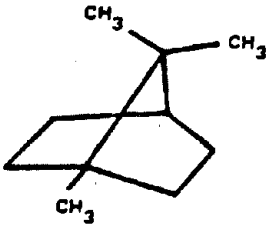
This chapter considers toxaphene as the chlorinated camphene mixture containing 67-69% chlorine; Holmstead et al. (1974) showed that at least 177 compounds are present in toxaphene. Saleh and Casida (1977) reported that about 85% of the glpc peak area (electron capture detector) is accounted for by 29 major peaks that individually vary from 1 to 8% of the total area.



CAMPHENE

Holmstead et al. (1974) showed that at least 177 compounds are present in the toxaphene mixture; about two thirds of these compounds are of $C_{10}H_{11}Cl_7$, $C_{10}H_{10}Cl_8$, and $C_{10}H_9Cl_9$ formulae. The remaining chemicals are

the $C_{10}H_{10}Cl_6$, $C_{10}H_{12}Cl_6$, $C_{10}H_9Cl_7$, $C_{10}H_7Cl_9$, $C_{10}H_8Cl_{10}$, and $C_{10}H_7Cl_{11}$ chlorinated derivatives of camphene. Since both ionic and free radical reactions probably occur during the chlorination of camphene, such a complex reaction mixture is reasonable. Many studies on the identification of various components of toxaphene and their associated toxicities have been reported (Chandurkar et al. 1978; Turner et al. 1977; Saleh et al. 1977; Palmer et al. 1975; Turner et al. 1975; Khalifa et al. 1974). Most compounds identified thus far are of the polychlorinated bornane structure; Saleh et al. (1977) stated that the octachlorobornane toxaphene components A-1 and A-2 (see below) are major contributors to the acute toxicity of toxaphene.



BORNANE

Although it would be preferable to focus on the toxic chemicals of the mixture, lack of environmental information on these components makes such an approach futile. Focus on components may also disregard environmental studies that have been conducted using the toxaphene mixture; this chapter identifies components using terms as described in literature (i.e., "higher molecular weight fraction," "less soluble," "higher chlorinated compounds," etc.).

Important Note: As a mixture of variously chlorinated structures, all toxaphene components do not have similar properties that provide parallel or even similar fates (and toxicity). Most data on sorption, solubility, bioaccumulation, and biotransformation were reported as total toxaphene because of the analytical difficulty of separating the individual components. However, most authors also report that marked qualitative differences occur in the glpc profiles of "toxaphene" after sorption, biotransformation, reduction, or bioaccumulation. Thus, the total concentration of toxaphene should be difficult to correlate in an assessment or prediction of a specific environmental or ecological effect when the effect is possibly due to the activity of a small component of the total toxaphene measured. Accordingly, the argument that a rapid "detoxification" of toxaphene minimizes pollution hazards may be a fallacy, since the absence of an acute toxicity effect does not necessarily correlate with the absence of chronic toxic effect.

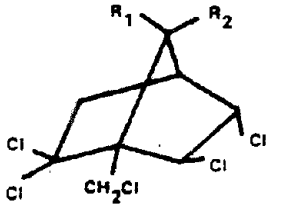
Alternate names and CAS and TSL numbers for toxaphene are given below.

(No structure is unique for toxaphene; structures for a few toxaphene components are given below.)

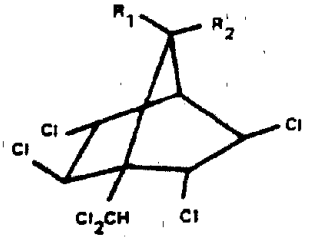
CAS No. 8001-35-2
TSL No. XW 52500

Alternate Names

Toxaphene
Camphechlor
Hercules 3956
Alltex
Toxakil



R_1	R_2	Name*	References
CH_2Cl	$CHCl_2$	A-1	Turner et al. 1975
$CHCl_2$	CH_2Cl	A-2	Turner et al. 1975
$CHCl_2$	CH_2Cl	B	Khalifa et al. 1974



CH_2Cl	$CHCl_2$	Ac	Chandurkar et al. 1978

*The names below are as presented in the respective literature citations.

35.3 Physical Properties

The general physical properties of the toxaphene mixture are:

Molecular weight	343 for $C_{10}H_{10}Cl_6$ 517 for $C_{10}H_7Cl_{11}$
Melting point (Brooks 1974)	range 70-95°C
Boiling point (Brooks 1974)	decomp. > 120°
Vapor pressure at 25°C (Brooks 1974)	0.2 torr to 0.4 torr
Solubility in water at 25°C	
(Brooks 1974)	about 3 ppm
(Weil et al. 1974) at 25°C	0.740 ppm
(Paris et at. 1977)	0.500 ppm
Log octanol/water partition coefficient (Paris et al. 1977)	3.3±0.4

35.4 Summary of Fate Data

35.4.1 Photolysis

Wolfe et al. (1976) reported photolysis studies on several pesticides and found that the glpc profile of toxaphene was unchanged on exposure to uv light filtered through borosilicte glass (> 290 nm). They also reported that the relative photoreactivities of toxaphene, malathion, and 2,4-D-BEE (2,4 dichlorophenoxyacetic acid, butoxyethyl ester) were < 1, 1, and 300, respectively. The sunlight photolysis half-life of 2,4-D-BEE was determined to be 12-14 days. Assuming that the relative reactivity of 2,4-D-BEE and toxaphene is at least 300:1 in sunlight, a half-life of over 10 years is probable for toxaphene photolysis. Since 2,4-D-BEE surely absorbs more light in the solar spectral region than toxaphene, the 10 year half-life estimate is probably too short but it does serve to show that photolysis is not an important process for toxaphene in aqueous systems. No reliable, environmentally relevant data on photolysis studies were found

in literature to substantiate the often-found statement that sunlight is important in detoxification of toxaphene.

35.4.2 Oxidation

No information is available on the oxidation of toxaphene in aquatic systems.

35.4.3 Hydrolysis

Wolfe et al. (1976) reported that toxaphene was unchanged after 2 days at 65°C in aqueous solutions at pH values of 3.7 and 10.0. Using this information, and allowing for a two-fold decrease in hydrolysis rate for every 10°C interval with extrapolation to more moderate pH values, the hydrolysis half-life of toxaphene at environmental pH values (5 to 8) and 25°C is greater than 10 years.

35.4.4 Volatilization

No data were found on the toxaphene volatilization from aquatic systems. Calculation of volatilization half-lives using the procedure of Mackay and Leinonen (1975) is difficult to interpret because of the many polychlorinated structures constituting toxaphene. However, it is possible that the very low solubility of the higher chlorinated bornane structures, which are highly toxic, may contribute to volatilization of the components from aquatic systems. This transport process in addition to the sorption on particulate-deposition transport process may explain the moderate detoxification rates observed in some shallow lakes.

35.4.5 Sorption

Paris et al. (1977) reported the adsorption and equilibrium of toxaphene with bacteria, fungi, and algae. Distribution coefficients $K_d = C_m/C_w$, where C is the concentration of toxaphene (mg/mg) in microorganism (C_m) and water (C_w) were as follows:

Microorganism	$K_d \times 10^{-3}$
2 Bacteria	3.4 ± 0.5, 5.2 ± 0.2
1 Fungus	17 ± 2
1 Alga	17 ± 1
1 Field sample (algae and bacteria)	6.6 ± 0.2

The time for sorption equilibrium was 10 minutes for algae, 30 minutes for bacteria, and 2 hours for fungi; desorption and equilibrium were attained in similar times and the same K_d values were obtained. Equilibrium in the field sample was reached within 1 hour.

These authors also found that the less soluble toxaphene components (with longer retention time and higher molecular weights) were preferentially sorbed by the microorganisms. The importance of sorption of toxaphene onto plankton and subsequent deposition into sediment has also been described by Veith and Lee (1971).

35.4.6 Bioaccumulation

Sorption of toxaphene on biota is rapid (Paris et al. 1977) and significant uptake occurs in natural waters (cf. reviews by Hughes 1970; and Holt 1977). The ratios of the concentration of toxaphene in organisms to the toxaphene concentration in water obtained in laboratory studies by Sanborn et al. (1976) and Schimmel et al. (1977) are representative. Sanborn et al. (1977) reported ratios of 6900 for an alga, 9600 for a snail, 8900 for mosquito larvae, and 4200 for fish in microcosms. Schimmel et al. reported ratios of 3100-21,000 for fish and oysters in 96-hr tests and 400 to 1200 for shrimp. Ratios of 4200 to 60,000 were obtained (whole-body basis) for fish in 280 day tests. Terriere et al. (1966) also reported significant uptake and concentration of toxaphene in aquatic plants and invertebrates and fishes over several years in two lakes, with concentration ratios of 500 for aquatic plants, $(1-2) \times 10^3$ for aquatic animals other than fish, and $(1-2) \times 10^5$ for rainbow trout in a shallow lake rich in biological life. Terriere, et al. also found that the toxaphene component profiles were different among the commerical toxaphene mixture and toxaphene residues recovered from aquatic plants or trout.

35.4.7 Biotransformation and Biodegradation

Parr and Smith (1976) reported a 50% loss of toxaphene in 6 weeks due to biological transformation of toxaphene in anaerobic, unstirred, flooded soils but found no transformation in aerobic sediments. The resistance of toxaphene to biotransformations in aerobic systems was also found in microcosm experiment reported by Sanborn et al. (1976) and in the single culture experiments of Paris et al. (1977).

