

James W. Moore S. Ramamoorthy

Organic Chemicals in Natural Waters

Applied Monitoring and Impact Assessment

With 81 Figures



Springer-Verlag
New York Berlin Heidelberg Tokyo

James W. Moore

Alberta Environmental Centre
Vegreville, Alberta
T0B 4L0 Canada

S. Ramamoorthy

Alberta Environmental Centre
Vegreville, Alberta
T0B 4L0 Canada

Library of Congress Cataloging in Publication Data

Moore, James W., 1947–

Organic chemicals in natural waters.

(Springer series on environmental management)

Bibliography: p.

Includes index.

1. Water chemistry. 2. Organic chemicals—

Analysis. I. Ramamoorthy, S. II. Title.

III. Series.

GB9855.M653 1984 628.1'6 84-10507

© 1984 by Springer-Verlag New York Inc.

Softcover reprint of the hardcover 1st edition 1984

All rights reserved. No part of this book may be translated or reproduced in any form without written permission from Springer-Verlag, 175 Fifth Avenue, New York, New York 10010, U.S.A.

The use of general descriptive names, trade names, trademarks, etc., in this publication, even if the former are not especially identified, is not to be taken as a sign that such names, as understood by the Trade Marks and Merchandise Marks Act, may accordingly be used freely by anyone.

Typeset by Ampersand Inc., Rutland, Vermont

9 8 7 6 5 4 3 2 1

ISBN-13: 978-1-4613-9540-9 e-ISBN-13: 978-1-4613-9538-6

DOI: 10.1007/978-1-4613-9538-6

Series Preface

This series is dedicated to serving the growing community of scholars and practitioners concerned with the principles and applications of environmental management. Each volume is a thorough treatment of a specific topic of importance for proper management practices. A fundamental objective of these books is to help the reader discern and implement man's stewardship of our environment and the world's renewable resources. For we must strive to understand the relationship between man and nature, act to bring harmony to it, and nurture an environment that is both stable and productive.

These objectives have often eluded us because the pursuit of other individual and societal goals has diverted us from a course of living in balance with the environment. At times, therefore, the environmental manager may have to exert restrictive control, which is usually best applied to man, not nature. Attempts to alter or harness nature have often failed or backfired, as exemplified by the results of imprudent use of herbicides, fertilizers, water, and other agents.

Each book in this series will shed light on the fundamental and applied aspects of environmental management. It is hoped that each will help solve a practical and serious environmental problem.

Robert S. DeSanto
East Lyme, Connecticut

Preface

This is the second of two volumes on monitoring and impact assessment of chemical pollutants in natural waters. Our intention is to provide a review of data, methods, and principles that are of potential use to individuals involved in environmental management and research. The first volume dealt with the most common heavy metals in natural waters, including arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc. The second volume considers organic compounds outlined in the priority pollutant list (EPA) and Environmental Contaminants Act (Canada) and includes aliphatic compounds, aromatic compounds, chlorinated pesticides, petroleum hydrocarbons, phenols, polychlorinated biphenyls, and polychlorinated dibenzo-*p*-dioxins. Most of these chemicals are widespread in the environment and toxic to fish and humans; many are mutagenic, carcinogenic, and teratogenic. As in the first volume, a multidisciplinary approach is emphasized. There are extensive reviews of the chemistry, production, uses, discharges, behavior in natural waters, uptake, and toxicity of organics. This is followed by a description of criteria for prioritizing chemical hazards posed to users of aquatic resources. Several recommendations are made with the intention of improving current monitoring techniques.

We would like to acknowledge the assistance of staff from the Alberta Environmental Centre in the preparation of this volume. We relied heavily on Sita Ramamoorthy for the compilation and indexing of the literature. Sita Ramamoorthy and Jim Bradley also proofread the various drafts. Mrs. Diana Lee from the library handled all of our literature requests, Mrs. Arhlene Hrynyk arranged for typing of the drafts, and Mr. Terry Zenith was responsible for figure preparation. Finally, we would like to acknowledge Dr. R.S. Weaver (Executive Director, Alberta Environmental Centre) and Dr. L.E. Lillie (Head, Animal Sciences Wing) for their support during this project.

