PREDICTION OF THE ENVIRONMENTAL FATE OF CHEMICALS

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Published in association with
The British Petroleum Company p.l.c.

ELSEVIER APPLIED SCIENCE
LONDON and NEW YORK

ELSEVIER SCIENCE PUBLISHERS LTD
Crown House, Linton Road, Barking, Essex IG11 8JU, England

Sole distributor in the USA and Canada
ELSEVIER SCIENCE PUBLISHING CO., INC.
655 Avenue of the Americas, New York, NY 10010, USA

WITH 55 TABLES AND 54 ILLUSTRATIONS

British Library Cataloguing in Publication Data

Samiullah, Yusaf
Prediction of the environmental fate of chemicals.
1. Environment. Pollution by chemicals. Pollution of environment by chemicals. Simulations. Models
I. Title II. British petroleum company
628.5

ISBN 1-85166-450-5

Library of Congress Cataloging-in-Publication Data

Samiullah, Yusaf.
Prediction of the environmental fate of chemicals/Yusaf Samiullah.
p. cm.
'Published in association with the British Petroleum Company.'
Includes bibliographical references.
ISBN 1-85166-450-5
1. Pollution—Environmental aspects. I. British Petroleum Company. II. Title.
TD196.C45S36 1990
628.5'2—dc20 89–48129
CIP

Printed in Northern Ireland by The Universities Press (Belfast) Ltd.

Foreword

Concern over the effects of chemicals in the environment has been increasing for many years. Environmental contamination by DDT, Aldrin, Dieldrin, mercury, PCBs, organotins and many other substances are all part of the public consciousness and have led to widespread attention to this topic. Some of the concerns have arisen because human health has been affected when contaminants have been consumed via the food chain—for instance in the case of 'Minimata disease' in Japan. In other cases, direct effects on other components of ecosystems have given cause for alarm.

The toxic effects which any chemical can cause are a function of exposure and innate toxicity, i.e. of the ability to reach in sufficient quantity a site where a biological process can be disrupted and of the tendency to cause disruption when it gets there.

The processes by which chemicals reach sites of toxic action are the subject of this book, and are a fundamental consideration in ecotoxicology. When a chemical enters the environment e.g. via a spillage or in an effluent, it is potentially subject to a wide variety of processes which may eliminate it from the environment completely, modify it into a more or less harmful substance, or transfer it to another part of the environment. The processes involved are complex and highly variable, but it is essential to increase our understanding of them.

If the toxic effects of chemicals are to be controlled it is essential that the way that these processes occur can be predicted. Only then can the probable environmental hazards posed by new chemicals be assessed and appropriate control measures defined before the substance reaches the environment.

The need for methods to predict the environmental hazards posed by chemicals is internationally recognized, and various regulatory

schemes are in place to ensure that relevant data is gathered before the chemical is marketed. An essential element of such schemes is the ability to predict fate and behaviour of chemicals, often based on limited experimental data.

This book sets out some of the methods and principles which can be used in predicting and understanding the fate of chemicals in the environment. It is based on a report initially produced by MARC for BP, which was intended to summarize and review the data available. We are pleased to have been able to update the information and to publish it as a contribution to the development of a complex, but important, topic.

DR D. C. MONK
BP International Ltd

Acknowledgement

The author is grateful to Group Environmental Services, The British Petroleum Company, London, for sponsorship towards the preparation of this book under contract numbers XEC-935-176-1 and XEC-935-287-1/ZL47.

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Chapter 1

Introduction

This book was commissioned to review the state of the art of predicting the environmental fate of chemicals. It is intended to be a significant bibliographic resource, highlighting major developments in empirical and theoretical approaches to fate prediction. A very wide range of topics are considered, the intention being to provide the reader with insight into the nature of the task that may be required. Coverage of any particular subject may be expanded by reference to the appropriate paper(s) cited in the References and Bibliography.

Other than a means of recording present-day achievements and ambitions for chemical fate prediction in the air, water and soil, the book should provide sufficient information to enable science students, scientists, municipal administrators, politicians and the environmentally concerned general public to ask pertinent questions of those purporting to be experts in chemical fate prediction. Thus, given a list of potentially useful physicochemical parameters it should be possible to request not only that a commissioned study should incorporate some such parameters, but also that the study should justify the exclusion of others.

A primary aim of the book is to outline what it is about a chemical that determines where it will go in the environment if released. Inevitably it is impossible to consider a chemical in isolation—the medium to which it may be released and with which it may interact is an integral part of the fate prediction equation. Emphasis is placed on the final environmental medium to which a substance will migrate. The enormous area of chemical toxicity to living organisms is treated only in so far as bioconcentration can be anticipated.

