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**RESEARCH AND DEVELOPMENT OF
METHODS FOR ESTIMATING
PHYSICOCHEMICAL PROPERTIES OF
ORGANIC COMPOUNDS OF
ENVIRONMENTAL CONCERN**

FINAL REPORT, PHASE I

by

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of

Arthur D. Little, Inc.

and

David H. Rosenblatt, Ph.D.

US Army Medical Bioengineering Research and Development Laboratory

February 1979

Supported by

US Army Research and Development Command

Fort Detrick

Frederick, Maryland 21701

Contract No. DAMD 17-78-C-8073

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Acorn Park

Cambridge, Massachusetts 02140

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle)		5. TYPE OF REPORT & PERIOD COVERED
RESEARCH AND DEVELOPMENT OF METHODS FOR ESTIMATING PHYSICOCHEMICAL PROPERTIES OF ORGANIC COMPOUNDS OF ENVIRONMENTAL CONCERN.		Final Report, September 1978 - February 1979 on Phase I.
6. PERFORMING ORG. REPORT NUMBER		7. AUTHOR(s)
ADL-C-82426		Warren J. Lyman, Ph.D. Leslie H. Melken Judith C. Harris, Ph.D. David H. Rosenblatt, Ph.D.
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Arthur D. Little, Inc. Acorn Park Cambridge, MA 02140		62720A 3E162720A835/00.082
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE
US Army Medical R&D Command Fort Detrick Frederick, MD 21701		1980
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES
Folger		135
16. DISTRIBUTION STATEMENT (of this Report)		15. SECURITY CLASS. (of this report)
Approved for public release; distribution unlimited.		UNCLASSIFIED
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
18. SUPPLEMENTARY NOTES		
Phase II of this program, the actual preparation of the estimation methods handbook, was initiated in May 1979.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Estimation methods; Environmental fate; Physicochemical properties; Environmental fate models; Organic chemicals; Hazard ranking; (cont'd. over)		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
This study was the first phase of a program designed to prepare a handbook of estimation methods for the environmentally-important physicochemical properties of organic chemicals. A review of environmental fate models, hazard ranking schemes, federal regulations and other material led first to the identification of about 50 physicochemical properties of interest. Those properties that are estimable with available methods were then identified; these properties will be included in the handbook to be prepared in the next phase.		

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19. Key Words (cont'd.)

solubility; vapor pressure; octanol/water partition coefficient; adsorption coefficient; bioconcentration factor; volatilization; hydrolysis; dissociation; activity coefficient; diffusion coefficient; density; boiling point; heat of vaporization; surface tension; interfacial tension; viscosity; heat capacity; thermal conductivity; atmospheric residence time; dipole moment; refractive index; biodegradation; photolysis; hydroxyl radical; free radical oxidation; biochemical oxygen demand; chemical oxygen demand; melting point; mean lifetime; reactivity; flammability; flash point; heat of solution; dielectric breakdown voltage; particle size; reaction rates.

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documents.

Arthur D. Little, Inc.

EXECUTIVE SUMMARY

This report describes the results of Phase I of a program currently being carried out by Arthur D. Little, Inc. for the US Army Medical Research and Development Command. The purpose of this program is to prepare a handbook which will contain details and recommendations on the available methods to estimate, for organic chemicals, selected physico-chemical properties related to the environmental fate and transport of these chemicals.

The Phase I program was, essentially, a problem definition study to develop a ranked list of properties or parameters to be included in the handbook. The ranked list of properties was developed following an analysis of the physicochemical properties required in environmental transport and fate models, legally mandated lists of chemicals and properties, hazard and ranking schemes, and other pertinent material (including expert opinion). The rank of each property was based upon a consideration of its general importance and frequency of occurrence in the models, ranking schemes, and regulations, etc.

The Phase I program identified over 40 properties or parameters (associated with environmental concerns of organic chemicals) for which estimation techniques are desirable. However, estimation techniques having some degree of general applicability appear to be available for only one half of these properties at present. These are listed as numbers 1-25 in Table 1. Also listed in Table 1 (nos. 26 and 27) are two additional properties, rates of biodegradation and rate of aqueous photolysis, which will be qualitatively discussed in the handbook to be prepared even though reliable (or generally applicable) estimation methods are not currently available for these properties. These two properties are considered to have a ranking equal to the estimable properties at the top of the list in Table 1. Their addition to the list* of properties to be considered in Phase II reflects not only this high ranking, but also the specific interests and needs of other federal agencies who will be contributing to the support of the Phase II work.

Table 1 also lists two properties, flash point (no. 16) and solubility in other solvents (no. 17), that were not in the original list of estimable properties submitted in the Phase I draft report. Discussions held subsequent to the completion of the Phase I work led to the conclusion that these properties were also estimable.

This Phase I report, in addition to documenting the identification and ranking of the properties of interest, also provides an overview of the available estimation techniques, a general description of recent work in the area of environmental fate modeling, and a bibliography of articles, reports and books that were collected for review.

* The addition was made subsequent to the completion of the Phase I work.

TABLE 1

PROPERTIES TO BE STUDIED IN PHASE II

1. Solubility
2. Vapor Pressure
3. Oct./Water Partit. Coef.
4. Adsorption Coef.
5. Bioconcentration Factors
6. Rate of Volatilization
(Water)
7. Rate of Hydrolysis
8. Dissociation Constant
9. Activity Coef.
10. Rate of Volatilization
(Soils)
11. Diffusion Coef. (air)
12. Diffusion Coef. (water)
13. Density
14. Boiling Point
15. Heat of Vaporization
16. Flash Point
17. Solubility in Other Solvents
18. Surface Tension
19. Interfacial Tension with Water
20. Viscosity
21. Heat Capacity
22. Thermal Conductivity
23. Atmospheric Residence Time
24. Dipole Moment
25. Refractive Index
26. Rate of Biodegradation
27. Rate of Aqueous Photolysis

TABLE OF CONTENTS

	<u>Page</u>
<u>EXECUTIVE SUMMARY</u>	2
<u>I. SUMMARY</u>	9
A. Introduction	9
B. Properties Proposed for Inclusion in the Handbook	9
C. Properties for Which Estimation Methods Are Not Available	10
D. Report Overview	13
<u>II. BASIC FINDINGS</u>	15
A. Sources Used	15
B. Properties Used in Environmental Fate Models	16
C. Properties Associated with Federal Regulations and Hazard Ranking Schemes	29
D. Properties Suggested for Studies of Environmental Transport and Fate of Organic Chemicals	44
<u>III. SELECTION AND DESCRIPTION OF PROPERTIES</u>	47
A. Selection and Ranking of Properties	47
B. Description of Estimable Properties	50
C. Overview of Available Estimation Methods	54
D. Errors and Their Propagation in Estimation Methods	74
E. Potential Cost Savings Associated with the Use of Estimation Methods	76
<u>IV. ENVIRONMENTAL FATE MODELING - AN OVERVIEW</u>	80
A. Introduction	80
B. Objectives of Models	81
C. Models Principally Considering Bulk Transport and Dispersion	83
D. Chemical Fate Models	88
E. Soil/Groundwater Models	95
F. Chemical Spill Models	97

TABLE OF CONTENTS (cont.)

	<u>Page</u>
<u>V. SCOPE AND APPROACH FOR PHASE II</u>	101
A. Scope of Work	101
B. Approach	101
<u>VI. BIBLIOGRAPHY</u>	107
A. Other Bibliographies Used	107
B. Articles, Books, and Reports	110
<u>VII. DISTRIBUTION LIST</u>	134

LIST OF TABLES

<u>Table No.</u>		<u>Page</u>
1	Properties to be Studied in Phase II	3
2	Environmentally Important Properties which can be Estimated for Many Organic Compounds	11
3	Environmentally Important Properties for which Estimation Methods are Not Available	12
4	List of Visits and Contacts Made	17
5	Properties Important for Chemical Fate and Runoff/River Modeling of Organic Chemicals	21
6	Examples of Environmental Fate Models of Chemicals	23
7	Parameters Used in Soil/Groundwater Models of the Fate and Transport of Organic Chemicals	28
8	Properties Used in Modeling Chemical Spills in Water	30
9	Properties Required by Federal Regulations or by Hazard Assessment Schemes	32
10	Physical and Chemical Properties Included on Proposed TSCA Premanufacture Notification Form	34
11	Physical and Chemical Properties Used in Scoring System of the TSCA Interagency Testing Group	35
12	Physical and Chemical Data Requirements Related to Product Chemistry	37
13	Physical and Chemical Data Requirements Related to Environmental Chemistry	38
14	Physical and Chemical Properties Related to Hazardous Waste Characteristics	39
15	Physical and Chemical Properties Used in Ranking Pollutants for EPA ORD/OHEE STARS Reports	42
16	Physical and Chemical Properties Identified as Required in MITRE Study for the Federal Republic of Germany	43

LIST OF TABLES (cont.)

<u>Table No.</u>		<u>Page</u>
17	Properties Cited as Being Important for an Understanding of the Fate and Transport of Organic Chemicals in the Environment	46
18	Sources for List of Estimable Properties	48
19	Sources for List of Nonestimable Properties	49
20	Examples of Chemical-Specific Input Data Requirements for Various Property Estimation Methods	57
21	Estimated Costs for Laboratory Measurement of Selected Parameters	78
22	Parameters Required for Modeling Vinyl Chloride in Aquatic Ecosystems - Worst Case Model Parameters	91
23	Programs Available for Chemical Spill Modeling in the U.S. Coast Guard's Hazard Assessment Computer System	100
24	Schematic Outline of the Phase II Final Report	106

LIST OF FIGURES

<u>Figure No.</u>		<u>Page</u>
1	Some Possible Pathways for Property Estimation	55
2	Schematic Diagram of Intercompartmental Flows of Emitted Chemical	85
3	Compartmental Model for the Distribution of a Volatile Solvent Emitted into the Troposphere (Dow Chemical Co.)	87
4	Pathways for Toxic Substances (TXSB) in the Physicochemical Environment System	89
5	Working Conceptual Model of Vinyl Chloride Interactions in an Aquatic System (U.S. EPA, Athens, GA)	90
6	Schematic of Fish-Food Chemical Fate Model Developed by Dow Chemical Co.	93
7	Schematic Diagram of the First Branch of the ADL System for Selecting and Ranking Chemicals of Environmental Concern	94
8	Hazard Assessment Tree: (Events Chart) for Use in U.S. Coast Guard's Chemical Hazards Response Information System	99

I. SUMMARY

A. Introduction

This report describes the results of Phase I of a program currently being carried out by Arthur D. Little, Inc. for the U.S. Army Medical Research and Development Command, Fort Detrick, Frederick, Maryland. The purpose of this program is to prepare a handbook which will contain details and recommendations on the available methods to estimate, for organic chemicals, selected physicochemical properties related to the environmental fate and transport of these chemicals. The handbook is to be published in book form, and the methods described incorporated - to the extent possible - in an interactive computer program.

It is expected that this handbook (to be prepared in Phase II) will prove to be a valuable tool to both scientists and managers, in both industry and government, who must consider the probable impact of potentially harmful organic chemicals in our environment. Environmental assessments do not, in general, require data with a high degree of accuracy. When laboratory data are not available, it thus appears that estimated values of certain properties may be entirely adequate for use in environmental fate modeling studies, in hazard assessments, in filling data gaps of large chemical data bases, and in several other endeavors. A laboratory measurement could subsequently be made for any property where the error probable in the estimate resulted in a significant uncertainty in the model results or environmental assessment.

Phase I of this program was, essentially, a problem definition study to develop a ranked list of properties or parameters to be included in the handbook. The ranked list of properties was developed following an analysis of the physicochemical properties required in environmental transport and fate models, legally mandated lists of chemicals and properties, hazard ranking schemes, and other pertinent material (including expert opinion). An initial review of the availability of estimation methods for these properties was also undertaken. Properties for which no reliable estimation methods are currently available will not be included in the handbook. We expect, however, to be able to propose how additional research might be directed to obtain estimation methods for the more important properties in this last category.

B. Properties Proposed for Inclusion in the Handbook

The Phase I program identified over 40 properties or parameters (associated with environmental concerns of organic chemicals) for which estimation techniques are desirable. However, estimation techniques appear to be available for only one half of these properties at present. The properties for which estimation methods are available include many

of the more important parameters (solubility, vapor pressure, adsorption coefficients, bioconcentration factors, etc.). In some cases, however, the methods will only be applicable to selected classes of organic chemicals. Also, while method errors may be relatively large for some properties, it is felt that these errors (which will be documented) will be well within the acceptable error range associated with the probable uses of such estimates.

The complete list of 23 properties which was initially proposed for study in Phase II is shown in Table 2. (Subsequent discussions led to the addition of the following properties for study in Phase II: (1) flash point; (2) solubility in other solvents; (3) rate of biodegradation; and (4) rate of aqueous photolysis.)* The properties in Table 1 have been listed in rough order of priority (highest first); they have also been separated into three groups for Phase II cost proposal purposes. The priority of a property or parameter was derived from considerations of its frequency of use and relative importance in environmental fate models, hazard ranking schemes, federal regulations (e.g., TSCA requirements), as well as from expert opinion.

For each property or parameter listed in Table 2, we have identified one or more estimation techniques that will be evaluated** and, if appropriate, included in the handbook. In a few cases (nos. 1, 2, 5 and 6 of Table 2) we have identified some additional (secondary) properties or parameters, which are related to the principal property, for which estimation methods would also be evaluated. For example, the critical pressure and temperature are listed under vapor pressure. These two properties are required in several of the more important vapor pressure estimation methods; since data on a chemical's critical properties are seldom available, these properties must also be estimated.

C. Properties for Which Estimation Methods Are Not Available

The Phase I program identified a number of properties or parameters for which estimation methods would be desirable (Table 3). The investigations undertaken in Phase I did not identify any available estimation techniques for these parameters. The properties in Table 3 are listed in rough order of priority (highest first). The priority, as for the listing in Table 2, was derived from considerations of the frequency of use and relative importance in environmental fate models, hazard ranking schemes, federal regulations, and expert opinion.

A number of the properties listed in Table 3, especially 1, 2 and 3, are extremely important for an adequate understanding of the fate of organic chemicals in the environment. In some cases a rough estimate of

* The reasons for these changes are given in the executive summary.

** A brief overview of these estimation techniques is given in Section III.

TABLE 2

ENVIRONMENTALLY IMPORTANT PROPERTIES WHICH CAN
BE ESTIMATED FOR MANY ORGANIC COMPOUNDS

GROUP I

1. Solubility in water
 - Solubility in salt water
2. Vapor pressure
 - Critical temperature and pressure
3. Octanol/water partition coefficient
4. Adsorption coefficient (at equilibrium) for soils and sediments.
5. Bioconcentration factors for aquatic life
 - Biosorption factors for aquatic microorganisms
6. Rate of volatilization from surface waters
 - Henry's Law constant
 - Gas- and Liquid-Phase mass transfer coefficients
7. Rate of hydrolysis in water
8. Dissociation constant in water.

GROUP II

9. Activity coefficient (w/relationships to 1,3,6)
10. Rate of Volatilization from soils
11. Diffusion coefficient in air
12. Diffusion coefficient in water
13. Density
14. Boiling point
15. Heat of vaporization

GROUP III

16. Surface tension
17. Interfacial tension with water
18. Viscosity
19. Heat capacity
20. Thermal conductivity
21. Atmospheric residence time*
22. Dipole moment
23. Refractive index

*Available correlation derived principally from data on inorganic chemicals.

TABLE 3

ENVIRONMENTALLY IMPORTANT PROPERTIES FOR WHICH
ESTIMATION METHODS ARE NOT AVAILABLE

1. Rate of biodegradation (in water, soils or sewage treatment plants).
2. Rate of photolysis (in air and water; direct and catalyzed).
 - absorption spectra (especially UV)
 - quantum yields
3. Rate of reaction with hydroxyl radical (in air).
4. Rate of adsorption and desorption with soils and sediments.
5. Adsorption coefficient (at equilibrium) when hysteresis is apparent.
6. Coefficient n in Freundlich equation for soil or sediment adsorption isotherms ($X = KC^{1/n}$).
7. Rate of uptake by aquatic life.
8. Rate of clearance by aquatic life.
9. Apparent diffusion coefficient in unsaturated soils.
10. Rate of oxidation in water (e.g., by $RO\cdot$ or $RO_2\cdot$ radicals).
11. Biochemical oxygen demand, and chemical oxygen demand.
12. Rate of metabolism by aquatic life.
13. Rate constants for transfer from atmosphere to lithosphere/hydrosphere (wet and dry fallout).
14. Extent of adsorption (absorption) on (in) atmospheric particulates.
15. Mean lifetime, or overall "decay" rate, for a chemical in any major environmental compartment. (May be possible for atmosphere; see no. 21 in Table 1.).
16. Melting point.
17. Solubility in various solvents (other than water).
18. Reactivity (general; or with specific compounds or materials; when exposed to light, heat, shock, etc.);
19. Flammability limits (in air).
20. Flash point.
21. Heat of solution.
22. Dielectric breakdown voltage.
23. Particle size (a property of the bulk formulation).
24. Schmidt number (= Viscosity/[Density x Diffusion Coefficient]).
25. "Conductivity Parameter" for a chemical in a soil.

the possible range of a property in this list may be made, and should this be considered sufficiently valuable, it may be possible to include that property in the handbook. For example, if rough estimates of the UV absorption of a chemical and the quantum efficiency of the photodegradation reaction could be obtained, then it would be possible to use this information to estimate the rate of photolysis under natural conditions in the environment. Concerning biodegradation and hydroxyl radical reactivity (properties 1 and 3 in Table 3), there is, at present, both a lack of sufficient understanding about the mechanisms involved and a lack of a sufficiently large, self-consistent data base from which adequate estimation methods can be obtained.

Some of the "properties" listed in Table 3 may depend more on environmental and/or metabolic conditions than on the properties of the specific chemical. It has been suggested, for example, that for most neutral organics, the rate of uptake in fish (no. 7 in Table 3) is mostly dependent on the metabolic activity of the fish and - to a first approximation - independent of the chemical. [209]* Other "properties" which may not vary from chemical to chemical, under similar environmental conditions, are those listed as nos. 6 and 13. Other properties (e.g., no. 9) are associated with complex systems; no self-consistent data base of any size exists.

Some of the properties in Table 3 can probably be estimated following a minimal amount of research. For example, the solubility of a chemical in other solvents may be estimable through the use of solubility parameters or through correlations with water solubility and/or octanol/water partition coefficients.** In the latter case, one might make use of existing correlations between octanol/water partition coefficients and other solvent/water partition coefficients to derive the solubility in the other solvent. This might give reasonable estimates if the solvent had a very low solubility in water.

Finally, it may be preferable in many cases to measure some of the properties in Table 3 rather than to estimate them. Properties which may be easily and quickly measured include the melting point, flash point, dielectric breakdown voltage, and the absorption spectra.

D. Report Overview

Section II of this report describes the details of the work undertaken in Phase I and provides specific information on the environmental

* All citations used in this report (except for Section III-C) are listed in the bibliography in Section VI-B.

** As noted in the Executive Summary, this property was subsequently considered to be adequately estimable and will thus be included in the proposed handbook.

fate models, regulations, hazard ranking schemes, personal contacts, etc., that were used to derive the ranked list of physicochemical properties.

Section III focuses on the 23 properties proposed for inclusion in the handbook. It summarizes the basis for their selection, their importance and the nature of the available estimation techniques. Some additional information is also given for those properties which cannot be included in the handbook.

Section IV provides an overview of environmental fate modeling, discussing - in particular - the state-of-the-art of chemical fate models, soil/groundwater models, chemical spill models, and others.

Section V includes the details of our proposed scope and approach for Phase II. This information was also included in our Technical Proposal for Phase II submitted on April 16, 1979.

Section VI contains a bibliography of articles, reports and books that resulted from our literature search efforts. An initial list covers other bibliographies that were used in our work while the main list, given in alphabetical order (by author name), contains the bulk of the material. All reference numbers used in the text of this report (except for Section III-C) refer to the material in this main list (Section VI-B).

II. BASIC FINDINGS

A. Sources Used

A number of different sources were used to obtain the information desired for this program. They included:

- (1) Previously compiled bibliographies of literature covering the environmental field;
- (2) Machine searches of the recent literature by both Arthur D. Little, Inc. and the Defense Documentation Center; and
- (3) Contacts and visits with several experts in the field of environmental chemistry, including Drs. R. Reid and G. Fred Lee who consulted with us on this program.

The bibliographies used are listed in Section VI-A. Of principal interest are those compiled over a number of years by Oak Ridge National Laboratories (ORNL) with funding from the National Science Foundation.* A detailed subject index is provided by ORNL for most of this material.

Machine searches by Arthur D. Little, Inc. (ADL) of the current literature (approximately 1970-present) were conducted using the National Technical Information Service (NTIS) and Chemical Abstracts (CA) files. In addition, we requested the Defense Documentation Center (Alexandria, VA) to conduct a machine search of the reports in their files. The search strategy used by ADL focussed on those properties most frequently associated with the fate of organic chemicals in the environment (hydrolysis, photolysis, biodegradation, adsorption, volatilization, etc.) using combinations of key words that included not only the property of interest, but also key words relating to testing, estimation, correlation, data sets, and modeling. Special key words were used to search for material on environmental fate models. The search strategy used by the Defense Documentation Center focussed on three levels of search terms:

<u>First Level</u>	<u>Second Level</u>	<u>Third Level</u>
Approximately 125 organic chemicals or specific chemical classes (e.g., phenols). General terms for organic chemicals also used (e.g., organic compounds).	Adsorption Bioaccumulation Biodegradation Diffusion Diffusion coefficients Hydrolysis Ionic mobility Mathematical models Photolysis Reaction kinetics Solubility Transport properties Volatilization Water vapor	Atomic structures Chemical reactions Chemical structures Correlations Equations Models Molecular structures Theory

* Numbers 3-6, 10 and 11 in Section VI-A.