Contents

<i>Series Preface</i>	v
<i>Preface</i>	vii
1. Introduction	1
Multidisciplinary Studies	1
Objectives	2
2. Physico-Chemical Concepts on the Fate of Organic Compounds	4
Physico-Chemical Properties	4
Physico-Chemical Processes	6
Chemical Transformations	8
Metabolic Transformations	13
References	14
3. Aliphatic Hydrocarbons	16
Production, Uses, and Discharges	16
Behavior in Natural Waters	21
Residues	28
Toxicity	33
References	38

4. Aromatic Hydrocarbons—Monocyclics	43
Production, Uses, and Discharges	43
Behavior in Natural Waters	47
Residues	53
Toxicity	57
References	62
5. Aromatic Hydrocarbons—Polycyclics	67
Production, Uses and Discharges	68
Behavior in Natural Waters	69
Residues	74
Toxicity	80
References	83
6. Chlorinated Pesticides	88
Production, Uses, and Discharges	88
Behavior in Natural Waters	89
Residues	92
Toxicity	105
References	110
7. Petroleum Hydrocarbons	115
Production, Uses, and Discharges	116
Behavior in Natural Waters	122
Residues	127
Toxicity	130
References	135
8. Phenols	141
Production, Uses, and Discharges	142
Behavior in Natural Waters	146
Residues	155
Toxicity	160
References	164
9. Polychlorinated Biphenyls	168
Production, Uses, and Discharges	169
Behavior in Natural Waters	173
Residues	180
Toxicity	185
References	186

10. Polychlorinated Dibenzo-<i>p</i>-dioxins (PCDD)	192
Production, Uses, and Discharges	192
Behavior in Natural Waters	195
Residues	203
Toxicity	208
References	209
11. Prioritization and Hazard Assessment of Chemicals	213
Environmental Distribution	214
Prioritization for Detailed Assessment	222
Screening of Toxic Chemicals	225
Predictive Capability of Transport and Fate Processes	228
Impact on Biological Species	233
Assessment of Hazards	234
References	241
Appendices	
A. Chemical Formulae of Compounds Cited in This Book	244
B. Physical and Chemical Terms Cited in This Book	272
C. Common and Scientific Names of Fish Cited in This Book	274
D. Equations for the Evaluation of Physico-Chemical Fate Processes	277
Index	283

1

Introduction

Multidisciplinary Studies

Priorities in environmental research and management change. Ten years ago, we were largely concerned with eutrophication and warm water discharges into rivers. Although most scientists and managers were aware of the symptoms of poisoning by mercury, cadmium, and organo-chlorines, chemical disease was an area that the majority of environmentalists did not study. Consequently, there has been a surprising number of cases involving the exposure of humans and other organisms to chemicals. Some of the most significant examples include the Love Canal and Michigan incidents (Smith, 1980) and the closure of commercial fisheries in the lower Great Lakes. In retrospect, eutrophication and warm water do not seem that important, and it is easy to suggest that research money should have been spent in other areas.

The foregoing scenario would have been largely avoided if researchers and managers had taken a broader outlook on problem solving. All of us have to avoid the tendency to be narrow in our thinking. In most cases, we have to make a conscious attempt to expand our knowledge into different disciplines. The need for a broad outlook is generally more important in environmental studies than in other areas. The complexity and diversity of environmental problems require knowledge of chemistry, life sciences, and engineering. The effective implementation of recommendations from such studies also requires an empathy for social, political, economic, and legal factors. In short, perturbations on the sum of conditions that influence an organism or

population (the environment) cannot be effectively studied using a restricted approach.

Multidisciplinary research involves the use of several disciplines to reach a common goal. The disciplines have to be diverse in nature, spanning the physical, chemical, life, and engineering sciences. Each component should contribute substantially to the common goal and not be restricted to a service role. Active and strong input from individuals with diverse training will produce a broad understanding of the long-term consequences of specific environmental problems. This will in turn lead to improvement in the means of prioritizing research needs.