Ideally, environmental fate prediction requires the acquisition of

three sets of data. Firstly, information is required on the physical and chemical properties of the substance under consideration. Secondly, data need to be collected on the routes of transfer to and through the environment for that substance. Finally, the resulting distribution of the substance in the various environmental phases should be ascertained. In practice, however, our current knowledge may cover, and then only partially, one or two of these sets of data. Predicting the environmental fate of chemicals may therefore call for extrapolation from confirmed fact to speculative distribution. Conversely, a knowledge of environmental distribution can itself provide clues as to the physical and chemical properties of molecules and yield information on likely environmental transfer and transformation processes.

The prediction of the environmental fate of chemicals may therefore be considered as an integrated process utilizing both preproduction information on chemical structure and properties, and postproduction information about the distribution of that chemical in the environment. An information hierarchy can be envisaged, with data on fundamental molecular properties of structure and energy being used to predict molar or bulk chemical properties dependent on molecular aggregations. Some molar properties, such as solubility, vapour pressure and partition coefficient, may be used, in conjunction with knowledge of natural chemical and physical pathways in the environment, to anticipate eventual environmental fate. For instance, the rate of volatilization of a chemical may be deduced from Henry's Law constant which in turn is derived from information on solubility and vapour pressure. These last two parameters are themselves calculable from a knowledge of molecular structure and boiling temperature. The relationships between molecular and molar properties of chemicals and the prediction of volatilization rate are illustrated in Fig. 1.1. Information on potential marketing trends, possible use, transport, storage and disposal of chemicals may provide a more obvious means of establishing primary sites of environmental contamination.

Further down the hierarchy, the environment itself may be conceptually split into three components, viz. the soil, aquatic and atmospheric phases. Prediction of ultimate chemical fate may require the subdivision of these units into smaller, and mathematically more manageable, portions. Such a multicompartmental construction can then be used to indicate data requirements for modelling studies. Data may simply be chemical concentrations measured in a number of media, or may involve quantified rates of chemical transfer between compartments or suppositions about degradative processes.

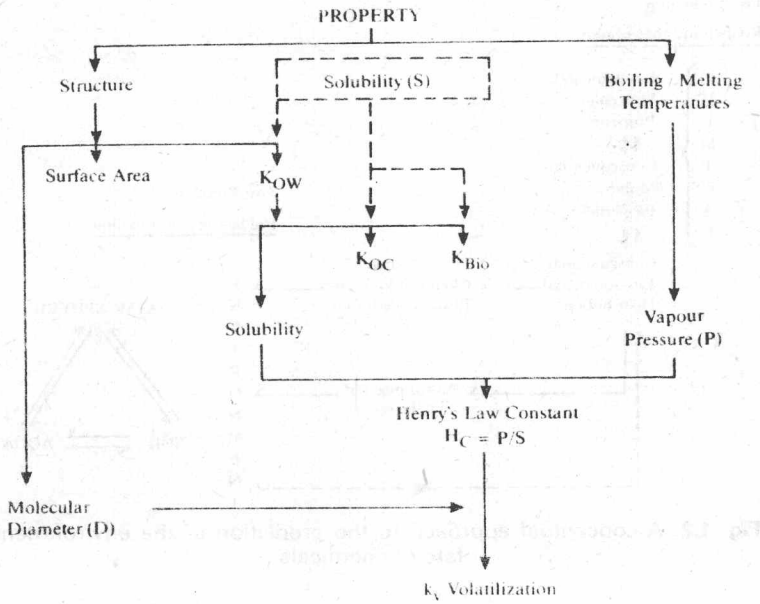


Fig. 1.1. The relationship between molecular and molar properties of chemicals and physical transport constants. K_{OW}, Water/octanol partition coefficient; K_{OC}, water/soil or sediment partition constant; K_{Bio}, water/biota partition coefficient. Reproduced from Mill (1981).

Once equilibrium has developed, chemical distribution in the environment provides a source of information on the properties and behaviour of the chemical. Thus, a two-way information transfer mechanism exists within the conceptual hierarchy. Figure 1.2 outlines these concepts and illustrates the hierarchical nature of environmental fate prediction. This figure also provides a guide to the rationale behind the structure of the book. A decision as to whether data need be collected on all or only some of the stages indicated should be determined by present knowledge of chemical behaviour and properties, environmental distribution and persistence, and potential hazard to biological systems.

