Chemical Fate and Transport in the Environment 2nd Ed

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SECOND EDITION

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PREFACE

This textbook is expanded and extensively revised from the first edition of *Chemical Fate and Transport in the Environment*. It is intended for a one-semester course covering the basic principles of chemical behavior in the environment. The approach is designed to include students who are not necessarily pursuing a degree in environmental science, but whose work may require a basic literacy in environmental transport and fate processes.

Written as a survey text suitable for graduate students of diverse backgrounds, this book may also be appropriate for use in some undergraduate curricula in environmental engineering. Concepts are developed from the beginning, assuming only prior familiarity with basic freshman chemistry, physics, and math. Certain simplifications are made, and the material is intentionally presented in an intuitive fashion rather than in a rigorously mathematical framework. Nevertheless, the goal is to teach students not only to understand concepts but also to work practical, quantitative problems dealing with chemical fate and transport.

Depending on the nature of the class, the instructor may wish to spend more time with the basics, such as the mass balance concept, chemical equilibria, and simple transport scenarios; more advanced material, such as transient well dynamics, superposition, temperature dependencies, activity coefficients, redox energetics, and Monod kinetics, can be skipped. Similarly, by omitting Chapter 4, an instructor can use the text for a water-only course. In the case of a more advanced class, the instructor is encouraged to expand on the material; suggested additions include more rigorous derivation of the transport equations, discussions of chemical reaction mechanisms, introduction of quantitative models for atmospheric chemical transformations, use of computer software for more complex groundwater transport simulations, and inclusion of case studies and additional exercises. References are provided

with each chapter to assist the more advanced student in seeking additional material.

This book was originally based on notes for a class titled Chemicals in the Environment: Fate and Transport, which the first author has taught for 10 years at the Massachusetts Institute of Technology. Several classes have now used the first edition of the textbook; each time, we have benefited from thoughtful feedback from students and teaching assistants, and we have included many of their suggestions in this second edition. We hope to hear of the experiences of others, students and instructors alike, who use this text in the coming years. We hope you find the book helpful, even enjoyable, and come away sharing both our enthusiasm for the fascinating environment we inhabit and our desire to treat the environment from a basis of appreciation and understanding.

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Basic Concepts

1.1 INTRODUCTION

"By sensible definition any by-product of a chemical operation for which there is no profitable use is a waste. The most convenient, least expensive way of disposing of said waste—up the chimney or down the river—is the best" (Haynes, 1954). This quote, describing once common industrial waste disposal practices, reflects the perception at that time that dispersal of chemical waste into air or water off the factory site meant that the chemical waste was gone for good. For much of the 20th century, many industries freely broadcast chemical waste into the environment as a means of disposal. Other human activities, including use of pesticides and disposal of household waste in landfills, also contributed enormous loads of anthropogenic chemicals to the environment.

Today, however, not only have the gross pollution effects of emissions from stacks, pipes, and dumps become evident, but more subtle and less predictable effects of chemical usage and disposal have also manifested themselves. Some lakes, acidified by atmospheric deposition from power plants, smelters, and automobiles, have lost fish populations, while other lakes have burgeoned with unwanted algal growth stimulated by detergent disposal,

septic leachate, and urban and agricultural runoff. Municipal wells have been shut down due to chemical contamination emanating from landfills. Populations of several species of birds of prey have been decimated by pesticides that have become concentrated in their tissues and have adversely affected their reproduction. Humans have been poisoned by polychlorinated biphenyls (PCBs) and by mercury acquired from the environment via the food chain. Even nontoxic, seemingly harmless chlorofluorocarbons (CFCs) from spray cans and refrigerators have threatened the well-being of humans as well as the functioning of ecosystems by creating a hole in Earth's protective ozone shield.

Nevertheless, it is neither possible nor desirable for modern societies to stop all usage or environmental release of chemicals. Even in prehistoric times, tribes of troglodytes roasting hunks of meat over their fires were unknowingly releasing complex mixtures of chemicals into the environment. It is imperative, however, that modern societies understand their environment in sufficient detail so that accurate assessments can be made about the environmental behavior and effects of chemicals that they use. This includes an understanding of both chemical *transport*, referring to processes that move chemicals through the environment, and chemical *fate*, referring to the eventual disposition—either destruction or long-term storage—of chemicals. It then can be hoped that societies will make intelligent, informed decisions that will protect both human health and the environment, while allowing human beings to enjoy the benefits of modern technology.