We hope that the need for multidisciplinary studies is apparent to environmentalists. If not, the example of the hazards posed by 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) in water should perhaps be considered. Short-term exposures of coho salmon to TCDD showed that there was no measurable impact on food consumption, weight gain, or survival during a 60-day postexposure period (Miller *et al.*, 1979). This type of testing is far more sophisticated than the routine monitoring programs conducted in many government laboratories and should have been reasonably well suited for the protection of aquatic resources. However, more detailed studies have shown that growth and survival of the salmon decreased after a 114-day exposure to higher concentrations of TCDD. In addition, the body burden of TCDD increased with both the level and duration of exposure. Similarly, although there is histological evidence of liver degeneration in rainbow trout fed TCDD at a concentration of 2.3 mg g⁻¹ food (Hawkes and Norris, 1977), histological methods are relatively insensitive in testing for TCDD toxicity (Wallace, 1979). On the other hand, the mutagenic and carcinogenic properties of TCDD to higher animals can be directly attributed to its induction of aryl hydrocarbon hydroxylase and accumulation of the intermediates (Kouri *et al.*, 1973). It is also important to point out that laboratory exposures of TCDD to animals may not reflect the chemical nature of the environment, thereby neglecting potential synergistic actions (Franklin, 1976; Gori, 1980). Obviously, the foregoing investigations would be largely unnecessary if TCDD is rapidly photodecomposed in the environment. We hope that environmentalists who have read this section will realize that unidiscipline investigations could have led to misevaluations of the hazards of TCDD.

Objectives

Our objective is to provide the manager and scientist with information on organic chemicals that can be used during monitoring, impact assessment, and decision-making processes. Initially, there is a treatment of the chemistry of organics in natural waters and tissues. This is followed by a more detailed discussion on the production, source, use, and discharge of organics into

water, air, and land. Such information is intended to help the manager predict the potential for contamination in natural waters. The next section describes the effect of the environment on the chemistry, toxicity, and fate of organics, followed by a review of residues in water, sediments, precipitation, effluents, emissions, and tissues in lakes, rivers, and coastal marine waters. This will allow comparisons to be made between the extent of contamination in a manager's jurisdiction and other areas. The toxicity of organics to different groups of organisms, including aquatic plants, invertebrates, fish, and humans is then reviewed.

The chemical formulas of compounds cited in this book are listed in Appendix A. Appendices B and C are glossaries of physical and chemical terms and scientific names of fish, respectively. Appendix D consists of equations for the evaluation of physico-chemical fate processes, referred to in Chapter 2.

References

- Franklin, M.R. 1976. Methylene dioxyphenyl insecticide synergists as potential human health hazards. *Environmental Health Perspectives* **14**:29–37.
- Gori, G.B. 1980. The regulation of carcinogenic hazards. *Science* **208**:256–261.
- Hawkes, C.L., and L.A. Norris. 1977. Chronic oral toxicity of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) to rainbow trout. *Transactions of the American Fisheries Society* **106**:641–645.
- Kouri, R.E., R.A. Salerno, and C.E. Whitmire. 1973. Relationships between aryl hydrocarbon hydroxylase inducibility and sensitivity to chemically induced subcutaneous sarcomas in various strains of mice. *Journal of the National Cancer Institute* **50**:263–268.
- Miller, R.A., L.A. Norris, and B.R. Loper. 1979. The response of coho salmon and guppies to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) in water. *Transactions of the American Fisheries Society* **108**:401–407.
- Smith, R.J. 1980. Swifter action sought on food contamination. *Science* **207**:163.
- Wallace, D. 1979. TCDD in the environment. *Transactions of the American Fisheries Society* **108**:103–109.

2

Physico-Chemical Concepts on the Fate of Organic Compounds

The concentration, behavior, and eventual fate of an organic compound in the aquatic environment are determined by a number of physico-chemical and biological processes. These processes include sorption-desorption, volatilization, and chemical and biological transformation. Solubility, vapor pressure, and the partition coefficient of a compound determine its concentration and residence time in water and hence the subsequent processes in that phase. The movement of an organic compound is largely dependent upon the physico-chemical interactions with other components of the aquatic environment. Such components include suspended solids, sediments, and biota.

Physico-Chemical Properties

Solubility

Although precise determination of solubility data is critical in evaluating the transformation process, such measurements still remain elusive for many compounds. In fact some of the data on aqueous solubility are no more than estimates. The problem is aggravated by the extremely low solubility of many environmentally significant contaminants. For example, the reported solubility of polychlorinated biphenyls (PCBs) varies by a factor of 2–4 depending on the procedures used (Haque and Schmedding, 1975; Wallhofer *et al.*, 1973). Several techniques are documented in the literature, but the one

by Moriguchi (1975) seems to be simple and sound. This technique is based on factoring water solubility of an organic compound into two intrinsic components: free molecular volume and hydrophilic effect of polar groups.

