The Handbook of EnvironmentalChemistry

Volume 2 Part A

Reactions and Processes

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Edited by O. Hutzinger

Preface

Environmental Chemistry is a relatively young science. Interest in this subject, however, is growing very rapidly and, although no agreement has been reached as yet about the exact content and limits of this interdisciplinary discipline, there appears to be increasing interest in seeing environmental topics which are based on chemistry embodied in this subject. One of the first objectives of Environmental Chemistry must be the study of the environment and of natural chemical processes which occur in the environment. A major purpose of this series on Environmental Chemistry, therefore, is to present a reasonably uniform view of various aspects of the chemistry of the environment and chemical reactions occurring in the environment.

The industrial activities of man have given a new dimension to Environmental Chemistry. We have now synthesized and described over five million chemical compounds and chemical industry produces about hundred and fifty million tons of synthetic chemicals annually. We ship billions of tons of oil per year and through mining operations and other geophysical modifications, large quantities of inorganic and organic materials are released from their natural deposits. Cities and metropolitan areas of up to 15 million inhabitants produce large quantities of waste in relatively small and confined areas. Much of the chemical products and waste products of modern society are released into the environment either during production, storage, transport, use or ultimate disposal. These released materials participate in natural cycles and reactions and frequently lead to interference and disturbance of natural systems.

Environmental Chemistry is concerned with reactions in the environment. It is about distribution and equilibria between environmental compartments. It is about reactions, pathways, thermodynamics and kinetics. An important purpose of this Handbook is to aid understanding of the basic distribution and chemical reaction processes which occur in the environment.

Laws regulating toxic substances in various contries are designed to assess and control risk of chemicals to man and his environment. Science can contribute in two areas to this assessment; firstly in the area of toxicology and secondly in the area of chemical exposure. The available concentration ("environmental exposure concentration") depends on the fate of chemical compounds in the environment and thus their distribution and reaction behaviour in the environment. One very important contribution of Environmental

Chemistry to the above mentioned toxic substances laws is to develop laboratory test methods, or mathematical correlations and models, that predict the environmental fate of new chemical compounds. The third purpose of this Handbook is to help in the basic understanding and development of such test methods and models.

The last explicit purpose of the Handbook is to present, in concise form, the most important properties relating to environmental chemistry and hazard assessment for the most important series of chemical compounds.

At the moment three volumes of the Handbook are planned. Volume 1 deals with the natural environment and the biogeochemical cycles therein, including some background information such as energetics and ecology. Volume 2 is concerned with reactions and processess in the environment and deals with physical factors such as transport and adsorption, and chemical, photochemical and biochemical reactions in the environment, as well as some aspects of pharmacokinetics and metabolism within organisms. Volume 3 deals with anthropogenic compounds, their chemical backgrounds, production methods and information about their use, their environmental behaviour, analytical methodology and some important aspects of their toxic effects. The material for volume 1, 2 and 3 was each more than could easily be fitted into a single volume, and for this reason, as well as for the purpose of rapid publication of available manuscripts, all three volumes were divided in the parts A and B. Part A of all three volumes is now being published and the second part of each of these volumes should appear about six months thereafter. Publisher and editor hope to keep materials of the volumes one to three up to date and to extend coverage in the subject areas by publishing further parts in the future. Plans also exist for volumes dealing with different subject matter such as analysis, chemical technology and toxicology, and readers are encouraged to offer suggestions and advice as to future editions of "The Handbook of Environmental Chemistry".

Most chapters in the Handbook are written to a fairly advanced level and should be of interest to the graduate student and practising scientist. I also hope that the subject matter treated will be of interest to people outside chemistry and to scientists in industry as well as government and regulatory bodies. It would be very satisfying for me to see the books used as a basis for developing graduate courses in Environmental Chemistry.

Due to the breadth of the subject matter, it was not easy to edit this Handbook. Specialists had to be found in quite different areas of science who were willing to contribute a chapter within the prescribed schedule. It is with great satisfaction that I thank all 52 authors from 8 contries for their understanding and for devoting their time to this effort. Special thanks are due to Dr. F. Boschke of Springer for his advice and discussions throughout all stages of preparation of the Handbook. Mrs. A. Heinrich of Springer has significantly contributed to the technical development of the book through her conscientious and efficient work. Finally I like to thank my family, students and colleagues for being so patient with me during several critical phases of preparation for the Handbook, and to some colleagues and the secretaries for technical help.