This book begins with a chapter on the fundamental properties of chemicals. Molecular connectivity is commended both as a way of utilizing data on fundamental molecular properties and predicting unknown molecular and molar properties. Deemed the most useful of

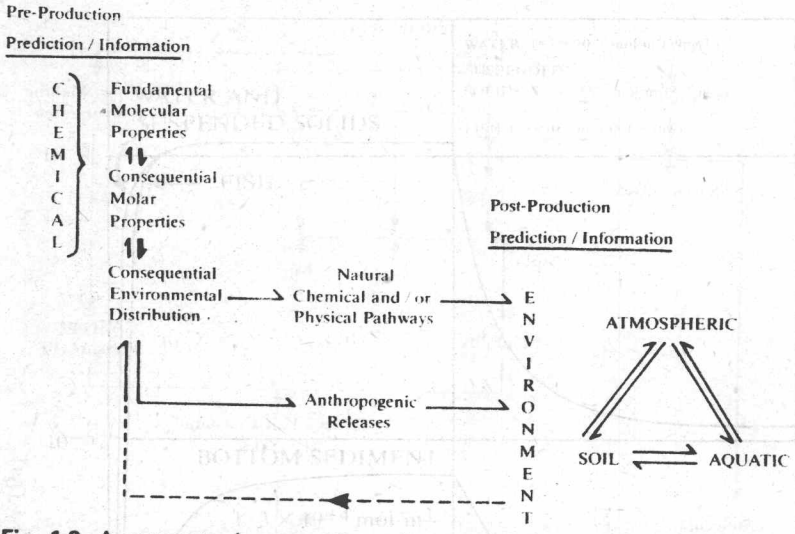


Fig. 1.2. A conceptual approach to the prediction of the environmental fate of chemicals.

the consequential molar properties, partition coefficients are discussed in detail. Natural chemical and physical pathways and transfers are outlined, as are potential anthropogenic releases of synthetic chemicals, be these associated with manufacturing processes or hazardous waste disposal. Next, various modelling strategies and philosophies are covered and, by way of recommendation, a whole section is devoted to modelling procedures utilizing the concept of fugacity. The natural world is discussed in three chapters on soil, aquatic and atmospheric environments. Intercompartmental transfers and significant degradative processes are detailed within the relevant chapter.

Within the context of specific equations, the book indicates data requirements throughout the various chapters. Wherever appropriate, published theory is cited and examples of existing fate predictive models are presented. Notwithstanding the apparent complexity of environmental fate prediction, it is hoped that it has been demonstrated that great progress in our understanding of the processes involved has been made over the last two decades, and that whilst data may be as yet una ilable, at least we are now in a position to recognize that fact and take steps to rectify omissions.

Chapter 2

Fundamental Properties of Chemicals

2.1 INTRODUCTION

There are over two million known chemicals of which some 70 000 are presently in commercial use worldwide. These include metals, metal compounds, metalloids and an enormous variety of synthetic organic chemicals. Testing a new chemical for its likely adverse biological effects may cost from a few thousand US dollars for simple acute toxicity tests or laboratory measurement of bioconcentration potential to over one million US dollars for longer-term epidemiological studies on humans. Even then, in only 20% of all cases can health hazard assessments fulfil rigorous scientific and technical criteria (NRC, 1984). Furthermore, such testing procedures may not account adequately for the complex series of transformations undergone by chemicals once they are subjected to environmental processes. Thus, it is clear that some form of early screening is necessary, even if only to identify those chemicals likely to require further testing.

A logical point at which to begin such a first check is to consider those aspects of chemical property and structure amenable to theoretical prediction. These may be considered in two distinct yet interrelated groups, namely molecular properties and molar properties. Molecular properties are independent of state and are intrinsic to the single molecule and include such fundamental parameters as the heat of formation (ΔH_f) and heat of atomization (ΔH_a). Molar properties, however, depend on molecular aggregations, examples being the heat of vaporization (ΔH_{vap}) boiling point, liquid density or water solubility.

The behaviour of chemicals in soil, water or the atmosphere is

ultimately determined by the interaction of the molecular or molar forces and properties of the substance with those of the relevant medium. Therefore, what has to be the goal in the theoretical fate prediction is a measure of the probability that a given property will behave in a certain way towards a defined abiotic or biotic receptor.

Since chemical properties are a consequence of molecular structure and electronic charge, many studies have been carried out into the relationship between chemical activity and structure. This field of endeavour has now developed into what are generally termed investigations into Quantitative Structure–Activity Relationships (QSAR) and these are widely used in chemistry in the prediction of both properties and the course of reactions.

