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PRE-SCREENING FOR ENVIRONMENTAL HAZARDS –

A SYSTEM FOR SELECTING AND PRIORITIZING CHEMICALS

APRIL 1977

PHASE 1 REPORT

ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF TOXIC SUBSTANCES
WASHINGTON, D.C.

PRE-SCREENING FOR ENVIRONMENTAL HAZARDS --

A System for Selecting and Prioritizing Chemicals

REPORT TO THE

Office of Toxic Substances
U.S. Environmental Protection Agency
Washington, D.C. 20460

APRIL 1977

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SUMMARY

This report presents the results of a study whose objective was the development of a conceptual scheme for ranking chemicals emitted into the environment in order of their hazard potential. Although the major focus is on preliminary screening of chemicals prior to full commercial production, the scheme we recommend could also be used for evaluating the potential hazard of chemicals already in production.

We have explored a number of alternatives for ranking chemicals so that subsequent research efforts may be properly focused. The method we recommend for subsequent development has the potential of fulfilling the needs. Basically, the method consists of selecting chemicals for further attention by comparing the concentration of each chemical that may be expected in the environment to the concentration levels of that chemical which are of concern.

The proposed method for estimating the eventual environmental level is based on a multi-compartment model of the environment. In order to provide estimates with moderate effort the model is substantially simplified. The emphasis has been on ensuring that the model does not underestimate the eventual levels, and that overestimation is kept within reasonable bounds.

The proposed method for estimating levels of concern was also selected on the basis of simplicity and accuracy. A test using available information on tolerable air concentrations indicates that the estimated levels would be adequate for preliminary screening.

The method also provides the capability of ranking the selected chemicals into more refined priorities by estimating the time horizon during which regulatory action would prevent significant deleterious effects.

Before the conceptual scheme can be implemented additional research is required. The main area of research to be pursued is the development of improved methods of predicting levels of concern from available information on chemical composition. The performance of the system with a number of test chemicals also needs investigation.

INTRODUCTION

A. BACKGROUND

The hazards posed to the total environment by certain substances is now widely appreciated. These substances affect the environment, threaten the integrity of ecological niches, or endanger man by a variety of modes of action ranging from direct effects, through effects of their decomposition products, bioaccumulation in prey-predator chains, synergism, and interaction products.

It is generally recognized that the potential for damage could often be anticipated if there were adequate data on the toxicity of the substances involved in a variety of relevant species. Yet, the collection of an adequate data base on chronic toxicity would entail substantial expenditures and extended periods of time.

In an economy that relies heavily on new materials to improve the quality of life, decrease the cost of goods and thereby improve their distribution to people of all income levels, the potential delays and costs associated with thorough testing prior to production is viewed with substantial concern. This concern is quite justified if we realize that the eventual distribution of substances in the environment is not easy to predict and, in fact, it may take decades before it can be estimated accurately enough to relate these levels to the toxicological information. A further cause for concern is that in some compartments of the environment the concentrations may continue to increase well beyond the time at which release of the substance has been discontinued.

In spite of and because of these difficulties, it is essential that some methodology be developed that will allow an orderly review of environmental contaminants and will lead to the selection of some subset of these as being of sufficient concern as to warrant the development of an adequate toxicological data base or, in extreme cases, a reduction in the level of emissions into the envirnoment.

The recently enacted Toxic Substances Control Act requires the testing of chemical substances and mixtures which "may present an unreasonable risk of injury to health or the environment." Test data might be required, for example, to establish potential risks of acute toxicity, subacute toxicity, chronic toxicity, persistence, carcinogenicity, mutagenicity, teratogenicity, behavioral disorders, etc. The Act recognizes the need for prioritizing chemicals for testing, and provides for the establishment of a list of chemicals, not to exceed 50 at any time, for which test data are most urgently required.