I consider it a privilege to see my chosen subject grow. My interest in Environmental Chemistry dates back to my early college days in Vienna. I received significant impulses during my postdoctoral period at the University of California and my interest slowly developed during my time with the National Research Council of Canada, before I could devote my full time to Environmental Chemistry, here in Amsterdam. I hope this Handbook may help deepen the interest of other scientists in this subject.

Amsterdam, May 1980 O. Hutzinger

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Transport and Transformation of Chemicals: A Perspective

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Introduction

Transport and transformation processes affecting chemical substances have been examined intensively since the beginnings of the environmental sciences. Most studies of chemical pollutants have been directed toward monitoring the distribution, concentration, and sometimes transformation products that result from releases of chemicals into the environment. Knowledge gained from these studies has often been enhanced when the investigations were guided or complemented by laboratory studies designed to indicate possible transformation pathways. Monitoring data, however, can rarely be generalized because little rationale exists for the direct extrapolation of monitoring results to other chemicals or other sites. Generalizing from the insights gained through monitoring programs and laboratory studies is primarily an exercise in perspective.

In this chapter, a specific aspect of transport and transformation – predicting the behavior of toxic organic chemicals in aquatic ecosystems – is examined from a systems perspective. This particular problem has only been a focus of research for a few years, but the general approach can be applied to many kinds of ecosystems, regional-scale problems, and chemicals. One result of this research has been the development of systematic and economical approachs for evaluating chemical behavior under the mandate of laws such as the U.S. Toxic Substances Control Act and for guiding product development. A primary concern behind these evaluations is the desire to curtail exposure of humans and other unintended receptors to deleterious levels of toxicants. The definition of those levels is in the province of toxicologists, who along with others may make a determination of "risk" or "hazard". Forecasting the toxicant concentrations (climate) that will prevail as a result of given input loadings, however, is a technical problem in the extrapolation of transport and transformation data to chemicals as yet unstudied and ecosystems as yet unpolluted.

Predicting the Fate of Organic Toxicants

Only in the recent past has research begun in earnest on the formidible problem of predicting the behavior of aquatic pollutants, although conceptually similar approaches have long been applied to air contaminants. In practice, the problem is often reduced to one of predicting the time-varying or ultimate concentration of a specific compound in various environmental compartments (epilimnion, hypolimnion, benthic sediments, etc.). Unfortunately, transformation of an organic toxicant does not always result in formation of a less objectionable compound. Thus impact may be related to the presence of products as well as the parent molecule. In this case, modeling the chemical species that causes the adverse impact requires treating the products exactly as parent compounds subject to distributed loadings (possibly with regeneration of the parent). Fortunately, this may not be necessary in practice for most organic compounds.

Physical Models

Two basic approaches are available for predicting the behavior of aquatic pollutants: physical or mathematical. The physical approach in one variation or another has led to much of our current understanding of environmental behavior. These methods range from laboratory and microcosm studies to full scale field experiments. Laboratory studies of microbial metabolism and photochemistry have long been guides to probable transformation products and, in the absence of degradation, have been cited as evidence of stability. Microcosms have contributed to our understanding of transport processes such as bioconcentration, volatilization, and sorption. They have been used extensively by Metcalf et al. [20] and others (Sanborn et al. [29]; Witherspoon et al. [36]; Isensee and Jones [6]), to indicate environmental behavior and to relate behavior to chemical properties. Microcosm work and field studies are increasingly important in the testing and validation of mathematical ecosystem models.

Physical simulations are likely to remain invaluable in environmental studies, especially for examining transformation pathways. On the other hand, like monitoring studies, they generally lack explicit rationale for direct extrapolation to other compounds or environments. Consequently, results from these studies are more indicative of what might happen than of what is probable in a given natural environment. Most importantly, microcosm results cannot be used for directly forecasting expected environmental concentrations.