One machine search for publications by a particular author (J.M. Prausnitz) was made because of his important contributions in several areas of property estimation (vapor pressure, activity coefficients, and others).

These machine searches yielded several hundred citations which, after review, provided about one hundred considered potentially important to this program. Additional machine searches in Phase II will focus more on the specific properties selected for inclusion in the handbook and the individuals who appear to be prominent in the measurement and estimation of these properties.

Our contacts and visits with various experts brought us in touch with about 40 individuals. A list of the visits and contacts made is given in Table 4. These contacts provided up-to-date and useful information about the importance of various physicochemical properties, the methods in which they are measured and (for some) estimated, recent environmental fate modeling efforts, and an overview of current work by other U.S. researchers in these areas.

B. Properties Used in Environmental Fate Models

We considered five basic types of environmental fate models that have been developed in recent years:

- Atmospheric models - principally dispersion models or models of the chemical reactions related to smog formation.
- Chemical fate models that focus on the fate and transport, principally in the surface water-sediment compartment.
- Soil/groundwater models, less complex than those above, which focus principally on transport and dispersion in soil systems.
- Runoff/river models, which tend to focus (in the first case) on the runoff of pollutants from land to streams and (in the latter or combined case) on the general impacts of water quality of these pollutants.
- Chemical spill models, which are used to predict the fate of a chemical spilled onto water. These models consider such processes as dispersion in water (and vapor dispersion where vapors are formed), sinking, spreading, etc., but do not consider degradation.

Current atmospheric modeling efforts for organic molecules are, as mentioned above, either dispersion models (which take no account of the nature of the pollutant being modeled) or models of complex chemical reaction sequences thought to be important in smog formation. These models seldom require any physicochemical properties of interest to this program. It is expected, however, that future models may also include

TABLE 4

LIST OF VISITS AND CONTACTS MADE

A. VISITS (Nos. 1 and 2 by Drs. W. Lyman and J. Harris)

1. U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, Ga. (Nov. 14, 1978).
2. Dow Chemical Co., Midland, Mich. (Nov. 27-28, 1978).
3. Dr. G. Fred Lee (consultant) at A.D. Little, Inc. (Nov. 11, 1978).
4. Robert Reid (consultant) at A.D. Little, Inc. (various dates).

B. INDIVIDUALS CONTACTED (including those from trips)

<u>Name</u>	<u>Affiliation</u>
James W. Falco	EPA/Athens
George Baughman	"
David Brown	"
Samuel Karickhoff	"
W.C. Steen	"
Doris Paris	"
Richard Zepp	"
Lawrence Burns	"
N. Lee Wolfe	"
Raymond Lassiter	"
Asa Leifer	EPA, Office of Toxic Substances
Bruno Vasta	"
Arthur Stern	"
Rizwanul Haque	EPA, Office of Research and Development
Gunter Zweig	EPA, Office of Pesticide Programs
Carter Schuth	NSF, Integrated Basic Research

TABLE 4 (cont'd)

LIST OF VISITS AND CONTACTS MADE

<u>Name</u>	<u>Affiliation</u>
Farley Fisher	NSF, Research Applications
Jack Hahn	National Institutes of Health
William Milne	"
Donald Mackay	U. of Toronto, Canada
Martin Alexander	Cornell U., Ithaca, NY
Richard Park	Rensselaer Polytechnic Institute, Troy, NY
Robert Carlson	U. of Minnesota, Duluth, MN
Cary T. Chiou	Oregon State U., Corvallis, OR
Robert L. Metcalf	U. of Illinois, Urbana, ILL.
Anthony Hopfinger	Case Western Reserve U., Cleveland, OH
D.D. Huff	Oak Ridge National Lab., Oak Ridge, TN
Stephen Herbes	"
Alan Eschenroeder	Arthur D. Little, Inc., Cambridge, MA
Conrad Miller	Dow Chemical Co., Midland, MI
Dean Branson	"
W. Brock Neely	"
Wendell Dilling	"
Gary Blau	"
Gary Agin	"
Alan Syverud	"
Dennis Laskowski	"
Phillip McCall	"

TABLE 4 (cont'd)

LIST OF VISITS AND CONTACTS MADE

<u>Name</u>	<u>Affiliation</u>
Robert Swan	Dow Chemical Co., Midland, MI
Eugene Kenaga	"
Robert Bailey	"
Evan Buck	Union Carbide, Charleston, W.VA

consideration of such processes as adsorption on atmospheric particulates, wet and dry fallout, and reaction with the OH radical. While fluid mechanical processes may play a large part in the rate of fallout (or transfer to the stratosphere), the degree of adsorption on particulates will depend on such properties as water solubility and vapor pressure. The three degradation processes considered most important for organic chemicals are attack by hydroxyl radical, attack by ozone and direct photolysis. The available data, which are quite limited for all three processes, indicate that attack by OH radical may be the most important of the three.

Chemical fate models*, the type currently being considered for use in risk assessments of chemicals in the environment, do require a number of chemical-specific properties and parameters. A summary list of these properties, ranked in rough order of importance (highest first), is given in Table 5.** An indented listing is somewhat less important than - but related to - the unindented property under which it is listed. The availability of one or more appropriate estimation methods for each property is indicated by the lack of an asterisk (*).

The chemical fate, river/runoff and chemical spills models we investigated in this program (excluding soil/groundwater and atmospheric models) are listed in Table 6. Those that fall into the general class of chemical fate models are numbers 1-11, and 13-18 in this Table. This Table also provides basic information about the environmental compartments considered, the chemicals considered, and the fate and transport processes considered. Additional discussion of chemical fate models is given in a following section (Section IV).

A relatively large number of soil/groundwater models have been proposed although they do not differ much in their basic approach. The basic goal of these models is to predict the movement of chemicals or other pollutants, often starting with an assumed application near the soil surface, through the various unsaturated and saturated layers of a soil or surface layer of the lithosphere. In general, the only processes considered that involve chemical-specific parameters are adsorption and diffusion. Thus, as indicated in Table 7, the principal properties desired are adsorption and diffusion coefficients. In some cases an overall rate of "decay", taken to represent all possible degradation processes (hydrolysis, biodegradation, etc.) is used in the model. Additional information on the soil/groundwater models reviewed is given in Section IV.

* The term "chemical fate model" is used here to mean any model that focuses on the transport and degradation pathways of a particular organic chemical. Uptake by aquatic life is generally considered as well.

** Parameters used in runoff/river models were also considered in the preparation of this Table.

TABLE 5

PROPERTIES IMPORTANT FOR CHEMICAL FATE AND RUNOFF/RIVER
MODELING OF ORGANIC CHEMICALS

Adsorption coefficient, K or K_{oc} (at equilibrium) for soils and sediments

Octanol/water partition coefficient

Rate of adsorption*

Rate of desorption*

Desorption coefficient (at equilibrium) when hysteresis is apparent*

Bioconcentration factor (at equilibrium) for aquatic life (especially fish)

Rate of uptake*

Rate of clearance*

Octanol/water partition coefficient

Adsorption coefficient for adsorption on microbial populations(*?)

Rate of volatilization from surface waters and soils

Henry's Law constant (H)

Solubility in water (fresh water and salt water)

Vapor pressure and/or partial pressure

Gas and liquid phase mass transfer coefficients(*?)

Diffusion coefficients in air and water

Apparent diffusion coefficient in unsaturated soils or other systems*

Molar refractivity radius

Rates of various chemical reactions

Hydrolysis (in water)

Photolysis (in water and, less importantly, in air)*

Oxidation, e.g., with $RO\cdot$ (in water)*

Reaction with hydroxyl radical (in air)*

Rate of biodegradation (in water, soil and treatment plants)*

Biochemical oxygen demand (or rates of related reactions)*

Rate of metabolism by aquatic life*

TABLE 5 (cont'd)

PROPERTIES IMPORTANT FOR CHEMICAL FATE AND RUNOFF/RIVER
MODELING OF ORGANIC CHEMICALS

Dissociation constant

Rate constant for transfer from air to water or land*

Rate constant for transfer from troposphere to stratosphere*

"Conductivity parameter" for chemical in soil*

Mean lifetime of chemical in any major compartment or overall rate constant for "decay" in the compartment†

*Properties for which: (1) estimation methods appear to be of either limited applicability or uncertain reliability at present; and/or (2) no information on any estimation method is currently available.

†An estimation method to determine the mean atmospheric residence time has been proposed, but its utility has not yet been assessed.

TABLE 6

EXAMPLES OF ENVIRONMENTAL FATE MODELS FOR CHEMICALS

MODEL I.D.	Author	REFERENCE (Year)	ESF. No.	PRINCIPAL ENVIRONMENTAL COMPARTMENTS CONSIDERED	CHEMICALS CONSIDERED	PROCESSES CONSIDERED (EXCLUDING RELEASE, BULK TRANSPORT, AND DISPERSION)	PHYSICO-CHEMICAL PROPERTIES RELEVANT
1. SRI - Environmental Pathways	(Smith et al.)	1977	249	-Surface waters -Sediments (up to total of 9 compartments) -Biota	Organic chemicals (11)	Photolysis; hydrolysis; oxidation; volatilization; biodegradation; adsorption on sediments; bioconcentration	-Bioconcentration factor -Adsorption partition coefficient -Photolysis rate -Hydrolysis rate -Oxidation rate -Volatilization rate -Biodegradation rate
2. EPA - Vinyl chloride	(Mill et al.)	1976	128	-Surface waters -Sediments -Biota	Vinyl chloride	Volatilization; chemical and biological degradation (as above); adsorption on sediments; bioconcentration (food chain); transport across thermocline	-Rates of chemical and biological degradation -Rate of volatilization -Sinks by filter feeders -Sinks by other aquatic organisms -Adsorption coefficient for sediments
3. ABL - Freezing	(Venzien)	1977	273	-Air, air moisture, particulates; -Surface waters (Lakes, streams, ocean) -Soil moisture (various depths) -Ground water (various depths) -Soil (various depths)	Any organic chemical	Transport between all compartments; degradation (by means unspecified); sorption; bioconcentration	-Molecular weight -Solubility -Vapor pressure -Octanol/water partition coefficient -Half life in air and water -Molar refractivity radius -Air/water partition coefficient
4. ERT - Profile Models (DOT)	(Bechhoefer et al.)	1978	75	-Aquatic community (others discussed)	DOT	Bioaccumulation (food chain); toxic effects. (Others discussed include atmospheric reactions, photooxidation, and transformations in solution) Respiration rate (of biota)	-Bioconcentration factor
5. Global DOT	(Gramer)	1972	56	-Atmosphere -Land -Shallow sea -Aquatic plankton	DOT	Rates of chemical and biological decay; transfer between compartments; adsorption	-Reaction and transfer constants (i.e., air to land) -Degradation rate -Rate of direct microbial adsorption

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TABLE 6

EXAMPLES OF ENVIRONMENTAL FATE MODELS FOR CHEMICALS (cont.)

MODEL I.P.	Author.	REFERENCE (Year)	Ref. No.	PRINCIPAL ENVIRONMENTAL COMPARTMENTS CONSIDERED	CHEMICALS CONSIDERED	PROCESSES CONSIDERED (EXCLUDING RELEASE, BULK TRANSPORT, AND DISPERSION)	PHYSICO-CHEMICAL PROPERTIES REQUIRED
6. PCBs in Great Lakes	(Whitmore, 1977)	1977)	279	-Atmosphere -Surface waters (lakes) -Suspended solids -Sediments -Aquatic biota	PCBs	Volatilization; adsorption on suspended solids and sediments; bioconcentration; degradation (for PCBs with 3-5 Cl atoms)	-Partition coefficient for water/medium -Partition coefficient for biota/water -Evaporation rate constant -Rate of uptake and clearance by fish (of PCBs) -Degradation decay constant
7. DDT Transport	(Harrison <u>et al.</u> , 1970)	1970)	115	-Atmosphere -Sediments, soil, detritus -Ground and surface water -Food chain	DDT	Bioconcentration; metabolism; volatilization	-Rate of storage per trophic level -Rates of ingestion, excretion
8. DDT Transport	(Barbarot <u>et al.</u> , 1971)	1971)	70	-Aquatic food chain	DDT	Bioconcentration; long and short term retention in compartments	-Rate constants and transfer coefficients for individual salt marsh species
9. DDT Circulation on Earth	(Woodwell <u>et al.</u> , 1971)	1971)	288	-Soil -Troposphere -Oceans: mixed layer and abyss	DDT	Transfer between compartments; chemical and biological degradation discussed but not considered significant	-None
10. Durban [®] - Simulated Ecosystem	(Blau <u>et al.</u> , 1975)	1975)	35	-Soil and plants -Water -Fish	Durban [®]	Partitioning and uptake by fish; plant-water-soil equilibrium; biological degradation and excretion	-Rate of adsorption/desorption with soils and plants -Rate of uptake and excretion from fish -Rate of metabolism by fish
11. Volatilization of Pesticides	(Meyer <u>et al.</u> , 1974)	1974)	194	-Soil (porous) -Air layer above soil	Lindane Dieldrin	Volatility; adsorption	-Diffusion coefficient in air
12. Nonpoint Source Pesticide Loadings	(Falco <u>et al.</u> , 1976)	1976)	78	-Surface waters -Rivers	Malathion	Hydrolysis; microbial degradation; elimination due to loss (death) of aquatic organisms	-Hydrolysis and elimination rate constants -Microbial degradation rate

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TABLE 6

EXAMPLES OF ENVIRONMENTAL FATE MODELS FOR CHEMICALS (cont.)

MODEL I.D.	(Author, Year, Ref. No.)	PRINCIPAL ENVIRONMENTAL COMPARTMENTS CONSIDERED	CHEMICALS CONSIDERED	PROCESSES CONSIDERED (EXCLUDING RELEASE, BULK TRANSPORT, AND DISPERSION)	PHYSICO-CHEMICAL PROPERTIES REQUIRED
17. Atmospheric Material Balance	(Neely, 1977) 206	-Oceans -Atmosphere	Trichlorofluoromethane carbon tetrachloride	Transfer between air/water	-Solubility -Vapor pressure -Vapor pressure -Water solubility -Rate of uptake and clearance by fish -Rate of uptake and release by soil -Rate of hydrolysis -Rate of metabolism by fish
18. Predicting Environmental Exposure Concentration - PECC	(Neely, 1977) 209	-Surface waters -Sediments -Aquatic biota	Neutral organic molecules	Bioconcentration; adsorption/desorption; volatilization; metabolism by fish; hydrolysis	-Solubility -Fremdlich adsorption and desorption coefficients (K _a) -Apparent diffusion coefficient in water -Diffusion coefficient in air -Conductivity parameter -Overall decay rate for various degradation processes
19. Pesticide Movement in Agricultural Watersheds - SEMAN	(Adams et al., 1976) 3	-Surface water (runoff) -Ground water -Soils	Pesticides	Adsorption/desorption; volatilization (from soil); chemical and microbial degradation	-Adsorption coefficient -Overall rate constant for all degradation pathways
20. Adsorption and Transport of Agricultural Chemicals	(Preere, 1973) 88	-Surface and ground water -Soil -Plants	Pesticides and fertilizers	Adsorption; degradation; (Volatilization discussed but not modeled)	-Adsorption coefficient -Overall rate constant for all degradation pathways
21. SEMATEA (Sediment and Concomitant Transport Model)	(Grismrud et al., 1976) 98	-Surface waters -Sediments (3 size fractions)	Radionuclides (may be applicable to other constituents or chemicals)	Adsorption; degradation	-Adsorption coefficient -General "decay" rate to cover all types of degradation
22. EXPLORE - 1 (Extended and Modified Storm Water Management Model)	(Grismrud et al., 1976) 98	-Surface waters (rivers, estuaries, reservoirs) -Phytoplankton and zooplankton	BOD (3 types); TOC; phosphorus (3 types); nitrate (4 types); tox; pounds, DO	"Decay" of toxic compounds; processes affecting concentration of DO	-General "decay" constant for toxic compounds -Interactions for DO, BOD, TOC, N, P

TABLE 6

EXAMPLES OF ENVIRONMENTAL FATE MODELS FOR CHEMICALS (cont.)

MODEL I.D.	Author	REFERENCE Year, Ref. No.	PRINCIPAL ENVIRONMENTAL COMPARTMENTS CONSIDERED	CHEMICALS CONSIDERED	PROCESSES CONSIDERED (EXCLUDING RELEASE, BULK TRANSPORT, AND DISPERSION)	PHYSICO-CHEMICAL PROPERTIES REQUIRED
23. AEM - Agricultural Runoff Management Model	(Grimerud <i>et al.</i> , (Donigan <i>et al.</i> ,	1976) 98 1976) 67	-Surface waters (runoff) -Sediments -Soil	Pesticides	Adsorption; degradation	-Adsorption coefficient -Overall rate constant for all degradation pathways
24. MPS - Nonpoint Source Pollutant Loading Model	(Grimerud <i>et al.</i> ,	1976) 98	-Surface waters (runoff, streams) -Sediment	PO, mineral pollutants, nutrients, pesticides, and biodegradable pollutant.	Adsorption; others (?)	-Adsorption coefficient
25. QUAL - 1	(Grimerud <i>et al.</i> ,	1976) 98	-Surface waters	PO, BOD	BOD decay	-Interactions for BOD, BOD (e.g., BOD decay, re-aeration)
26. DOM - River Spill	(Neely <i>et al.</i> ,	1976) 211	-Surface waters (river) with bottom layer of chloroform -Boundary layer between two compartments	Chloroform or other partially soluble chemical with $\rho > 1 \text{ g/cc}$	Transport between all compartments; volatilization	-Volatilization rate -Diffusion rate constant for transport across boundary layers (empirical)
27. Chemical Spills in Surface Waters	(Raj <i>et al.</i> , (Raj <i>et al.</i> ,	1977) 231 1973) 232	-Bulk chemical -Surface waters -Atmosphere	Organics	Vaporization; dissolution and mixing in water; spreading; sinking; vapor dispersion; boiling; cooling; burning	-Solubility -Vapor pressure -Density -Boiling point -Viscosity -Surface tension -Interfacial tension (with water) -Heat of vaporization -Diffusion coefficient in water -Heat capacity -Thermal conductivity -Specific heat -Freezing point -Schmidt No. -Critical temperature

*Personal communication to W. Lyman, Arthur D. Little, Inc., November, 1978.

**Used to calculate rate constants for movement across the air/water interface.

TABLE 7

PARAMETERS USED IN SOIL/GROUNDWATER MODELS OF THE FATE
AND TRANSPORT OF ORGANIC CHEMICALS

Adsorption coefficients: K, n* from Freundlich equation[†]

Desorption coefficients: K'* , n'* from Freundlich equation[†]

Diffusion coefficient in air

Diffusion coefficient in water

Apparent diffusion coefficient (in moist, porous soils)*

Rate constant for "decay" (i.e., for any first order degradation or loss being considered)*

[†]The Freundlich equation, which is taken to represent equilibrium conditions, is expressed as

$$X = KC^{1/n}$$

where X is the amount adsorbed per unit weight of adsorbent, and C is the concentration in solution. The parameter n is often assumed equal to 1.0.

*Properties for which: (1) estimation methods appear to be of either limited applicability or uncertain reliability at present, and/or (2) no information on any estimation method is currently available.

A number of runoff/river models were investigated. Examples are given by numbers 12, and 19-25 in Table 6. An important process these models generally do consider is soil (or sediment) adsorption; a single adsorption coefficient is required. The second most common feature is the use of an overall "decay" rate to represent all forms of degradation of the chemical species being considered (e.g., hydrolysis, photolysis, biodegradation). Finally, these models generally consider the effect of organic discharges, in combination, on the dissolved oxygen content of the stream. However, in this case the interactions require only a knowledge of the biochemical oxygen demand (BOD) of the combined organic discharge, rather than the BOD of an individual chemical. In rare cases specific degradation processes may be considered (e.g., hydrolysis in no. 12, Table 6); volatilization from soils may also be considered in some cases (no. 19, Table 6). The use of various physicochemical parameters in runoff/river models was considered in the preparation of Table 5.

A number of chemical spill models, prepared for the U.S. Coast Guard's Chemical Hazards Response Information System (CHRIS)*, were reviewed to determine the physicochemical parameters required. Table 8 provides a summary list of these parameters, ranked in order of priority (highest first) based on general importance in determining not only the initial action of a spill (dissolves vs. floats or sinks or vaporizes) but also the modeling of subsequent processes such as dispersion, spreading, etc. Because of the variety of processes considered, and because most of them act on the bulk phase of the chemical (rather than a very dilute solution as in chemical fate modeling), the list of parameters shown in Table 8 is quite diverse. Some additional information on the CHRIS is given in Section IV.

C. Properties Associated with Federal Regulations and Hazard Ranking Schemes

A number of federally-mandated lists of chemicals and chemical regulatory acts require input information concerning the physical and chemical properties of particular substances or categories of substances. The physical and chemical property data requirements may be implicit, as in cases where a specified list of chemical pollutants is regulated, or explicit, as in cases where test data must be submitted to obtain certification or registration of a product. In this section, the information requirements associated with the following have been reviewed.

- Toxic Substances Control Act (TSCA)
- Federal Insecticide, Fungicide and Rodenticide Act (FIFRA)
- Resource Conservation and Recovery Act (RCRA)

* See Section IV-F for a description of CHRIS.

TABLE 8

PROPERTIES USED IN MODELING CHEMICAL SPILLS IN WATER

Solubility
Vapor pressure
Density
Boiling point
Viscosity
Surface tension
Interfacial tension with water
Heat of vaporization
Diffusion coefficient in water
Heat capacity
Thermal conductivity
Freezing point*
Schmidt number(*?)†
Critical temperature

*Properties for which: (1) estimation methods appear to be of either limited applicability or uncertain reliability at present, and/or (2) no information on any estimation method is currently available.

†Since the Schmidt number is related to the viscosity, density and diffusion coefficient (all of which may be estimated in certain cases) some estimation may be possible.