Prioritization is of key importance to protecting health and the environment, without imposing both major economic burden on the chemical industry and a major administrative review burden on the EPA. The National Institue of Occupational Safety and Health "Registry of Toxic Effects of Chemical Substances" (formerly called "The Toxic Substances List") 1976 Edition, for example, includes nearly 22,000 different chemicals, and the numbers expected to be included in subsequent editions is currently estimated at about 100,000 unique toxic substances. Development of a full battery of health and environmental effects test data for all of them is clearly impractical within a realistic time frame. The alternative described in this report is aimed at the development of an objective prioritization methodology capable of (1) classifying chemical substances with respect to the probable risk they present to human health and/or the environment; and (2) identifying the kinds of test data that would assest in determining whether or not the probable risks are "unreasonable."

If such a methodology is to be effective in reducing the amount of data which must be developed, while at the same time directing data development efforts to the most crucial problem area, it should have the following characteristics:

(1) The screen should "pass" a significant fraction of chemical substances, on the grounds that they have such a low probability of presenting unreasonable risks under current and projected conditions of use, that additional data development does not appear to be worthwhile. (This assumes of course that a large number of chemical substances can defensibly be categorized in this way.)

(2) Ideally the screen should also provide some indication of the nature of the probable risk for substances that do not "pass" (i.e., indicate whether the risk is to air, water, and/or ground pollution, and whether it is carcinogenicity, teratogenicity, mutagenicity, chronic toxicity, etc., to humans; phytoxicity; persistance; bioaccumulation; synergism, etc.)

The list of substances which "pass" the screen would include substances such as those on the FDA's GRAS list and substances which, though potentially damaging at some concentrations, are not likely to reach concentrations which pose unreasonable risks to health or environment. They would be substances, which on the basis of current knowledge and perceptions, appear to be sufficiently safe to require no further testing at the moment. As new knowledge develops and perceptions change, the list would have to be reexamined and reevaluated.

To say that a chemical substance is *not* hazardous to human health and/or the environment is to imply that the substance does not induce a whole variety of potential adverse effects traditionally associated with chemicals. To say that a chemical substance *is* hazardous is to imply that the substance exhibits at least one adverse human health or environmental effect. If only one such effect is suspected, then that is the effect for which data development should be prescribed. Even if there is a high probability that a chemical substance may produce several adverse effects, it may not be necessary to document all of them. If, for example, a substance is a suspected human carcinogen and also may lead to fires in landfills, data development could probably most usefully be focused on the question of carcinogenicity.

A reasonable and defensible chemical screening system is not a substitute for experimental data. A screening system is nothing more than a systematic mechanism for reviewing available data, and for prioritizing future data needs, so that resources (which are always limited) may be directed as early as possible into the most crucial problem areas. This report is concerned with the development of an objective screen based on the amounts of chemical substances released into the environment and the kinds of problems associated with the projected levels of such substances in the environment. Prioritization of the problems identified with respect to their need for attention and with respect to the kinds of data that should be sought is a subjective matter which is well beyond the scope of the present effort.

B. PURPOSE AND SCOPE

The overall goal of this project is to design, implement and install within the Office of Toxic Substances an identification system for selecting and ranking chemicals, chemical classes or use classes by objectively assessing their environmental hazards. The project has been organized into two phases - the first focused on systems design and the second directed towards implementation. This report summarizes the results of Phase I.

Phase I encompassed the following tasks:

- Task 1 - System Design Criteria - Criteria were developed to guide the design and development of an environmental hazard identification system that would meet the needs of the Office of Toxic Substances.

- Task 2 - Analysis of Information Needs - Minimum input parameters were defined that should enable a system to select and rank chemicals potentially hazardous to the environment.

- Task 3 - Formulation of System Concepts - A number of potential system concepts were formulated to serve as informal models against which to evaluate selected systems.

- Task 4 - Evaluation of Existing Identification Systems - Prior work had shown that *none* of the many existing systems were readily adaptable to meeting the specific needs of the Office of Toxic Substances.[1] Several of the more promising approaches, however, were evaluated against the design criteria, information requirements, and system concepts developed in Tasks 1-3 in order to define their shortcomings more precisely.

- Task 5 - Resolution of Information Gaps - The problem of data availability, not just for specific chemicals, but in whole areas of health and environmental concern, was consciously and seriously considered, but not entirely resolved.