Moriguchi chose Quayle's parachor (molecular volume) over five other additive parameters relating to molecular volume for predictive purposes (Quayle, 1953). Quayle's parachor value is calculated by considering the molecule as a sum of its functional groups. Each group is assigned a certain value, based on its empirical data. Thus, the molecular volume is calculated from the structure of the compound. The second component, hydrophilicity of polar groups, which accounts for solute-solvent and solvent-solvent interactions, is calculated for various functional groups from their empirical data (Moriguchi, 1975). Finally, using Quayle's parachor and the appropriate hydrophilic reference factor, aqueous solubility of an organic compound can be estimated (Appendix D-1).

Vapor Pressure

In simple terms, equilibrium vapor pressure can be interpreted as the solubility of the compound in air from the liquid phase. For some organic compounds, the solids possess a finite vapor pressure that should also be considered in the evaluation of its behavior in the environment. This is particularly important for compounds of low solubility. Vapor pressure at 25°C can be calculated directly where the constants are available at that temperature or by interpolation from other temperatures. The equation of Weast (1974) can be used for several priority pollutants for the calculation of vapor pressure (Appendix D-2).

In cases of insufficient data, tables in Dreisbach (1952) can be used from the knowledge of the boiling point at 760 torr and the chemical family to which the compound belongs. The tables developed the "Cox Chart" chemical families using Antoine's equation, a modified version of equation D-2 (Appendix D). Charts are available for several organic compounds such as naphthalenes, halobenzenes with side chains, and phenols. The appropriate table is then referred to for an estimated vapor pressure.

The third method of calculating the vapor pressure is using the Clausius-Clapeyron equation (Appendix D-3). Calculations from this equation provide only a rough estimate of vapor pressure.

Partition Coefficient

Partition coefficient is a measure of the distribution of a given compound in two phases and expressed as a concentration ratio, assuming no interactions other than simple dissolution. In reality, the situation could be more complex as a result of dissociation/association of the molecule altering the speciation and stoichiometry. Partition coefficient values are valuable in describing the

environmental behavior of the compound. Since partition coefficients are additive in nature, such values for a complex compound could be calculated from the values of the parent compound by adding on the values of the substituents (transfer constants). The organic compound is considered a sum of its functional groups, which cause a certain proportion of the partitioning between octanol/water phases. An index value called the “pi” value, which can be positive or negative, has been estimated for many of the common functional groups (Tute, 1971). Calculated and experimental values for some PCBs have shown good agreement. Equations have been developed for converting partition coefficient values from one set of solvents system to another (Leo *et al.*, 1971).

Physico-Chemical Processes

Sorption-Desorption

The term sorption used here covers both adsorption and absorption, which are difficult to distinguish in most situations. In general, the more hydrophobic the organic compound is, the more likely it is that it will be sorbed to the sediment. The solubility of an organic compound depends primarily upon the sorption-desorption characteristics of the sorbate (organic compound) in association with the sorbent (soil, sediment, or synthetic matrix such as resin-coated organic strips). The physico-chemical characteristics of (i) the sorbent such as surface area, nature of charge, charge density, presence of hydrophobic areas, and organic matter such as humic and fulvic acid, and (ii) the sorbate such as water solubility and the ionic form determine the extent and the strength of sorption.

Sorption can be expressed in terms of the equation,

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

where C_s and C_w are the concentrations of the organic compound in solid and water phases respectively, K_p = partition coefficient for sorption, and $1/n$ = exponential factor. At environmentally significant concentrations that are low compared with the sorption capacities of the surface components, the term $1/n$ approximates to unity. It should be emphasized here that in the measurement of K_p , sufficient time must be allowed for the equilibration between phases to be established. This time could vary from a few minutes to several days depending on the organic compound. For neutral organic compounds, the sorption was shown to correspond to the organic content of the particulates (Kenaga and Goring, 1980). K_{oc} (K_p /fraction of organic carbon) was shown to correlate well with water solubility and K_{ow} (K for octanol/water mixture). However, this relationship between K_p and K_{oc} has

limited predictability since many neutral organic compounds are also sorbed by materials with little or no organic content. Also, the field concentrations of organic compounds are often much lower than laboratory concentrations, and the span of the concentration in a given isotherm (for example, the pesticide concentration in soil) is generally less than an order of magnitude. Usually, laboratory concentration conditions were chosen to approximate the field conditions at the time of pesticide application and/or to meet analytical detection requirements. Thus, in many cases equation (1) has not been adequate to describe the extrapolation of sorption measurements to out-of-range (low concentration levels) field situations.