The susceptibility of toxaphene to reduction (i.e., loss of chloride from structure by hydrogen substitution or elimination) by biochemical and chemical methods has been clearly demonstrated. Casida et al. (1975) found that toxaphene was partially metabolized in rats and concluded that on the average about half of the C-Cl bonds in toxaphene were metabolically labile; they specifically pointed out, however, that the various

components in toxaphene will show different reactivities and extent of reduction because of different degrees of chlorination and structures of the components themselves.

Khalifa et al. (1976) reported that hematin (ferriprotoporphyrin hydroxide) reduced toxaphene, as did a rat liver microsome-NADPH system. The reduced toxaphene species were determined by the reduced glpc retention times and reduced sensitivity in detection by the electron capture detector. Toxaphene components A (A-1 and A-2) and B were reduced by these systems through dechlorination and dehydrochlorination mechanisms.

Subsequent work by Saleh and Casida (1978) reported that toxaphene component B (a heptachlorobornane; see Section 35.2) was reduced in bovine rumen fluid, in sewage primary effluent and in vivo in houseflies as well as in rats.

The results of these studies, and those of chemical reduction studies (see Section 35.4.8) and field studies in lakes (see Section 35.4.9), indicate that toxaphene will be reduced in eutrophic, anaerobic environments, but that different toxaphene components and even different chlorinated sites within a component's molecular structure will be reduced at different rates (see Section 35.2). It is also significant to note that the moderate "detoxification" rates of some toxic, higher chlorinated toxaphene components in eutrophic, shallow lakes are probably partially due to removal by the preferential sorption of these lower solubility components to particulate and sediment, with subsequent reduction in these anaerobic environments.

35.4.8 Other Reactions

Williams and Bidleman (1978) reported that toxaphene was reduced in anaerobic unsterile and sterile wet estuarine sediments and in sterile sand containing a Fe(II)/Fe(III) couple. Although they could not quantitate the transformation rates, the authors found marked changes in the toxaphene glpc profile after only several days; the results of a sterile sand-distilled water control experiment with the Fe(II)/Fe(III) couple showed that chemical processes were occurring in sterile systems. It was not determined whether biological transformations were also occurring in the unsterile sediments.

Khalifa et al. (1976) reported reduction of toxaphene as well as its individual toxicants A and B by reduced hematin (see Section 35.4.6). Saleh and Casida (1978) reported that toxicant B is also reduced by free radical-triphenyltin hydride reactions in hexane and by photolysis in hexane solution with uv light > 220 nm.

35.4.9 Microcosm Studies, Field Studies, and Modelling

Several groups reported studies of toxaphene persistence in lakes. Data from these studies suggest that toxaphene may persist in lakes for periods of several months to more than 6 years as measured by acute toxicity to fish. This toxicity criteria obviously measures the persistence of the more acutely toxic toxaphene components and does not include less toxic components that are possibly more persistent and may accumulate in the food chain. Toxaphene persistence data indicates that transformations (either chemical or biological) will occur fastest where the rate of transfer to sediment/anaerobic systems is most rapid and where biologically rich systems are also present (i.e., shallow, biologically rich lakes give faster toxaphene reduction/detoxification than deep, oligotrophic lakes).

Stringer and McMynn (1960) reviewed the detoxification of toxaphene in lakes as determined by survival of fish in cages. Detoxification times in 14 lakes ranged from 11 to 48 months with an average of 29 months. The authors state that high turbidity and shallow lakes increase detoxification of toxaphene.

Terriere et al. (1966) reported the persistence of toxaphene in two mountain lakes. In a shallow lake rich in aquatic life (Davis Lake), initially treated at 88 ppb toxaphene, the concentration of toxaphene in water after 1, 2, and 3 years was 0.63, 0.41, and < 0.2 ppb, respectively, (each concentration is an average of 6 samples). In a deep, biologically sparse lake (Miller Lake) initially treated at 40 ppb toxaphene, concentrations in water of 2.10, 1.20, and 0.84 ppm were found after 4, 5, and 6 years. Data for uptake and bioaccumulation in aquatic plants and invertebrates fish and bottom mud in the two lakes showed higher concentrations in Miller Lake species than in Davis Lake species, with average concentrations in trout exceeding 2 ppm in all analyses (also see Section 35.4.7). The authors also stated that trout could not be restocked in Miller Lake for six years because of the toxaphene levels that persisted.

Lee and coworkers reported a series of studies on the persistence of toxaphene in lakes (Johnson et al. 1966; Hughes et al. 1970; Hughes 1970; Veith and Lee 1971; Hughes and Lee 1973; Lee at al. 1977). The 1966 paper reported that lakes treated with 0.1 ppm toxaphene 3 to 9 years before analysis contained toxaphene as 1-4 ppb in water, 0.2 to 1 ppm in sediments and 0.05 to 0.4 ppm in aquatic plants. The paper also states that sorption onto particulate is one detoxification mechanism, and suggested that the components of the toxaphene mixture are degraded at different rates and have different toxicities. The 1971 paper reported that in a toxaphene-treated lake the concentration of toxaphene in the sediment increased for 190 days and then decreased by a factor of 2 for each subsequent 120 day period. Citing work in their group, the authors found a

significant mechanism for accumulation in sediment is sorption of toxaphene on particulate matter with subsequent deposition in sediment. They also report that toxaphene accumulated on sediments under the natural lake conditions could not be desorbed from sediment by pure water in the laboratory, suggesting that desorption from sediment is not a significant process in the aquatic environment. In the 1977 paper, Lee and coworkers found that toxaphene extracted from sediment was less toxic to fish than commercial toxaphere preparations, demonstrating that some toxic components of toxaphene were transformed in sediments.

Sanborn et al. (1976) explored the fate of toxaphene in small microcosms, but did not identify products, although they did quantify the concentrations of 6 unknown components in the water and the organisms. At the end of one month, 60% to 80% of the radiolabelled material in the organisms remained in the form of toxaphene.

35.5 Data Summary

Table 35-1 summarizes the data on the aquatic fate of toxaphene.

Table 35-1

Summary of Aquatic Fate of Toxaphene

Environmental Process[a]	Summary Statement	Rate	Half-Life $t_{\frac{1}{2}}$	Confidence of Data
Photolysis	Not an important process.	-	> 10 years	High
Oxidation	Probably not an important process.	-	-	Medium
Hydrolysis	Not an important process	-	> 10 years	High
Volatilization	May be an important process.	-	-	Low
Sorption	Is an important process.	-	< 2 hours for uptake by microorganisms	High
Bioaccumulation	Is an important process.	-	-	High
Biotransformation/ Biodegradation	Degraded in anaerobic systems but not in aerobic systems.	-	Will depend on transport to anaerobic environment	Low

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

35.6 Literature Cited

Brooks, G. T. 1974. Chlorinated insecticides: Volume I:Technology and applications. CRC Press, Cleveland, OH., 249 pp.

Casida, J. E., R. L. Holmstead, S. Khalifa, T. R. Knox, and T. Ohsawa. 1975. Toxaphene composition and metabolism in rats. Environ. Qual. Saf., Suppl. 3(Pesticides):365-369.

Chandurkar, P. S., F. Matsumura, and T. Ikeda. 1978. Identification and toxicity of toxicant Ac, a toxic component of toxaphene. Chemosphere 7(2):133-139.

Holmstead, R. L., S. Khalifa, and J. E. Casida. 1974. Toxaphene composition analyzed by combined gas chromatography-chemical ionization mass spectrometry. J. Agric. Food Chem. 22(6):939-944.

Holt, B. R. 1977. Population exposure to toxaphene (chlorinated camphenes). SRI-Int. CRESS Report No. 36, Prepared for Environmental Protection Agency, 68-01-4314, 69pp.

Hughes, R. A., 1970. Studies on the persistence of toxaphene in treated lakes. Ph.D. Thesis. University of Wisconsin. 289pp. University Microfilms, Ann Arbor, Mich., Order No. 70-24, 751 (Diss. Abstr. Int. B 1971, 31(11):6989).

Hughes, R. A., J. D. Welch, and G. F. Lee. 1970. Gas chromatographic analysis of toxaphene in natural waters, fish, and lake sediments. Water Research 4:547-558.

Hughes, R. A., and G. F. Lee. 1973. Toxaphene accumulation in fish in lakes treated for rough fish control. Environ. Sci. Technol. 7(10):934-939.

Johnson, W. D., G. F. Lee, and D. E. Spyridakis. 1966. Persistence of toxaphene in treated lakes. Air Water Pollut. 10(8):555-560.

Khalifa, S., T. R. Mon., J. L. Engel, and J. E. Casida. 1974. Isolation of 2,2,5-endo,6,9,10-heptachlorobornane and octachloro toxicant from technical toxaphene. J. Agric. Food Chem. 22(4):653-657.

Khalifa, S., R. L. Holmstead, and J. E. Casida. 1976. Toxaphene degradation by iron(II) protoporphyrin systems. J. Agric. Food Chem. 24(2):277-282.