- Task 6 - Proposed System - A basic system with a number of variations of increasing complexity, has been developed for selecting and prioritizing environmental hazards.

- Task 7 - System Test Methodology - A methodology for testing the applicability and reliability of the basic system, and for evaluating the potential benefits of the more complex variations is presented in the final section of this report and concludes the Phase I effort.

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[1] *Literature Search and State-of-the-Art Study of Identification Systems for Selecting Chemicals or Chemical Classes as Candidates for Evaluation* (EPA-560/1-74-001), Environmental Protection Agency, Office of Toxic Substances, Washington, D.C., November 1974.

C. DEVELOPMENT OPTIONS

1. System Design Criteria

Some of the criteria developed to guide the design of a workable environmental hazard identification and prioritization system include:

(1) Objectivity. Policy decisions with respect to potentially toxic substances in the environment must of necessity be subjective. The subjective decisions, however, are generally required to be reasonable and defensible in the legal sense. This usually means that they must stem from an even handed interpretation of objective facts. The desired identification system must be objective, in terms of input requirements and procedures or rules to be followed in selecting and ranking chemicals. Use of the output results in decision making is subjective and need not, in fact cannot, be addressed by the objective system sought. The necessity of objectivity implies that the system would accept only a modicum of external judgment or personal interpretation. To the extent that it may be desirable or necessary to distinguish hazards to target populations, OTS has established the following order of importance (descending): a) man, b) economically significant animals and plants, and c) ecologically important species and then, presumably, the inanimate environment.

(2) Reproducibility. The identification system(s) must be capable of producing identical results (at any given point in time) when operated by different people. This is not a trivial problem due to the plethora of information sources and the likelihood that some judgment may be required even in the most objective system.

(3) Credibility. The system must possess demonstrable credibility in selecting and prioritizing potential chemical environmental hazards. The results should be statistically credible, i.e., at most a small percentage of the substances ranked as non-hazardous should turn out to give rise to major health or environmental problems; and at most a small percentage of the chemicals ranked as highly hazardous should in fact prove to be benign.

(4) Specificity. The system should classify chemicals, chemical classes, or use classes into their probable major hazard categories, e.g., carcinogenicity, mutagenicity, teratogenicity, oral toxicity, dermal toxicity, inhalation toxicity, aquatic toxicity, bioaccumulation. It may also be desirable to rank chemicals according to the perceived risk presented to different target populations, i.e., man, animals, plants, and the inanimate environment.

(5) Discrimination. The system must possess the ability to scale chemicals according to their associated risks of environmental hazard. A process of discrimination is needed to distinguish among different potential hazard levels and thereby achieve a prioritization. In general, it may be expected that the simpler systems will yield coarser gradations.

(6) State-of-the-Art Concepts. The system should utilize only proven state-of-the-art techniques, methodologies, information sources, etc., and not attempt to incorporate heretofore untested or incompletely developed approaches. For example, a new and unknown theory relating chemical structure to biological activity should be incorporated into the system only as a last resort because its merit would not be known beforehand. The same consideration would hold, for example, in deciding whether to include a new information center under development and not yet operational.

(7) Response Time. A realistic time must be established for the system to return results once it is set in motion.

(8) Personnel Requirements. The system must be designed in conformance with anticipated personnel skill levels and numbers. A system demanding unavailable technical skills must be avoided.

(9) Expansion. The system should be devised so that it may evolve without undue hardship as new information sources and techniques become available in the future.

(10) Built-In Hierarchy. In recognition of the many potential information sources and voluminous data (not all of which is necessarily pertinent), it would be desirable to develop a hierarchical system which would produce results of increasing specificity and credibility the further the process was followed. That is, an early indication of probable chemical toxicity (but one with limited credibility) might be achieved by following the recommended process to a predetermined point. Succeeding stages of evaluation requiring more information and analysis would lead to improved predictions of hazard classes and levels.

(11) Gaps in Knowledge. The system should identify the existence of information gaps which, if filled, would permit improved predictions.