The first part of this chapter provides a brief introduction to the background to studies demonstrating the utility of structure–activity relationships (SAR), representative of individual molecules or molar aggregations. Their role as a predictive tool in toxicology and ecotoxicology has been reviewed comprehensively by Goldberg (1983), ECETOC (1986) and Nirmalakhandan and Speece (1988). In spite of the apparent potential of QSAR predictions, it should always be borne in mind that these are only as good as the biological and chemical data upon which they are based. In addition, particularly when considering predictions of toxicity, the effects of metabolic intermediates, animal species differences, synergistic and antagonistic mixtures of substances, and individuals susceptibilities, are often not accounted for in the initial data set.

The chapter then concentrates on the partition coefficient (K) which has proved to be one of the most useful molar parameters both in environmental fate prediction and in the estimation of bioconcentration potential. Ways of determining K are discussed, and examples are given of the use of partition coefficient in bioconcentration factor studies.

2.2 MOLECULAR AND MOLAR PROPERTIES

2.2.1 Molecular structure

The concept that molecules consist of atoms bound together into stable and identifiable entities has played a vital role in modern chemistry. Physical properties, stability, reactivity and other characteristics are described and explained in molecular terms.

At the moment, quantum mechanics offers the most fundamental approach to the quantification of molecular structure. In principle, given the coordinates and atomic numbers for a collection of atoms, the Schroedinger equation can be solved for the eigen values and eigen vectors that describe energy and electron distribution. The stable arrangement of these atoms in molecular form corresponds to their lowest energy arrangement. Ordinarily, a chemist cannot accurately describe the electronic structure or energies of two isomers (e.g. butane and isobutane) without a quantum mechanical calculation. At a less fundamental level it is possible to deduce the structural formulae of isomers based on notions of valence and chemical bonding. This intermediate level of structural information is the bonding or branching pattern in the molecule and may be classified topologically.

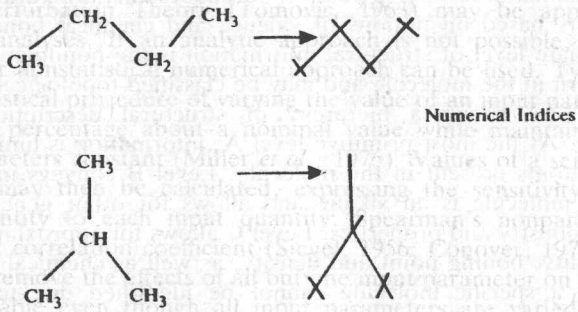
Figure 2.1 shows a hierarchy of structural descriptions for a molecule. At the most primitive level A, information is limited to the type of atoms present in the molecule. Level B conveys information that the molecule is an alkane and allows for other generalizations about chemistry and properties. Level C allows for approximate values of solubility, boiling point and density, as well as chemical reactivity, although a specific molecule cannot be identified due to isomeric possibilities. Level D informs on how the atoms in the molecule are organized or connected. At level E, the quantum mechanical description, all of the information about the molecule is contained in principle.

However, in practice, especially for interacting systems, quantum mechanical calculations have not produced adequate methods for predicting the properties of large molecules. This is due to two main problems. Firstly, because of the complexity of dealing with all the interactions between particles as required by the Schroedinger equation, there are practical problems of computation and computer time. Secondly, a quantity such as total bonding energy is only a tiny fraction of the total calculated energy of a molecular system. A small but acceptable error in terms of the total energy becomes a major portion of the chemical bonding energy. For example, even a stable diatomic molecule with a strong bond such as N_2 (945 kJ (225 kcal)) has a total molecular energy of more than 420 000 kJ (100 000 kcal) (Kier & Hall, 1976). It is not feasible to ask for a calculation based on the Schroedinger equation to yield results better than to within one part per 100 000. Thus, for such reasons, more efforts have been directed at less complex descriptions than those of quantum mechanics.

A. C, H

B. C_nH_{2n+2}

C. C_4H_{10}

D. 

E. $\psi_1 = c_1\phi_1 + c_2\phi_2 + \cdots\cdots$

$\psi_n = c'_1\phi'_2 + c'_2\phi'_2 \cdots\cdots$

Fig. 2.1. A hierarchy of structural descriptions.

2.2.2 Additive and constitutive properties

Molecular properties may be divided into two general classes. Those such as molecular mass, which may for all practical purposes be obtained as a sum of the corresponding values for the constituent parts, are termed additive, whereas properties that depend heavily on details of the arrangement of the constituent atoms are termed constitutive. Boiling point, for instance, is constitutive, as is the water solubility of organic compounds.

Molecular weight is strictly additive in terms of the numbers and kinds of atoms in the molecule, as is demonstrated in Table 2.1. This additivity is fundamental to the concept of homologous series in organic chemistry.