Lee, G. F., R. A. Hughes, and G. D. Veith. 1977. Evidence for partial degradation of toxaphene in the aqueous environment. Water, Air, Soil Pollut. 8:478-484.

Mackay, D., and P. J. Leinonen. 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 9(13):1178-1180.

Palmer, K., R. Wong, R. Lundin, S. Khalifa, and J. Casida. 1975. Crystal and molecular structure of 2,2,5-endo,6,-exo,8,9,10-heptachlorobornane, $C_{10}H_{11}Cl_7$, a toxic component of toxaphene insecticide. J. Am. Chem. Soc. 97(2):408-413.

Paris, D. F., D. L. Lewis, and J. T. Barnett. 1977. Bioconcentration of toxaphene by microorganisms. Bull. Environ. Contam. Toxicol. 17(5):564-572.

Parr, J. F., and S. Smith. 1976. Degradation of toxaphene in selected anaerobic soil environments. Soil Sci. 121(1):52-57.

Saleh, M. A., and J. E. Casida. 1977. Consistency of Toxaphene Composition analyzed by open tubular column gas-liquid chromatography. J. Agric. Food Chem. 25(1):63-68.

Saleh, M. A., W. V. Turner, and J. E. Casida. 1977. Polychlorobornane components of toxaphene: Structure-toxicity relations and metabolic reductive dechlorination. Science 193:1256-1258.

Saleh, M. A., and J. E. Casida. 1978. Reductive chlorination of the toxaphene component 2,2,5-endo,6-exo,8,9,10-heptachlorobornane in various chemical, photochemical, and metabolic systems. J. Agric. Food Chem. 26(3):583-590.

Sanborn, J. R., R. L. Metcalf, W. N. Bruce, and P.-Y. Lu. 1976. The fate of chlordane and toxaphene in a terrestrial-aquatic model ecosystem. Environ. Entomol. 5(3):533-538.

Sanborn, J. R., B. M. Francis, and R. L. Metcalf. 1977. The degradation of selected pesticides in soil: A review of the published literature. U.S. NTIS, PB Rep. PB-272353, 633pp.

Schimmel, S. C., J. M. Patrick, Jr., and J. Forester. 1977. Uptake and toxicity of toxaphene in several estuarine organisms. Arch. Environ. Contam. Tox. 5:353-367.

Stringer, G. E., and R. G. McMynn. 1960. Three years' use of toxaphene as a fish toxicant in British Columbia. Can. Fish Cult 28:37-44.

Terriere, L. C., U. Kiigemagi, A. R. Gerlach, and R. L. Borovicka. 1966. The persistence of toxaphene in lake water and its uptake by aquatic plants and animals. J. Agric. Food Chem. 14:66-69.

Turner, W. V., J. L. Engel, and J. E. Casida. 1977. Toxaphene components and related compounds: Preparation and toxicity of some hepta-, octa-, and nonachlorobornanes, hexa- and heptachloronenes, and a hexachlorobornadiene. J. Agric. Food Chem. 25(6):1394-1401.

Turner, W. V., S. Khalifa, and J. E. Casida. 1975. Toxaphene toxicant A. Mixture of 2,2,5-endo,6-exo,8,8,9,10-octachlorobornane and 2,2,5-endo,6-exo,8,9,9,10-octachlorobornane. J. Agric. Food Chem. 23(5):991-994.

Vieth, G. D., and G. F. Lee. 1971. Water chemistry of toxaphene-role of lake sediments. Environ. Sci. Technol. 5(3):230-234.

Weil, L., G. Dure and K. E. Quentin. 1974. Solubility in water of insecticide chlorinated hydrocarbons and polychlorinated biphenyls in view of water pollution. Z. Wasser Abwasser Forsch. 7(6):169-175.

Williams, R. R., and T. F. Bidleman. 1978. Toxaphene degradation in estuarine sediments. J. Agric. Food Chem. 26(1):280-282.

Wolfe, N. L., R. G. Zepp, G. L. Baughman, R. C. Fincher, and J. A. Gordon. 1976. Chemical and photochemical transformation of selected pesticides in aquatic systems. U. S. Environ. Prot. Agency, Off. Res. Dev., EPA 600/3-76-067, 151pp.

SECTION IV: PCBs AND RELATED COMPOUNDS

Chapters 36 & 37

36. POLYCHLORINATED BIPHENYLS

36.1 Statement of Probable Fate

Polychlorinated biphenyls (PCBs) are a family of compounds which vary widely in physical, chemical, and biological properties. For those compounds with four or fewer chlorine atoms per molecule, biodegradation appears to be the dominant fate process and results in significant destruction and transformation. Polychlorinated biphenyls with five or more chlorine atoms per molecule have been photolyzed in experimental situations but it is difficult to extrapolate these results to environmental conditions.

Non-destructive processes which affect the distribution and transport of polychlorinated biphenyls are adsorption, volatilization, and bioaccumulation. In natural water systems, the greatest concentration of these compounds is sorbed to suspended and bed sediments due to the very low solubility in water. The tendency of polychlorinated biphenyls for adsorption increases with the degree of chlorination and with the organic content of the absorbent. The biota are another environmental compartment into which these compounds are strongly partitioned (measured bioconcentration factors range up to 10^6).

Volatilization and transport as an aerosol followed by fallout with dust or rain is the probable cause of the ubiquitous distribution of polychlorinated biphenyls. The more highly chlorinated species are less volatile than the lighter species. The presence of suspended solids tends to reduce volatilization, presumably because the solids adsorb the polychlorinated biphenyls and reduce the concentration in solution.

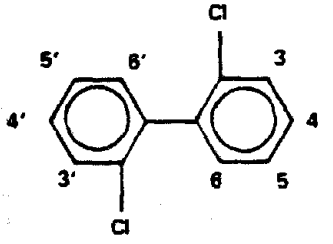
The available empirical evidence indicates that polychlorinated biphenyls, especially those with four or more chlorines, are persistent in the environment. The composition of polychlorinated biphenyls in the atmosphere is similar to that of Aroclor 1242 or 1016, while those in surface waters (mostly adsorbed to suspended solids) approach the composition of Aroclor 1254. Polychlorinated biphenyls in biota are heavier and more chlorinated still, and approximate the composition of Aroclor 1260. Thus the processes controlling distribution are somewhat selective, with the lighter species more likely to volatilize and the heavier species more likely to be incorporated into sediments and biota.

36.2 Identification

The Aroclors are technical mixtures of a number of the individual polychlorinated biphenyls made by the partial chlorination of biphenyl in the

presence of a suitable catalyst. In the designation of the individual Aroclors (Monsanto TM) a set of four digits was used, the first two, 12, to designate that the preparation is a mixture. The second set of two numbers is used to denote the approximate chlorine content by weight. Thus, Aroclor 1242 is a mixture having an average chlorine content of 42 percent. When it was determined that there was a significant environmental problem associated with the more heavily chlorinated species, Monsanto (the major American manufacturer) prepared a new mixture that was limited primarily to the mono, di and trichloro isomers. This product carried the designation Aroclor 1016.

Of the total of 209 possible compounds resulting from the partial or total chlorination of biphenyl, some 100 individual compounds have been detected in the various Aroclors (Hutzinger et al. 1974). The structure of a typical (2,2'-dichlorobiphenyl) member of the class of polychlorinated biphenyls is shown below.



CAS NO.: Each of the polychlorinated biphenyls compounds has been given an individual CAS number. The CAS numbers of the Aroclors are listed in Table 36-2.

TSL NO.: TSL numbers NZ32800, NZ3300, and NZ33500 have been assigned to three polychlorinated biphenyls mixtures. However, none of these mixtures coincide with the molecular composition of Aroclor species as listed by Monsanto.

The appropriate molecular compositon of the Aroclors is shown in Table 36-1.

36.3 Physical Properties

Individual polychlorinated biphenyls vary widely in their physical properties according to the degree and position of chlorination. However, all have a very low water solubility, low vapor pressure, and a high dielectric constant. The properties that make these compounds so widely used in industrial applications include excellent thermal stability, strong resistance to both acidic or basic hydrolysis, and general inertness (Gustafson 1970). The environmentally relevant physical properties of the Aroclors are presented in Table 36-2. Again, it is important to remember that the Aroclors are mixtures of many different polychlorinated biphenyls species. The physical properties of a mixture cannot be properly defined as

Table 36-1

Approximate Molecular Composition of Aroclors

(Percent) [Hutzinger et al. 1974]

Empirical Formula	Aroclor Number						
	1016	1221	1232	1242	1248	1254	1260
$C_{12}H_{10}$	<0.1	11	<0.1	<0.1	ND*	<0.1	ND
$C_{12}H_9Cl$	1	51	31	1	ND	<0.1	ND
$C_{12}H_8Cl_2$	20	32	24	16	2	0.5	ND
$C_{12}H_7Cl_3$	57	4	28	49	18	1	ND
$C_{12}H_6Cl_4$	21	2	12	25	40	21	1
$C_{12}H_5Cl_5$	1	<0.5	4	8	36	48	12
$C_{12}H_4Cl_6$	<0.1	ND	<0.1	1	4	25	38
$C_{12}H_3Cl_7$	ND	ND	ND	<0.1	ND	6	41
$C_{12}H_2Cl_8$	ND	ND	ND	ND	ND	ND	8
$C_{12}H_1Cl_9$	ND	ND	ND	ND	ND	ND	ND
Average Molecular Weight	257.9	200.7	232.2	266.5	299.5	328.4	375.7

*ND denotes none detected.