(12) Statistical Confidence. If possible, hazard predictions should be accompanied by statements of statistical confidence, however approximate these might be. The measure of statistical confidence can be viewed as an indicator of the need for additional information. A hazard evaluation accompanied by a low confidence level indicates that more data may be required to yield a stronger statement.

(13) Input Data Requirements. The system should be capable of selecting and prioritizing potential chemical environmental hazards on the basis of data normally provided by the manufacturer.

(14) Ability to Deal with Degradation Products. Chemically induced health and environmental effects may be due not only to manufactured chemical substances, but also, and sometimes entirely, to degradation products. Where such products and their properties are known, the system should be capable of handling them in a normal way. When the routes of degradation of a chemical substance are unknown or very complicated, it is unlikely that any simple identification and priorization system will be able to flag the potential hazards accurately.

(15) Ability to Deal with Synergism. The goal of the project (cf. section I.B.) is to design an objective system for selecting and ranking chemicals, chemical classes or use classes, based on their environmental hazards. It is implied that any selection or ranking algorithms that may be developed will be applied to individual chemical substances or chemically related groups of substances. Environmental hazards, however, may result from or be amplified by synergistic interactions between or among unrelated chemical substances. There is very little data on the importance of synergism in the environment, and even if there were more, it would not be easy to incorporate synergistic effects into an objective system design. For the subjective regulatory viewpoint, the problem of synergism would be even more difficult to deal with.

2. Analysis of Information Needs

The primary rationale for an early warning or pre-screening system for environmental hazard identification and prioritization stems from the desirability of reducing the requirements for extensive experimental data development. A complete experimental evaluation of the potential environmental impact of a chemical substance would involve toxicological, pharmacological, and metabolic studies in a number of species (e.g., mice, rats, dogs, rabbits, domestic animals, fish, wildlife, lower aquatic organisms, plants); transport mechanism and persistence studies in air, water, and various soil types; potentiation studies; bioaccumulation studies; degradation studies and evaluation of the hazardous effects of degradation products. Not only would such an experimental program be time consuming and expensive, but so much data would be developed that it would be difficult to sort out what the real problems are. Technical resources would be more effectively utilized in developing data in

particular areas for specific chemical substances where there is good reason to believe that serious health or environmental effects may be found. Choosing productive areas to work on is not an easy task for anyone. Nonetheless, it is not possible to do everything, and the choice is made, with greater or lesser degrees of success, by individuals, corporations, and agencies. An early warning system should be an effective tool for helping to guide data development efforts towards major problems.

The more data that must be developed experimentally as input to an early warning system, the less useful it can be as a planning tool for focusing future technical effort, i.e., the more effort required to develop routine input data, the less effort available to investigate specifically identified potential problem areas.

For chemicals that are either produced commercially or under consideration for commercial production, the manufacturer can usually supply a data sheet which includes:

- Common and/or trade name;
- Chemical class and/or structural formula;
- Physical properties (e.g., melting point, boiling point, vapor pressure, solubility, etc.);
- Chemical properties (e.g., reactions with air and moisture, if any, and other relevant reactions); and
- Suggested applications.

A large chemical company has reported that they would normally make some additional measurements during the course of development of a new product specifically to provide some preliminary indications of potential environmental impacts.[2] One parameter that might be experimentally determined is the octanol/water partition coefficient, which appears to be correlated with bioconcentration in the environment. Another is five-day biological oxygen demand (BOD_5), which provides some indication of the possibility of microbial decay in aquatic or soil environments. In addition, some initial toxicological tests would be carried out. These might include, for example, a determination of acute oral, inhalation, dermal, and/or ocular toxicity to rats or mice.

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[2] *Papers of a Seminar on Early Warning Systems for Toxic Substances* (EPA-560/1-75-003), Environmental Protection Agency, Office of Toxic Substances, Washington, D.C., July 1975, p. 167.

Most chemically induced health and environmental effects (with the possible exception of cancer) are concentration dependent. Even a rough assessment of possible environmental hazard, therefore, requires some knowledge of the concentration levels to which potentially affected populations might be exposed. The primary data likely to be available that might be related to environmental concentrations are planned production and major uses. Manufacturers usually have such data, but would generally be reluctant to release it unless required by law to do so.