This book presents the principles that govern the fate and transport of many classes of chemicals in three major environmental media: surface waters, soil and groundwater (the subsurface), and the atmosphere. These several media are treated in one book for three related reasons. First, this is primarily an introductory textbook, and a broad scope is most appropriate to the student who has not specialized in a particular environmental medium. Second, chemicals released into the environment do not respect the boundaries between air, water, and soil any more than they respect political boundaries. Because exchanges among these media are common, modeling a chemical in any single medium is unlikely to be adequate for obtaining a full description of the chemical's fate. Third, a great deal of insight can be gained by comparing and contrasting chemical behavior in surface waters, soil and groundwater, and the atmosphere. For example, although the fact is not immediately apparent in much of the literature, the mathematics describing physical transport in each medium are almost identical; the transport equation that models the mixing of industrial effluent into a river is also useful for describing the movement of contaminants in groundwater or the mixing of air pollutants in the atmosphere. Contrasts are also instructive; for example, the dominant fate process for a chemical in the atmosphere may be photode-
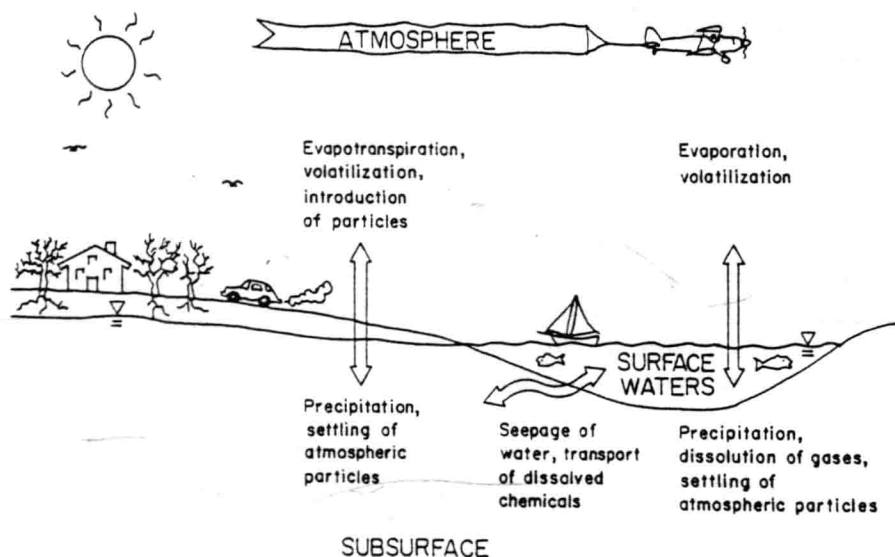
FIGURE 1-1   Three major environmental media: surface waters, the subsurface (soil and groundwater), and the atmosphere. Although each medium has its own distinct characteristics, there are also many similarities among them. Few chemicals are restricted in their movement to only one medium; thus chemical exchanges among the media must be considered. Several very generalized exchange processes between media are shown.

gradation, whereas in the subsurface environment, biodegradation of the chemical may dominate.

Knowledge of the principles underlying the fate and transport of chemicals in the environment allows problems ranging from local to global scales to be defined and analyzed. This first chapter presents fundamental concepts that apply universally to any environmental medium. The subsequent three chapters focus on surface waters, the subsurface environment, and the atmosphere, respectively; see Fig. 1-1 for a diagram of some of the interrelationships among these media. In each chapter, each medium is discussed in terms of its basic physical, chemical, and biological attributes; then the fate and the transport of introduced chemicals are considered.

1.2 CHEMICAL CONCENTRATION

Perhaps the single most important parameter in environmental fate and transport studies is chemical *concentration* (C). The concentration of a chemical is a measure of the amount of that chemical in a specific volume or mass of air, water, soil, or other material. Not only is concentration a key quantity in fate

and transport equations; a chemical's concentration in an environmental medium also in part determines the magnitude of its biological effect.

Most laboratory analysis methods measure concentration. The choice of units for concentration depends in part on the medium and in part on the process that is being measured or described. In water, a common expression of concentration is mass of chemical per unit volume of water. Many naturally occurring chemicals in water are present at levels of a few milligrams per liter (mg/liter). The fundamental dimensions associated with such a measurement are $[M/L^3]$. The letters M, L, and T in square brackets refer to the fundamental dimensions of mass, length, and time, which are discussed further in the Appendix. For clarity in this book, specific units, such as (cm/hr) or (g/m^3), either are free-standing or are indicated in parentheses, not in square brackets.

Another common unit of concentration in water is *molarity*. Recall that a *mole* of a chemical substance is composed of 6.02×10^{23} atoms or molecules of that substance. Molarity refers to the number of moles per liter of solution and is denoted M, with neither parentheses nor square brackets around it in this book.

A related unit, *normality* (N), refers to the number of *equivalents* of a chemical per liter of water. An equivalent is the amount of a chemical that either possesses, or is capable of transferring in a given reaction, 1 mol of electronic charge. If a chemical has two electronic charge units per molecule, 1 mol of the chemical constitutes two equivalents [e.g., a mole of sulfate (SO_4^{2-}) is equal to two equivalents, and a one molar (1 M) solution of sodium sulfate (Na_2SO_4) is two normal (2 N)].

In soil, a chemical's concentration may be measured in units such as milligrams per cubic centimeter (mg/cm^3). Expressing concentration as mass per unit volume for soil, however, carries the possibility of ambiguity; soils undergo volume changes if they are compressed or expanded. Accordingly, it is often more useful to express soil concentration as mass per unit mass, such as (mg/kg) because the mass of soil does not vary with changes in the degree of compaction of the soil.