Table 36-2

Properties of Aroclors[a,b]

Property	1016	1221	1232	1242	1248	1254	1260
Appearance	Clear Oil	Clear Oil	Clear Oil	Clear Oil	Clear Oil	Light Yellow Viscous Liquid	Light Yellow Sticky Resin
Chlorine (Percent)	41	20.5-21.5	31.4-32.5	42	48	54	60
Density (gm/cm^3) (25°C)	1.33	1.15	1.24	1.35	1.41	1.50	1.58
Distillation Range (°C)	325-356	275-320	290-325	325-366	340-375	365-390	385-420
Evaporation loss (%) 100°C/6 hrs	NA	1-1.5	1-1.5	0-0.4	0-0.3	0-0.2	0-0.1
Aqueous Solubility (mg/l)	0.42[c]	[15.]	[1.45]	0.24 0.34[c] 0.11[d]	0.054	0.012[d] 0.027[d] 0.05[e]	0.0027
Vapor Pressure (mm Hg @ 25°C)	[4×10^{-4}]	[6.7×10^{-3}]	[4.06×10^{-3}]	4.06×10^{-4}	4.94×10^{-4}	7.71×10^{-5}	4.05×10^{-5}
Octanol/Water Partition Coefficient (log P)	4.38[c] >5.58[e,f]	[2.8] 4.09[f,g]	[3.2] 4.56[f,g]	4.11[c] >5.58[e,f]	[5.75][h] >6.11[e,f]	[6.03][h]	[7.14][h] >6.11[e,f]
CAS NO.		111-042-82	111-411-65	534-692-19	126-722-96	11-976-91	110-968-25

a. All values not subscripted are from Monsanto (1974).
b. Bracketed data are estimated.
c. Paris et al. (1978).
d. Dexter and Pavlou 1978.
e. Chiou et al. 1977.
f. Partition coefficient of lowest chlorinated polychlorinated biphenyl present in significant quantities.
g. Tulp and Hutzinger 1978.
h. Hansch et al. 1973 and Chiou et al. 1977.
i. Haque et al. 1974.

constants. The true solubility of a mixture for example is undefined because the water concentration at equilibrium is controlled by partitioning of the individual components between water and the mixture itself. The physical properties of the individual polychlorinated biphenyls are not identical, and, consequently, selective solubilization of the more soluble lower chlorinated components will occur. Conversely, the more highly chlorinated compounds will be selectively partitioned into the mixture. The measured solubilities or the equilibrium mass concentration as well as the other properties of the mixture will be an average of the properties of the individual chlorinated biphenyls. Theoretically, from a knowledge of the equilibrium mass concentrations, the individual solubilities can be determined or visa versa (Dexter and Pavlou 1978; Paris et al. 1978; Tulp and Hutzinger 1978). In Table 36-2, the physical properties of several mixtures are presented.

36.4 Summary of Fate Data

36.4.1 Photolysis

Irradiation of polychlorinated biphenyls with short-wave ultraviolet light has been shown to produce partial dechlorination in the vapor phase (Maugh 1973) and, in water with ozone, essentially complete destruction (Versar 1976). Experimental results of Bunce and Kumar (1978) indicate that the more highly chlorinated species are susceptible to photolysis, resulting in the formation of dehalogenated or substituted products. These products may be accompanied by chlorinated biphenylenes and chlorinated dibenzofurans (Safe et al. 1976). Photoproducts of polychlorinated biphenyls isomers are listed in Table 36-3 (from Safe et al. 1976). There is some doubt as to the applicability of these experiments to environmental conditions, however, since such experiments are carried out in media other than water due to the low aqueous solubility of polychlorinated biphenyls.

Safe and co-workers (1976) suggest the following mechanism for photochemical breakdown or transformation of polychlorinated biphenyls:

"The accepted route for the photochemical excitation of aromatics in the 280-320 nm region occurs by a transition of electrons in the π ground state to an excited state (π^*). From the excited state, which can be of singlet or triplet multiplicity, the carbon-halogen bond undergoes fission giving rise to an aryl and a hydrogen radical. The radicals then abstract hydrogen from the medium or dimerize and, in addition, a hydrogen halide can also be detected. Prior to bond fission an alternative reaction between the excited state and a nucleophilic species can occur giving the appropriate substitution product at the C-X bond."

Table 36-3

PHOTOPRODUCTS OF PCB ISOMERS (from Safe et al. 1976)

PCB Isomer	Photoproducts	Solvent
4,4'-dichlorobiphenyl	4-chlorobiphenyl	methanol
2,4,6-trichlorobiphenyl	2,4-dichlorobiphenyl 4-chlorobiphenyl	cyclohexane
2,4,5-trichlorobiphenyl	3,4-dichlorobiphenyl 4-chlorobiphenyl	cyclohexane
3,4,2'-trichlorobiphenyl	3,4-dichlorobiphenyl	cyclohexane
2,2',4,4'-tetrachlorobiphenyl	2,4,4'-trichlorobiphenyl 4,4'-dichlorobiphenyl 2,4,4'-trichloro-2'-methoxy-biphenyl	methanol
2,2',5,5'-tetrachlorobiphenyl	2,5,2'-trichlorobiphenyl 3,3'-dichlorobiphenyl 3-chlorobiphenyl trichloromethoxybiphenyl dichlorodimethoxybiphenyl chlorohydroxybiphenyls	dioxane-water
2,2',3,3'-tetrachlorobiphenyl	2,3,3'-trichlorobiphenyl 3,3'-trichlorobiphenyl trichloromethoxybiphenyl	methanol
2,2',6,6'-tetrachlorobiphenyl	2,2',6-trichlorobiphenyl 2,2'-dichlorobiphenyl trichloromethoxybiphenyl	methanol
3,3',4,4'-tetrachlorobiphenyl	3,4,4'-trichlorobiphenyl 4,4'-dichlorobiphenyl trichloromethoxybiphenyl	methanol
3,3',5,5'-tetrachlorobiphenyl	3,3',5-trichlorobiphenyl	methanol
2,3,4,5-tetrachlorobiphenyl	3,4,5-trichlorobiphenyl 3,4-dichlorobiphenyl	cyclohexane
2,3,5,6-tetrachlorobiphenyl	2,3,5-trichlorobiphenyl 3,5-dichlorobiphenyl	cyclohexane
2,2',4,4',6,6'-hexachlorobiphenyl	dechlorinated product (mono pentachlorobiphenyls quaterphenyls, diphenylene dibenzofurans, chloro-methoxybiphenyls	hexane and methanol
2,2',4,4',5,5'-hexachlorobiphenyl	dechlorinated products chlorinated quaterphenyls	hexane and methanol
2,2',3,3',4,4',5,5'-octachloro-biphenyl	dechlorinated products	
Aroclor 1254	dechlorinated, hydroxylated and hydrated photoproducts	dioxane-water

When the rate of polychlorinated biphenyls photolysis in oxygen-saturated solutions is compared with the rate in anoxic solutions, it is evident that oxygen supresses photolysis, apparently by acting as a free radical quencher. This supports the contention that an intermediate triplet excited state is involved in the photolytic reaction (Safe et al. 1976). Since in natural waters the photic zone corresponds to the most oxygen-rich zone (due to photosynthesis), dissolved oxygen is an inherent limitation on the rate of aqueous polychlorinated biphenyl photodegradation.

Bunce and Kumar (1978) measured photolysis of several polychlorinated biphenyl species in a 4:1 acetonitrile-water solution and calculated the approximate rate of dechlorination under environmental conditions. For shallow waters and typical environmental PCB concentrations, they predicted that up to 5% of the lightly chlorinated polychlorinated biphenyls molecules might lose a chlorine atom in one year, but that at least one chlorine atom should be lost from each highly chlorinated molecule annually. The authors stress the limitations of the assumptions made in this calculation, but if accurate, it is very significant since the less-chlorinated species can be biodegraded while the heavier species cannot. Furthermore, Bunce and Kumar point out the fact that if polychlorinated biphenyls concentrate heavily in the surface film, the photolytic rates would be much higher than those calculated.

Thus it is possible that photolysis results in the breakdown of the more highly-chlorinated polychlorinated biphenyl species. Even though the rate of such breakdown is slow, it is significant since none of the other fate processes result in degradation of the heavier species.

36.4.2 Oxidation

Polychlorinated biphenyls are extremely resistant to oxidation (Hutzinger et al. 1974). Gustafson (1970) cites a Monsanto technical bulletin that "they can be heated to 140°C under 260 p.s.i. of oxygen pressure without showing any evidence of oxidation as judged by development of acidity or formation of sludge." Thus chemical oxidation is not important as an environmental fate process.

36.4.3 Hydrolysis

Polychlorinated biphenyls are strongly resistant to both acidic and basic hydrolysis (Gustafson 1970; Hutzinger et al. 1974). Hydrolysis does not appear to be important in terms of environmental fate.