Recently, methods have been developed to estimate the equilibrium sorption behavior of hydrophobic pollutants applicable to environmental conditions (Karickhoff, 1981). This method is also based on the organic-carbon referenced sorption approach developed earlier by Goring (1967), Hamaker and Thompson (1972), Lambert (1968), Lambert *et al.* (1965), and Briggs (1973). In addition, it includes thermodynamic rationale to establish the relationship of sorption parameters to other physical properties of the sorbate, making the extrapolation to other sediments or structurally similar sorbates valid. At low pollutant concentration (aqueous phase concentration less than half the solubility), sorption isotherms were linear, reversible, and characterized by a partition coefficient (Karickhoff, 1981). Partition coefficients normalized to organic carbon, K_{oc} ($K_{oc} = K_p / \text{fraction organic carbon}$) varied only twofold in a set of sediments and soils collected throughout the US. This can be compared with a 20- to 30-fold variation in K_p (without normalization for organic carbon).

From his findings as well as from those of Hassett *et al.* (1980) and Kenaga and Goring (1980), Karickhoff (1981) generalized that for neutral organic compounds of limited solubility ($<10^{-3}$ M) and not susceptible to speciation changes, sorption was "controlled" by organic carbon and amenable to quantification by K_{oc} format. In addition to organic carbon, sediment particle size governed the sorption of hydrophobic chemicals to natural sediments; the fine particles dominate the sorption and sand acting as diluent (10- to 40-fold reduction of K_{oc}). The K_{oc} for the whole sediment approximates that of the finest fraction. Karickhoff (1981) also derived equations for estimating K_{oc} from water solubility (including crystal energy) and octanol/water partition coefficients. The use of solubility data with no crystal energy correction was shown to introduce considerable error in the estimation of K_{oc} for organic solids containing polar groups (triazenes and carbamates) and for anomalously high melting compounds (β -BHC and anthracene). On the other hand, this corrected solubility equation apparently failed to extrapolate to high molecular weight chlorinated compounds (DDT, methoxychlor, hexachloro PCBs). The predictive capabilities of the equation were tested on literature sorption data for a wide variety of organic compounds and were found to agree within a factor of two.

Volatilization

The transport of a compound from the liquid to the vapor phase is called volatilization and it can be an important pathway for chemicals with high vapor pressures or low solubilities. Some early studies on the fate of chemicals misinterpreted volatilization losses as chemical or biological transformations. In the recent past, volatilization loss became recognized as a discrete process in the fate of organic compounds. Evaporation depends upon the equilibrium vapor pressure, diffusion (generally increasing inversely with molecular weight of the compound, and proportionally to turbulence), dispersion of emulsions, solubility, and temperature.

In general, the volatilization rate, R_v , is a first-order kinetic process (Appendix D-4; Liss and Slater, 1974; Mackay and Leinonen, 1975). For highly volatile compounds and for Henry's law constant $H_c > 3000$ torr M^{-1} , volatilization rate is determined by the diffusion through the liquid-phase boundary layer (Appendix D-5). In cases where $H_c < 10$ torr M^{-1} , the diffusion through the gas-phase boundary layer limits the volatilization rate. For conditions between 3000 and 10 torr M^{-1} , both liquid and gas phase are significant. In these cases, the mass transport coefficients of the chemical in the water column are estimated from representative values of mass transport coefficient for oxygen reaeration and water where liquid-phase resistance and gas-phase resistance are controlled, respectively.