- Federal Water Pollution Control Act (FWPCA, - Hazardous Substances Designation
- Federal Hazardous Substances Act and the Poison Prevention Packaging Act
- EPA: Systems for Rapid Ranking of Environmental Pollutants
- Regulation of Toxic Substances in the Federal Republic of Germany

A summary of the properties required is presented in Table 9. The properties have been listed in rough order of importance (highest first).

The data requirements of these reports and regulations are designed to allow an assessment of the potential hazard of a chemical to man and the environment. (We have not listed here the toxicological data requirements.) In some cases, a ranking scheme is given (e.g., EPA: "Systems for Rapid Ranking...")* and in others rules are given for selecting chemicals to be designated "hazardous" or "non-hazardous"; but the majority of the reports and regulations reviewed do not spell out a specific hazard ranking scheme. Such schemes may be developed in the near future and may involve environmental fate modeling.

1. Toxic Substances Control Act (15. U.S.C. 2604)

40 CFR Part 720

Federal Register 44 (7), pp. 2242-2348, January 10, 1979

"Toxic Substances Control: Premanufacture Notification Requirements and Review Procedures."

This Act requires that a premanufacture notice be submitted to EPA 90 days before a person intends to manufacture or import any new chemical substances. New substances are those not included in the inventory of chemicals published by EPA under Section 8 of the Act.

The Act does not establish a certification or regulation program for new chemical substances. It does require submission of data that are "known to" or "reasonably ascertainable by" the submitter, relevant to the health and environmental effects. The data are to be submitted on forms developed by EPA. EPA may decide to regulate manufacture of the new substance if it determines that there is a reasonable basis for concluding that its manufacture, distribution and/or use will present an unreasonable risk to health or the environment.

Section 8, the premanufacture notification requirements, does not explicitly require any testing. However, the section allows the Agency to prohibit manufacture if it finds that insufficient test data are submitted.

* Discussed in item 7 below.

TABLE 9

PROPERTIES REQUIRED BY FEDERAL REGULATIONS OR
BY HAZARD ASSESSMENT SCHEMES

<u>ENVIRONMENTAL PROPERTIES</u>	<u>BULK PROPERTIES</u>
Solubility in water	Melting point*
Solubility in other solvents*	Boiling point
Soil adsorption coefficient (K or K_{oc})	Vapor pressure
Rate of adsorption*	Stability and/or reactivity*
Rate of desorption*	Rxn. with water, acids, bases, metal ions, etc.
Leachability(*?)	Rxn. with metals (corrosion)
Octanol/water partition coefficient	Sensitivity to heat, flame, light, etc.
Rate of volatilization	Density
Bioconcentration factor (aquatic life)	Spectral properties (UV, Vis., IR, etc.)*
Rate of uptake*	Flammability limits*
Rate of release*	Flash point*
Rate of biodegradation* (in water, soils, sludge)	Viscosity
Biochemical oxygen demand*	Particle size*
Chemical oxygen demand*	Index of refraction
Reactivity with various species	Dielectric breakdown voltage*
Rate of hydrolysis (aqueous)	
Rate of photolysis (aqueous and atmospheric)(*?)	
Rate of oxidation and reduction (aqueous)*	
Rate of degradation (atmospheric) by all processes*	
Atmospheric reactivity (various rxns.) *	
Dissociation constant in water	
pH of water solution	
Vapor phase sorption properties (*?)	
Mean lifetime in the environment *(air(*?))	

*Properties for which: (1) estimation methods appear to be of either limited applicability or uncertain reliability at present, and/or (2) no information on any estimation method is currently available.

Several specific chemical and physical properties of new substances are called out in the reporting requirements. Table 10 lists the properties and chemical reactivity data (excluding toxicity effects test results) that are itemized in the Premanufacture Notification Form (Fed. Reg. 44 (7), pp. 2291-3, January 10, 1979). There is also space on the form to enter known or readily ascertainable "other environmental effects", such as stratospheric ozone depletion. The text of the Proposed Rules also calls for reporting any results of:

Tropospheric degradation and transformation studies
Stratospheric degradation studies
Atmospheric transport studies
Octanol/water partition coefficient (measurements and calculations)
Vapor pressure sorbent studies
Olfactory threshold studies
Combustion and pyrolysis studies and theoretical analyses
Measurements of the permeability of the chemical through gloves used by workers or consumers
Any environmental fate studies in natural waters.

2. Initial Report of the TSCA Interagency Testing Committee to the Administrator, Environmental Protection Agency

January 1978: EPA 560-10-78/001, pp. 1-48 (also published in Federal Register 42 (197), pp. 55026-55080, October 12, 1977)*

The mandate of the Interagency Testing Group is the selection of substances or categories of substances as high priority for testing under TSCA. A preliminary list of 330 substances/categories was developed based on potential for human exposure and environmental release. The list was narrowed to 80 substances/categories after considering available information and/or lack of information related to potential for carcinogenic, mutagenic, teratogenic and chronic toxic effects, ability to bioaccumulate and ability to cause deleterious environmental effects. The scoring system used to narrow the list to 80 substances/categories explicitly considered the physical and chemical properties listed in Table 11.

3. Federal Insecticide, Fungicide and Rodenticide Act (7 U.S.C. 136 et seq.)

40 CFR Parts 162,163,181
Federal Register 43 (132), pp. 29696-29741, July 10, 1978

"Proposed Guidelines for Registering Pesticides in the United States

The Act authorizes the Administrator to specify "the kinds of information which will be required to support the registration of a pesticide." The 1978 Guidelines are the result of consideration of public

* See reference no. 12 in Section VI-B for full citation.

TABLE 10

PHYSICAL AND CHEMICAL PROPERTIES INCLUDED ON
PROPOSED TSCA PREMANUFACTURE NOTIFICATION FORM
(Federal Register 44 (7), 2291-3, January 10, 1979)

<u>PROPERTIES</u>	<u>CHEMICAL REACTIVITY</u>
Spectra (UV, Vis., IR)	Photochemical Degradation
Density	Hydrolysis
Solubility in Water	Chemical Oxidation
Melting Point	Chemical Reduction
Boiling Point	Chemical Incompatibility
Sublimation Point	Flammability
Vapor Pressure	Explodability
Dissociation Constant	Other
Particle Size Distribution	Biodegradation
pH	Adsorption/Desorption Characteristics
Other (specify)	Formation of Persistent Transformation Products
<u>EFFECT</u>	
Bioconcentration	

TABLE 11

PHYSICAL AND CHEMICAL PROPERTIES USED IN SCORING SYSTEM
OF THE TSCA INTERAGENCY TESTING GROUP

(Federal Register 42 (197), pp. 55026-55080, October 12, 1977)

<u>PROPERTY</u>	<u>FACTOR ACTUALLY SCORED</u>
Volatility	General population exposure; exposure intensity and penetrability into body
Water Solubility	Bioaccumulation
Octanol/Water Partition Coefficient	Bioaccumulation
Chemical Reactivity	Quantity released to environment; lifetime years, days or hours
Reaction with Stratospheric Ozone	Ecological effects; ozone depletion.

comments on 1975 Proposed Guidelines.** Testing requirements for pesticides are both extensive and intensive, since the end use formulations are deliberately introduced into the environment. The proposed Guidelines specify reporting requirements for: (1) Chemistry, (a) Product Chemistry and (b) Environmental Chemistry and (2) for Hazard Evaluation, (a) Avian and Mammalian Testing and (b) Aquatic Organism Testing.

The physical and chemical properties required by Parts 163.61, Product Chemistry, and 163.62 Environmental Chemistry, are presented in Tables 12 and 13, respectively.

4. Resource Conservation and Recovery Act of 1976, PL94-580
(42 USC 6901)

40 CFR Part 250
Federal Register 43 (243), pp. 58946-59028, December 18, 1978

This Act requires promulgation of several regulations providing "comprehensive control of hazardous waste from its generation to its final disposal." Under Section 3001 of the Act, two mechanisms are provided for determining whether a waste is hazardous. A waste must be managed according to the RCRA regulations if it exhibits the specified characteristics of a hazardous waste (40 CFR Part 250.13), or if it is included in the list of hazardous wastes (40 CFR Part 250.14).

Characteristics of a waste that qualify it as hazardous, according to Part 250.13, are of four types: ignitability, corrosivity, reactivity and toxicity. The physical and chemical properties that are required to determine characteristics of hazardous waste are listed in Table 14. Toxic wastes are defined in terms of extractable levels of eight specified metal and six specified pesticide contaminants.

Criteria for listing a waste as hazardous in Part 250.14 included: having the characteristics described above; containing infectious agents or radioactive substances; containing mutagenic, carcinogenic or teratogenic substances; containing toxic organic substances; and containing substances that bioaccumulate. The specific definition of bioaccumulation potential is an octanol-water partition coefficient $>10^3$, as measured by a High Performance Liquid Chromatography (HPLC) method applied to a methylene chloride extract of the waste. (Appendix XI of 40 CFR 250, Subpart A).

5. Federal Water Pollution Control Act (33 USC 1251 et. seq.)

40 CFR (proposed), Part 116, Section 311b
Federal Register 39 (164), pp. 30466-30471, August 22, 1974,
also 43 (49), pp. 10479-10506, March 23, 1978

"Hazardous Substances: Designation of and Determination of Removability."

** Federal Register, 40, p. 26802.

TABLE 12

PHYSICAL AND CHEMICAL DATA REQUIREMENTS
RELATED TO PRODUCT CHEMISTRY
(40 CFR Part 163.61)

<u>Property</u>	<u>Test Substance</u>		
	<u>Technical Chemical</u>	<u>Manufacturing Use Product</u>	<u>Formulated Product</u>
Color	X		
Odor	X		
Melting Point	X		
Solubility	X		
Stability (to acids, bases, moisture, light, etc.)	X		
Octanol/Water Partition Coefficient	X		
Physical State	X	X	X
Density or Spec. Gravity	X	X	X
Boiling Point	X	X	X
Vapor Pressure	X	X	X
pH	X	X	X
Storage Stability		X	X
Flammability		X	X
Oxidizing or Reducing Action		X	X
Explosiveness		X	X
Miscibility		X	X
Viscosity		X	X
Corrosion Characteristics		X	X
Dielectric Breakdown Voltage			X

TABLE 13

PHYSICAL AND CHEMICAL DATA REQUIREMENTS
RELATED TO ENVIRONMENTAL CHEMISTRY
(40 CFR, Part 163.62)

Hydrolysis Rate	Acidic, basic, neutral pH Two concentrations, two temperatures.
Photodegradation	Water, soil, vapor phase
Leachability	Four soils
Volatility	Vapor pressure above soil at 0, 12 hrs., 1, 230 days
Adsorption/Desorption	Minimum of one soil, four concen- trations
Fish Accumulation/Depuration	

TABLE 14

PHYSICAL AND CHEMICAL PROPERTIES
RELATED TO HAZARDOUS WASTE CHARACTERISTICS
(40 CFR Part 250.13. Fed. Reg. 43 (243), Dec. 18, 1978).

<u>PROPERTY</u>	<u>COMMENT</u>
Flash Point	If $< 60^{\circ}\text{C}$, liquid waste is defined as ignitable.
pH	If ≤ 3 or ≥ 12 , aqueous waste is defined as corrosive.
Reaction with water	If violent, or if toxic gases are generated, waste is defined as reactive. If flammable species formed, waste is defined as ignitable.

The approach proposed in this citation is to designate hazardous substances by list, rather than by specifying properties or values of properties per se. Criteria EPA used in determining whether to list a substance included:

- a. LC₅₀ and LD₅₀ limits for several routes of exposure to aquatic organisms or animals.
 - b. Potential for being discharged - production quantities, modes of transport, etc.
 - c. Removability - solubility, density, physical state, dispersion characteristics, potential for leaving a residue and detectability in the water body.
6. Federal Hazardous Substances Act (15 U.S.C., 1261-1274), Hazardous Substances Standards (16 CFR Part 1500), and Poison Prevention Packaging Act (15 U.S.C., 1471-1476)

Both acts authorize the Administrator of the Consumer Product Safety Commission to specify the labelling and packaging requirements for substances defined to be hazardous or toxic. A partial definition of a hazardous substance includes "any substance or mixture of substances which (i) is toxic, (ii) is corrosive, (iii) is an irritant, (iv) is a strong sensitizer, (v) is flammable or combustible, or (vi) generates pressure through decomposition, heat or other means "such that substantial injury or illness may result from reasonable handling and use, or ingestion by a child. In this definition, "corrosive" refers to the destruction of living tissue brought about by the chemical action of the substance in contact with the skin.

The flammability and combustibility of a substance is defined by its flashpoint as determined by the Tagliabue Open Cup Tester. The terms "extremely flammable," "flammable," and "combustible" are divided as follows:

- extremely flammable - flash point $\leq 20^{\circ}\text{F}$
- flammable - $20^{\circ}\text{F} < \text{flash point} \leq 80^{\circ}\text{F}$
- combustible - $80^{\circ}\text{F} < \text{flash point} \leq 150^{\circ}\text{F}$

Extremely flammable solids are those which ignite and burn at 80°F or less, when the substance is subjected to friction, percussion, or an electrical spark.

A substance which generates pressure through decomposition heat or other means is identified when positive results occur from the following tests:

- explosion as a result of an electrical spark, percussion, or five-second exposure to a candle flame.

- explosion of the container closure, or rupture of the container when the substance is held at or below 130°F for two days or less.
- eruption from the opened container after storage at 130°F or less for two days in the closed container.

One criterion by which a product is judged to be exempt from special labelling requirements is viscosity. Substances with a high viscosity, such as a floor wax, do not require a labelled "danger" statement as a preventative measure against swallowing.

Special packaging requires a scientific evaluation of the interaction of the substance and the package to determine that the chemical and physical characteristics of the substance do not inhibit or interfere with the proper functioning of the package. The exact properties to consider are not stated.

7. Systems for Rapid Ranking of Environmental Pollutants

EPA-600/5-78-012, June 1978 (NTIS PB 258168)*

The EPA Office of Health and Ecological Effects (OHEE) in the Office of Research and Development (ORD) is producing a series of Scientific and Technical Assessment Reports (STARs), each of which will summarize available knowledge about a particular pollutant. The STARs are intended as input to the regulatory process.

Technical personnel from EPA and SRI International investigated systems for ranking candidate pollutants for STAR reports. The two most promising approaches were felt to be those based either on expert judgment by a committee ("expert system") or on a mathematical model ("objective subsystem"). Table 15 lists the physical and chemical properties that were considered to be important for ranking.

8. Information Required for the Regulation of Toxic Substances (in the Federal Republic of Germany)

Report prepared by the MITRE Corporation, June 1978**

In a program undertaken for the Federal Republic of Germany, MITRE compared the toxic chemical regulatory legislation of several countries including Canada, Japan, the United States and European Common Market members. The focus was to define information needs and appropriate analysis methodologies for the German government to use in implementing the proposed German Environmental Chemical Law. Physical and chemical property data that were identified as required for regulation are presented in Table 16.

*See reference no. 26 in Section VI-B for full citation.

**See reference no. 136 in Section VI-B for full citation.

TABLE 15

PHYSICAL AND CHEMICAL PROPERTIES USED IN
RANKING POLLUTANTS FOR EPA ORD/OHEE
STARs REPORTS (EPA-600/5-78-012)

<u>Property</u>	Required For	
	<u>"Expert System"</u>	<u>"Objective Subsystem"</u>
Melting Point	*	
Boiling Point	*	
Vapor Pressure	*	*
Decomposition Point	*	
Combustion Products	*	
Flash Point	*	
Density	*	
Flammability Limits	*	
Explosive Limits	*	
Solubility in Water	*	
Solubility in Non-Polar Solvents	*	
Water/Octanol Partition Coeff.	*	*
Biological Oxygen Demand	*	*
Chemical Oxygen Demand	*	
Rate of Oxidation in Air, Water	*	
Hydrolysis Rate	*	
Uptake/Release Rates		
- Environmental Media	*	*
- Organisms	*	
Bioconcentration Factors	*	
Volatilization from Water		*
Half-Life in the Environment		*

TABLE 16

PHYSICAL AND CHEMICAL PROPERTIES IDENTIFIED AS
REQUIRED IN MITKE STUDY FOR THE FEDERAL REPUBLIC OF GERMANY

Physical Properties

State/Color/Texture

Density

Index of Refraction

Transition Temperatures:

melting, boiling, freezing
flash point

Vapor pressure

Vapor density

Solubility

water, organics
water/octanol partition
coefficient

Spectral properties

UV, Vis, IR, NMR, Mass
spectrum, X-ray diffraction,
Fluorescence, Optical Rotation

Persistence

Atmosphere, Hydrosphere,
Lithosphere

Chemical Properties

pH

Reactivities with water, acid
bases; Redox; photoreactivity;
nucleophilicity; electrophilicity;
thermal

Dissociation constants

D. Properties Suggested for Studies of Environmental Transport and Fate of Organic Chemicals

In addition to seeking relevant properties from environmental fate models and regulations, we also sought to obtain a list from what might be considered "expert opinion". This was accomplished, as detailed in Section II-A above, (1) by reviewing numerous publications which discussed the general problems associated with understanding the fate and transport of organic chemicals in the environment, and (2) through discussions with persons knowledgeable in this field.

A very large number of the publications included in our bibliography might be considered pertinent to this task. The short list cited below, however, is considered to contain some of the better descriptions of the relationships of various physicochemical properties to fate and transport:

<u>Reference Number*</u>	<u>Publication</u>
44	"Estimating the Hazard of Chemical Substances to Aquatic Life," ASTM (1978). This publication contains at least eight papers relevant to the subject.
9	"Assessing Potential Ocean Pollutants," NAS (1975).
16	"Principles for Evaluating Chemicals in the Environment," NAS (1975).
83	"Chemodynamics: Transport and Behavior of Chemicals in the Environment - A Problem in Environmental Health," Freed <u>et al.</u> (1976).
132	"Determining the Fate of Chemicals," Howard <u>et al.</u> (1978).
112	"Environmental Dynamics of Pesticides," Haque and Freed (Eds.) (1975).
95	"Organic Chemicals in the Soil Environment," Goring and Hamaker (Eds.) (1972).
151	"Pesticides in Aquatic Environments," Khan (Ed.) (1977).

*See Section VI for full citation.

Of particular interest to this program is the work currently being conducted by the American Society for Testing and Materials (ASTM) subcommittee E-35.21.01 on Environmental Chemistry Fate Modeling which is being led by Dr. G. Fred Lee (Colorado State University, Ft. Collins). This committee is currently focusing its attention on, and developing test methods for the following seven properties: solubility; water → air transfers of a chemical (Henry's Law constant); adsorption and desorption from sediments; photolysis in water; octanol/water partition coefficient; hydrolysis in water; and biological transformations (i.e., degradation). (Bioaccumulation is not being considered by the E-35.21.01 subcommittee since it has already been considered and included under a different subcommittee.) This list of properties was selected from a fairly large list of properties that were considered to be potentially important to an understanding of a chemical's transport and fate in the environment. The need for such parameters in environmental fate modeling was one of the more important factors in the final selection of the seven properties for which test methods will be evaluated and recommended. Numerous representatives from both industry and government had a voice in the selection of the final property list, and, thus, it deserves special attention.

In Table 17, we have summarized the properties considered important by the sources and "experts" used. They have been separated into three groups: properties, partition coefficients and rate constants. Within each group the properties are listed in rough order of priority (highest first).

The list of properties in Table 17 is, not surprisingly, quite similar to the lists given in Sections II-B and C above with one exception. This is the activity coefficient. The activity coefficient of a substance, A, in solution (γ_A) is equal to a_A/X_A , where a_A is the activity of the substance and X_A is its mole fraction in the solution. Activity coefficients are particularly useful for describing the behavior of non-ideal solutions.* (For an ideal solution: $\gamma = 1$ and $a = X$.) In particular, they may be used to obtain a more accurate estimate of Henry's Law constant (used in estimating rates of volatilization from surface waters). For organics with low aqueous solubilities they may also be used to estimate the solubility limit. In addition, if the activities in the mutually saturated phases of a two-phase octanol/water system can be estimated, then an octanol/water partition coefficient may be calculated. Other solvent/water partition coefficients might be estimated in a similar fashion. Obtaining activity/coefficients, until recently, required the use of the equilibrium vapor/liquid data which are available for only a small number of common, high-volume industrial chemicals. Recent group contribution methods have, however, made it possible to estimate these coefficients from the structure alone. (See Section III for additional discussion.)

*In an ideal solution, the intermolecular forces between all species are the same, and the solution obeys Raoult's Law: $p/p^\circ = X$, where p is the partial pressure of a solute above a solution, p° is the vapor pressure of the pure solute and X is the mole fraction of the solute.

TABLE 17

PROPERTIES CITED AS BEING IMPORTANT FOR AN
UNDERSTANDING OF THE FATE AND TRANSPORT OF
ORGANIC CHEMICALS IN THE ENVIRONMENT

<u>PROPERTIES</u>	<u>PARTITION COEFFICIENTS</u>
Water solubility	Octanol/water
Vapor pressure	Air/water (Henry's Law constant)
Adsorption spectra (UV, visible)*	Sediment or soil/water
Dissociation constant (in water)	Biota/water
Latent heat of solution*	Atmosphere/Atmospheric particulate*
Heat of vaporization	
Dipole moment	
Activity coefficient	
<u>RATE CONSTANTS</u>	
Adsorption on soils and sediments*	
Desorption from soils and sediments*	
Uptake by (aquatic) organisms*	
Release by (aquatic) organisms*	
Volatilization	
Chemical degradation (especially hydrolysis)	
Biodegradation*	
Photolysis (UV, vis.)(*?)	
Overall "decay" rate (or $t_{1/2}$)* (air ^(*?))	

*Properties for which: (1) estimation methods appear to be of either limited applicability or uncertain reliability at present, and/or (2) no information on any estimation method is currently available.