36.4.4 Volatilization

Volatilization and/or aerosol dispersion of polychlorinated biphenyls is thought to account for their ubiquitous distribution. Atmospheric transport followed by fallout with dust or rain is largely responsible for the fact that polychlorinated biphenyls have been detected in air over Baltimore, Maryland (Paris, et al. 1978) in "rainwater in England, brown seals off the coast of Scotland, white-tailed eagles in Sweden, cod in the Baltic Sea, mussels in the Netherlands, Adelie penguins in the Antarctica, brown pelican eggs in Panama, Arctic terns, shrimp in Florida, river water in Japan (and) waters in the Great Lakes" (Gustafson 1970). Although these compounds have a fairly high molecular weight and low vapor pressure, they have a remarkably high activity coefficient in water which causes a high equilibrium vapor partial pressure (Mackay and Wolkoff 1973). As a result, the rate of volatilization is somewhat higher than might be expected.

Mackay and Wolkoff (1973), and later Mackay and Leinonen (1975) calculated the evaporative half-life of Aroclors 1242, 1248, 1254, and 1260 in a water column 1 meter deep on the basis of an approach assuming thermodynamic equilibrium. The estimated half-lives for the Aroclors published by Mackay and Leinonen range from 9.5 hours for Aroclor 1248 to 12.1 hours for Aroclor 1242 (see Table 36-4). The Mackay and Wolkoff (1973) model suggests that volatilization results from the entrainment of solute molecules in the stream of evaporating water molecules. The rate at which the solute molecules are so carried off is determined by the effective surface concentration of the solute and by the evaporative rate of the water. The model proposed by Mackay and Leinonen (1975) is based on the assertion that equilibrium will be reached when the chemical potential for the solute in the air and in the aqueous phases are equal; the driving force is the actual inequality of these chemical potentials. Here, again, the controlling concentration is that of the solute at the surface. Neither of these models are directly concerned with those processes that act in the aqueous phase to control the surface concentration and thus are based on the assumption of sufficiently perfect mixing within the aqueous phase so that the surface phenonmena are rate-controlling in the volatilization process. Since the Mackay and Leinonen (1975) model has a more acceptable thermodynamic basis, the results presented herein are calculated from this model rather than from Mackay and Wolkoff (1973).

It should be noted that, even though the Aroclor mixtures 1016, 1221 and 1232 have larger proportions of the more volatile (i.e., higher vapor pressure) mono-, di- and trichloro species that does 1242, they also exhibit higher ultimate aqueous solubility so that, without a direct measure of the Henry constant, it is not possible to assert that these species will volatilize more rapidly than does Aroclor 1242.

Table 36-4

Calculated Volatilization Half-Life at 25°C, in 1 m^3 water, 1 m deep

Preparation	Henry Law Constant [Atmos m^3/mole]	$t_{1/2}$ (hrs)
Aroclor 1242[a]	5.7×10^{-4}	12.1
Aroclor 1248[a]	3.5×10^{-3}	9.5
Aroclor 1254[a]	2.8×10^{-3}	10.3
Aroclor 1260[a]	7.1×10^{-3}	10.2
Aroclor 1016[b]	-	9.9

[a] MacKay and Leinonen 1975.

[b] Paris et al. 1978.

Haque et al. (1974) demonstrated that volatilization of Aroclor 1254 is much slower from soil than from sand or unadulterated PCB solution. Apparently adsorption by organic materials in the soil greatly reduces the concentration of "free" PCB's in solution which can evaporate.

The reduction of volatilization by adsorption may explain the fact that polychlorinated biphenyls in most natural water samples evaporate at a much slower rate than that predicted by Mackay and Wolkoff (1973) or Mackay and Leinonen (1975). Oloffs et al. (1972) showed that volatilization loss of Aroclor 1260 from solutions of 100 µg/l in river water was only 67% after 12 weeks. When sediment was added to the system maximum loss was only 34% after 12 weeks (Oloffs et al. 1973). Tucker et al. (1975) demonstrated volatilization rates of 4.2 and 3.6% for Aroclor, 1221 and 1016, respectively over a 24-hour period in aerated samples exposed to activated sludge.

All of the above measurements indicate volatilization half-lives considerably longer than those estimated by Mackay and Wolkoff (1973) and Mackay and Leinonen (1975). The estimated half-life resulting from the Oloffs et al. (1973) experiment would be of the order of 1260 hours, which is to be compared to the Mackay and Leinonen (1975) estimate of 10.2 hours.

Although empirical evidence shows that volatilization is slow under natural conditions, the lack of destructive processes for the more highly chlorinated polychlorinated biphenyls indicates that volatilization is an important transport process. The persistence of these compounds, along with the transport afforded them by volatilization, is probably the major factor in their widespread distribution.

36.4.5 Sorption

Adsorption to sediments is the major non-destructive process affecting polychlorinated biphenyls after introduction to the aquatic environment. The combination of low water solubility (.0027-15 mg/l) and high octanol/water partition coefficient (2.8-7.4) (also see Table 36-2) indicates that polychlorinated biphenyls will have a high affinity for suspended solids, especially those high in organic carbon (Hamelink et al. 1971). This has been confirmed by a number of experiments which have shown that polychlorinated biphenyls are quickly adsorbed and that the greatest amount is usually associated with sediments or soils in soil-water systems (Oloffs et al. 1973; Haque et al. 1974; Hetling et al. 1978; Moein 1976; Moein et al. 1976; Paris et al. (1978). Paris et al. (1978) found the partition coefficients for polychlorinated biphenyl between water and a variety of bacteria, seston, and sediments to be only an order of magnitude less than the corresponding octanol/water partition coefficient.

When contamination becomes sufficiently high, sediments may serve as a reservoir for re-solution of polychlorinated biphenyls (Veith and Comstock 1975). This fact has important ramifications for areas where polychlorinated biphenyls are spilled; even after the initial degradation in water quality, release of these compounds by sediments can cause long-term pollution. For example, Wilson and Forester (1978) report that for 7 years following a spill, oyster tissue (Crassostrea virginica) still contained measurable quantities of Aroclor 1254 even though the amount in water was below detectable levels.

Polychlorinated biphenyls have an even greater affinity for oil than for sediments (Sayler and Colwell 1976). In areas polluted by both oil and polychlorinated biphenyls, microbes capable of degrading each of the pollutants separately appear to be inhibited by the high concentrations in combination.

The preferential sorption of polychlorinated biphenyls on the organic fraction of the suspended solids coupled with the entrance of these suspended solids into the sediments is thought to be a major mechanism for the immobilization in aquatic systems. The persistance of these chemicals, however, makes re-solution a possibility for years after they have entered the sediments.

36.4.6 Bioaccumulation

Since polychlorinated biphenyls are adsorbed strongly to organic sediments, it is not surprising to find that they are also strongly bioaccumulated. Their resistance to biodegradation implies that they will be quite persistent in organisms. This is indeed the case.

The potential for bioaccumulation of polychlorinated biphenyls species is directly related to the number of chlorines for two reasons: first, the more highly chlorinated species have a greater octanol/water partition coefficient, and secondly, the heavier polychlorinated biphenyls species are more resistant to biodegradation (Metcalf et al. 1975; EPA 1977).

Numerous authors have published the concentrations of polychlorinated biphenyls in various aquatic and terrestrial organisms. Although the ambient concentrations are not often reported along with the in vivo concentrations, it is suggested that bioaccumulation factors are usually on the order of 10^4 -10^6. Although these factors are very high, it is probable that the total reservoir of polychlorinated biphenyls in the oceanic water column is higher than the total reservoir in oceanic biota (Clayton et al. 1977).

Polychlorinated biphenyls can be passed along a food chain; however, biomangification is apparently not a controlling factor in attaining the levels found in aquatic organisms (Metcalf et al. 1975; Clayton et al. 1977). Scura and Theilacker (1977) found that the partition coefficient for each organism in an aquatic food chain determined the ultimate level and not the food chain itself.

36.4.7 Biotransformation and Biodegradation

Individual polychlorinated biphenyl species vary widely in their susceptibility to biodegradation. The mono-, di-, and tri-chlorinated species can be degraded by an array of organisms ranging from bacteria to man. Polychlorinated biphenyls with five or more chlorines per molecule are quite resistant to biodegradation.

The mechanism of polychlorinated biphenyl biodegradation has been investigated thoroughly (Hutzinger et al. 1972; Metcalf et al. 1975; Branson et al. 1975; Berlin et al. 1975; Kaiser and Wong 1974; Wong and Kaiser 1976; Furakawa et al. 1978). For the purposes of this study, it suffices to say that biodegradability of these compounds is a function of the number of C-H bonds available for hydroxylation by microsomal oxidation. Adjacent unchlorinated carbons allow the formation of arene oxide intermediates and thus facilitate metabolism. There are exceptions to this simple rule however. For example, in a study of the biodegradation of 31 isomers of polychlorinated biphenyls by Alcaligenes and Actinobacter, chlorinated biphenyl containing two chlorines on either the ortho position of a single ring (i.e., 2.6-) or both rings (i.e., 2,2'-) showed very poor degradability (Furakawa et al. 1978). Whether this will be a general phenomenon for all organisms is yet to be determined.

