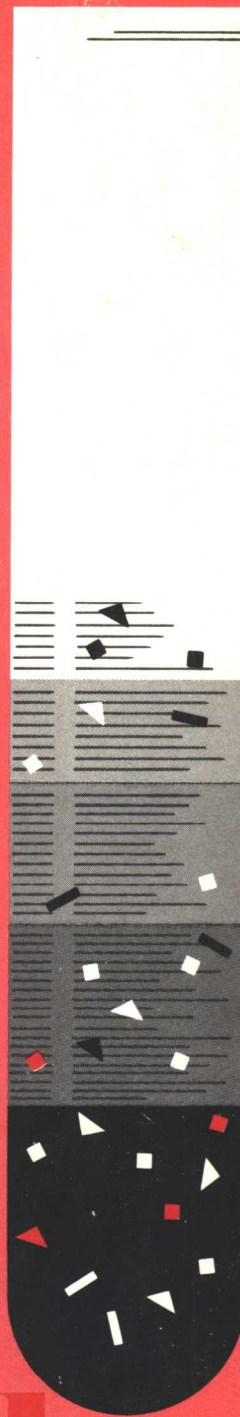


Chemical Concepts In Pollutant Behavior

Ian J. Tinsley

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Edited by: Robert L. Metcalf and Werner Stumm



Chemical Concepts in Pollutant Behavior

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SERIES PREFACE

Environmental Science and Technology

The Environmental Science and Technology Series of Monographs, Textbooks, and Advances is devoted to the study of the quality of the environment and to the technology of its conservation. Environmental science therefore relates to the chemical, physical, and biological changes in the environment through contamination or modification, to the physical nature and biological behavior of air, water, soil, food, and waste as they are affected by man's agricultural, industrial, and social activities, and to the application of science and technology to the control and improvement of environmental quality.

The deterioration of environmental quality, which began when man first collected into villages and utilized fire, has existed as a serious problem under the ever-increasing impacts of exponentially increasing population and of industrializing society. Environmental contamination of air, water, soil, and food has become a threat to the continued existence of many plant and animal communities of the ecosystem and may ultimately threaten the very survival of the human race.

It seems clear that if we are to preserve for future generations some semblance of the biological order of the world of the past and hope to improve on the deteriorating standards of urban public health, environmental science and technology must quickly come to play a dominant role in designing our social and industrial structure for tomorrow. Scientifically rigorous criteria of environmental quality must be developed. Based in part on these criteria, realistic standards must be established and our technological progress must be tailored to meet them. It is obvious that civilization will continue to require increasing amounts of fuel, transportation,

industrial chemicals, fertilizers, pesticides, and countless other products; and that it will continue to produce waste products of all descriptions. What is urgently needed is a total systems approach to modern civilization through which the pooled talents of scientists and engineers, in cooperation with social scientists and the medical profession, can be focused on the development of order and equilibrium in the presently disparate segments of the human environment. Most of the skills and tools that are needed are already in existence. We surely have a right to hope a technology that has created such manifold environmental problems is also capable of solving them. It is our hope that this Series in Environmental Sciences and Technology will not only serve to make this challenge more explicit to the established professionals, but that it also will help to stimulate the student toward the career opportunities in this vital area.

Robert L. Metcalf
Werner Stumm

Preface

The objective of this text is to demonstrate how chemical concepts can be applied to define the behavior of chemicals in the environment and to present such an analysis at a level comprehensible to those who have had two years of college chemistry. The outline has been developed over the past seven years while teaching a course with this focus.

The emphasis is on the properties of the chemical as they relate to environmental behavior rather than the chemistry of pollution control systems. Two fundamental questions need to be addressed—What is the potential for a compound to move from the site of release? What is its tendency to be transformed in the environment to derivative compounds?

Answers to the first question involve those properties of a chemical which determine its tendency to adsorb on or leach through soil, evaporate into the atmosphere, or be absorbed across a biological membrane. Chapter 1 is concerned primarily with physical chemical properties as they relate to these processes.

After release into the environment a compound may be photochemically degraded, oxidized or reduced, hydrolyzed, or metabolized by organisms. The important considerations are: Which compounds react in a given transformation process? What products will be formed? At what rate do these changes occur? These are discussed in Chapter 2.