For air, which is highly compressible, expression of chemical concentration as mass per volume is even more ambiguous. The volume of a given mass of air changes significantly with changes in pressure and temperature, and thus the chemical concentration, when expressed as mass per volume, also changes. Consider the following situation: if initially there is 1 μg of benzene vapor (C_6H_6) per cubic meter of air and the barometric pressure decreases by 5%, the concentration of benzene as expressed in units of mass per volume also decreases by 5%, because the air expands while the mass of benzene remains constant. Expressing the benzene concentration as mass of benzene per mass of air removes all ambiguity because changes in temperature and pressure do not affect the mass of air present.

Ambiguity can also arise when a laboratory reports the concentration of a chemical that can exist in more than one form *(species)* without reference to a particular species. For example, if the concentration of nitrogen in a water sample is reported simply as 5 mg/liter, it is unclear whether 1 liter contains 5 mg of nitrogen atoms (N) or 5 mg of one of the nitrogen species present, such as nitrate (NO_3^-), nitrite (NO_2^-), ammonia (NH_3), or ammonium (NH_4^+). In such a situation, clarification from the laboratory performing the measurements must be obtained to understand the actual chemical mass present. Furthermore, if the species associated with a concentration is not known, a conversion from mass to moles is not possible. [Recall that to convert mass to moles, the molecular weight of the species measured must be known; the number of moles is then equal to the mass (in grams) divided by the molecular weight.]

Numerous other options exist for specifying a concentration; common ones are parts per thousand (ppt or ‰), parts per million (ppm), or parts per billion (ppb). For the soil and air cases just mentioned, ppm on a mass basis is numerically equal to milligrams (mg) of chemical per kilogram (kg) of soil or air. Parts per million is also sometimes used on a volume basis. This may be inferred from context or made clear by the term ppm(v); 1 ppm(v) of helium in air would correspond to 1 ml of helium in 1000 liters (1 m^3) of air. For water, the density of which is approximately 1 g/cm^3, parts per million corresponds to milligrams of chemical per liter of water (mg/liter) in dilute solutions.

No matter which units are used, however, concentration is the measure of interest for predictions of a chemical's effects on an organism or the environment. Concentration is also critical in one of the most important concepts of environmental fate and transport: the bookkeeping of chemical mass in the environment.

1.3 MASS BALANCE AND UNITS

1.3.1 MASS BALANCE AND THE CONTROL VOLUME

Three possible outcomes exist for a chemical present at a specific location in the environment at a particular time: the chemical can remain in that location, can be carried elsewhere by a *transport* process, or can be eliminated through *transformation* into another chemical. This very simple observation is known as *mass balance* or *mass conservation*. Mass balance is a concept around which an analysis of the fate and transport of any environmental chemical can be

organized; mass balance also serves as a check on the completeness of knowledge of a chemical's behavior. If, at a later time in an analysis, the original mass of a chemical cannot be fully accounted for, then there is an incomplete understanding of how transformation and transport processes are affecting that chemical. Accurate fate and transport modeling results from an understanding of every process contributing to the mass balance of a chemical.

Implicit in the application of the mass balance concept is the need to choose a *control volume*. A control volume is any closed volume, across whose boundaries we propose to account for all transport of a chemical, and within whose boundaries we propose to account for all the chemical initially present (stored), as well as all processes (*sources* or *sinks*) that produce or consume the chemical. The *mass balance expression* for any chemical in any control volume during any time interval can be written as

Change in storage of mass = mass transported in − mass transported out

+ mass produced by sources − mass eliminated by sinks.   [1-1a]

The mass balance expression in a control volume can also be written in terms of rates, that is, mass per time [M/T]:

Rate of change in storage of mass = mass transport rate in

− mass transport rate out + mass production rate by sources

− mass elimination rate by sinks.   [1-1b]

Control volumes are chosen to be convenient and useful. While the choice of a good control volume is somewhat of an art and depends on both the chemicals and the environmental locations that are of interest, the control volume boundaries are almost always chosen to simplify the problem of determining chemical transport into and out of the control volume.

As an example of an environmental pollution problem requiring the choice of a control volume, consider a lake that is receiving industrial effluent from a discharge pipe. To establish a useful volume within which we could describe the fate and transport of chemicals in the effluent, we might choose the entire lake, as shown in Fig. 1-2. The upper boundary of the control volume is then the lake surface; transport across this boundary is described by the general principles that govern chemical transport between water and air. For some *nonvolatile* chemicals (i.e., chemicals that do not rapidly move from a dissolved phase in the water to a gaseous phase in the air), this transport rate is negligible. For many other chemicals, enough knowledge exists to make reasonable estimates of the air/water exchange rate (based on factors such as the volatility of the chemical, the rate of chemical diffusion in water, and the amount of turbulence in the lake). The lower boundary of the control volume