On the basis of a structural formula, a few easily obtainable physical and chemical properties, a five-day BOD, an indication of acute toxicity, and some estimate of production and use, it is *not* possible to *predict with certainty* the human or environmental hazards of a chemical or chemical class. If only the minimal data base is available, then, the real question is whether a system can be developed which will identify potentially hazardous chemicals, chemical classes or use classes with sufficient accuracy to justify its implementation.

3. Formulation of System Concepts

The one guiding principle used in formulating system concepts was simplicity. There are several reasons for assigning paramount importance to simplicity. One is that the current state of knowledge about factors that produce environmental hazards is so primitive as to preclude any but the simplest of identification systems. Another is that to a simple or even simplistic system, refinements and embellishments may be added as needed. Every additional refinement however will usually entail greater efforts at data collection, information processing, and finally interpretation of results. It is clear that any contemplated system must not entail greater effort at selection and ranking than would be involved in the experimental pre-screening tests themselves. For example, it might be of interest to develop for each selected chemical to be prioritized a comprehensive statement of the conditions of exposure pertaining to the principal plant, animal, and inanimate populations at risk. The enormity of this undertaking alone would seem to overwhelm the basic objective of developing a tool for selecting pre-screening candidates.

A prior report, *Literature Search and State-of-the-Art Study of Identification Systems for Selecting Chemicals or Chemical Classes as Candidates for Evaluation,*[3] reached the conclusion that *none* of the numerous existing systems reviewed are readily adaptable to the problem at hand. We concur in that conclusion, and only discuss here a number of systems concepts that address the early warning problem directly.

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[3] *Op. cit.*

(1) Systems Based on Clinical and Epidemiological Studies. One approach to early warning is to monitor the concentrations of toxic substances in the environment, track various health indices (urine analysis, blood analysis, pulmonary function, etc.) in the exposed populations, and look for correlations.[4] Apart from obvious practical difficulties (e.g., deciding which of thousands of substances to monitor and selecting relevant health indices), the results are not likely to be obtained early enough to avert serious problems.

(2) Laboratory Model Ecosystems. Model terrestrial-aquatic systems have been used to evaluate bioconcentration, bio-and chemical degradation, and toxicity of chemical substances to fish, snail, mosquito, daphnia, and algae. The experiments are quite time consuming, and the toxicity results are not readily extrapolated to man.

(3) Cost-Risk-Benefit Analysis. Most of the identification system concepts for selecting and ranking chemicals focus on the risk of hazardous health and environmental effects. The higher the risk is, the higher the priority that is assigned to the chemical for further attention. Another possible prioritization concept is based on an evaluation of the benefits that accrue from accepting a risk, and the costs of reducing or eliminating the risk.[5] This concept is fundamentally sound, but large scale implementation is almost totally impractical. Definition and quantification of environmental risks requires that a great deal more be known about the fate of a chemical in the environment than could be estimated from a few simple tests. If non-economic costs and benefits are included in the analysis (and they must be to assure credibility), their identification and quantification is also extremely difficult.

(4) Delphi. Industry, government, university, and public interest leaders or experts in the fate of toxic substances in the environment frequently must (and do) make decisions on priority problems without the benefit of a great deal of objective data. They rely very heavily on their own experience in interpreting and weighting the data that are available, and generally have some rationale for reaching an essentially subjective conclusion. Prioritization systems based in the Delphi technique rely on the development of consensus among experts acting independently as part of a panel. The National Science Foundation recently assembled a Delphi panel to select and prioritize organic compounds hazardous to the environment.[6]

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[4] *Op. cit.*, pp. 5, 82, and 154.

[5] *Ibid.*, p.93.

[6] *Final Report of NSF Workshop Panel to Select Organic Compounds Hazardous to the Environment* (AEN 74-14553A02), Institute of Environmental Medicine, New York University Medical Center, October 1975.