III. SELECTION AND DESCRIPTION OF PROPERTIES

A. Selection and Ranking of Properties

The selection and ranking of physicochemical properties of interest to this program followed these basic steps:

1. Identification of properties used in environmental fate models, hazard ranking schemes and federal regulations, or considered important by experts. Details of this step were given in Section II.
2. A rough assessment of the relative importance of the properties was made for each of the lists prepared in step 1. The ranking considered frequency of use and the importance of the property. The summary tables in Section II listed the properties ranked in order of this priority.
3. A determination was made as to whether or not one or more methods existed by which each property could be estimated for a reasonable number of organic chemicals. The summary tables in Section II identified those properties for which: (a) estimation methods appear to be of either limited applicability or uncertain reliability at present, and/or (b) no information on any estimation is currently available. The determination of estimability for each property was made following a review of the literature and discussions with our consultants and experts (see Section II-A).
4. All properties were separated into two groups, estimable and non-estimable, and a ranked list of each group prepared that correlated, to the extent possible, with the rank in the original listings.

Tables 18 and 19 summarize the final ranking and original sources, for the estimable and non-estimable properties, respectively*. Three general points should be made with regard to these tables. First, the final rank order presented is based, in part, on subjective considerations. Thus, no particular significance should be given to the ranking of any parameter relative to other parameters immediately above and below it. Second, some liberty was taken in combining "properties" from the initial lists (in Section II) to a common property in Tables 18 and 19. For example, the "rate of volatilization from water" (no. 6 in Table 18) was considered equivalent to "air/water partition coefficient", "Henry's Law constant plus gas and liquid phase mass transfer coefficients," and (more liberally) "atmospheric transport studies." Third, there do appear to be some natural breakpoints in the relative

*The executive summary contains a slightly revised list as a result of discussions subsequent to the Phase I work.

TABLE 18
SOURCES FOR LIST OF ESTIMABLE PROPERTIES

Parameter (from Table 1)	Environmental Fate Models			Regulations and Hazard Assessment		Expert Opinion	
	Chemical Fate	Soil/ Groundwater	Chemical Spill	Regulations: TSCA, FIFRA, RCRA, etc.	Hazard Assessment	ASTM E-35:21.02	Other
1. Solubility	*		*	*	*	*	*
2. Vapor pressure	*		*	*	*		*
3. Oct./Water partition coefficient	*			*		*	*
4. Adsorption coefficient	*	*		*	*	*	*
5. Bioconcentration factor	*			*	*	(*) ¹	*
6. Rate of volatilization (water)	*			*	*	*	*
7. Rate of hydrolysis	*			*	*	*	*
8. Dissociation constant	*			*			*
9. Activity coefficient							*
10. Rate of volatilization (soils)	*	*		*			*
11. Diffusion coefficient (air)	*	*					
12. Diffusion coefficient (water)	*	*	*				
13. Density			*	*	*		
14. Boiling point			*	*	*		
15. Heat of vaporization			*				*
16. Surface tension			*				
17. Interfacial tension			*				
18. Viscosity			*	*			
19. Heat capacity			*				
20. Thermal conductivity			*				
21. Atmospheric residence time				*	*		*
22. Dipole moment							*
23. Refractive index					*		

¹. Being covered by another ASTM subcommittee.

TABLE 19

SOURCES FOR LIST OF NON-ESTIMABLE PROPERTIES

Parameter (from Table 2)	Environmental Fate Models			Regulations and Hazard Assessment		Expert Opinion	
	Chemical Fate	Soil/ Groundwater	Chemical Spill	Regulations: TSCA, FIFRA, RCRA, etc.	Hazard Assessment	ASTM E-35:21.02	Other
1. Rate of biodegradation	*			*		*	*
2. Rate of photolysis (spectra)	*			*		*	*
3. Rate of reaction with OH radical	*			(*) [†]			
4. Rate of soil adsorption, desorption	*			*	*	*	*
5. Adsorption coeff. with hysteresis	*			(*)			
6. Coeff. n in Freundlich equation		*		(*)			
7. Rate of uptake by aquatic life	*			*	*	[*] [†]	*
8. Rate of clearance by aquatic life	*			*	*	[*]	*
9. Apparent diffusion coeff. in soils		*					
10. Rate of oxidation in water	*			*	*		
11. BOD, COD					*		
12. Rate of metabolism by aquatic life	*						
13. Rate of wet and dry fallout	*			(*)			
14. Adsorp. coeff./atmospheric particles				(*)		*	
15. Mean lifetime in air/water/soils etc.	*	*		(*)	*		*
16. Melting point			*	*	*		
17. Solubility in various solvents					*		
18. Reactivity				*	*		
19. Flammability limits in air				*	*		
20. Flash point				*	*		
21. Heat of solution							*
22. Dielectric breakdown voltage				*			
23. Particle size				*			
24. Schmidt number			*				
25. "Conductivity" parameter	*						

[†] () implies property is only indirectly referred to; [] implies being considered by another ASTM subcommittee.

ranking of properties in Tables 18 and 19. For example, in Table 18 the first seven properties were cited in four to six sources (average = 4 sources); the second seven properties (with the exception of the activity coefficient) were cited in two to four (average = 2.7) sources; and the last eight properties are only cited in one to three sources (average = 1.3).

The properties with the greatest importance for the fate and transport of trace concentrations of organic chemicals in the environment would include numbers 1-12 in Table 18 and 1-15 in Table 19. Most of the properties generally associated with bulk quantities of the pure compound, with the notable exceptions of solubility and vapor pressure, are found in the lower ranks of these tables.

In two cases the final ranking of a property was adjusted to reflect some consideration other than just the frequency of use or general importance in the sources used. In the first case activity coefficients were given a higher ranking than would have normally resulted because: (1) they can provide a more accurate estimate of Henry's Law constant (and, thus rates of volatilization from water); (2) they can provide an additional route for the estimation of water solubilities (ranked no. 1 in Table 18); (3) they may allow an additional route for the calculation of octanol/water partition coefficients (ranked no. 3 in Table 18); and (4) recent research has resulted in group contribution methods for the estimation of activity coefficients.

In the second case, atmospheric residence time (no. 21 in Table 18) was given a lower ranking than would have normally resulted because (1) the information required in the identified estimation method, the standard deviation of the measured atmospheric concentration, is unlikely to be available except for a very few compounds, and (2) the data base from which the estimation method was derived was principally for inorganic chemicals with relatively long residence times; its applicability to organic chemicals is thus in question.

B. Description of Estimable Properties

The identity and importance of each property identified in this program will be clear to most readers. We have, however, included below a brief description of each of the 23 estimable properties to make it clear just what will be covered in the handbook.

1. Solubility refers to the solubility limit of an organic chemical in water (or salt water). While some chemicals (e.g., acetone) may be miscible with water in all proportions, others may have solubility limits down in the parts per billion range. The solubility of a chemical is an important indicator of its mobility in any part of the environment where liquid water is present.

2. Vapor pressure is the pressure exerted by the vapors of a chemical at some stated temperature, which will usually be ambient temperatures (0-30°C). The vapor pressure is an important indicator of a chemical's tendency to change from the liquid (or solid) state to a vapor, and thus relates to the probable importance of atmospheric transport in the dispersion of the chemical. The critical temperature and pressure (used in the estimation of vapor pressure) relate to the critical point of a substance. Above a substance's critical temperature, only one fluid phase can exist no matter how great the pressure applied to the system. The pressure that would just suffice to liquefy a substance held at its critical temperature is called the critical pressure.

3. Octanol/water partition coefficient is defined as the ratio of the concentration of a substance in octanol to the concentration in water when equilibrium (of the substance) exists between the two-phase octanol/water system. This coefficient has found much use in describing the hydrophobic/hydrophylic character of chemicals. Hydrophobic chemicals (which will have a large octanol/water coefficient) will preferentially associate with organic materials (e.g., body fat, soil organic matter, etc.) while hydrophilic chemicals will preferentially associate with water.

4. Adsorption coefficient is a measure of the degree of adsorption in a sediment/water or soil/water environment. Most of the adsorption in soils and sediments is thought to take place in the organic fraction of the material. The adsorption coefficient usually estimated, $K_{o.c.}$, is defined as $K/(o.c.)$, where K is the adsorption coefficient (under equilibrium conditions) in the Freundlich equation and $o.c.$ is the organic carbon content of the soil or sediment.

5. Bioconcentration factor is the ratio of the concentration of a chemical in some species of aquatic life (usually a fish) to the concentration in the surrounding water. Different factors may result from different test conditions (e.g., static vs flow-through tests) and if different parts of the organism (skin, flesh, internal organs, etc.) are considered rather than the whole organism. This factor then describes the extent to which aquatic life accumulates various chemicals from water, and stores them in its body. A large fraction of the data which have been used in correlations with this property derive from two species of fish, mosquito fish and trout.

6. Rate of volatilization refers to the rate at which a chemical will move from a well-mixed surface water body (where it is present in dissolved form and in generally low concentrations) into the air space above the water. An overall first-order "reaction" is usually assumed. This parameter is thus a measure of how fast a chemical may be lost from a river, pond or lake into the atmosphere. Henry's Law constant (H) is the constant of proportionality between the concentration of a gas in a liquid (X) and its partial pressure (P) in the gas phase (valid at low partial pressures).* The liquid and gas phase mass transfer coefficients are used, in conjunction with a concentration gradient driving force, to

*Thus $P = HX$

derive a mass flux associated with the transfer of the chemical across a critical boundary within the respective phase. The rate of volatilization will depend on the air and water speed as well as other factors.

7. Rate of hydrolysis is the rate at which a chemical is degraded (initial reaction) by aqueous hydrolysis. The nature of the reaction may vary depending on the pH of the solution, i.e., the initial reaction may be with OH^- , H_2O or H_3O^+ and may involve species of the compound being hydrolyzed that differ from each other in the degree of protonation. Hydrolysis is considered to be an important degradation pathway for many organic chemicals although for others it may, because of its slowness, play no practical role in the eventual destruction of the chemical.

8. Dissociation constant is defined as the ratio of the concentrations of the dissociated species of a molecule (e.g., $[\text{H}^+]$ and $[\text{CH}_3\text{COO}^-]$ in acetic acid) multiplied together, to the concentration of the undissociated chemical (e.g., $[\text{CH}_3\text{COOH}]$ for acetic acid) in water. The degree of dissociation may be strongly affected by pH. A highly dissociated chemical may have markedly different solubility, adsorption, bioconcentration and toxic characteristics than the corresponding neutral chemical.

9. Activity coefficient (in aqueous solution) is defined as the ratio of the chemical's activity (a) to its mole fraction (X) in solution. The activity of a substance may, in turn, be related to its fugacity or chemical potential, and provides a measure of how "active" the material is relative to some standard state. As described elsewhere in this report, the activity coefficient may be used in obtaining Henry's Law constant (H), in estimating solubilities for some chemicals of low solubility, and in estimating octanol/water partition coefficients.

10. Rate of volatilization from soils refers to the rate at which a chemical will be lost from the surface or bulk surface layer of a soil into the air space above this soil. This parameter is especially important in assessing the importance of atmospheric transport in the loss of pesticides that have been applied to agricultural lands or other pest control areas.

11. Diffusion coefficient in air is the constant of proportionality between a concentration gradient of a substance over some distance in air and the diffusive flux of the substance across this distance. Movement is due to pure diffusion alone and is not due to air turbulence, etc.

12. Diffusion coefficient in water is the constant of proportionality between a concentration gradient of a substance over some distance in water and the diffusive flux of the substance across this distance. As above, movement is due to pure diffusion alone. Air and water diffusion coefficients are useful in assessing the importance of pure diffusion in various transport phenomena where bulk transport and turbulent dispersion may play only a minor role (e.g., in the air spaces and soil moisture of a soil).

13. Density is the mass of a pure substance divided by its volume. This property is important, for example, in determining the initial fate (i.e., floats vs sinks) of a chemical spilled into water.

14. Boiling point is the temperature at which the vapor pressure of a material is equal to the ambient pressure (76 cm Hg for the normal boiling point). The boiling point is thus just one special point on the vapor pressure-temperature curve (which may be obtained under #2 above); but it also serves as a general indicator of volatility and standard state.

15. Heat of vaporization is the amount of heat required to vaporize a given quantity of a substance at a specified temperature (often the boiling point). This parameter will give some indication of how readily a pure substance will volatilize under a given set of environmental conditions.

16. Surface tension is a measure of the intermolecular forces of a liquid material which tend to reduce the surface area of the liquid in contact with air. This property will influence the rate of spreading of a spill on any surface.

17. Interfacial tension with water refers to the intermolecular forces which will tend to keep the organic/aqueous phases separate and the surface energies minimized. This property is important in the rate of spreading of a liquid spilled on water.

18. Viscosity is a measure of a fluid's resistance to change in form when moving, a sort of internal friction. It is important in considering, for example, the ease with which a chemical may be pumped.

19. Heat capacity is the quantity of heat required to increase the temperature of the pure substance one degree of temperature. The property would be important in some chemical spill situations where the spill was exposed to heat.

20. Thermal conductivity is the time rate of transfer of heat by conduction, through the pure substance of unit thickness, cross-section area and temperature differential. This property would also be important in some chemical spill situations where the spill was exposed to heat.

21. Atmospheric residence time is the mean lifetime of a chemical in the (lower) atmosphere considering all degradation and loss mechanisms. This is an important indicator of the likelihood that a chemical may be a serious atmospheric pollutant.

22. Dipole moment for molecules is associated with the transfer of charge within the molecule and the distance separating the charge differential.

23. Refractive index of a substance is the ratio of the velocity of light in a vacuum to its velocity in the substance. It will vary with the wavelength of the light used. The property is sometimes used as an indicator, in analytical work, of the purity of a substance.

C. Overview of Available Estimation Methods

A diversity of types of estimation methods exists for the properties listed in Table 2; and, in most cases, more than one estimation method is available for each property. In general, estimates may be based on theory, on correlations of experimental values, or on a combination of the two. In many cases it is possible to estimate some property from a knowledge of the chemical structure alone, although such methods are frequently limited to chemicals of relative simplicity with regard to both atomic composition and structural bonding.

Figure 1 shows schematically a number of pathways for property estimation. Structure, through group contribution methods, is seen to be involved in a number of pathways. In some cases these pathways involve equations based on the form of a theory, with empirical correlations (with structural fragments or other properties) of the constants which the incomplete theory does not provide. In other cases, structure may be used (again via fragment constants) in a straightforward correlation with the desired property. A good example of this latter case is the use of fragment constants for the estimation of octanol/water partition coefficients. In this particular case, fragment constants for relatively large fragments (several containing five or six atoms) are available; this allows more accurate (and rapid) estimates to be made than in other cases where, for example, only atomic "fragment" constants might be available.

The importance of two-parameter correlations, and the central role of the octanol/water partition coefficient is also clear from the lower portion of Figure 1. One of the more important correlations, for example, is that between the water solubility (S) and the octanol/water partition coefficient ($K_{o/w}$) with equations of the form

$$\log (1/S) = a \log K_{o/w} + b$$

where a and b are constants which are obtained by fitting a straight line to a plot of $\log (1/S)$ vs. $\log K_{o/w}$ using data for a number of chemicals. Different values of a and b may be derived for different classes of chemicals which will generally lower the probable error in the estimates obtained. Because of their simplicity, completely empirical correlations such as this are tempting to use outside of the range of chemical classes and values on which they are based, but such uses may involve substantial errors in the resulting estimates and are to be avoided.

Input data requirements for the available estimation methods vary widely. In the simplest of cases the structure or one other property

value may be required. In some of the worst cases, three, four or more input parameters may be required; and if data are not available, these parameters will, in turn, have to be estimated as well. In such cases, the problem of error propagation in the overall estimation method becomes quite complex and it may be difficult to obtain a reasonable estimate of the probable error in the estimate derived.* Table 20 provides a summary of the chemical-specific input data requirements for a number of property estimation methods. No attempt was made to list the input requirements of all available methods, but just enough to provide an indication of the variety involved.

The remaining part of this section provides more specific information on some of the available estimation methods for the 23 properties listed in Table 2. The references cited in this subsection are given at the end of the subsection in order to save time for the reader wishing to see the references cited. Most of the references cited are also included in the bibliography given in Section VI-B.

1. Solubility in Water

Some of the more interesting (and recent) estimation methods for water solubility are based upon correlations with such parameters as the octanol/water partition coefficient ($K_{o/w}$), with bioconcentration factor (BCF), and soil adsorption coefficients (K_{oc}). A set of nine correlations with $K_{o/w}$ for nine different chemical classes was prepared some years ago by Hansch et al. (1968) [1]. Another correlation with this parameter has been reported by Chiou et al. (1977) [2]. The correlations with BCF and K_{oc} are more likely to be used to estimate those parameters when the water solubility is known; such correlations are referenced in the subsections on those parameters. Kenaga and Goring (1978) [3] have reviewed (and expanded on) many of the reported correlations between water solubility, $K_{o/w}$, BCF and K_{oc} .

The solubility of polynuclear aromatic hydrocarbons (PAH) has been shown to be estimable from the molecules' effective molar volume (Leinonen et al., 1971) [4] or their carbon number (Mackay and Shiu, 1977) [5]. In the latter study, the relationship to the infinite dilution activity coefficient was also demonstrated. For regular hydrocarbons up to C_{10} , McAuliffe (1969) [6] has also shown a good correlation between water solubility and carbon number. McAuliffe (1966) [7] has also shown that correlations with hydrocarbon molar volumes may be used if various classes (e.g., saturated paraffins, olefins, diolefins, aromatics, etc.) are considered separately. The parachor, which is a measure of molar volume, has also been correlated with water solubility for organics (McGowan, 1954) [8]. Stefanye (1977) [9] has correlated the solubilities of substituted benzenes with a modified sigma substituent constant (a linear free-energy relationship parameter).

*Additional discussion of error propagation in estimation methods is given in Section III-D.

References for this section are given on page 69.

TABLE 20

EXAMPLES OF CHEMICAL-SPECIFIC INPUT DATA REQUIREMENTS FOR
SOME OF THE MORE COMMON PROPERTY ESTIMATION METHODS

(Different methods identified by a, b, c ... etc.)

1. Solubility in water

- a. Octanol/water partition coefficient
- b. Bioconcentration factor
- c. Soil or sediment adsorption coefficient ($K_{o.c.}$)
- d. Molar volume or parachor
- e. Carbon number (for polynuclear aromatic hydrocarbons)
- f. Activity coefficient (for chemicals of low solubility)
- g. Modified sigma constant (a linear free-energy relationship parameter)
- h. Melting point and heat of fusion (for solids in liquids)
- i. Henry's Law Constant and fugacity (for gases in liquids)

2. Vapor pressure

- a. Boiling point, critical temperature and critical pressure (3 methods)
- b. Three parameters in (a) plus heat of vaporization
- c. Coefficients A, B, C for Antoine equation*
- d. Coefficients A, B, C, D (or B, C plus critical temperature and pressure) for Frost-Kalkwarf-Thodos equation*

3. Octanol/water partition coefficient

- a. Fragment constants (π values in some cases)
- b. Fragment constants plus value of $K_{o/w}$ for structurally related chemical
- c. Solvent/water partition coefficient for some other solvent
- d. Water solubility
- e. Soil or sediment adsorption coefficient ($K_{o.c.}$)
- f. Bioconcentration factor

*These coefficients are tabulated for a limited number of chemicals.

TABLE 20 (cont.)

4. Adsorption coefficient for soils and sediments ($K_{o.c.}$)
 - a. Octanol/water partition coefficient
 - b. Water solubility
 - c. Bioconcentration factors
 - d. Fragment constants or parachor
5. Bioconcentration factors for aquatic life
 - a. Octanol/water partition coefficient
 - b. Water solubility
 - c. Adsorption coefficient for soil or sediment
 - d. Molecular weight (for polycyclic aromatic hydrocarbons)
6. Rate of volatilization from water

Henry's Law constant, gas and liquid phase mass transfer coefficients (or an overall mass transfer coefficient)
7. Rate of hydrolysis in water
 - a. Group or substituent values (for use in a linear free-energy relationship) and the rate of hydrolysis for a structurally related compound (various methods available)
 - b. pK_a of product plus correlation between pK_a and rate of hydrolysis for structurally related compounds
8. Dissociation constant

Group or substituent values (for use in a linear free-energy relationship) and the dissociation constant for a structurally related compound (various methods available)
9. Activity coefficients
 - a. Group contribution factors (2 methods available)
 - b. Vapor-liquid equilibrium data
 - c. Solubility parameters and molar liquid volumes
10. Rate of volatilization from soils

Vapor pressure and diffusion coefficient in air (plus diffusion coefficient in water in wet or saturated soils)

TABLE 20 (cont.)

11. Diffusion coefficient in air
 - a. Molecular weight, collision integral, characteristic length. (Collision integral may be obtained from dipole moment, molar volume, boiling point and a characteristic energy parameter.)
 - b. Molecular weight and atomic structural diffusion-volume increments
12. Diffusion coefficient in water

Viscosity and molar volume
13. Density (for liquids)
 - a. Pitzer acentric factor (derived from the vapor pressure at a reduced temperature of 0.7), a scaling parameter (obtainable from the acentric factor and the critical temperature and pressure), and the critical temperature. (For saturated-liquid volumes only)
 - b. Critical temperature, pressure and compressibility factor
 - c. Above in (b) plus acentric factor
14. Boiling point
 - a. Group contribution factors (several available)
 - b. Molar refraction, parachor and a constant that depends on the chemical class of the chemical (alcohol, amine, ether, etc.)
15. Heat of vaporization
 - a. Critical temperature and acentric factor
 - b. Critical temperature and pressure, boiling point, and compressibility factor
 - c. Vapor pressure-temperature data (laboratory or estimated) plus compressibility factor
16. Surface tension
 - a. Parachor, vapor density and liquid density
 - b. Critical temperature and pressure, and boiling point
 - c. Molar refraction and refractive index

TABLE 20 (cont.)