Two shorter chapters, 3 and 4, discuss the tendency for compounds to bioconcentrate and distribute in food chains and the analysis of environmental samples. Bioconcentration is treated as a kinetic process and the discussion of biological distribution shows the interface between chemical properties and some physiological and ecological processes. The objective of the analytical section is to provide the reader with sufficient perspective to make a judgment as to the validity of reported analytical information. Consequently the limitations of analytical techniques are discussed rather than the procedural details. The final chapter analyzes several situations

involving the distribution of chemicals in the environment, providing a synthesis of some of the concepts presented.

An understanding of these ideas is important to professionals in many areas. Environmental health scientists concerned with the toxicological effects of environmental agents can use these concepts to define exposure and predict hazard. Information on environmental behavior also provides a basis for developing strategies for preventing or minimizing exposure. Effective use of pesticides—maximum effect on the pest with minimum side effects—in agriculture, forestry, and public health is predicated on the definition of their environmental behavior. Distribution of chemical pollutants is often an important consideration in water pollution biology. Formal training in any of these fields requires background in chemistry, at least through organic chemistry, hence the level of presentation in this text. This is not to say that these concepts are not of interest to chemistry students who respond positively to the realization that physical chemistry can be very practical!

Only in recent years has environmental behavior become a significant consideration in the use of all industrial chemicals. In the United States, congressional action has given regulatory agencies the responsibility of reviewing thousands of compounds from this perspective. One consideration in such an analysis has to be the chemical properties of these different compounds. A comprehensive analysis of the impact of a chemical in the environment requires input from many disciplines. Hopefully this text illustrates this while clearly defining the role of the chemist.

For the most part, the outline of this text parallels research programs in the Department of Agricultural Chemistry at Oregon State University. In teaching the course and in preparing the manuscript I have relied heavily on my colleagues specializing in these areas for critical discussions of subject matter, providing illustrative material, and so on. In particular the assistance of Dr. D. R. Buhler, Dr. C. T. Chiou, Dr. M. L. Deinzer, and Mr. M. L. Montgomery has been invaluable. The encouragement and support of Dr. V. H. Freed, head of the department, is also acknowledged. The final draft was typed by Mrs. K. Miller, and Mrs. L. Haygarth drew the figures. Mrs. C. Day's patience in handling the initial transcriptions and ability to manage many of the other details involved in the preparation of the manuscript are much appreciated.

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Corvallis, Oregon
January 1979

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I

Chemodynamics

If a chemical is introduced into the environment, there is a certain probability that it can move from the point where it was released. The distribution of some chemicals may even be global in scope. This may result from their use over a broad geographical area or it may involve their ability to move in the environment. It is possible that problems associated with the widespread distribution of chemicals in the environment could have been avoided or at least minimized if the chemodynamic properties of each compound were better understood when the compound was first introduced. However, having been faced with the problem has provided the incentive to outline the concepts and assemble necessary information to define the phenomenon. Such an exercise will hopefully provide a better understanding of present situations and give the basis for making predictions which will eliminate future problems.

The different pathways are summarized in Fig. 1.1. First of all, there can be movement within each compartment; for example, a chemical introduced into an aquatic environment can move to the extent that the water is moving, whether or not the chemical is in solution or adsorbed on a particle. This type of movement would be defined by the appropriate hydrological parameters. The chemical may also find its way into the atmosphere where it might be transported in the atmospheric currents: in this situation the appropriate meteorological phenomena will determine the rate and direction of movement. A similar situation prevails in the biological compartment, where the distribution of a chemical in an animal or a plant is dependent upon the transport processes in the organism. In an animal this would be the vascular system; in a plant, it would depend on transport in the phloem. In a much broader context, the transport of a chemical in an ecosystem must have some relationship to the overall mass flow in the system since the chemical moves with the food constituents of the various components in the ecosystem.