The panel members identified chemicals of concern solely on the basis of their own experience, and refined their judgments based on available data in production, import, uses, disposal, and toxicity. Through successive examinations by the panel, individually and together, in progressively greater detail, a prioritized list was developed. The system is certainly not objective. It is probably not reproducible (a different panel might reach a different consensus). It does have a modicum of credibility, at least among those who value and respect expert opinion. While experts are sometimes wrong, they generally establish their reputations as "experts" because they are more often right.

(5) Hierarchical Testing and Evaluation. A hierarchical system for assessing the probable impacts of chemical substances on the environment has been proposed by Robert J. Moolenaar of the Dow Chemical Company.[7] From some simple measurements on the basic physical, chemical and biological properties of a chemical, problem areas (if any) for more detailed experimental evaluation are identified. Strategies are devised for averting potential environmental problems confirmed by the detailed evaluation. Actual environmental problems that may not have been anticipated in earlier stages of testing are assessed by field observations and monitoring of the effects of handling, use and disposal.

The basic system is shown schematically in Figure 1. Interpretation of the basic property measurements to determine the additional data needed for environmental impact assessment can be done fairly objectively. In the illustration shown in Figure 2, the substance has a high vapor pressure, a low solubility in water, does not degrade readily, does bioconcentrate, and is acutely toxic to mammals via the inhalation route. Such a substance could be an air pollution problem, but is unlikely to be a water pollution problem. Further work might involve subacute and chronic inhalation toxicity studies in rats, mice and/or dogs (including pathological examination for cancer), and bioconcentration studies in a model ecosystem. The fundamental screening parameter is taken to be environmental degradation; i.e., if a substance degrades rapidly to nontoxic products in air and water, it is not likely to present an unreasonable risk, even if its octanol/water partition coefficient is high.

The initial (Level I) property measurement can be done relatively rapidly and relatively inexpensively. Certain types of problems will be missed. For example, the need for detailed toxicology will only be triggered for substances which are acutely toxic and/or which bioconcentrate. Chronically toxic substances which do not bioconcentrate would not be flagged.

(6) Stressor Matrix System. David L. Morrison of Battelle has developed a systematic approach for organizing and evaluating the multitude of data which relates to environmental hazard identification.[8] From

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[7] *Op. cit.*, p. 167.

[8] *Ibid.*, p. 175.