17. Interfacial tension with water

Surface tension of pure components, molar volume, and a constant which depends on the size and type of organic molecule

18. Viscosity

- a. Density of liquid at boiling point (for liquids at boiling point)
- b. Thermal conductivity (for liquids at boiling point)
- c. Liquid density, critical temperature and a constant derived from group contribution factors (for liquids)
- d. Critical volume and temperature (for gases)

19. Heat capacity (liquids)

- a. Group contribution factors (several available)
- b. Critical temperature, acentric factor (for polar fluids), the polar factor, and the heat capacity at constant pressure

20. Thermal conductivity

- a. Heat capacity at constant volume and pressure, viscosity and molecular weight (for gases)
- b. Molecular weight, critical temperature and pressure, and the heat capacity at constant volume (for gases)
- c. Boiling point and molecular weight (for liquids)
- d. Liquid density, heat capacity at constant pressure, critical temperature, boiling point, heat of vaporization, and two constants (which are tabulated for a limited number of chemical classes) which depend on the chemical class and the liquid density (for liquids)

21. Atmospheric residence time

Mean and standard deviation of the concentration in the atmosphere

22. Dipole moment

Vector group-contribution factors

23. Refractive index (liquids)

- a. Liquid density and a constant
- b. Molar refraction, molecular weight, liquid density

More basic approaches to solubility, considered separately for gases, liquids and solids, have been reviewed in several texts (Reid et al., 1977; Hildebrand and Scott, 1950; and Shinoda, 1978) [10,11,12]. One can, for example, estimate the solubility of a solid in a liquid (e.g., in water) if the melting point and heat of fusion (or entropy of fusion) are known. These approaches are, in comparison with the simple correlations mentioned previously, somewhat more complicated and, in addition, require data that are less likely to be available.

The influence of salinity on the solubility of organic compounds has been considered by several researchers. The work of Eganhouse and Calder (1976) [13] indicates one method, involving the use of an empirical salting parameter (K_s), which can be used to estimate solubilities in brackish or salt waters. We are aware of other work in this area but have not yet had time to obtain and review the relevant publications.

2. Vapor Pressure

Reid et al., (1977) [10] have reviewed most of the methods for vapor pressure estimation that we may want to consider. Most methods require that the boiling point, critical temperature and critical pressure be known (or be estimated first). Other methods may also require the heat of vaporization. The methods reviewed by Reid et al., (1977) [10] are generally only considered to be accurate for vapor pressures ≥ 10 mm Hg, although some researchers have indicated that several of the methods may be adequate at much lower pressures.

Some work on the estimation of low vapor pressures (as would be the case for many pesticides) has apparently been carried out by Dr. J. Prausnitz at the U. of California. We have not yet had an opportunity to review his work in this area.

3. Octanol/Water Partition Coefficients ($K_{o/w}$)

This parameter, which has found such wide use in the estimation of other parameters, can be estimated in a number of ways. One basic approach is based upon fragment constants (π values in some cases) which are derived for individual atoms or groups of atoms in a molecule. One of the best reviews of the subject is given by Leo et al., (1971) [4]. Leo and his co-workers at Pomona college have prepared a much expanded list of fragment constants and bond factors, along with a data base of $K_{o/w}$ values for thousands of chemicals. Some of the revised fragment constants have been published (Leo, 1976; Hansch et al., 1973) [15,16], but much of this work has yet to be published in final form. The accuracy of this method is much improved if the measured $K_{o/w}$ value for a structurally related compound is available. Work on estimation techniques for $K_{o/w}$ - similar

*References for this section are given on page 69.

to that of Leo and Hansch - is currently being carried out by Hopfinger and Potenzzone at Case Western Reserve (see: Hopfinger and Battershell, 1976; Potenzzone et al., 1977) [17,18]. Some of their work has allowed the whole estimation technique to be computerized.

Leo et al., (1971) [13] have also shown that $K_{O/W}$ values may be estimated, via regression equations, from a chemical's partition coefficient between some other solvent and water. Constants (for a regression equation) for about twenty different solvents have been given.

Finally, as mentioned in subsection 1 above, $K_{O/W}$ values may be estimated from the water solubility via a number of available correlation equations.

4. Adsorption Coefficients for Soils and Sediments

The adsorption coefficient usually estimated, K_{OC} , is defined as $K/o.c.$, where K is the adsorption coefficient in the Freundlich equation, and $o.c.$ is the organic carbon content of the soil. The parameter K_{OC} has been shown to correlate well with the octanol/water partition coefficient, $K_{O/W}$ (Karickhoff et al., 1978; Briggs, 1973) [19,20], and also with water solubility (Karickhoff et al., 1978) [19]. These relationships, and others with bioconcentration factors, have been reviewed and expanded by Kenaga and Goring (1978) [3]. The relationships assume (and it appears to be quite valid) that the organic carbon content of the soil or sediment is the determining factor in the adsorption process, and that the nature of this organic carbon material is relatively unimportant.

Some additional approaches to the estimation of K (or K_{OC}) have been reported in the literature and, although they do not appear to have the same degree of usefulness and ease of use as those described above, they will be evaluated in any case. Of some interest, for example, are the works of Lambert (1967 and 1968) [21,22], Hance (1969) [23], Helmer, et al., (1968) [24], and Bark and Graham (1966) [25].

5. Bioconcentration Factors for Aquatic Life

Bioconcentration factors (BCF) have been correlated principally with octanol/water partition coefficients ($K_{O/W}$) and water solubilities (WS). The better known correlations are those of Neely et al., (1974) [26] for rainbow trout muscle, Lu and Metcalf (1975) [27] and Metcalf et al., (1973) [28] for mosquito fish, and Chiou et al., (1977) [2] for rainbow trout; a significant amount of additional data does, however, exist. Several of these correlations have been reviewed and expanded by Kenaga and Goring (1979) [3]. Unpublished reviews (which we have not yet been able to obtain) of work in this area have apparently been prepared by Metcalf (U. of Illinois) and the EPA laboratory in Athens, Ga. In some cases (e.g., with polycyclic aromatic hydrocarbons), it may be possible to use a correlation of BCF with molecular weight (Herbes et al., 1976; Southworth et al., 1978) [29,30].

*Reference for this section are given on page 69.

Data exist for several other species of aquatic life (see for example, Lu *et al.*, 1978; Coats *et al.*, 1976; Clayton *et al.*, 1977; Southworth *et al.*, in press) [31,32,33,34] including snails, mosquito larvae, alga, and zooplankter. The processes involving microorganisms may involve more surface adsorption than internal bioconcentration, thus requiring special correlation equations for these species. However, for those species that allow a relatively easy interchange of a chemical between the water and the internal parts of the organism (e.g., via gills), the bioconcentration factors derived from fish studies may be adequate. It will be necessary in our work to make a distinction between those studies conducted under static conditions and those conducted under flow-through conditions since different bioconcentration factors are obtained.

6. Rate of Volatilization from Water

The rate of volatilization from surface waters may be estimated if Henry's Law constant (H) and the gas and liquid mass transfer coefficients (k_g , k_l) are known. H may be easily (if roughly) estimated from the pure chemical's vapor pressure and water solubility, while k_g and k_l are somewhat more difficult to estimate. The early work on estimation methods (Dilling, 1977; Neely, 1976; Mackay and Wolkoff, 1973; Mackay and Leinonen, 1975) [35,36,37,38] generally considered evaporation from a well mixed surface layer of water, but did not explicitly consider the effect of air and water velocities on the rates of evaporation. Some of the more recent work has, however, considered these effects, including the effect of waves (Cohen *et al.*, 1978; Southworth, in press; Southworth, 1977) [39,40,41]. Additional work in this area is currently being undertaken by Dr. Mackay (U. of Toronto) and Dr. J. Smith (SRI). It is not clear if any of this current research is investigating the concentration build-up effect that occurs in the air on the up-wind side of a water body; this tends to reduce the rate of volatilization on down-wind portions of the water body. Some work in this area has been conducted at A.D. Little for the U.S. Coast Guard.

7. Rate of Hydrolysis in Water

Rates of hydrolysis can be estimated for many organic species by application of appropriate linear free energy relationships (LFER's). Methods for estimation of hydrolytic reactivity are feasible primarily because there is an extensive data base. Reaction rates have been determined for a variety of organic species. Hydrolysis reaction mechanisms are also generally understood in some detail, and fall into a fairly small number of categories. Therefore, it is usually possible to select an appropriate model system and corresponding LFER for estimation of unknown hydrolysis rates.

*References for this section are given on page 69 .

Solvolysis mechanisms (Streitwieser, 1962) [42] and LFER's (Leffler and Grunwald, 1963; Wells, 1968) [43,44] have been reviewed. The types of LFER's that will be valuable in estimating hydrolysis rates include the following:

- | | |
|---------------------|---|
| Hamett eqn. - | Substituent effects on side chain reactions or aromatics. |
| Taft eqn. - | Substituent (polar) effects on aliphatic compound reactions. |
| Swain-Scott - | Nucleophilic displacement reactions. |
| Brønsted type - | Correlations with leaving group pK_a . |
| Grunwald-Winstein - | Effect of solvent changes. (Useful in converting data base values from non-aqueous to aqueous media). |

The most difficult challenge in preparing this section of the handbook is going to be writing unequivocal directions for choosing a model reaction system and LFER. We can anticipate that there will usually not be one - and only one best-choice model for a given organic species. The uncertainty in selecting models implies that estimated values may frequently be uncertain by 1-3 orders of magnitude. The estimated values of hydrolysis rate, therefore, may be most useful in establishing boundaries of environmental concern. For example, if one estimates a hydrolytic half-life of $> 10^4$ years, one generally will not need a finer estimate because other environmental processes will dominate the behavior of that organic species. If the estimated half-life is on the order of days, however, a measurement of the rate constant may be in order to define whether it is 0.1 day or 10 days.

Dissociation Constant

The dissociation constant can be estimated for most organic acids and bases by application of an appropriate LFER. There is an abundant data base of model compound dissociation constants. The dissociation reaction is relatively simple and well understood, so selection of appropriate model systems is facilitated. The Hammett substituent constants for aromatics and the Taft substituent constants for aliphatics will generally be appropriate. (Leffler and Grunwald, 1963; Wells, 1968) [43,44].

9. Activity Coefficients

Although methods have been available for some time to estimate activity coefficients from vapor-liquid equilibrium data (see Reid, et al.,

*References for this section are given on page 69.

1977) [10], it is only recently that group-contribution methods have been available. Such methods require only that the structure of the molecule be known and that the group-contribution factors be available for the various "groups" in the molecule. Two such methods, called ASOG ("Analytical Solutions of Groups") and UNIFAC ("Universal Functional-group Activity Coefficients"), currently exist (Palmer, 1975; Fredenslund et al., 1975; Fredenslund et al., 1977) [45,46,47]. While we have not yet had an opportunity to study these two (somewhat complex) methods in detail, it does appear that they have the capability to provide fairly accurate estimates of activity coefficients for a somewhat limited selection of chemical classes.

10. Rate of Volatilization from Soils

Volatilization or evaporation from soils requires a consideration of chemical location (e.g., on soil surface or mixed in soil), chemical concentration, adsorption on soil, atmospheric relative humidity, and soil temperature and moisture content. A number of researchers have investigated this process and proposed estimation techniques (Hartley, 1969; Lloyd-Jones, 1971; Freed et al., 1972) [48,49,50], and it appears that reasonable estimates can be obtained.

When evaporation from surfaces is being considered, a knowledge of the vapor pressure and rate of diffusion (in air) of the chemical may be the only chemical-specific information required. For evaporation from a mixed soil, additional information may be required (e.g., the diffusion coefficient in water or an apparent diffusion coefficient for the soil) (Mayer et al., 1974) [51].

11. Diffusion Coefficient in Air

Available estimation methods have been reviewed by Reid et al., (1977) [10], and these methods are expected to be appropriate for chemicals of environmental concern unless the molecules tend to agglomerate (in which case diffusion is reduced). Polar and nonpolar molecules may have to be considered by different methods. A number of different input parameters are required in these methods.*

12. Diffusion Coefficient in Water

Available estimation methods have been reviewed by Reid et al., (1977) [10], and these methods are expected to be quite applicable to chemicals of environmental concern. One of the more widely used methods (Wilke-Chang) requires a knowledge of the chemicals viscosity and molar volume.*

*It may be necessary to include, in our handbook, methods to estimate or derive some of these input parameters from more basic information.

**References for this section are given on page 69.

13. Density

Reid et al., (1977) [10] have reviewed the available methods for estimating liquid densities. All are based on some form of the law of corresponding states and are algebraically complex. Input parameters may involve molar volumes, acentric factors, and critical-compressibility factors.* The density of a gas may be derived from any appropriate equation of state for gases. The densities of solids cannot be easily estimated.

14. Boiling Point

Although various methods for estimating normal boiling points are available, they are not especially accurate (Reid et al., 1977) [10]. Most involve group-contribution techniques, which are devised for homologous series with no more than one functional group attached to a hydrocarbon framework. The methods were reviewed in Reid and Sherwood's 2nd edition of The Properties of Gases and Liquids (McGraw-Hill, 1966).

15. Heat of Vaporization

Reid et al., (1977) [10] have also evaluated various estimation methods for the heat of vaporization. One approach requires finding dP_{VP}/dT either from a vapor-pressure-temperature correlation or from actual vapor-pressure data. In both cases, it is also necessary to know the compressibility factor of the chemical (gas and liquid states). A second approach requires a knowledge of the critical temperature and acentric factor. A third approach (for estimating values at the boiling point) involves such input parameters as the critical temperature and pressure, boiling point, and compressibility factor. This value can then be corrected to other temperatures.

16. Surface Tension

Available methods for estimating surface tension have been reviewed by Reid et al., (1977) [10]. For pure liquids, methods based upon the law of corresponding states and upon the parachor are considered the most accurate. In many cases the parachor can be estimated via a fragment (group) contribution approach. Input parameters (other than parachor) for methods applicable to organic liquids include the liquid and vapor densities in one method and - in a second method - the critical temperature and pressure, and the boiling point. Some difference in applicability between methods is seen for hydrogen-bonded liquids and non-hydrogen-bonded liquids.

*References for this section are given on page 69.

17. Interfacial Tension With Water

According to Autonoff's rule, the interfacial tension, σ_i , is equal to the difference between the individual surface tensions of the two mutually saturated phases under a common vapor or gas:

$$\sigma_i = \sigma_{1s} - \sigma_{2s}$$

If pure component surface tensions are used, the rule proves quite inaccurate (Perry and Chilton, 1973) [52]. If, however, the saturated-phase values are used, estimates within ~15% can usually be made. The basic problem then is to estimate the saturated-phase values. Reid et al. (1977) [10] have reviewed two methods to estimate such numbers for binary organic-aqueous mixtures. One, primarily for organic chemicals of low solubility, requires the use of a constant which has been tabulated for a limited number of chemicals. The second method, more generally applicable to organics of any solubility, requires molal volumes and a constant, g (a function of the type and size of the organic chemical), for input parameters.

18. Viscosities

Viscosities of most liquids, at their normal boiling point, may be estimated with reasonable accuracy from either the liquid density or--for nonpolar liquids--the thermal conductivity. At temperatures other than the boiling point, Thomas's equation may be used which requires not only the density, but also a parameter derived from the reduced temperature, and atomic and group contributions [52].

19. Heat Capacity

Estimation methods for the heat capacities of both liquids and gases have been reviewed by Reid et al. (1977) [10]. For liquids, a number of approaches are available including group contribution methods, corresponding-states methods, and others. Input parameters for the non-group methods include the critical temperature, acentric factor, and others. Similarly, a number of approaches for estimating ideal gas heat capacities are available, including one, fairly accurate, group contribution method (Method of Benson).

20. Thermal Conductivity

Estimation methods for the thermal conductivity of gases and liquids have been reviewed by Reid et al. (1977) [10]. A variety of input parameters are required. In one quick method, to obtain approximate values for liquids, only the boiling point and molecular weight are used. One relatively simple method for gases requires the heat capacity at constant volume, the heat capacity at constant pressure and the viscosity.

*References for this section are given on page 69.

21. Atmospheric Residence Time

Junge (1974) [53] has proposed that the atmospheric residence time of trace gases (in the troposphere) can be correlated with the variability of the measured concentration of the gas in the atmosphere. His correlation derives from data on H₂O, Rn, O₃, CO, CH₄, N₂O, H₂, CO₂, and O₂. The residence times covered by these species range from about five days for radon (Rn) to almost 10,000 years for O₂. In particular, Junge found that when a plot of the log relative standard deviation (of the atmospheric concentration) is plotted versus the log of the residence time, a straight line (negative slope) is obtained. That is, the residence time increases as the standard deviation decreases. The model used by Junge contains a number of assumptions (e.g., no significant time, seasonal, or locational variations), and the estimated residence times may thus have uncertainties of at least one order of magnitude. The input data for this correlation are adequate measurements of the global atmospheric concentration of the chemical from which a mean and standard deviation can be obtained.

22. Dipole Moment

Dipole moments of molecules have been tabulated for a large number of molecules (for references to data bases see Reid et al. (1977) [10]). When necessary, dipole moments can be estimated by vector group-contribution methods, although such methods apparently require considerable effort (Reid et al., 1977) [10].

23. Refractive Index

For most types of liquids, the viscosity may be estimated fairly accurately from the empirical Eykman equation, which requires only the density and one constant for input. A rougher approximation may be obtained for organic liquids with the Lorentz-Lorentz equation which relates the refractive index to the molar refraction (values of which are obtained via group contribution methods) and the molar volume (which may be obtained from the density and molecular weight). [52]

For hydrocarbons only, the effect of temperature on the refractive index can be estimated if data on the density at the two temperatures in question are available [52].

*References for this section are given on page 69.

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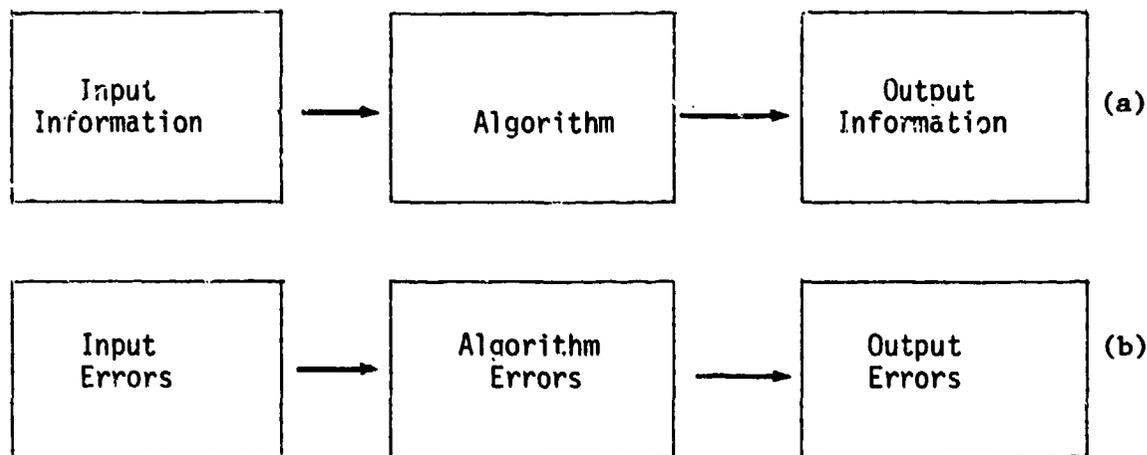
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51. Mayer, R., J. Letey and W.J. Farmer, "Models for Predicting Volatilization of Soil-Incorporated Pesticides," Soil Sci. Soc. Am. Proc., 38(4):563-568 (1974).
52. Perry, R.H. and C.H. Chilton (Eds.), Chemical Engineers' Handbook, 5th edition, McGraw-Hill Book Co., New York (1973).
53. Junge, C.E., "Residence Time and Variability of Tropospheric Trace Gases," Tellus, 26:477-488 (1974).

D. Errors and Their Propagation in Estimation Methods

The development and evaluation of methods for estimating physico-chemical properties involves computing required numerical results from given numerical data. The given data are input information, the required results are the output information, and the method is known as the algorithm. These essential ingredients of the methodology are summarized in Figure (a).



Frequently, several algorithms are available for producing the required output information, and a choice must be made between them. There are various reasons for preferring one algorithm over another, but two obvious criteria are speed and accuracy. The issue of accuracy leads us inexorably to the question of errors and their propagation. Rarely will output information be exact, since it ordinarily comes from measurement devices of some sort or from other algorithms. And usually the computing algorithm introduces further error. The output information, therefore, contains error from both these sources, as suggested in Figure (b).

What is desired is not so much a method for completely eliminating or compensating for the errors, as a technique for evaluating the uncertainty in the output information. Depending on the nature of the input information and the form of the algorithm, the techniques are myriad, and are best exemplified by examples.

Linear Regression: One independent variable.

This type of algorithm gives the relationship between an independent variable x and a dependent variable y , e.g.,

$$y = mx + b$$

where m is the slope of the line and b its intercept (value of y at $x = 0$).

Often the statistics of the regression are given: the standard deviation, S_{yx} , and the correlation coefficient, r . For a calculated value of the dependent variable y' , from a value of x in the applicable range of the regression formula, the uncertainty in y' is given by $\pm S_{yx}$ (i.e., $y = y' \pm S_{yx}$). However, there is only a 68% confidence level associated with this range. Other confidence levels are obtainable from the formulas given below.

<u>Range</u>	<u>Confidence Level</u>
$y' \pm S_{yx}$	68%
$y' \pm (1.96)S_{yx}$	95%
$y' \pm (2.58)S_{yx}$	99%

Unfortunately, use of these formulas imply that the value of x is known with certainty; this is seldom the case. Associated with each value of the independent variable may be an error S_x , such that its range of values is $X \pm S_x$. Thus,

$$y = mx + b \pm mS_x$$

where mS_x is the uncertainty associated with the calculated value of y , resulting from uncertainty in x . The error propagation formulas for random errors associated with two statistically independent variables x and y for a number of common operations are given below.