Rates of biodegradation vary widely, depending on the composition and distribution of biota, concentration of polychlorinated biphenyls, availability of other nutrients, temperature, and other factors. Tucker et al. (1975) reported the rates listed below for degradation of mixtures of polychlorinated biphenyls in an acclimated semi-continuous activated sludge experiment with 48-hour exposure:

Aroclor	% Degradation
1221	81 ± 6
1016	33 ± 14
1242	26 ± 16
1254	19 ± 38

Tulp et al. 1978, in contrast, found that the metabolism of th single compound 4,4'-dichlorobiphenyl by a mixed culture of bacteria lated from activated sludge was almost totally suppressed by alte-

carbon sources such as glucose, glycerol, peptone, yeast extract, humic acid or activated sludge. Though the interpretation of the latter result is trivial it points out the difficulty in extrapolating conclusions drawn from laboratory studies to the environment.

Wong and Kaiser (1976) published data on the degradation of 2-mono-chlorobiphenyl (0.05%) and 4-monochlorobiphenyl (0.05%) by a mixed culture of bacteria (predominately Achromobacter sp) isolated from lake waters. Interpolating from a graph presented in their paper, the half-life of the former was about 100 hours and the latter was 175 hours.

Metcalf and co-workers (1975) studied the behavior of 2,5,2'-trichlorobiphenyl; 2,5,2',5'-tetrachlorobiphenyl; and 2,4,5,2',5',-pentachlorobiphenyl in a model ecosystem. After 33 days, the concentrations of the parent materials and metabolites in the water column and organisms were measured. The trichlorobiphenyl species was degraded considerably, but the tetra- and penta-chlorinated forms were, for the most part, unchanged and were strongly bioaccumulated.

The polychlorinated biphenyl species composing the heavier Aroclor mixtures are essentially non-biodegradable. Oloffs et al. (1972) showed that there was no degradation of the polychlorinated biphenyls in Aroclor 1260 over 12 weeks in natural water samples. In a study of the distribution and fate of Aroclor 1254 after a spill of transformer fluid, Moein et al. (1976) concluded that "no detectable reduction in the concentration of this mixture in the soil has occurred as the result of chemical transformation or biodegradation". This study compared the polychlorinated biphenyls found in soil samples in 1975 to those found in mixtures (askarels) used in the transformer in 1973.

To summarize, biodegradation is very likely to be an important fate process for the mono-, di-, and tri-chlorinated biphenyls, but does not have a signficant effect on polychlorinated biphenyls with five or more chlorines. The tetra-chlorinated biphenyls are intermediate in their susceptibility to biodegradation.

36.5 Data Summary

Biodegradation is the only process known to transform polychlorinated biphenyls under environmental conditions, and only the lighter compounds are measurably biodegraded. There is experimental evidence that the heavier polychlorinated biphenyls (five chlorines or more per molecule) can be photolyzed by ultraviolet light, but there are no data to indicate that this process is operative in the environment.

Volatilization is probably responsible for the global disperson of polychlorinated biphenyls, but on the basis of mass, aqueous transport (either adsorbed to suspended solids or in "solution") is probably the more significant process.

Polychlorinated biphenyls are strongly partitioned to organic solids and biota. Their incorporation into deep sediments is an important sink resulting in immobilization. However, resuspension of these sediments could cause them to be released back into the water column.

The fate of polychlorinated biphenyls is summarized in Table 36-5.

Table 36-5

Summary of Aquatic Fate of Polychlorinated Biphenyls

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	May result in destruction of heavier PCBs.	-	-	Low
Oxidation	PCBs are stable to oxidation.	-	-	High
Hydrolysis	PCBs are stable to hydrolysis	-	-	High
Volatilization	Important mechanism for transport. Volatility depressed by presence of organic solids.	Varies widely	Varies widely	Medium
Sorption	PCBs strongly adsorbed by solids, especially with high organic content.	Typically rapid	-	High
Bioaccumulation	Bioaccumulation factors range from about 10^4 - 10^6.	Typically rapid	-	High
Biotransformation/ Biodegradation	The only proven mode of destruction of PCBs, but only important for those with fewer than 4 chlorines per molecule.	Varies widely	-	High

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

36.6 Literature Cited

Berlin, M., J. Gage and S. Holm. 1975. The distribution and metabolism of 2,4,5,2',5'-pentachlorobiphenyl. Arch. Environ. Health 30:141-147.

Branson, D.R., G.E. Blau, H.C. Alexander and W.B. Neely. 1975. Bioconcentration of 2,2',4,4'-tetrachlorobiphenyl in rainbow trout as measured by an accelerated test. Trans. Am. Fish. Soc. 4:785-792.

Bunce, N.H. and Y. Kumar. 1978. An assessment of the impact of solar degradation of PCB's in the aquatic enviornment. Chemosphere (2):155-164.

Chiou, C.T., V.H. Freed, D.W. Schmedding and R.L. Kohnert. 1977. Partition coefficients and bioaccumulation of selected organic chemicals. Environ. Sci. Technol. 11(5):475-478.

Clayton, J.R., Jr., S.P. Parlov, and N.F. Breitner. 1977. Polychlorinated biphenyls in coastal marine zooplankton: bioaccumulation by equilibrium partitioning. Environ. Sci. Technol. 11(7):676-682.

Dexter, R.N. and S.P. Pavlou. 1978. Mass solubility and activity coefficients of stable organic chemicals in the marine environment: Polychlorinated Biphenyls. Mar. Chem. 6:41-53.

Environmental Protection Agency. 1977. Review of the environmental fate of selected chemicals. Office of Toxic Substances, EPA 560/5-77-003. Washington, D.C. p. 79-82.

Furakawa, K., K. Tonomura, and A. Kamibayashi. 1978. Effect of chlorine substitution on the biodegradability of polychlorinated biphenyls. Appl. Environ. Microbiol. 35(2):223-227.

Gustafson, C.G. 1970. PCB's -prevalent and persistent. Environ. Sci. Technol. 4:814-819.

Hamelink, J.L., R.C. Waybrant and R.C. Ball. 1971. A proposal: Exchange equilibria control the degree chlorinated hydrocarbons are biologically magnified in lentic environments. Trans. Am. Fish. Soc. 100:207.

Hansch, C., A. Vittoria, C. Silipo, and P. Jow. 1974. Partition coefficients and the structure - activities relationship of the anesthetic gases. J. Med. Chem. 18(6):546-548.

Haque, R., D.W. Schmedding, and V.H. Freed. 1974. Aqueous solubility, adsorption, and vapor behavior of polychlorinated biphenyl Aroclor 1254. Environ. Sci. Technol. 8(2):139-142.

Hetling, L., E. Horn and J. Tofflemire. 1978. Hudson River PCB study results. (unpublished). N.Y. State Dept. of Env. Conservation. Albany, N.Y.

Hutzinger, O., D. M. Nash, S. Safe, A.S.W. DeFreitas, R.J. Norstrom, D.J. Wildish, and V. Zitko. 1972. PCB's: Metabolic behavior of pure isomers in pigeons, rats, and brook trout. Science 178:312-318.

Hutzinger, S., S. Safe and V. Zitko. 1974. The chemistry of PCBs. Chemical Rubber Publishing Co., Cleveland, Ohio.

Kaiser, K.L.E. and P.T.S. Wong. 1974. Bacterial degradation of PCBs: I. Identification of some metabolic products from Aroclor 1242. Bull. Environ. Contam. & Toxicol. 11(2):291-296.

Mackay, D. and P.J. Leinonen. 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 9(13):1178-1180.

Mackay, D. and A.W. Wolkoff. 1973. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 7(7):611-614.

Maugh, T.H. 1973. DDT, an unrecognized source of polychlorinated biphenyls. Science 180:578-582.

Metcalf, R., J.R. Sanborn, P.-Y. Lu and D. Nye. 1975. Laboratory model ecosystem studies of the degradation and fate of radiolabeled tri, tetra and penta chlorobiphenyl compared to DDE. Arch. of Environ. Contam. and Toxicol. 3(2):151-165.

Moein, G.J. 1976. Study of distribution and fate of PCBs and benzenes after spill of transformer fluid. EPA 904/9-76-014. Washington, D.C. 128 p.

Moein, G.J., A.J. Smith, Jr., and P.L. Stewart. 1976. Follow-up study of the distribution and fate of PCBs and benzenes in soil and ground water samples after an accidental spill of transformer fluid. in Proc. of 1976 Nat'l. Conf. on Control of Haz. Mat'l. Spills. Information Transfer, Inc. Rockville, Md. p. 368-372.

Monsanto Industrial Chemical Corp. 1974. PCBs-Aroclors Tech. Bull. O/PL 306A. St. Louis, Mo.

Oloffs, P.C., L.J. Albright, and S.Y. Szeto. 1972. Fate and behavior of five chlorinated hydrocarbons in three natural waters. Can. J. Microbiol. 18:1393-1398.

Oloffs, P.C., L.S. Albright, S.Y. Szeto and J. Lau. 1973. Factors affecting the behavior of five chlorinated hydrocarbons and their sediments. J. Fish. Res. Board, Canada. 30:1619.

Paris, D.F., W.C. Steen, and G.L. Baughman. 1978. Role of the physico-chemical properties of Aroclor 1016 and 1242 in determining their fate and transport in aquatic enviroments. Chemosphere. 7(4):319-325.

Safe, S., N.J. Bunce, B. Chittin, O. Hutzinger, and L.O. Ruzo. 1976. Photodecomposition of halogenated aromatic compounds. In: Identification and analysis of pollutants in water. L.H. Keith (ed.). Ann Arbor Sci. Publ., Ann Arbor, Mich. pp. 35-47.