FIGURE 1

SCHEMATIC DIAGRAM OF A HIERARCHICAL SYSTEM

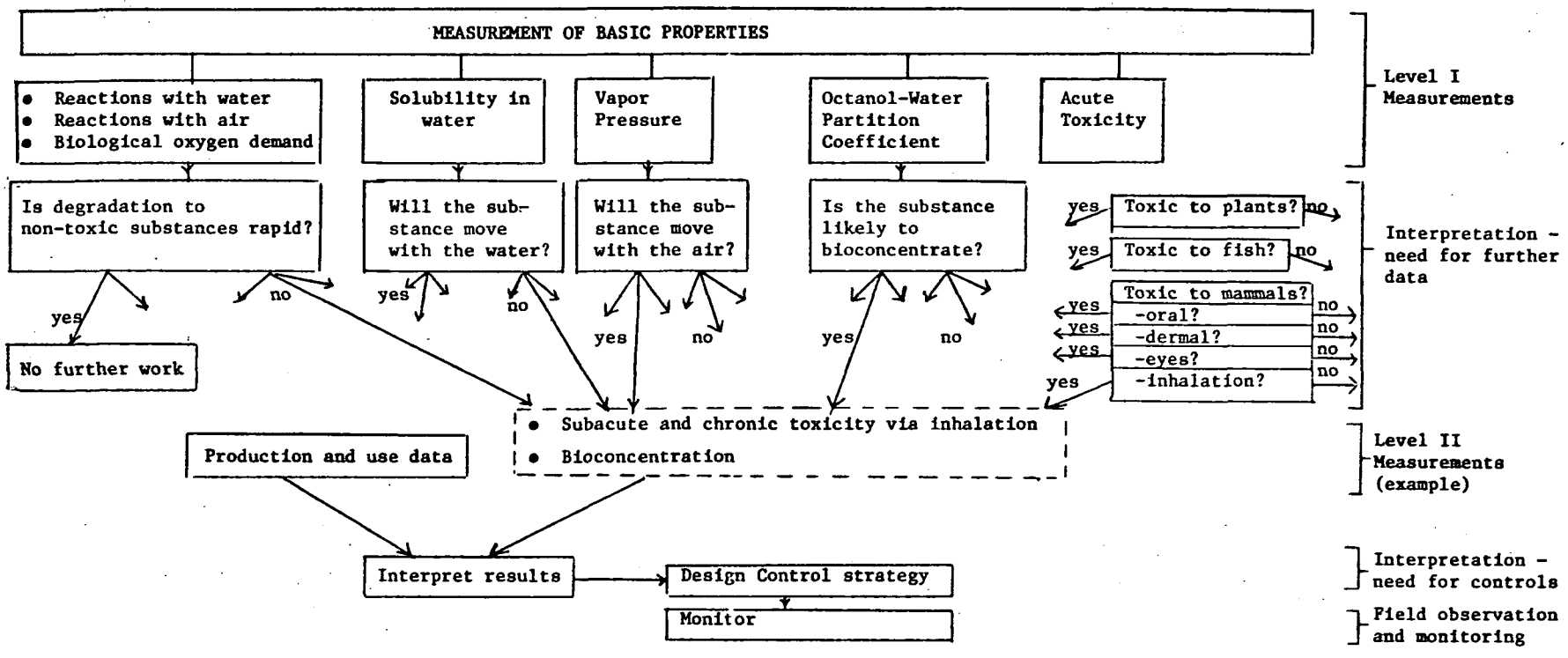
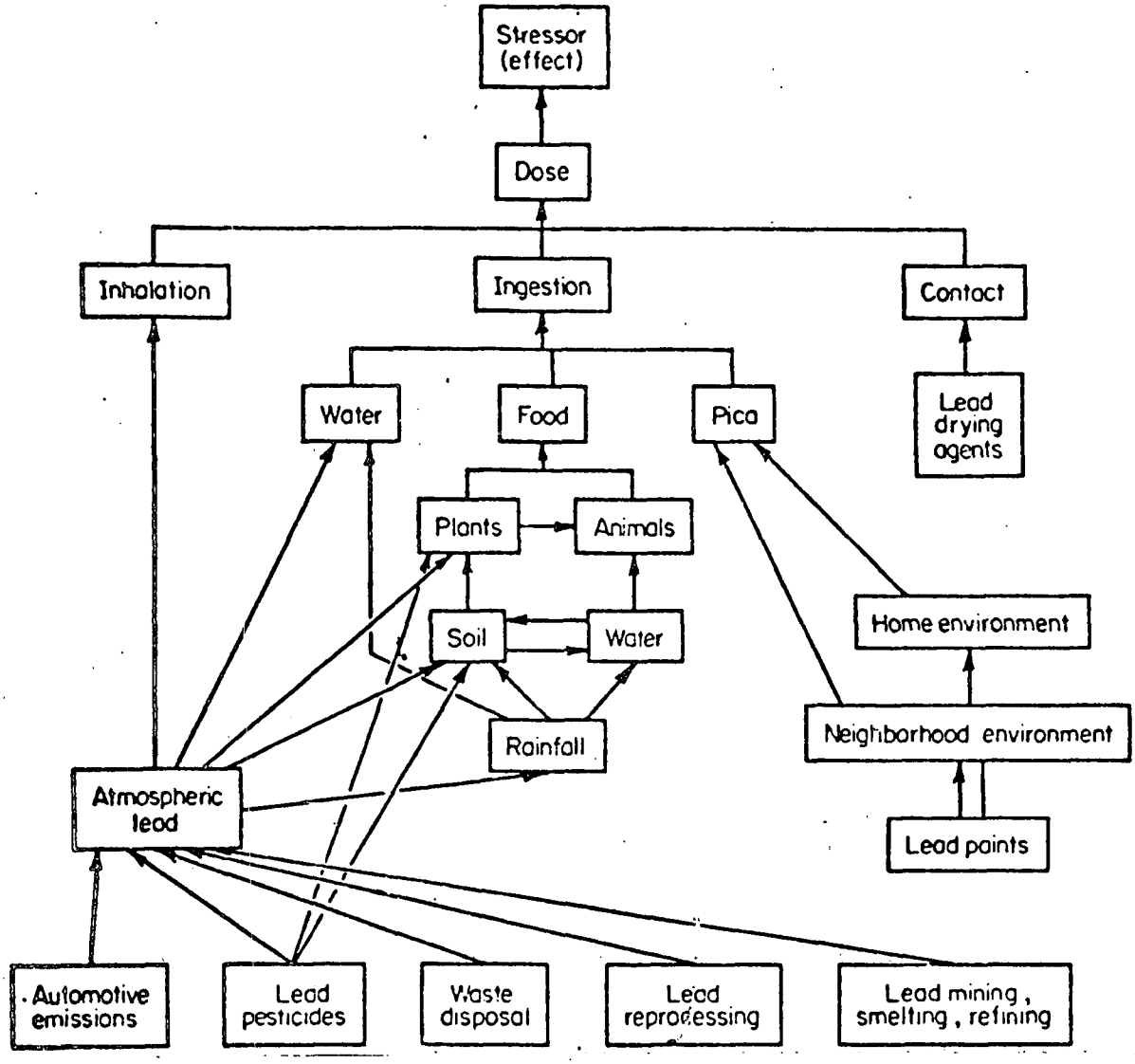