2 Chemodynamics

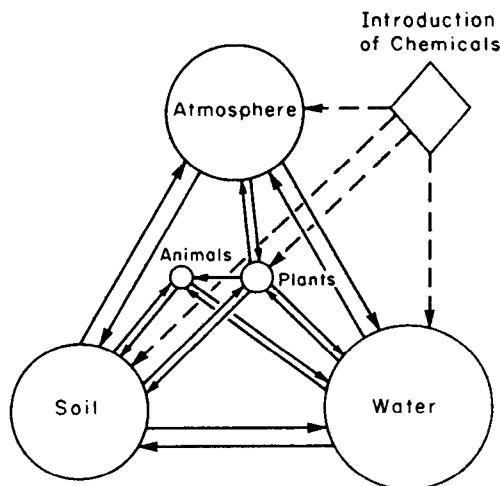


Fig. 1.1 Processes by which compounds are distributed in the environment.

The movement of a chemical in the soil environment is somewhat different from those examples cited above in that the movement of the chemical is accomplished primarily by a diffusion or mass transport process. The soil particles themselves may move in the air or water environment and carry adsorbed particles with them; in the latter cases, this movement would be a function of those factors governing the movement in air or water. In these situations, where the chemical is moving within a compartment, the movement is primarily a function of the characteristic transport processes of that compartment. The effect of the characteristics of the chemical being transported are minimal.

When one is concerned with the tendency of a chemical to move between compartments, the role of the chemical properties of the material become most significant. The determining parameters are the thermodynamic and the kinetic factors bearing on the transformations. In natural systems, one is not dealing with truly reversible equilibrium systems. However, an assumption of an equilibrium can provide some indication of the trend for a particular transformation between compartments.

If one considers the various interfaces, one can briefly enumerate those properties of the chemical that are of consequence in defining the possibility for movement between those compartments.

Water \rightleftharpoons Air

This interface is concerned primarily with the vapor pressure of the compound and its water solubility

Water \rightleftharpoons Soil	Movement of a chemical across this interface is primarily an adsorption-desorption process, involving the solubility of the chemical in water and the factors influencing its adsorption on the solid phase. Solubility, partition coefficients, and heats of solution become significant in this regard
Soil \rightleftharpoons Air	This is probably the most complex system in that one is concerned both with the adsorption of the chemical on the soil surface, its vapor pressure, and also the influence of water as it may affect the movement of the chemical to the soil-air interface
Physical \rightleftharpoons Biological	This interface is distinct from the other three in that one is concerned with the movement of a chemical across a membrane; an absorption process in contrast to a surface adsorption situation.

This discussion is concerned with the following topics:

Adsorption	}—soil–water interface
Movement through soil	
Evaporation	}—movement into air from soil or water
Absorption	

with primary emphasis being the definition of how the properties of the chemical are involved in these different processes. The following approach is used in discussing each topic:

1. Each process is defined as concisely as possible, that is, the adsorption equilibrium or absorption through a membrane.
2. The properties of a chemical that determine its response in that process are emphasized.
3. The overall significance of these factors in the environmental distribution of chemicals is evaluated.

The primary objective is to predict the distribution of a compound in the environment based on its chemical properties. This treatment has been termed **Chemodynamics**.¹

1. Physical Chemical Parameters

Before discussing these four processes a brief analysis of some of the more important physical chemical properties is appropriate.

1.1 Solubility

The tendency of a chemical to move from the pure solid into solution is usually expressed as the concentration of a saturated solution in equilibrium with excess solid. This equilibrium process is dependent on the balance between those forces holding the molecules or ions in the solid and the solvating ability of the particular solvent. The measurement of this parameter does not usually impose excessive demands on chemical techniques, however, the measurement of the solubility of very sparingly soluble compounds requires specialized procedures, and introduces some conceptual problems. This situation happens to be of some consequence in that many of those compounds that are known to be significant environmental contaminants are those that have very low water solubilities.

The problem is well illustrated by the variability in the values quoted for the solubility of DDT.² Values ranging from 1–1000 ppb have been reported.

In measuring the solubility of compounds such as DDT, one has to be concerned with the problem of adsorption to the glass vessels, the sampling containers, as well as the possibility of residues in the solution which might provide an adsorptive surface for the compound. Bowman et al.² reported a solubility for DDT of 1.2 ppb or less at 25°C using the following procedure:

1. An acetone solution of the radioactive DDT was added to a flask.
2. Acetone was removed under vacuum.
3. Distilled water was added.
4. The mixture was heated and shaken for 1 hr at 90–100°C.
5. The resulting solution was shaken for 1 week at 25°C.
6. The solution was then filtered through a fritted glass funnel with pores 4.5–5 microns.
7. Samples were taken and allowed to stand or centrifuged and the radioactive DDT extracted and counted.