<u>Operation</u>	<u>Error Propagation Formulas</u>
Addition	$X + Y \pm \sqrt{S_x^2 + S_y^2}$
Subtraction	$X - Y \pm \sqrt{S_x^2 + S_y^2}$
Multiplication	$XY \pm \sqrt{X^2 S_y^2 + Y^2 S_x^2}$
Division	$X/Y \pm \sqrt{\frac{S_x^2}{y^2} + \frac{X^2}{y^4} \cdot S_y^2}$
$f(x,y)$	$f(x,y) \pm \sqrt{\left(\frac{\partial f(x,y)}{\partial x}\right)^2 S_x^2 + \left(\frac{\partial f(x,y)}{\partial y}\right)^2 S_y^2}$

Alternatively, in those cases where only the regression formula, or algorithm is given, a measure of the overall uncertainty associated with a calculated value using the algorithm may be obtained by comparison of a series of calculated values with their experimental counterparts. If a representative range of input variables is used, and the resulting range of output variables is wide enough, an acceptable measure of the resultant (dependent variable) error may be realized. This type of analysis would also be applicable for higher order regressions as well. An added measure of certainty assurance may be obtained by regressing a series of calculated values against experimental values. Such a procedure has the advantage of determining the regression statistics (i.e., standard deviation and correlation coefficient) as well.

Ofentimes, insufficient input information may have been utilized in deriving the correlation equation. In such cases, sample calculations for a series of compounds can be tabulated, thus offering the researcher the benefit of order-of-magnitude values for at least a few compounds, one of which may be structurally and/or functionally related to the compound of interest.

E. Potential Cost Savings Associated with the Use of Estimation Methods

In the original technical proposal for this program (submitted August 7, 1978) as well as the technical proposal for Phase II (submitted February 6, 1979), we discussed the need for estimation methods and pointed out several specific areas in which they might be used. In particular, it was mentioned that estimated values of physicochemical properties would be very useful in:

- Models of the environmental fate and transport of chemical pollutants;
- Setting research priorities (e.g., for "new" chemicals registered under the Toxic Substance Control Act);
- Checking the reliability of reported data;
- The design of laboratory and/or field experiments; and
- Filling data gaps in large chemical data bases used by various agencies.

While property estimation has been a routine matter for some individuals in the past (e.g., chemical engineers who had to design a new process or plant), for most people the response to the need for a particular physicochemical property has been to: (1) conduct a literature search for previously reported (measured) values; and/or (2) measure the value themselves. If the literature contains no previously-reported values then the second step has to be taken. This second step is frequently taken even when other data are available.

The cost of conducting a literature search for one property of one chemical is difficult to estimate; it clearly depends upon several factors including: (1) the capabilities of the searcher; (2) the searcher's proximity and access to a good scientific library; (3) the relative obscurity of the chemical and the property; and (4) luck! Some chemical data bases have recently been prepared which are searchable by computer, but computer searches (via remote terminals) of the published literature will only yield citations and, in some cases, abstracts (which may or may not contain the property value desired). Considering all of the steps required to conduct a literature search, a typical cost range of \$50-500 seems reasonable for the determination of a single property of a single chemical. The higher end of this range would be associated more with obscure chemicals and properties (for which a manual search of up to 70 years of literature might be required), with those situations where it was desired to obtain all reported values rather than just any value, and where other difficulties (e.g., foreign language articles, inaccessibility to a good library, etc.) were present. Cost savings (on a per chemical basis) are clearly possible when several properties are being searched for. For example, in a recent (1978) contract issued by the U.S. Coast Guard, another federal laboratory was required to fill in the data gaps for the physiochemical properties of a large number of compounds; the literature search effort cost, on average, \$62 per data point.*

The costs of measuring various properties in the laboratory have been estimated for many properties. Table 21 presents some estimates for most of the estimable properties of interest to this program. The costs given are (in most cases) associated with the costs (time charges, chemical usage and laboratory overhead) to be expected at a laboratory which conducted such tests on a routine basis. The wide range of cost estimates seen for some parameters is clearly associated with the absolute value of the parameter and the type of chemical involved. For example, it would cost significantly more to measure the solubility of a chemical with very low solubility (e.g., DDT) where special care in every step of the analysis is required, than for a chemical of much higher solubility (e.g., benzene).

When the costs of literature search and laboratory measurement are considered together, costs of \$100-1000 per property per chemical will not be unusual. To obtain, by literature search and measurement, all 23 properties listed in Table 21 for a single compound would thus appear to involve costs ranging from \$9,000 to \$40,000! If all values were available in the literature, total costs might range from \$1,000-\$10,000.

* Personal communication from M. Parnarouskis (USCG) to W. Lyman (A.D. Little), March, 1979.

TABLE 21

ESTIMATED COSTS FOR LABORATORY MEASUREMENT OF SELECTED PARAMETERS

<u>Parameter</u>	<u>Estimated Cost (\$)</u> <u>per Compound</u>	<u>Footnote*</u>
1. Solubility in water	400 - 4,000	1
2. Vapor pressure	150 - 2,000	1
3. Octanol/water partition coefficient	150 - 1,000	1,2
4. Adsorption coefficient for one soil or sediment	200 - 2,000+ 7,500	1,2 3
5. Bioconcentration factor for fish (flowthrough)	1,500 - 2,000 20,000	2 3
6. Rate of volatilization from water	100	2
-Henry's Law Constant	450 - 600	2
7. Rate of hydrolysis in water	400 - 6,000 12,000	1,2 3
8. Dissociation constant in water	50 - 200	1,2
9. Activity coefficient	(500 - 5,000)	
10. Rate of volatilization from soils	1,000 7,500	2 3
11. Diffusion coefficient in air	?	
12. Diffusion coefficient in water	(1,000)	4
13. Density	10 - 50	1
14. Boiling point	20 - 50	1
15. Heat of vaporization	(500 - 2,000)	4
16. Surface tension	(50 - 100)	4
17. Interfacial tension with water	(100 - 200)	4
18. Viscosity (several points)	(100)	4
19. Heat capacity	(1,000)	4
20. Thermal conductivity	(1,000)	4
21. Atmospheric residence time	?	
22. Dipole moment	?	
23. Refractive index (several points)	(100)	4

*Footnotes are given on the following page.

The point of this discussion is that there should be, for many chemicals and chemical properties, a significant cost (and time) savings associated with the use of estimated properties. In most cases we expect that the proposed handbook of estimation methods will allow a trained person to obtain an estimated value of one property (for one chemical) in 5 to 20 minutes if the input data required are readily available. If one or more of the input data items are not readily available and must, in turn, be estimated, up to one hour may be required. Additional time and cost would be involved if the missing input data had to be obtained from a literature search.

We are not suggesting here that estimated values can be substituted for values from the literature or measured values in all applications. A significant difference in the uncertainty of the value is clearly involved in many (but not all) cases. We are suggesting that managers and scientists consider, whenever possible, the potential time and cost savings involved with estimation techniques.

Footnotes to Table 21

1. Personal communication from D. Shooter (Arthur D. Little, Inc.). Memorandum: "Estimation of Costs for Chemical Fate Testing" (12 September 1978). The cost estimates are by Arthur D. Little, Inc.; the communication also provided cost estimates, for some parameters, from: (1) SRI International, (2) "Experts", and (3) Commercial Laboratories.
2. See reference no. 136 in Bibliography. The cost estimates of this reference appear to include only direct laboratory costs (i.e., excluding overhead) and may be too low.
3. Cost estimates associated with the registration of pesticides. Fed. Reg., 43(173):39644 (6 Sept., 1978).
4. Rough estimates by Arthur D. Little, Inc. No real bases for these estimates were available and they are, thus, quite uncertain.

IV. ENVIRONMENTAL FATE MODELING - AN OVERVIEW

A. Introduction

While Phase I of this program did not specifically include a general review and assessment of the state-of-the-art of environmental fate modeling, we did have occasion to look at a large number of models and to discuss general problems with a number of experts. Since it is expected that property estimation methods may play a significant role in future environmental fate models, it is well worthwhile to include in this report an overview of environmental fate modeling. The extent of our literature search efforts and contacts in Phase I was limited and, thus, it cannot be stated with certainty that the following material accurately reflects the state-of-the-art in detail.

This overview focuses on four basic types of models (for organic pollutants) which, it appears, would benefit most from the expected output of this program:

1. Bulk transport and dispersion models;*
2. Chemical fate models;
3. Soil/groundwater models; and
4. Chemical spill models

One other type of model which might also benefit includes those focussing on biota in an ecosystem (as stressed by a particular toxic chemical). We have not reviewed any models in this category. The chemical fate models do, however, usually consider the uptake and clearance of a chemical from aquatic biota.

Bulk transport and dispersion models generally describe the advection and mixing of a pollutant in the medium. The models for the most part are independent of the physicochemical properties of the compound in question, and rely instead upon bulk transport mechanisms. Processes in atmospheric models which might require a knowledge of the chemical characteristics of the compound include smog formation, photolysis, particulate adsorption, and reactivity with atmospheric gases, such as ozone.

Chemical fate models on the other hand emphasize environmental fate processes which require chemical specific inputs. Degradation pathways such as photolysis, hydrolysis, biodegradation, and dissociation are most often considered, as well as routes involving bio-concentration within the biota of the ecosystem, adsorption and volatilization.

Environmental fate models may cover wide ranges of space and time. Roughly, the models may be defined according to the following scheme

*These may be easily modified in most cases to include one or more chemical-specific fate or transport process.

in which the numbers in parenthesis are the horizontal space scale, the vertical space scale and the range of time, respectively.

- Global ($\sim 10^3$ km; ~ 0 -150 km, ~ 10 yrs.)
- Regional ($\sim 10^2$ km; 0 -150 km, 1 yr.);
- Local (~ 50 km; ~ 0 -1 km; ~ 1 yr.);
- Large Point Source (~ 10 km, ~ 0 -1 km; ~ 1 - 10^3 hrs.);
- Spill (~ 10 km; ~ 1 cm; ~ 1 -100 hrs); vertical scale may vary widely.

Soil/groundwater models should actually be considered a sub-category of chemical fate models. However, due to the large number of such models, a separate category was established. Soil groundwater models are confined to one environmental compartment, the lithosphere. Accordingly, the only compartmental parameters which need be modeled are the soil, groundwater and the soil moisture. The processes which are most often considered by soil/groundwater models are particulate adsorption and desorption, molecular diffusion, and vapor phase transport through the soil pores.

The last model type refers to chemical spills, usually occurring in a river system. The primary purpose of these models is to describe the propagation and mixing of the pollutant within the river, during the transport process. As with atmospheric dispersion models, bulk transport processes play a major role in executing the model. However, chemical properties such as density, vapor pressure and solubility are often required inputs.

The models that may be employed in some of these schemes can range from simple graphs or arithmetic exercises to complex computer simulations. There are many paths to the needed answers. Which of the available methods is appropriate depends on the specific problem and objectives. In many cases, short deadlines have forced the use of extremely rudimentary methods; however, the recognition of the social costs of suggested controls has led to a deeper interest in scrutinizing the results of more elaborate models. The difficult balance between public health risks, severe socio-economic dislocation and large financial outlays suggests that casual calculations will be unacceptable.

B. Objectives of Models

At the heart of the problem of relating impacts on health and the environment to control programs for toxic and hazardous chemicals is a reliable method of prediction. This provides a rational basis for drafting regulations designed to meet the mandates of clean air,

clean water, resource recovery, and toxic and hazardous substance control.

Environmental fate models have been used to achieve a number of goals. One of these goals is for the model to act as a "monitoring" instrument. If information is available concerning the source inputs, environmental pathways, and sensitive environmental targets of a certain compound, a model can be used to monitor the effectiveness of chemical control programs. Future pollutant concentrations in the environment resulting from changing emission conditions may be assessed, and used to evaluate the effects over a large area resulting from an industry-wide abatement of a particular compound. Modeling may also serve to predict the environmental fate of yet unmarketed chemicals, based upon the physico-chemical characteristics of the molecule. By evaluating the environmental fate of a pollutant, levels of exposure to be expected for humans and wildlife can be determined. The results of these risk assessments can be used as a basis for legislation and regulations. Lastly, modeling is a useful tool in examining the progress of a pollutant involved in a real episode of a chemical spill. The mixing and dispersion of the compound within the medium over distance and time is important information in terms of evaluating the size of the population and area over which harmful concentrations of the pollutant will result.

Currently, the use of models has been largely restricted to dispersion studies, such as atmospheric pollution and chemical spills. However, federal agencies and contractors have become increasingly aware of the numerous applications of environmental fate models in the field of research. This is especially true for chemicals which have not been monitored in the environment.

In determining how well a model meets its objectives, several questions must be asked:

- Who will use the model? (Research scientist? Regulatory agency? Spill response team?)
- What questions must it be able to answer?
- How well is it adapted to the intended applications?
- Has the model been thoroughly tested against an adequate data base for its validation?
- Is it amenable to practical calculations and computer implementation?

Because of the importance of the questions of model availability and validation, they are discussed in more detail below.

In general, environmental fate modeling is in a preliminary developmental stage, and, while a number of models do exist, very few (if any) have been verified, e.g., by comparing model results with data from model ecosystems, field ecosystems, or ambient concentrations. In addition, if "availability" (of a model) is defined to mean that a model: (1) has been published and reviewed in the open literature; (2) has available a detailed description of the system modeled, processes included, assumptions made, data requirements, computer program listing, etc.; (3) has available a computer tape or card deck containing the program; and (4) has data for one or more test cases for use with the model; then, we know of very few such "available" models. They are principally standard air quality (atmospheric diffusion) models and surface water diffusion and transport models for rivers and lakes. Most of these models consider "toxic" pollutants to be conservative species; some may allow for the use of an arbitrarily chosen decay constant, which assumes an overall first-order "decay" rate for the chemical.

For the most part, environmental fate models have not been validated. The exceptions to the rule are atmospheric dispersion and chemical spill models. Here validation may be carried out either with tracer gases (for the atmospheric models) and soluble dyes (for the water models) or by comparing the model output with the measured ambient concentration of the chemical species in question. Through use and experience, it has been determined that these models can closely predict monitoring data. Soil groundwater models have been validated to some extent by simple laboratory experiments or with field lysimeter data.

In addition to the above-mentioned problems, there are some who feel that our basic understanding of chemical fate (i.e., degradation) and transport processes is not sufficiently good to allow them so simply modeled. They would thus call into question most chemical fate modeling results.

In spite of the problems identified above, there is a generally optimistic feeling about the current modeling efforts. Their usefulness in assessing air quality and stream quality (for conservative pollutants) is well documented, and it seems reasonable to expect that environmental fate models for non-conservative species will soon be close to reaching the objectives sought.

C. Models Principally Considering Bulk Transport and Dispersion

There are, as implied above, a number of models (of varying "availability") which focus on the dispersion of a pollutant, usually in a single medium, and in a well-defined portion of the environment. Such models include air dispersion models, river and lake dispersion

(or mixing) models, soil/groundwater dispersion models,* and models of chemical spills.* The primary focus of these models is usually the bulk transport of a pollutant (with air or water) and the mixing and/or dispersion of the pollutant during this transport process.**

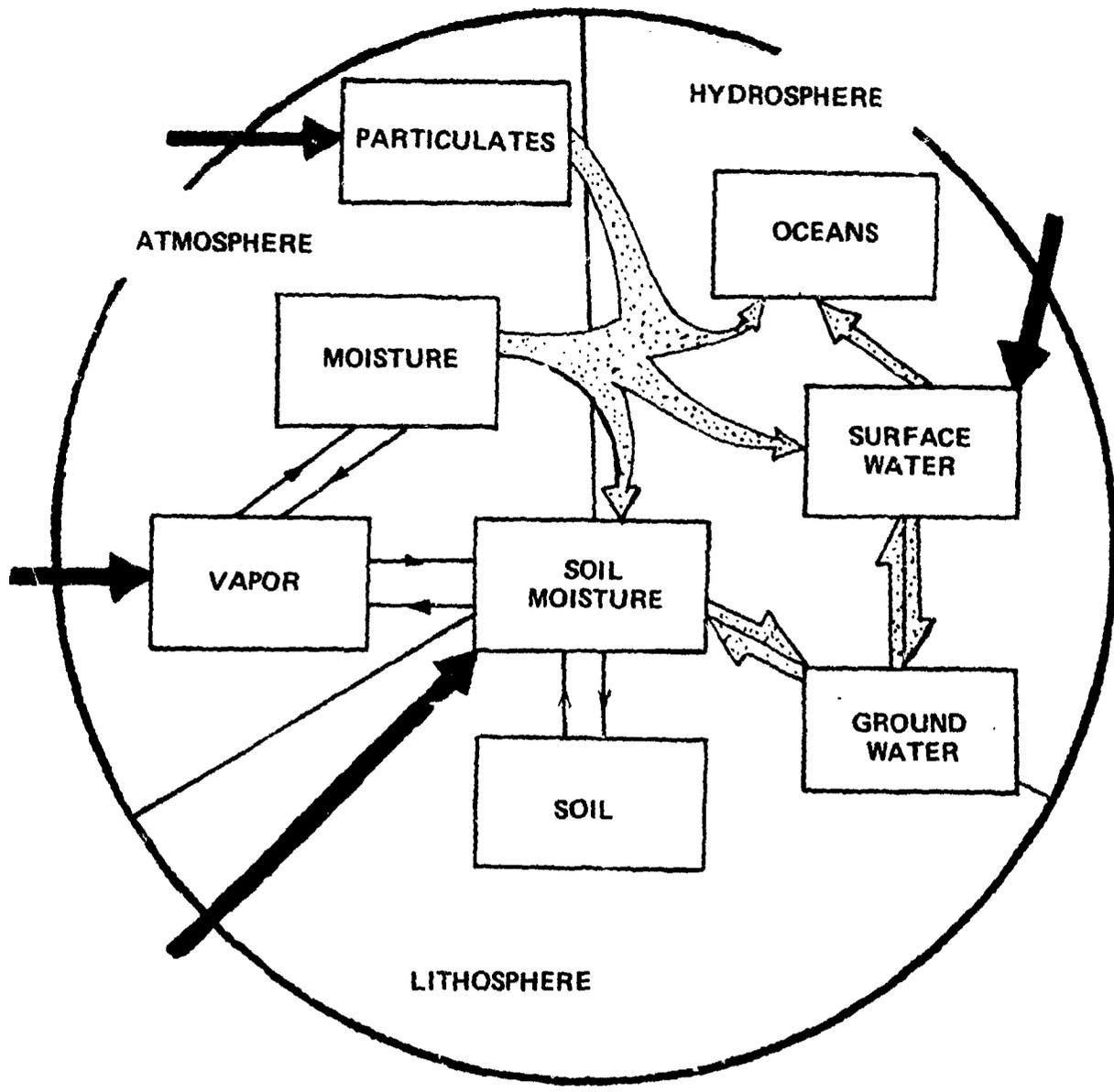
There have, to our knowledge, been few attempts to formulate general transport/dispersion models for the total environment, i.e., one that would include components of the atmosphere, hydrosphere and lithosphere as diagrammed in Figure 2. Such a model, to be sure, would only be applicable when long-lived chemicals were involved and large sectors of the global environment were of interest.

Most of these models are designed simply to estimate a pollutant concentration in a given environmental compartment, often at a particular time and location under dynamic equilibrium conditions but sometimes under some assumed equilibrium condition. It is then left to the model user to assess the impact of the calculated concentrations, and the sum of the impacts that a particular target system or organism (e.g., man) might be exposed to. With regard to human exposure, it is extremely rare to find a model that goes beyond simple compartmental concentrations to estimate exposures via a number of pathways (inhalation of air; ingestion of water and food; contact with drugs, cosmetics, dirt, etc.; industrial exposure; etc.) so that a clear picture of the total exposure of various segments of the population can be estimated. Some of the more detailed modeling efforts of this nature have been for such pollutants as lead and certain radionuclides (expected in fallout) and the models would not be useful for other pollutants without extensive modifications.

Atmospheric fate models have focused almost exclusively on the major atmospheric pollutants, such as particulates, NO_x, SO_x, CO, oxidants, and specific organic chemicals important in smog^x formation. In addition, a significant amount of work has focussed on the dispersion and fallout of radioactive material following a nuclear explosion. In the case of smog-forming chemicals it is not unusual to model a long chain of reactions (over 200 in some cases) when starting with a system containing initially only one organic chemical, NO_x, air and light. However, the consideration of specific chemical reactions is rare in those models that focus on just the fate of a general environmental pollutant. Recent work has indicated that, for many organic chemicals, one of the most important degradation pathways starts with a reaction with hydroxyl radicals in the atmosphere. Thus, this reaction - at a minimum - should be considered in any fate model for organics in the atmosphere. Adsorption of pollutants on atmospheric particulates is also seldom considered, perhaps because of our lack of knowledge about the fractions of various pollutants that are

*Discussed in subsequent subsections.

**More detailed information on this type of model is given in reference 217 (Section VI-B).



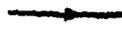
-  EMITTED CHEMICAL
-  BULK FLOW
-  DIFFUSIONAL OR CONVECTIVE FLOW

FIGURE 2 SCHEMATIC DIAGRAM OF INTERCOMPARTMENT FLOWS OF EMITTED CHEMICAL.
(man and biosphere omitts.)

associated with the wide variety of particulate matter that exists. Included, for example, are fugitive dusts, metal oxides, soot and other forms of unburnt carbon, water droplets, sea salt, and photochemically produced aerosols.