Sayler, G.S. and R.R. Colwell. 1976. Partitioning of mercury and polychlorinated biphenyl by oil, water, and suspended sediment. Environ. Sci. and Technol. 10(12):1142-1145.

Scura, E.D. and G.H. Theilacker. 1977. Transfer of the chlorinated hydrocarbon PCB in a laboratory food chain. Mar. Biol. 40(4):317-325.

Thom, N.S. and A.R. Agg. 1975. The breakdown of synthetic organic compounds in biological processes. Proc. Royal Soc. London 189:347-357.

Tucker, E.S., V.W. Saeger, and O. Hicks. 1975. Activated sludge primary biodegradation of polychlorinated biphenyls. Bull. Environ. Contam. Toxicol. 14(6):705-713.

Tulp, M.Th.M. and O. Hutzinger. 1978. Some thoughts on aqueous solubilities and partition coefficients of PCB, and the mathematical correlations between bioaccumulation and physico-chemical properties. Chemosphere. 7(10):849-860.

Veith, G.D. and V.M. Comstock. 1975. Sediments as a PCB source to aquatic systems. J. Fish. Res. Board, Canada. 32:1849.

Versar, Inc. 1976. Assessment of wastewater management, treatment technology and asssociated costs for the abatement of PCB concentrations in industrial effluents. NTIS PB 251-433/AS. Springfield, Va. 256pp.

Wilson, A.J. and J. Forester. 1978. Persistence of Aroclor 1254 in a contaminated estuary. Bull. Environ. Contam. Toxicol. 19:637-640.

Wong, P.T.S. and K.L.E. Kaiser. 1976. Bacterial degradation of PCBs: II. Rate Studies. Bull. Environ. Contam. and Toxicol. 13(2):249-255.

Yoshimura, H. and H. Yamamoto. 1973. Metabolic studies of polychlorinated biphenyls. I. Metabolic fate of 3,4,3',4'-tetrachlorobiphenyl in rats. Chem. Pharm. Bull. 21:1168.

37. 2-CHLORONAPHTHALENE

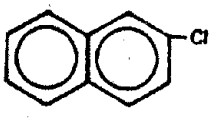
37.1 Statement of Probable Fate

Very little data specific to 2-chloronaphthalene were found; the aquatic fate of this compound is inferred from data summarized for naphthalene. The results of the data summary, which includes theoretical and emphirical evidence, suggests that 2-chloronaphthalene, a compound only slightly soluble in water (6.74 mg/l), will be adsorbed onto suspended particulates and biota and that its transport will be largely determined by the hydrogeologic conditions of the aquatic system. That portion of 2-chloronaphthalene dissolved in the water column may undergo direct photolysis. The ultimate fate of the 2-chloronaphthalene which accumulates in the sediment is believed to be biodegradation and biotransformation by benthic organisms.

37.2 Identification

2-Chloronaphthalene is present in the environment from anthropogenic sources. It is normally not found alone but as a complex mixture of naphthalenes having varying degrees of chlorination. Commercial preparations are marketed under the trade name Halowax with only 1000 and 1031 containing monochlorinated species (Kover 1975). As a group, chlorinated naphthalenes are not as widely distributed in the environment as the polychlorinated biphenyls. The survey of organics in water by Shackelford and Keith (1976) does not show, however, 2-chloronaphthalene to be a widespread pollutant. Crump-Wiesner et al. (1973) report the presence of 2-chloronaphthalene in sediment samples and Law and Goerlitz (1974) confirm its presence in the Guadalupe River of the San Francisco Bay area.

The chemical structure of 2-chloronaphthalene is shown below.



2-Chloronaphthalene

CAS No. 91-58-7
TSL No. OJ 22750

Alternate Names

Halowax
β-Chloronaphthalene

37.3 Physical Properties

The general physical properties of 2-chloronaphthalene are as follows.

Molecular weight (Weast 1977)	162.62
Melting Point (Weast 1977)	61°C
Vapor Pressure at 20°C	0.017 torr (calculated)
Solubility in water at 25°C	6.74 mg/l (calculated)
Log octanol/water partition coefficient (Calculated as per Leo et al. 1971)	4.12

37.4 Summary of Fate Data

37.4.1 Photolysis

2-Chloronaphthalene exhibits moderate adsorption in the 300 nm region and is, therefore, susceptible to direct photolysis or photooxidation (Radding et al. 1976).

Recent photolysis studies have shown a potential for photodegradation of polychlorinated naphthalenes in the environment (Ruzo et al. 1975). Experiments with various polychlorinated naphthalenes in methanolic solution irradiated at a peak energy output of 300 nm resulted in dechlorination and dimerization. They report a 15 percent dechlorination of 2-chloronaphthalene at a rate approximately $10^{-9}sec^{-1}$.

37.4.2 Oxidation

In natural water the principal oxidizing species are: (1) alkylperoxy ($RO_2\cdot$) and hydroperoxy (HO_2) radicals generated by photolytic cleavage of trace carbonyl compounds or from enzymatic sources, and (2) singlet oxygen. Singlet oxygen is thought to be the major oxidant species involved in the direct photolysis of organic molecules.

No data were found concerning the oxidation of 2-chloronaphthalene. Naphthalene, however, is believed to have a very long half-life toward oxidation by $RO_2\cdot$ radicals. The chlorine substituent on naphthalene (i.e., 2-chloronaphthalene) is thought to make it even less susceptible to free-radical oxidation. Oxidation is probably not an important fate process for 2-chloronaphthalene.

37.4.3 Hydrolysis

2-Chloronaphthalene does not contain groups amenable to hydrolysis. Hydrolysis, therefore, is not thought to be a significant fate process.

37.4.4 Volatilization

An actual volatilization rate is necessary to assess the importance of this transport process. Several authors have suggested ways to estimate volatilization rates of compounds from water using theoretical consideration (Mackay and Wolkoff 1973; Mackay and Leinonen 1975). These methods, however, are still under development, require a large amount of physical data for the compounds, and still may not predict the actual volatilization rate. Another method for determining the role of volatilization is that described by Hill et al. (1976) which employs the theory offered by Tsivoglou (1967). His theory states that the volatilization rate is directly related to the ratio of the compound's volatilization rate coefficient to the oxygen reaeration rate constant which is easily measured. Hill's method still requires a measurement of volatilization for the compound. Measured volatilization rates for 2-chloronaphthalene were not found in the literature and an accurate assessment of the role of volatilization is not possible without these rates. Work by Lee (1975) with naphthalene shows this compound to be rather volatile when present as part of an oil spill with the rate of volatilization dependent on air and water temperature, wind speed, and wave action

37.4.5 Sorption

The data reviewed did not reveal specific partition coefficients of 2-chloronaphthalene onto suspended particulate matter or biota. The calculated log octanol/water partition coefficient for 2-chloronaphthalene of 4.12 indicates that the compound should moderately adsorb onto suspended particulate matter, especially particulates high in organic matter.

Recent work by Lee and Anderson (1977) show that naphthalene will accumulate in sediments up to two orders of magnitude greater than the concentration in the overlying water. They also showed the importance of microoganisms (plankton and bacteria) in adsorbing and removing naphthalene from water. While no data specific to 2-chloronaphthalene were found, its log P octanol/water partition coefficient and the similarity to naphthalene indicate that adsorption could be an important transport process.

37.4.6 Bioaccumulation

Little specific data on the bioaccumulation of 2-chloronaphthalene were found. In one experiment Green and Neff (1977) measured the uptake and release by grass shrimp (Palaemonetes pugio) of three chlorinated naphthalene mixtures containing varying degrees of chlorination. Halowax 1000, containing 60% monochlorinated naphthalene was apparently accumulated much less than the mixture containing a greater amount of polychlorinated species. The apparent depuration rate ($t_{1/2}$ =12 hrs.) was also greater leading the authors to conclude that mono- and dichloro-species are metabolized and excreted faster than polychlorinated species.

Measurements of naphthalene content in zooplankton exposed to high concentrations show that significant uptake can occur (Lee and Anderson 1977). Work by Lee et al. (1972) reveals naphthalene is readily taken-up by aquatic organisms and concentrated in the liver where it is rapidly metabolized.

Since 2-chloronaphthalene has a calculated log octanol/water partition coefficient which is intermediate, the role of bioaccumulation is difficult to assess. It is probably adsorbed by biota to similar levels reported for naphthalene. Like naphthalene, bioaccumulation of 2-chloronaphthalene is probably short-term.

37.4.7 Biotransformation and Biodegradation

Walker and Wiltshire (1953) studied the decomposition of 1-chloronaphthalene by soil bacteria and found that two species of bacteria, isolated from the soil, would grow in a mineral salts medium with 1-chloronaphthalene as the sole carbon source. They report 8-chloro-1,2,-dihydro-1,2-dihydroxynaphthalene and 3-chlorosalicylic acid as the major bacterial metabolites. Similar results were reported for 2-chloronaphthalene by Canonica et al. (1957).

Okey and Bogan (1965) examined the rate of metabolism of 1 and 2-chloronaphthalene by sewage sludge bacteria that were enriched on unsubstituted naphthalene. The initial concentration of chlorinated substrate was 1 mg/l with the substrate being the only source of carbon. Their work showed that naphthalene was much more easily degraded than 2-chloronaphthalene which was more readily degraded than 1-chloronaphthalene.