Chemical Transformations

Chemical alteration of an organic compound in the environment could arise from one or more of the following reactions: (i) redox behavior, (ii) hydrolysis, (iii) halogenation-dehalogenation, and (iv) photochemical breakdown. The extent to which an organic compound breaks down to simple molecules in order to become part of natural biological processes will determine its persistence and toxicity. Studies have shown that some of these transformation processes can convert a compound into a derivative that may be substantially more hazardous and persistent. Examples are the photochemical degradation of hydrocarbons and nitrogen oxides to produce a smog that has more direct and active effect on the environment and its inhabitants. Thus, transformations magnify the environmental effects of organic compounds. Halogenation of aromatic compounds and aliphatic hydrocarbons are environmentally significant. Many active systems affecting such transformations occur in the biota owing to their catalytic enzymes and abundant bioenergy. Some of the transformation reactions are briefly described below.

Redox Behavior

A chemical reaction is one in which only neutral molecules and positively or negatively charged ions take part; electrons are not involved. An electrochemical reaction is one that involves, besides molecules and ions, negative electrons (e) arising from a metal or other substance. The reaction that liberates electrons is called an oxidation reaction, and the one that consumes electrons, a reduction reaction (Appendix D-6). pH and $P\epsilon$ are analogous, and the value of $P\epsilon$ will indicate the electrochemical direction of this environment; oxidation if this value is above the equilibrium potential, $P\epsilon^\circ$ and reduction if the $P\epsilon$ is below $P\epsilon^\circ$ value. Electrochemical thermodynamics, within limits, help to understand the complex transformation reactions and also predict certain species in the aqueous environment. It should be understood clearly that a thermodynamically feasible reaction need not take place unless it is kinetically fast. Hence, these equilibrium considerations should be used in conjunction with electrochemical kinetics to determine the affinity and the speed of a given redox reaction.

Many organic compounds can either accept or donate electrons, forming reduced or oxidized species. This is environmentally significant since the oxidized and reduced forms of an organic compound may have totally different biological and ecological properties. The rate of loss of a chemical by oxidation or reduction is generally a second-order kinetic reaction. For example, oxidation is expressed by equation (2):

$$-\frac{dc}{dt} = k_{ox} [ox] [C] \quad (2)$$

where k_{ox} = second-order rate constant for the oxidation of the chemical, C , and $[ox]$ and $[C]$ are the concentrations of oxidant and chemical, respectively. The use of k_{ox} in estimating oxidation half-lives of chemicals has been reviewed by Mill (1979) and Mill *et al.* (1979).

Hydrolysis

The ionic product (k_w) of water is $10^{-14} = ([H] + [OH^-])$ indicating low dissociation. However, the dissociated macro- and microsolute usually interact with water, changing the concentration of H^+ and OH^- ions substantially. Fresh waters generally vary in pH from 6.0 to 8.0. However, lower pHs are encountered with leachates from mine wastes. A hydrolysis reaction is one where hydrogen, hydroxyl radicals, or the water molecule interacts with the organic compound depending on the pH and polarity of the site of attack on the molecule. Hydrogen ions lacking electrons are called electrophiles and essentially attack a site with a negative charge or lone pair

of electrons or unsaturated compounds possessing a double bond. Typical examples are acid-catalyzed cleavage of ester linkage. On the other hand, nucleophiles, rich in electrons, interact with positive sites on the molecule being attacked.

The kinetics of the rate of hydrolysis of a chemical compound are described in Appendix D-7. The use of hydrolysis data in calculating the hydrolytic half-lives has been reviewed by Mabey and Mill (1978).

Halogenation-Dehalogenation

Halogenation of organic compounds occurs mostly under synthetic conditions or in drastic environments. Mild chlorination reactions are possible in natural waters in zones of mixing of different effluents or mixing of industrial with municipal effluents containing residual chlorine. Chlorine can be sorbed by algae and released with a time delay, and this could serve as a chlorine reservoir in natural waters.

Dehalogenation reactions occur in the environment and could be due to a combination of reactions such as hydrolysis and disproportionation reactions. The hydrolysis reactions can occur under neutral conditions with water nucleophile attack or under basic conditions, the OH^- ion being the nucleophile. The half-lives of some halogenated compounds at pH 7 and 25°C are given in Table 2.1. These conditions are relatively closer to the natural aquatic environment. Many halogenated compounds are susceptible to hydrolysis owing to charge separation between halogen atoms and carbon atoms. Chlorinated biphenyls are relatively inert to hydrolysis and consequent breakdown in the environment. Any breakdown of PCBs must be due to processes other than hydrolysis.