A final problem with most of the "available" atmospheric models (primarily dispersion models which might be easily modified to include reactions and adsorption) is the relatively short time-scale and small space-scale they are applicable to. One can classify such models by the time- and space-scales they focus on. Typical categories are as follows:

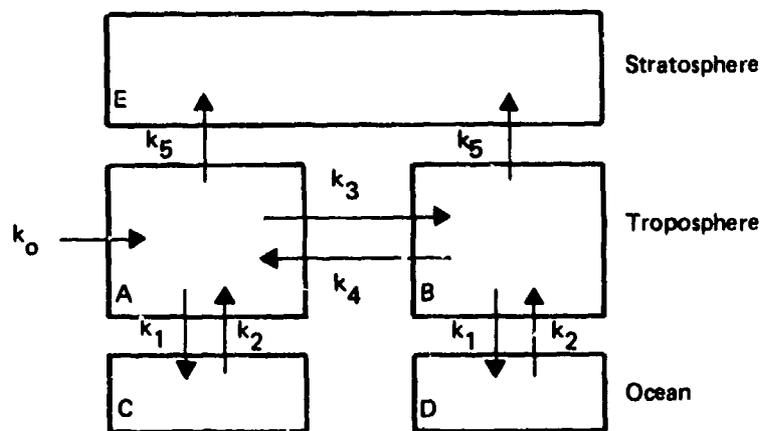
- A roadway impact model in the microscale (~0.1 km; ~10 min. to 1 hr.)
- Large-point-source or indirect-source model (~10 km; ~1 hr.)
- Urban regional scale model (~50 km; ~1 hr.)
- Urban-rural regional scale model (~300 km; ~1 hr. to 1 week).

If a continental or global atmospheric model were required, then processes such as rainout, dry deposition, reaction with ozone, and photolysis might also need to be considered in addition to hydrolysis (reaction with OH) and adsorption.

One example of a relatively simple global model where such processes were not used is that utilized by Woodwell, Craig and Johnson [288] to look at the probable levels of DDT in the troposphere and the mixed (surface) layer of the oceans. No physicochemical data on DDT were directly used in this model, which focussed on intercompartmental transport between the principal reservoirs: land surface, troposphere, mixed layer of the ocean, and oceanic abyss.

A second example of a relatively simple global model is the materials balance study of Neely for trichlorofluoromethane and carbon tetrachloride in the atmosphere [206]. This model did require some basic physicochemical information (water solubility and vapor pressure) in addition to the rates of flow between the principal reservoirs: oceans, troposphere and stratosphere (see Figure 3).

A second major category of environmental fate models focusing principally on bulk transport and dispersion includes those which consider the dispersion in rivers of pollutants which may be input from a variety of point and non-point sources. A specific example of a non-point source considered important is agricultural runoff, which may contain pesticides. Examples of such models are shown as numbers 12 and 19 to 26 in Table 6. Most of these models do, however,



- A = northern troposphere
 B = southern troposphere
 C = oceans north of equator
 D = oceans south of equator
 E = stratosphere
 k_1, k_2 = rate constants for movement across the air/water interface
 k_3, k_4 = rate constants for movement between the northern and southern troposphere
 k_5 = rate constant for transfer to stratosphere
 k_0 = rate of input

FIGURE 3 COMPARTMENTAL MODEL FOR THE DISTRIBUTION OF A VOLATILE SOLVENT EMITTED INTO THE TROPOSPHERE (DOW CHEMICAL CO.)

consider one or two additional processes such as adsorption, degradation (method usually not specified) or volatilization. In some cases, the major focus of the model is on the interaction of all organic material (measured in terms of BOD) and nutrients on the concentration of dissolved oxygen in the river under various conditions of river flows and BOD loadings (e.g., QUAL-1; no. 25 in Table 6). To such models it is relatively easy to append subroutines to calculate the concentration of conservative species that may also be in the river.

D. Chemical Fate Models

Chemical fate models go one step beyond transport/dispersion models by considering various processes that depend upon the specific properties of the chemical. Processes often considered include: adsorption (on soils and sediments); volatilization (from water to air); bioaccumulation (in aquatic organisms); biomagnification (in aquatic food webs); hydrolysis (in air and water); photolysis (in air and water); biodegradation (by soil and aquatic microorganisms); dissociation (for ionizable species); true diffusion; and other reactions that may be important. Even if degradation is not specifically considered, a variety of physicochemical parameters such as solubility, vapor pressure, rates of volatilization, adsorption coefficients and diffusion coefficients may be needed. Figure 4 diagrams a number of pathways and processes that might be considered in such models.

However, like the transport/dispersion models, the chemical fate models are generally constructed to consider either the atmosphere, the hydrosphere, or the lithosphere, but not a combination of these. A few "global" models (e.g., for DDT [56]) do exist which consider a combination of such compartments, but their numbers are few. Again, like the transport/dispersion models, the environmental fate models generally have as their output the concentrations of the pollutant expected in the compartments of the physical environment under study. Only in the case of models of the hydrosphere is it fairly common for uptake by (aquatic) biota to be modeled. But even here, it is rare for the model to go beyond direct uptake from water to consider such things as uptake from food (vs. uptake from water), food chain biomagnification, metabolism and excretion, and toxic effects.

The number of transport and reaction pathways that must be considered in models that do consider such processes can become quite large (see, for example, Figure 5), and as a result many parameters must be measured or estimated before the model can be used. In the example described in Figure 5 - the modeling of vinyl chloride in an aquatic ecosystem - a simplified (idealized) food web and chemical degradation system was eventually modeled by the researchers at EPA (Athens, GA) [128], and this model required a knowledge of the 15 parameters listed in Table 22. In one model currently being developed (again for an aquatic ecosystem) by Dr. R. Park at Rensselaer Polytechnic

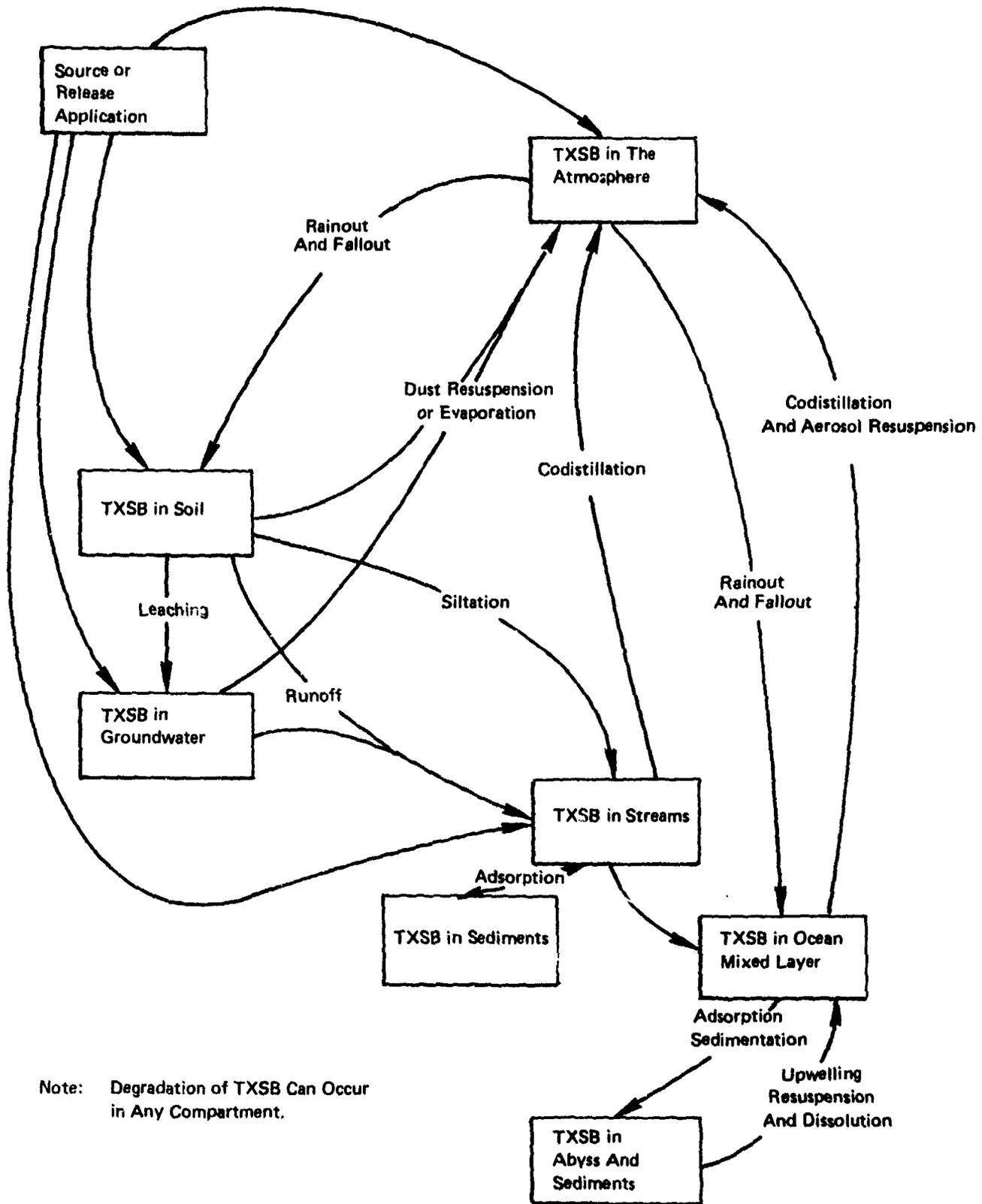


FIGURE 4 PATHWAYS FOR TOXIC SUBSTANCES (TXSB) IN THE PHYSICOCHEMICAL ENVIRONMENTAL SYSTEM

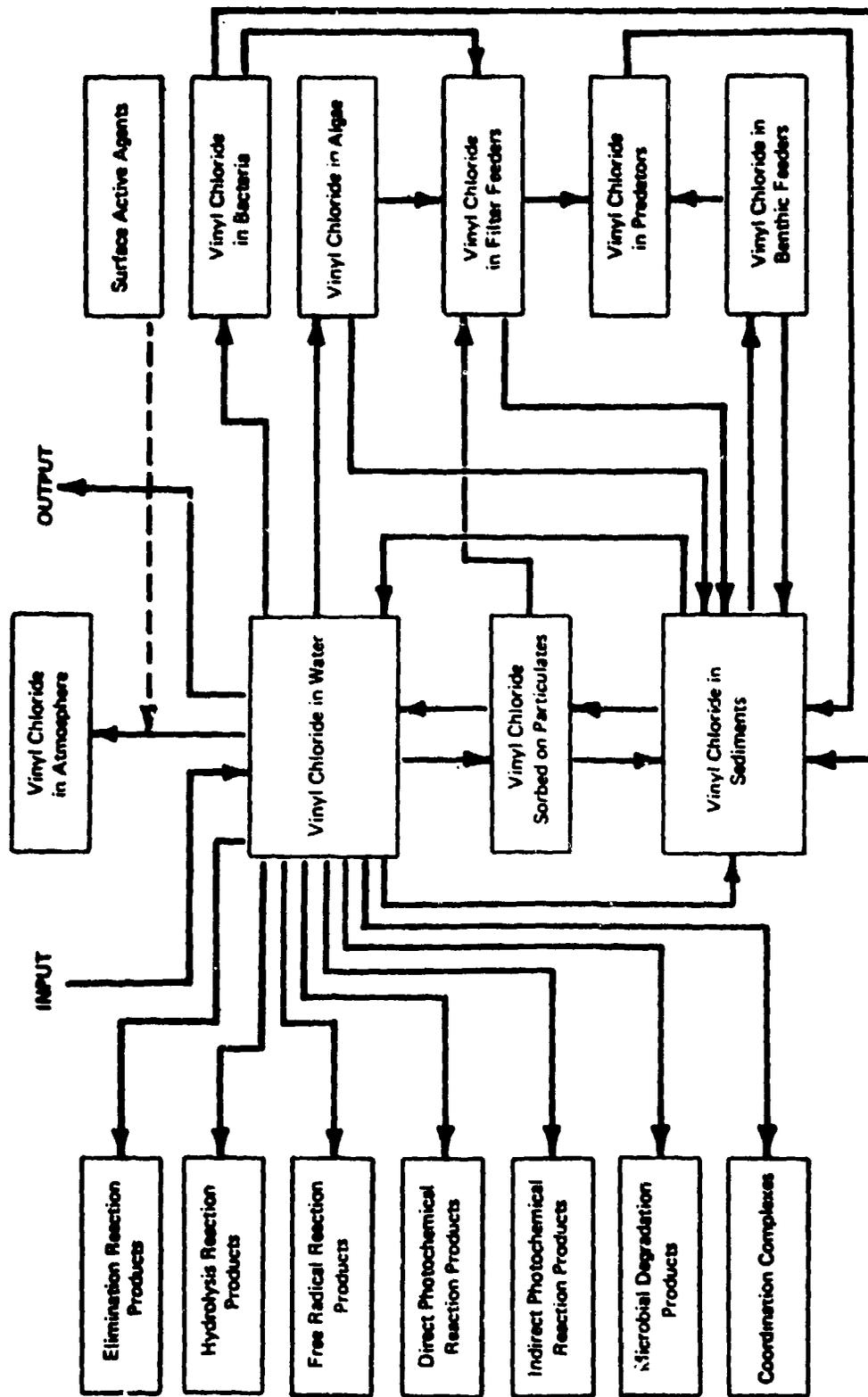


FIGURE 5 WORKING CONCEPTUAL MODEL OF VINYL CHLORIDE INTERACTIONS
IN AN AQUATIC SYSTEM
U.S. EPA, ATHENS, GA.

TABLE 22

PARAMETERS REQUIRED FOR MODELING VINYL CHLORIDE
IN AQUATIC ECOSYSTEMS - WORST CASE MODEL PARAMETERS

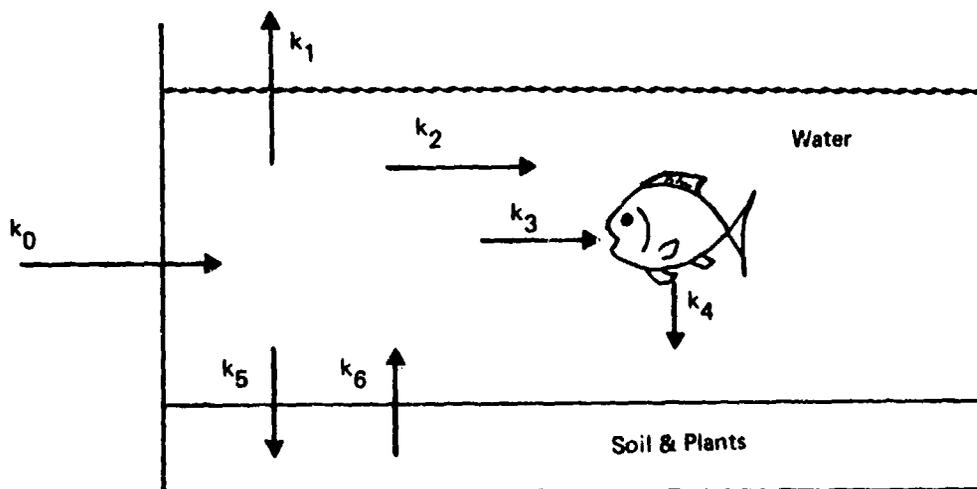
<u>Number of Parameters</u>	
1	Rate of volatilization
2	Combined chemical/biological degradation rate
2	Transport across thermocline
2	Uptake by filter feeding organisms
1	Uptake by benthic organisms
1	Uptake by predator
1	Uptake by omnivore
1	Turnover rate of organisms
1	Water to sediment transport
1	Sediment to water transport
1	Loss from compartment
1	Input to water

Institute for the EPA/Athens group, about 70 parameters are required to run the model; about 20 of these parameters are compound-specific [154, 221, 222].

Water/sediment fate models are the models most people think of when they think of "chemical fate models." As indicated above, these models may consider such processes as adsorption, hydrolysis, photolysis, biodegradation, volatilization and bioaccumulation. These models do not pretend, however, to describe the whole environment, nor even the total hydrosphere. Most models are for specific freshwater lakes and rivers; the oceans are not considered except as a permanent sink. Likewise, the atmosphere is generally considered as a permanent sink; the models allow for volatilization from the water to the air, but not for input from the air to the water. The variable degree to which these models consider the biotic compartment was described above. And finally, these models generally ignore the deep soil/groundwater compartment altogether. Good examples of such water/sediment fate models are: (1) the EPA/Athens model for vinyl chloride [128] described above; (2) the SRI model for certain energy-related pollutants and pesticides developed for EPA/Athens [249]; (3) an in-house model at EPA/Athens (EXAMS) that is similar to the SRI model; (4) the model (described above) being developed by Dr. Park at RPI (Troy, NY); and (5) a series of relatively simple fish-pond or lake models developed and used by researchers at the Dow Chemical Company (Midland, MI) [35, 205, 209, 210]. A schematic diagram of the processes considered in one of Dow's fish-pond models [210] is shown in Figure 6.

Chemical fate models for the total environment are very rare. While some work has focused on specific long-lived pollutants (e.g., DDT [56]) we know of only one attempt to create a general mass-balance/global model with a wide applicability to various chemicals. This model was prepared by Arthur D. Little, Inc. in order to assist EPA/OTS in screening and selecting chemicals or chemical classes as candidates for in-depth evaluation [273]. Of necessity, the model was designed to require a minimum of information for the chemical to be modeled since it was assumed that it would have to be used for "new" chemicals about which little was known. The number of environmental compartments considered by the model, however, is fairly large; dry air, air moisture and particulates; surface waters (lakes, streams and oceans); soil moisture (at various depths); and soil and groundwater (both at various depths). The model output is an estimate of the eventual equilibrium concentrations to be expected in each of these compartments. The general route of these calculations is shown schematically in Figure 7. The estimated compartmental levels were then to be compared, by EPA/OTS personnel, with "levels of concern" for each compartment so that a hazard evaluation and ranking could be made.

This model, as initially formulated, had two drawbacks with regard to realism. First, degradation (in any compartment) was only considered in a general way; there is no mechanism that allows input of data on



- k_0 = rate of input
- k_1 = rate const. for evaporation
- k_2 = rate const. for hydrolysis
- k_3 = rate const. for uptake by fish
- k_4 = rate const. for excretion by fish
- k_5 = rate const. for uptake by soil
- k_6 = rate const. for desorption by soil

FIGURE 6 SCHEMATIC OF FISH-POND CHEMICAL FATE MODEL DEVELOPED BY DOW CHEMICAL CO.

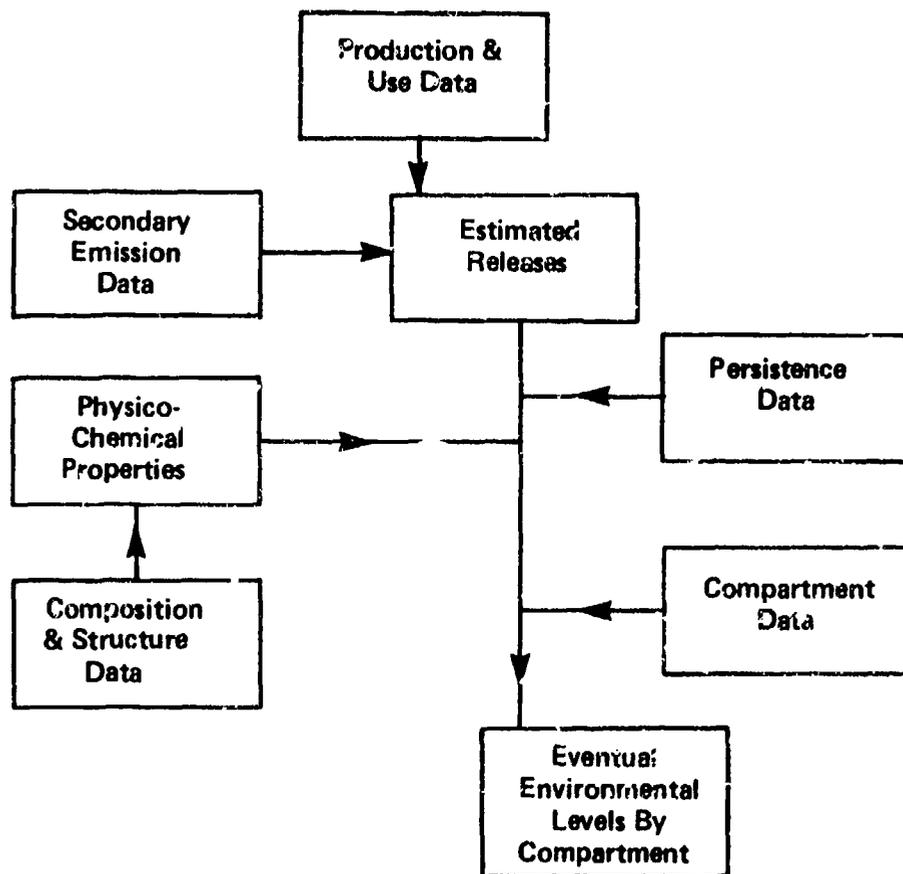


FIGURE 7 SCHEMATIC DIAGRAM OF THE FIRST BRANCH OF THE ADL SYSTEM FOR SELECTING AND RANKING CHEMICALS OF ENVIRONMENTAL CONCERN

rates of hydrolysis, photolysis, biodegradation, etc., although such data would be used to choose the first-order decay constants the model does require. Second, the model was designed to consider only an equilibrium situation so that the effect of changing emission rates (from industry, etc.) could not be evaluated. The latter drawback is currently being removed so that future versions of the model will yield time-dependent solutions.

E. Soil/Groundwater Models

Soil/groundwater models are concerned with the fate and transport processes of a pollutant within the soil/groundwater system (i.e., the lithosphere). In the models we reviewed*, the type of chemical considered is either organic (often a pesticide) or a plant nutrient. The characteristics of most soil/groundwater models seldom vary from one to another. The principal environmental compartments presented in these models are, as the title implies, the soil, soil moisture, and the groundwater. Sometimes the atmosphere is treated as a sink for volatile chemicals.

Bulk transport mechanisms, such as convection and dispersion, are most often incorporated in soil/groundwater models. Consequently, needed input characteristics about the soil arise, such as the soil porosity and/or permeability, moisture content, percent organic matter, soil profile and groundwater flow rates, to name a few.

With regard to the physicochemical properties of the pollutant, three inputs are often required - the adsorption-desorption coefficients, diffusion coefficients, and a "decay" constant. The decay constant is associated with any degradation or loss mechanism (e.g., hydrolysis) that the modeler may want to consider.