Ruzo et al. (1976) report that chloronaphthalenes are rapidly metabolized in the pig to their corresponding hydroxylated metabolites. Furthermore, the chloronaphthalenes are distributed in the various organs

and tissues whereas the metabolites were concentrated in the urine, bile, kidney and liver.

Data for naphthalene (Lee and Ryan 1976; Vernberg 1977; Lee and Anderson 1977) indicate it to be rapidly degraded by bacteria and metabolized by multi-cellular organisms. A biodegradation half-life of 1 day has been estimated for naphthalene from these data.

Thus, it appears that biodegradation and biotransformation of 2-chloronaphthalene is rapid enough to select these processes as the most probable in determining the aquatic fate of 2-chloronaphthalene.

37.5 Data Summary

Very little data were found for 2-chloronaphthalene. It will probably be adsorbed to suspended particulates, although the role of volatilization is unknown at this time. The 2-chloronaphthalene adsorbed to suspended sediment will most likely be taken up by benthic organism and metabolized at a rapid rate. That portion of 2-chloronaphthalene dissolved in the water column may undergo photolysis and will be biodegraded by bacteria. Table 37-1 summarizes the information found for 2-chloronaphthalene.

Table 37-1

Summary of Aquatic Fate of 2-Chloronaphthalene

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Dissolved portion may photolyze.	$\sim 10^{-9}$ m sec^{-1}	-	Low
Oxidation	Very slow process.	-	-	Medium
Hydrolysis	2-chloronaphthalene does not contain groups amenable to hydrolysis.	-	-	High
Volatilization	No data found.	-	-	-
Sorption	No quantitative data found; may moderately adsorb onto suspended sediments.	-	-	Low
Bioaccumulation	Probably a short-term process.	log P (calc) 4.12	-	Low
Biotransformation/ Biodegradation	2-chloronaphthalene is degraded by bacteria and metabolized by multi-cellular organism.	-	-	Medium

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

37.6 Literature Cited

Canonica, L., A. Fiecchi and V. Treuani. 1957. Products of microbial oxidation of some substituted naphthalenes. Rend.

Crump-Wiesner, H., R. Feltz and M.L. Yates. 1973. A study of the distribution of polychlorinated biphenyls in the aquatic environment. U.S. Geol. Sun. J. of Res. 1:603-607.

Green, F.A., Jr. and T. M. Neff. Toxicity, accumulation, and release of 3 polychlorinated naphthalenes (Halowax 1000, 1013, 1099) in postlarval and adult grass shrimp, Palaemonetes pugio. Bull. Environ. Contam. Toxicol. 17(4):399-407.

Hill, J., H.P. Kollig, D.F. Paris, N.L. Wolfe and R.G. Zepp. 1976. Dynamic behavior of vinyl chloride in aquatic ecosystems. U.S. Environmental Protection Agency, (Office of Research and Development) Athens, GA. (EPA 600/13-76-001).

Kover, F.D. Environmental hazard assessment report: chlorinated naphthalenes. EPA 560/8-75-001, PB-248834. 36p.

Law, L.M. and D.F. Goerlitz. 1974. Selected chlorinated hydrocarbons in bottom material from streams tributary to San Francisco Bay. J. Pesticides Monitoring 8(1):33-36.

Lee, R.F., R. Sauerherber, and G.H. Dobbs. 1972. Uptake, metabolism, and discharge of polycyclic aromatic hydrocarbons by marine fish. Marine Biol. 17(3):201-208.

Lee, R.F. and C. Ryan. 1976. Biodegradation of petroleum hydrocarbons by marine microbes, In Proceed. Third Intemat. Conf. on Biodegradation. Applied Publishers, London.

Lee, R.F. and J.W. Anderson. 1977. Fate and effect of naphthalenes: controlled ecosystem pollution experiment. Bull. Marine Sci. 27:127.

Lee, R.F. 1975. Fate of petroleum hydrocarbons in marine zooplankton. American Petroleum Institute Conf. 8:549-553.

Leo, A., C. Hansch, and D. Elkins. 1971. Partition coefficients and their uses. Chem. Rev. 71:525-616.

Mackay, D. and P.J. Leinonen. 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 9(13):1178-1180.

Mackay, D. and A.W. Wolkoff. 1973. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 7(7):611-614.

Okey, R.W. and R.H. Bogan. 1965. Apparent involvement of electronic mechanism in limiting microbial metabolism of pesticides. J. Water Poll. Control Fed. 37:692-712.

Radding, S.B., T. Mill, C.W. Gould, D.H. Lio, H.L. Johnson, D.C. Bomberger, and C.V. Fojo. 1976. The environmental fate of selected polynuclear aromatic hydrocarbons. U.S. Environmental Protection Agency, (Office of Toxic Sub.), Wash., D.C. 122p. (EPA 560/5--75-009).

Ruzo, L.O., N.W. Bunce, S. Safe, and O. Hutzinger. 1975. Photodegradation of polychloronaphthalenes in methanol solution. Bull. Environ. Contam. Toxicol. 14(3) :341-345.

Ruzo,. L.O., N.W. Bunce, S. Safe, and O. Hutzinger. 1976. Uptake and distributioin of chloronaphthalenes and their metabolites in pigs. Bull. Environ. Contam. Toxicol. 16(2):233-239.

Shackelford, W.N., and L.H. Keith. 1976. Frequency of organic compounds identified in water. U.S. Environmental Protection Agency, (Office of Research and Development), Athens, GA. 618p. (EPA 600/4-76-062).

Tsivoglou, E.C. 1967. Measurements of stream reaeration. U.S. Dept., Int., Washington, D.C.

Vernberg, F.J. (ed.). 1977. Physiological responses of marine biota to pollutants. Academic Press, New York. pp.323-340.

Walker, N. and G.H. Wiltshire. 1955. Decomposition of 1-chloro and 1-bromo-naphthalene by soil bacteria. J. Gen. Microbiol. 12:478-483.

Weast, R.C. (ed.). 1977. CRC Handbook of Chemistry and Physics, 58th Edition. CRC Press. Cleveland, Ohio.

*U.S. GOVERNMENT PRINTING OFFICE : 1980 O-311-726/ W71

TECHNICAL REPORT DATA
Please read Instructions on the reverse before completing

1. REPORT NO. EPA 440/4-79-029a	2.
3. RECIPIENT'S ACCESSION NO. PB80 204373	
4. TITLE AND SUBTITLE: Water-Related Environmental Fate of 129 Priority Pollutants, Volume I	5. December 31, 1979
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S): M. Callahan[1], M. Slimak[1], N. Gabel[2], I. May[2], C. Fowler[2], R. Freed[2], P. Jennings[2], R. Durfee[2], F. Whitmore[2], B. Maestri[2], W. Mabey[3], B. Holt[3], C. Gould[3]	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS: [2]Versar Inc., 6621 Electronic Dr., Springfield, Va. 22151; [3]SRI International, 333 Ravenswood Ave., Menlo Park, Calif. 94025	10. PROGRAM ELEMENT NO. 2BB156
	11. CONTRACT/GRANT NO. EPA 68-01-3852[2] EPA 68-01-3867[3]
12. SPONSORING AGENCY NAME AND ADDRESS: [1]United States Environmental Protection Agency, Monitoring and Data Support Division (WH-553), 401 M Street, SW, Washington, DC 20460	13. TYPE OF REPORT AND PERIOD COVERED: Final Report
	14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES
This is a combined Versar/SRI/EPA literature search.

16. ABSTRACT

This report is a literature search and summary of relevant data for the individual fate processes (hydrolysis, biodegradation, photolysis, etc.) which might be expected to occur if a pollutant were introduced into an aquatic system. The report is organized into 101 individual chapters for pollutants or small groups of pollutants, and four introductory chapters. Each chapter has its own references so the chapters can be used independently.

The approach taken by this report is to summarize data on the individual processes which might be important in describing the transport and fate of pollutants introduced at low concentrations (e.g., ppm or less) into aquatic environments. If transport processes will result in significant pollutant transfer to another medium (e.g., air, sediments), data are included where available to describe what happens to the pollutant in the medium to which the pollutant was transferred.

A list of the literature covered in the search is included.

Results of the literature search are that a significant amount of information on most pollutants was found, but that the information was more useful in making qualitative judgements about the pollutant transport and fate than for making quantitative predictions of concentrations in the environment. Availability of rate constants useful in mathematical fate models was limited.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Environments, Pollutants, Distribution, Transport, Water Pollution, Halogenated Hydrocarbons, Organic Nitrogen Compounds, Aromatic Polycyclic Hydrocarbons, Benzene, Toluenes, Phenols, Pesticides, Metals, Esters, Nitriles, Ethers	Priority Pollutants, Environmental Fate	06F, 07B, 07C, 07D, 08D, 97R, 57H, 68D, 68E, 68A, 99E

18. DISTRIBUTION STATEMENT: [illegible]li[illegible]ed	19. SECURITY CLASS (This Report): Unclassified	21. NO. OF PAGES
	20. SECURITY CLASS (This page): Unclassified	22. PRICE

EPA Form 2220-1 (9-73)