Table 2.1. Hydrolytic half-lives of some halogenated compounds.

Compound	Half-life ($t_{1/2}$)
CH_3F	30 years
CH_3Cl	339 days
CH_3Br	20 days
CH_3I	110 days
$\text{CH}_3\text{CHClCH}_3$	38 days
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$	26 days
$\text{C}(\text{CH}_3)_3\text{Cl}$	23 seconds
CH_2Cl_2	704 years
CHCl_3	3500 years
CHBr_3	686 years
CCl_4	7000 years
$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	15 hours

Source: Mabey and Mill (1978).

Photochemical Breakdown Processes

Structural changes of a molecule induced by electromagnetic radiation in the near ultraviolet-visible light range (240–700 nm) are called photochemical reactions. However, ionizing radiation is not present in a concentrated form to inflict any molecular alterations. Photochemical reactions could take place either by (i) direct absorption by the molecule of an incident radiation leading to an excited state with subsequent deactivation reactions, or (ii) electron or energy transfer through an intermediate called a photosensitizer. In some cases, photochemical reactions are followed by secondary dark (thermal) reactions. Photochemical absorption can occur only when the electronic changes of the molecule correspond to the wavelength of the incident radiation. Absorption of light energy in terms of photons results in the excitation of an electron from a lower to a higher orbital. The excitation of an electron can have several possible transitions as described in Figure 2.1.

Fundamental spectral data for organic molecules that undergo such electronic transitions, wavelength of maximum response (λ_{\max}), and their molar extinction coefficients (ϵ) (magnitude of the ability to absorb photons) are given in Table 2.2. The higher the value of λ_{\max} , the lower is the energy difference in electronic transitions. Thus, the structure of an organic compound will determine whether or not a photochemical reaction takes place in the environment. Ultraviolet absorption is common with many aromatic and unsaturated compounds. Generally, an increase in the number of conjugated double bonds in the molecule will decrease the energy required for an electronic transition.

Thus, the reactions that are normally possible at the far ultraviolet region become feasible at the near ultraviolet-visible range. Figure 2.2 presents the energies of electromagnetic radiations at different wavelength regions and dissociation energies of some typical diatomic chemical bonds. Comparison

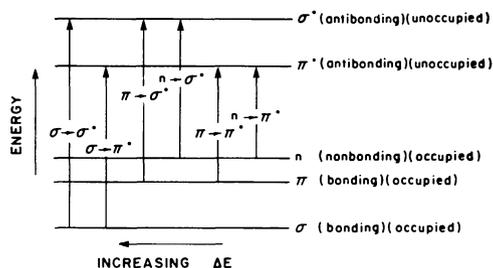


Figure 2.1. Transition of excited electrons from lower to higher orbitals. (From Tinsley, 1979).

Table 2.2. Spectral data of some chromophores.

Chromophore	Functional group	Electron transition	λ_{\max}	ϵ_{\max}
-O-	CH ₃ OH	n → σ^*	1830	500
-S-	C ₆ H ₁₃ SH	n → σ^*	2240	126
-N-	(CH ₃) ₃ N	n → σ^*	2270	900
-Cl:	CH ₃ Cl	n → σ^*	1730	100
-Br:	CH ₃ Br	n → σ^*	2040	200
-I:	CH ₃ I	n → σ^*	2580	378
-C=C-	H ₂ C=CH ₂	π → π^*	1710	15,500
-C≡C-	HC≡CH	π → π^*	1730	6000
>C=O	(CH ₃) ₂ CO	π → π^*	1890	900

Source: Tinsley (1979).

λ in Å unit, Å° = 0.1 nm

$$\epsilon = \frac{\text{O.D.}}{c \times d} \quad \text{where O.D.} = \text{optical density}$$

c = concentration in moles/L
 d = length of optical cell, in mm.

of incident radiation energies with bond dissociation energies will provide an estimate of bond cleavage in a given wavelength region (Figure 2.2).