The values obtained for the solubility of DDT were dependent on the procedures used, particularly whether or not the sample is centrifuged. The value of 1.2 ppb was obtained after centrifuging for 12 hr at 39,000 rpm. This raises a conceptual problem as to what really is the solution process of DDT in

TABLE 1.1 Solubilities of PCB Isomers Determined by Different Procedures

Isomer	Solubility Determined by Haque and Schmedding ^{3a} (ppm)	Solubility Determined by Wallnöfer et al. ^{4b} (ppm)
2, 4'-Dichloro-	0.638	1.85-1.90
2, 2', 5, 5'-Tetrachloro-	0.027	0.046
2, 4, 5, 2', 5'-Pentachloro-	0.0010	0.028-0.035

^a Compound dispersed in a large carboy and stirred for one day. Solution allowed to stand for 6 months before sampling. The solution was *not* stirred before sampling and precautions were taken to avoid losses through adsorption on the surface of sampling equipment.

^b Hexane solution pipetted into a flask and the hexane evaporated. Water was added and the solution shaken for 10 days at 30°C. After equilibration for 3 hr at 22-24°C, a sample was withdrawn through a filter and analyzed.

water. Are the particles sedimenting during centrifugation actually soluble, or what is their status?

Another illustration of this problem is summarized in Table 1.1 with several PCB isomers. Solubilities vary by a factor of from 2 to 4, with the different procedures used. One might conclude that the procedures used by Haque et al.³ would tend to be the more reliable since the possibility of suspended particles contributing to the solubility would have been minimized through the long standing period. The other procedure, with an extensive shaking over a 10-day period and only a 3-hr standing period, would suggest that too short a time was allowed for the system to equilibrate.

Since many of the chemicals of significance in the environment have very low solubilities, one needs to be aware of the problems involved in measuring this parameter. Thus, in searching the scientific literature for this information, one should be aware of the procedures used for obtaining these quantities. It will be a real advantage if more than one investigator has made a determination of solubility for a given compound.

1.2 Equilibrium Vapor Pressure

The equilibrium system involved is comparable to that of solubility in that one is measuring the escaping tendency from a liquid or solid. The equilibrium vapor pressure of a gas can be conceived as the solubility of the material in air. The vapor pressure of a liquid or solid is the pressure of the gas in equilibrium with the liquid or solid at a given temperature.

6 Chemodynamics

The thermodynamic expression (Clausius–Clapeyron equation) describing this equilibrium is

$$\frac{d \ln p}{d(1/T)} = \frac{-\Delta H}{R}$$

where ΔH is the heat of vaporization, T the absolute temperature, and R the universal gas constant. One often sees the equation expressed in an integral form:

$$\log p = A - BT$$

in which $B = -\Delta H/2.303R$ — ΔH is assumed to be constant. Since this relation is linear only over a relatively narrow temperature range other equations have been suggested such as the Antoine equation:

$$\log p = A - \frac{B}{t + C}$$

where A , B , and C are constants characteristic of the substance and temperature range and t the temperature in °C. Recent compendia of vapor pressures^{5,6} use the latter equation, while vapor pressure values listed in International Critical Tables use the former.

The natural tendency is to consider only those materials which are quite volatile as having significant vapor pressures. However, even though very small, the vapor pressure of solids can be significant under certain circumstances in defining the distribution of a chemical in the environment. For example, materials such as DDT and dieldrin* and lindane do have finite vapor pressures, that are certainly of some consequence in the behavior of these compounds in the environment.

The concentration term **vapor density** is often used in discussion of vapor phase systems. Vapor density is related to equilibrium vapor pressure through the equation of state for a gas:

$$PV = nRT$$

* It is not possible to incorporate structural formulas for the different compounds used to illustrate the different concepts. If needed, such information can be obtained from the following publications:

The Merck Index—An Encyclopedia of Chemicals and Drugs, Merck and Co., Inc., Rahway, N.J., 1976.

Pesticide Dictionary, Meister Publishing Co., Willoughby, Ohio, 1978.

E. Y. Spencer, Ed., *Guide to the Chemicals Used in Agriculture*, Research Branch, Agriculture Canada, Ottawa, Canada, 1973.