The adsorption/desorption terms occur in all the models referenced above. In addition, most of the authors choose to use the Freundlich isotherm equation as the best fit for observed data. The Freundlich adsorption isotherm is given as

$$S = KC^{1/n}$$

where S is the concentration of the adsorbed organic per unit mass, C is the concentration of the organic in solution and K and n are constants. When n is equal to 1.0, the adsorption isotherm becomes linear. Often, n is assumed to equal unity, although the values of 1/n reported for a number of agricultural chemicals range from 0.70-0.99 [167, 215]. Both K and n are found to be dependent on the nature of the adsorbant, adsorbate and temperature within the soil-water environment. The

*References 27, 37, 58, 130, 131, 155, 160, 161, 167, 172, 174-177 and 215 in Section VI-B.

Freundlich isotherm is based on the assumption that adsorption is an instantaneous, pointwise equilibrium process [174], which most authors assume to be true at low soil-water flow rates.

The process of desorption sometimes involves a different set of K and n parameters, due to the effects of hysteresis [58, 130, 131]. Hornsby and Davidson [130] have noted that the desorption constant is not a constant, but a function of the maximum amount of chemical adsorbed before desorption occurs. Hysteresis may also be dependent on the nature of the soils and the chemical nature of the adsorbate. In general, hysteresis is not significant for neutral organic molecules which do not contain any reactive sites or elements which would lead to any form of irreversible adsorption process.

Some models concern themselves with the rate at which adsorption equilibrium conditions are established. For these models, the kinetics or rate of adsorption, is important. Examples of this type are found in references 58, 130, 131, 167, 174, 177 and 215.

Another parameter inherent in the nature of the chemical is the diffusion coefficient in air and/or water. This coefficient is required by models referenced as 27, 37, 58, 130 and 161, 167, 172, 174-176. The coefficients are used to estimate movement or dilution in situations where bulk transport and dispersion are relatively slow. Diffusion through both the air spaces (of a porous soil) and the groundwater may thus be considered. Approximate values may be calculated for pesticides in both liquid and gas systems [167]. Otherwise, it is empirically determined from Fick's Law [37]. Since the net rate of chemical movement from areas of high to low chemical concentration is a function of the difference in concentrations, and the distance between the two areas, an empirical ratio was established in which the proportionality constant D is known as the diffusivity.

In some cases where transport through partially saturated (i.e., moisture containing) soil is being considered, diffusion through both the air spaces and soil moisture is taken into account with the use of a single coefficient called the apparent diffusion coefficient. Leistra [167] has observed three main factors which lead to the apparent diffusion coefficient in soil. They are: (1) diffusion of the chemical as a bulk quantity in the phase concerned, (2) the volume fraction of the phase, and related soil geometries, and (3) partitioning of a pesticide over the soil phases, with the processes of adsorption and solution acting to possibly retard diffusion.

In addition to these major physicochemical parameters used in soil-groundwater models, occasionally the "half-life" of the chemical is required for the consideration of assumed first-order decay processes [155].

F. Chemical Spill Models

Our review of chemical spill models was essentially limited to the models incorporated in the U.S. Coast Guard's Chemical Hazards Response Information System (CHRIS). The CHRIS manual is an official publication of the U.S. Coast Guard and consists of the following volumes:*

- CG-446-1 A Condensed Guide to Chemical Hazards
- CG-446-2 Hazardous Chemical Data
- CG-446-3 Hazard Assessment Handbook
- CG-446-4 Response Methods Handbook.

The manual provides timely information essential for proper decision-making by responsible Coast Guard personnel and others during emergencies involving the water transport of hazardous chemicals.

Of key interest to this program is the Hazard Assessment Handbook and the associated Hazard Assessment Computer System (HACS). The Handbook describes procedures to be used for estimating the quantity of a hazardous chemical that may be released accidentally during shipment. It also describes how to estimate its concentration in air and in water as a function of time and distance from the discharge. Methods for predicting the resulting toxicity, fire and explosion effects are also described. The details of the calculations are described in two separate documents [231,232]. (Some of the mathematical models employed have been independently reviewed [74]).

HACS is a computerized version of the Handbook. The calculations use data on the physicochemical properties of various chemicals as given in CG-446-2. Many of the data points in CG-446-2 are estimated values since literature values were not available. At present a physical properties data base for about 1500 chemicals is available for use in HACS.

In the initial steps involved in the use of HACS, a few basic properties of the spilled chemical (e.g., density, solubility, vapor pressure) and the environment (temperature, dimensions of stream, ignition or non-ignition of flammable chemicals, etc.) are used to select the appropriate branch(es) from a hazard assessment tree (Figure 8). Then, as necessary, additional data on the chemical and the environment are obtained and used in the mathematical model(s) available for that branch. Hazard assessment codes, which refer to various branches in Figure 8, are given below for a few sample chemicals.

*Most of these volumes were published in 1974 and are available through N.T.I.S.

<u>Chemical</u>	<u>Hazard Code (see Figure 8)</u>
Dichlorodifluoromethane	A-C and/or A-I-J
Ethylene	A, A-C, A-D-E, and/or A-D-F-G
Gasoline (automotive)	A-T-U and A-V-W
Polychlorinated biphenyl	A-II
Sodium	A-RR-C
Sodium fluoride	A-SS
Trichloroethylene	A-X-Y

Depending upon the details of the spill and the chemical's hazard code(s), various mathematical models from the HACS are called into use. The types of programs possible are shown by the boxes in Figure 8. A more detailed listing of available programs is given in Table 23.

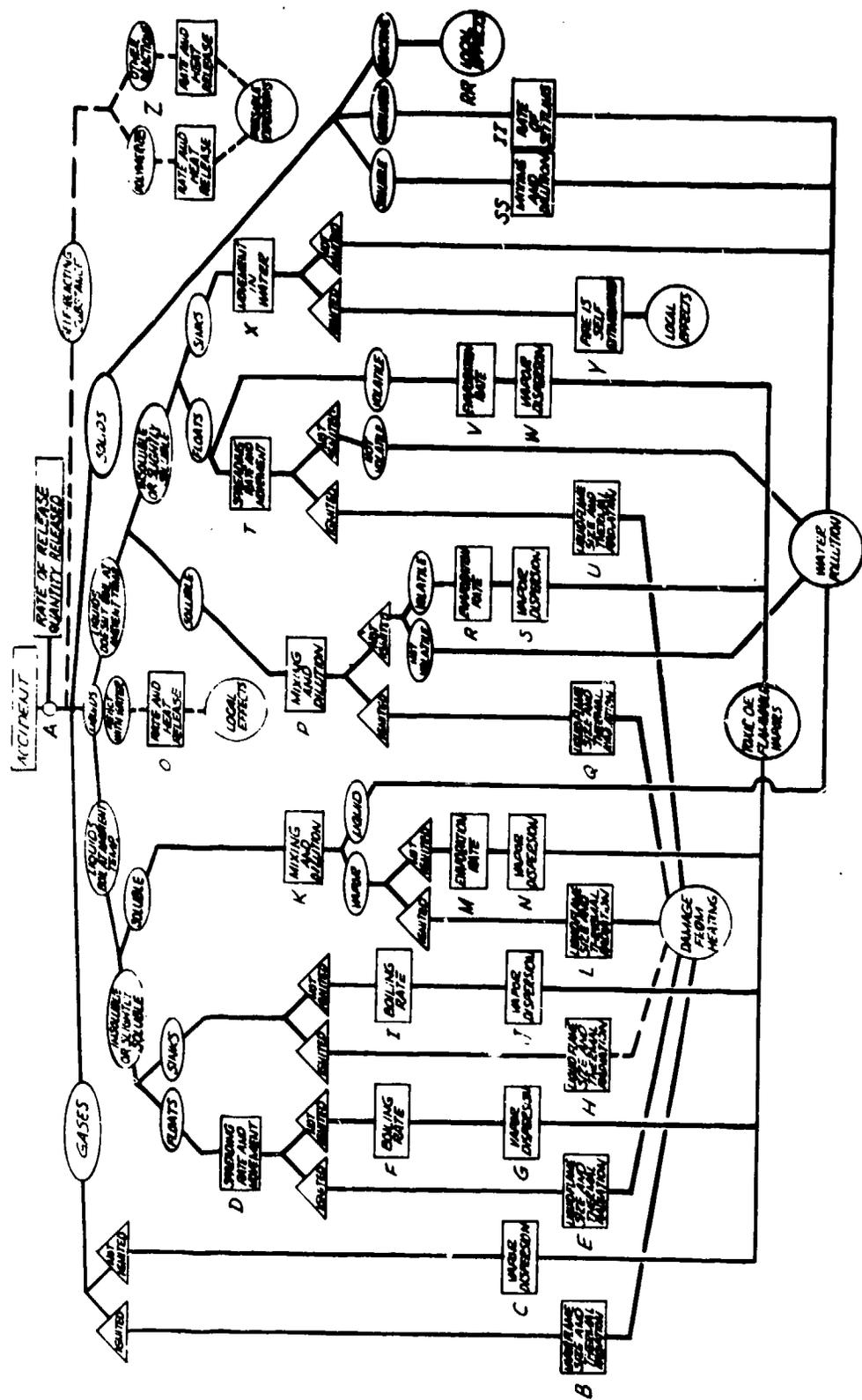


FIGURE 8 HAZARD ASSESSMENT TREE: (EVENTS CHART) FOR USE IN THE U.S. COAST GUARD'S CHEMICAL HAZARDS RESPONSE INFORMATION SYSTEM

TABLE 23

PROGRAMS AVAILABLE FOR CHEMICAL SPILL
MODELING IN THE U.S. COAST GUARD'S HAZARD
ASSESSMENT COMPUTER SYSTEM

1. Venting rate
2. Spreading of a liquid on water
3. Mixing and dilution
4. Vapor dispersion
5. Flame size
6. Thermal radiation from flames
7. Spreading of a low-viscosity liquid on a high-viscosity liquid
8. Simultaneous spreading and evaporation of a cryogen on water
9. Simultaneous spreading and cooling of a high-vapor-pressure chemical
10. Mixing and dilution of a high-vapor-pressure, highly-water-soluble chemical
11. Boiling rate model for heavy liquids with boiling temperatures less than ambient
12. Sinking to and spreading on the riverbed of an insoluble, heavier-than-water liquid chemical
13. Dissolution and dispersion of chemicals of finite solubility
14. Dissolution of cold and soluble chemicals under water
15. Spreading on the water surface of a continuously released, lighter-than-water, immiscible liquid
16. Heating, rupture and release of a pressurized cargo in a fire

V. SCOPE AND APPROACH FOR PHASE II

[Note: This information was included in the original Technical Proposal for Phase II. Also note, as described in the Executive Summary, that four properties were subsequently added to the list to be included in the handbook, two of which will be treated in a more qualitative manner.]

A. Scope of Work

We will prepare an estimation methods handbook which will evaluate and describe available estimation methods for the properties listed in Table 2. The scope of work may be limited to a subset of this list, at the discretion of the Government. The groups identified in Table 2 are associated with breakpoints in our cost proposal which is being submitted separately.

For each of the properties chosen, a study program will be designed and carried out which will look for and evaluate all available estimation techniques, correlation equations, etc. The study program will include literature searches, contact with the author(s) of key papers, and a subsequent critical evaluation to look at questions dealing with method applicability, method errors, ease of method's use and the availability of data for use in the method.

A draft final report will be prepared that includes a description of all estimation techniques considered appropriate for the handbook, along with all basic equations, tabular data, exemplar problems, and a description on how to estimate the method errors. Estimation techniques which, after evaluation, are not considered appropriate for inclusion may only be briefly described and the reason for the non-inclusion stated. The report will also contain recommendations for future research, especially in connection with those properties for which useful estimation techniques were not available.

The draft final report will be submitted to the sponsors for review. A final Phase II report will then be prepared and followed up with a Technical Transfer meeting at Fort Detrick.

B. Approach

The technical approach to the work in Phase II will involve the following basic steps:

- a. Assignment of responsibility to individuals for the work on specific parameters, and the initial formulation of a study program for each of the properties/parameters selected.
- b. Gathering of all relevant information for each property/estimation technique.
- c. Evaluation of available estimation techniques.
- d. Preparation of write-ups for each application estimation technique.

- e. Determination of future research requirements in the area of estimation technique development.
- f. Preparation of a draft final report.
- g. Preparation of a final report.
- h. Technical Transfer meeting.

Each of these steps is briefly described below:

- a. Each property/parameter will be assigned to a senior professional who will subsequently be responsible for the preparation of the handbook chapter(s) for those properties. In the Technical Proposal we have tentatively identified specific individuals who will be assigned such responsibility for each of the properties. The first task of these individuals would be the preparation of a detailed work plan for each property. In most cases, we already have a fairly clear overview of the estimation technique(s), correlation equations, data bases, etc., that are available. The plan would include not only actual work requirements (literature searches, evaluations, contacts with experts required, etc.), but time and budgetary restrictions as well.

The bulk of our work would focus on those properties for which one or more estimation technique or correlation equations existed, but where no critical review had been undertaken. Relatively little work would be required on properties such as those covered in Reid and Sherwood's The Properties of Gases and Liquids.

The plans would be reviewed by the key members of the case team, our consultant, the ADL Review Committee and the sponsors.

- b. The collection of the required information on each property and estimation technique would include both a careful literature search, as well as personal contact, where possible, with the originators of the more recent research papers on the subject.

The literature search strategy for each parameter/estimation method may differ somewhat and will be formulated - in part - on the basis of information obtained in Phase I. In Phase I we compiled a bibliography of nearly 300 reports, articles and books dealing with subjects pertinent to this program. In most cases, we have already obtained copies of the reports and reviewed them. From these reports we can identify key researchers in each property estimation field and contact them for the most recent information in the field. Personal contact may be required for most property estimation techniques since the published research papers seldom contain all the data required (for error estimation or method evaluation) and are often unclear as to applicable

units, limitations in use, or test conditions. We intend to request the raw data whenever it is apparent that the published data have been significantly reduced or limited for any purpose.

- c. The collected data and information are then used to evaluate each estimation technique or correlation equation. This specifically includes a determination of: (1) the applicability to different chemical classes, (2) the range of values (of the estimated parameter) the method is good for; (3) the nature and size of the errors involved; (4) the proper methods of use and the ease of use; and, (5) the quantity and quality of the data (e.g., parameter or substructure coefficients) available for use in the method.

The analysis of method errors will, as previously mentioned, be coordinated by one individual (Dr. M. Richards). He will, where appropriate, review reported error limits associated with estimation methods, prepare a uniform method for us to use in describing errors (or quality of "fit") associated with correlation equations, and set up procedures whereby we can derive our own estimate of the method errors. One possible mechanism for this is the use of two sets of chemicals in the evaluation of a method; one, the "teaching set", is used to evaluate the method and "determine" what the likely errors are; the other, the "test set", is subsequently used to check the previous findings. (The check involves a comparison of actual and estimated values.) This "teaching set"/"test set" concept can also be used in many cases to determine the range of applicability of a method, both in terms of chemical class and property range.

- d. The write-up on each estimation method, following from the above analysis, would be expected to follow the following basic format:
1. Introduction - A brief description of the property and the basis for the estimation methods available.
 2. Applicability - A clear description of the limits to the method applicability in terms of chemical class, range of values of the parameter, test conditions, etc.
 3. Method Description - This section will contain the basic equations, values of constants, tabular data, and any other information, and instructions needed for actual calculation of an estimate.
 4. Errors - This section will, to the extent possible, give a qualitative and quantitative description of the errors inherent in the method and indicate how the possible error in an estimated value can itself be estimated.
 5. Examples - One or more examples (several when the method is complex) will be given to show the proper use of the method, and the difference between the estimated and actual value of the parameter.

6. References - All references will be listed at the end of each section dealing with the estimation of a specific parameter.

Where more than one estimation method, or correlation equation is available for a given parameter, a discussion of the relative usefulness of each will also be included in the section dealing with that parameter.

We would expect to give each estimation-method write-up a "user's test" prior to acceptance for the final report. In this "user's test", a technical person unfamiliar with the method would be given the write-up and asked to estimate the property values and the probable errors for a set of chemicals. The difficulties the user encountered with the write-up would - to the extent possible - be removed by additional evaluative work and/or re-writing. If significant difficulties were encountered on the first test, a second test would be held.

We plan to have each initial draft of the write-up on a property undergo peer review by a knowledgeable person. The person may be from our own internal case team (including our consultant, Dr. Robert Reid) or from a University, Federal Agency or private company. We expect that such an independent peer review will add significantly to the completeness and quality of the final report. A second technical review will be required in any case where substantial changes result from the initial review.

- e. We will, for each property identified in the Phase I study, consider what additional research might be conducted to further develop estimation techniques for that parameter. This would be done whether or not an estimation technique or correlation equation already existed for the parameter, although special emphasis might be put on those properties for which no reliable estimation method was available. In different instances, these recommendations for future work might, for example, point out:
- The need for more basic data on actual values of the "property" under various test conditions.
 - The need for a better understanding of the mechanisms of the chemical or physical actions involved, with the possibility of theoretical treatments (including the formulation of equations).
 - The fact that data exists for additional correlations to be tested and developed from.
 - The fact that the property was probably related to structure in a manner similar to some other property for which detailed information on the property-structure relationship existed and that an estimation technique might, thus, be developed if a similar set of substructures and related coefficient values could be determined.

- f. The draft final report will contain the output from the work described in (d) and (e) above. Each of the method descriptions, as described in (d) above, would be grouped with all other method descriptions for the same parameter. A schematic outline of the report is given in Table 24.

We plan to have this draft final report undergo a careful review and editing process. A technical review will first be undertaken by the case leader and other key members of the case team, by at least one member of the review committee, and the project officer. The technically edited report will then be given to a professional editor (William F. Reehl) who will insure that the resulting report is well written, well organized and easy to read.

All tables, figures and any other art work will be put in final form at this time. Our Art Department will rework all graphs, charts, and figures, as appropriate, so that the finished figures can be used for the book planned for Phase III. In addition, we plan to process the final version of the text through our DecSet text-editing system so that future revisions are facilitated.

The final typed version of the draft final report will then be submitted to the sponsors for review.

- g. The comments from the sponsors will direct any changes required for the preparation of the final report.
- h. Following submission of the final report, a Technical Transfer meeting will be held at Fort Detrick to review the recently-completed Phase II work, and discuss plans for Phases III and IV.

TABLE 24

SCHEMATIC OUTLINE OF THE PHASE II FINAL REPORT

- I. Introduction (background, purpose, scope, etc.)
 - II. The Use of Estimation Methods
(Comments on symbols and units used, estimation errors, and general caveats on necessary checks for applicability, etc.)
 - III. Property A [e.g., Solubility in Water]
 - 1. Method (a); format as described in (d)
 - 2. Method (b)
 - etc.
 - n. Recommendations for Best Method
 - IV. Property B [e.g., Volatilization from Water, Rate of]
 - 1. Method (a)
 - 2. Method (b)
 - etc.
 - n. Recommendations
 - V. Property C
etc.
- etc.
- XX. Recommendations for Future Research
 - 1. Property A
 - 2. Property B
 - 3. Property C
 - etc.

VI. BIBLIOGRAPHY

A. Other Bibliographies Used

The eleven citations on the following two pages are of bibliographies that were used in the literature search efforts in Phase I of this program.

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2. Cavagnaro, D.M., "Atmospheric Modeling of Air Pollution. Volume 3. 1977-June 1978 (A Bibliography with Abstracts)," National Technical Information Service, Springfield, VA. (June 1978). (NTIS/P5-78/0631/8WP).
3. Copenhaver, E.D. (Ed.), **NSF-RANN Trace Contaminants Abstracts**, by Toxic Materials Information Center, Oak Ridge National Laboratory, Oak Ridge, TN:
 - (i) Vol. 1, No. 6 (July 1974) (Yearly Review Issue)
 - (ii) Vol. 2, No. 1 (August 1974)
 - (iii) Vol. 2, No. 2 (May 1975)
 - (iv) Vol. 2, No. 3 (June 1975)
 - (v) (December 1975)
 - (vi) (July 1976)
 - (vii) (September 1976)
 - (viii) (April 1977), Harnden, D.S. (Ed.)
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 - (Program terminated after this issue).
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10. Wilkinson, B.K., L.S. Corrill and E.D. Copenhaver, "Environmental Transport of Chemicals," Oak Ridge National Laboratory, Oak Ridge, TN (1974); Report No. ORNL-EIS-74-68.
11. Wilkinson, B.K. and S.K. Smith, "NSF-RANN Trace Contaminants Program," by Toxic Materials Information Center, Oak Ridge National Laboratory, Oak Ridge, TN (December 1975). (ORNL-EIS-83). Second directory, by P.A. Purnell, S.K. Smith and C.F. Wilkes (October 1976). (ORNL-EIS-97).

B. Articles, Books and Reports

The bibliography on the following pages lists, in alphabetical order by author, all of the articles, books and reports that resulted from our literature search efforts (through December, 1978) in Phase I. We have obtained and reviewed about 95 percent of these listings. (Copies of the remainder have been ordered but not yet received.) Subsequent to our review of these documents, we have found that a relatively small number contain little or no information of importance to this program; these will be removed from future bibliographies prepared for this program.

Since December, 1978, we have identified about one hundred additional articles, reports or books that may be of use in this program. Citations for these will be added to any revised bibliography prepared.

In addition to the new entries, mentioned above, we hope to have time to prepare a subject and author index for the expanded bibliography prior to the formal initiation of Phase II.

1. Abrams, D.S. and J.M. Prausnitz, "Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems," *AIChE J.*, **21** (1): 116 (1975).
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9. Anon., **Assessing Potential Ocean Pollutants**, National Academy of Sciences, Washington, D.C. (1975).
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11. Anon., **Decision Making for Regulating Chemicals in the Environment**, National Academy of Sciences, Washington, D.C. (1975).

12. Anon., "Initial Report of the TSCA Interagency Testing Committee to the Administrator, Environmental Protection Agency," U.S. Environmental Protection Agency Report No. EPA 560-10-78-001 (January 1978).
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