The excited organic molecule decays rapidly, returning either to the ground state after energy loss through collision and/or secondary radiations and/or chemical changes. The last category includes (i) ionization of the molecule resulting from ejection of an electron, (ii) molecular disproportionation yielding free radicals, (iii) molecular isomerization, and (iv) dark, thermal reactions involving free radicals and other molecules present in the environment. The rate of loss of a chemical ($-dc/dt$) by either direct or indirect photochemical reactions may be expressed by simple first-order kinetic expressions (Appendix D-8 and D-9).

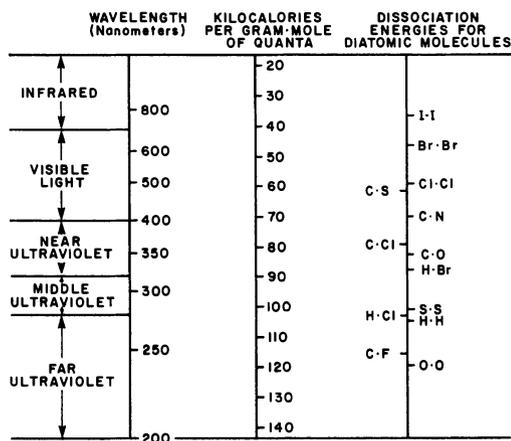


Figure 2.2. Comparison of radiation and bond energies. (From Tinsley, 1979.)

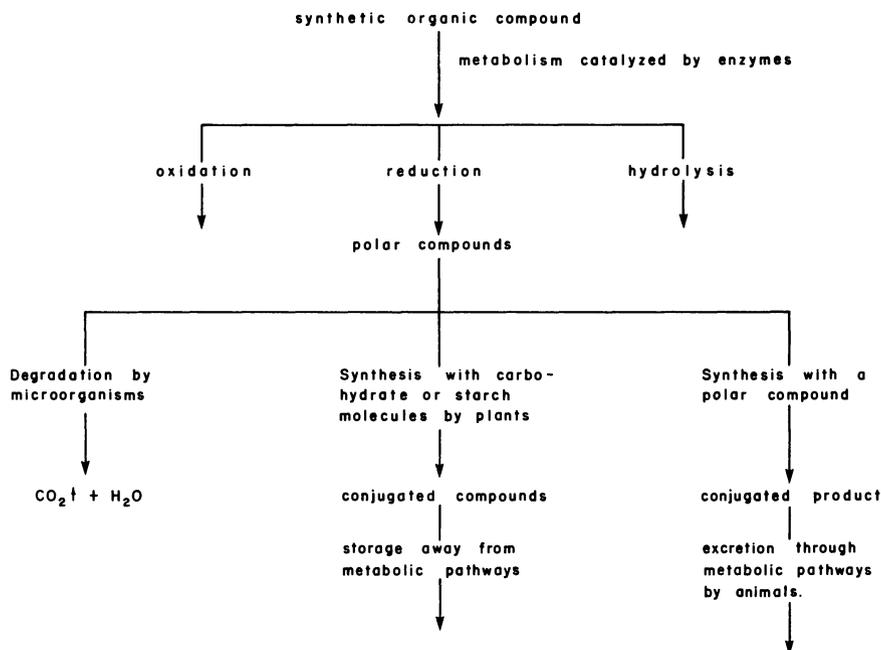


Figure 2.3. Possible pathways of enzymatic transformations of organic compounds.

Metabolic Transformations

Many microorganisms and biota in general develop resistance to most organic chemicals and transform them to compounds that are not toxic to themselves but may be toxic to the total environment. In general, the following enzyme-catalyzed reactions are possible in the metabolic transformation of organic compounds (Figure 2.3).

It is essential to determine the kinetics of these transformation reactions as a function of environmental variables to assess the half-life of the chemical under consideration. The rate for the biotransformation will be a function of the biomass and the chemical's concentration under given environmental conditions. When the organic compound is utilized as a carbon source, the growth rate of the organism is dependent upon the concentration of the former (Appendix D-10, D-11, D-12, and D-13). The half-life of the chemical under degradation ($t_{1/2}$ at a given cell concentration) can be calculated (Appendix D-14). In deriving this equation (Appendix D-14), it is assumed that the microbial community has already been acclimated to the chemical and that there is no lag time involved in the production of the necessary level of biodegrading organisms or mutants or the enzyme(s). However, when the chemical is newly introduced to the environment, the