FIGURE 2

POLLUTION CHAIN DIAGRAM FOR THE ENVIRONMENTAL STRESSOR LEAD



information on sources of a chemical substance; distribution of emissions in the atmosphere, hydrosphere, lithosphere, and biosphere; transport paths; and effects or consequences of exposure, a pollution chain diagram may be constructed. An example of such a diagram for *lead* is shown in Figure 2. The various pathways shown can be analyzed mathematically, if sufficient data are available, to yield an integrated exposure to humans. The system does not address the question of what exposure levels represent "unreasonable risk." However, it is not entirely clear that such a judgment can be made objectively. It is interesting to note that the diagram neglects at least three paths:

- lead shot uptake by bottom-feeding birds, which leads to lead poisoning;
- lead vapor in shooting galleries which leads to high occupational exposures; and
- lead pipes, glasses.

(7) Structure/Toxicity Correlation. One approach considered in this program was based on the hypothesis that there is a correlation between chemical structure or substructure and toxicological effects. The screening and ranking procedure, as shown schematically in Figure 3, would begin by identifying the principal substructures, functional groups, or elements contained in the chemicals of interest that are frequently associated with health or environmental hazards. A search would then be made via CHEMLINE for chemical analogs containing the substructure of interest. Sources of toxicity and related data, such as MEDLINE and Chemical Abstracts, would next be consulted to identify the hazardous characteristics associated with the structural analogs. Finally correlation equations or algorithms would be developed relating substructures in analogous compounds to various classes of toxicological hazard, and to degrees of hazard within each class. The substructure correlations would be used to classify and rank the chemicals of interest.

Reasoning by analogy is far from perfect, but certain physical and chemical properties can be fairly well predicted from a knowledge of structure, and in specific instances some toxic effects have been shown to be related to structure. Conceptually, the structure/toxicity approach is appealing in that, if it could be implemented, it would provide guidance on the types of toxicity to anticipate and hence on productive areas for subsequent testing and research. Implementation, however, depends upon the existance of toxicological data related to carcinogenicity, mutagenicity, teratogenicity, central nervous system action, etc., for a wide range of chemicals of different structural characteristics. If the data exist, they have certainly not been compiled in a readily retrievable form. Services such as MEDLINE, TOXLINE, CAS, provide literature references, not data. The data are yet to be retrieved from the literature, compiled, tabulated and correlated. Furthermore, a brief review of the literature suggests that the range of data required to develop meaningful structural correlations for even major toxicological hazards is in fact not available.

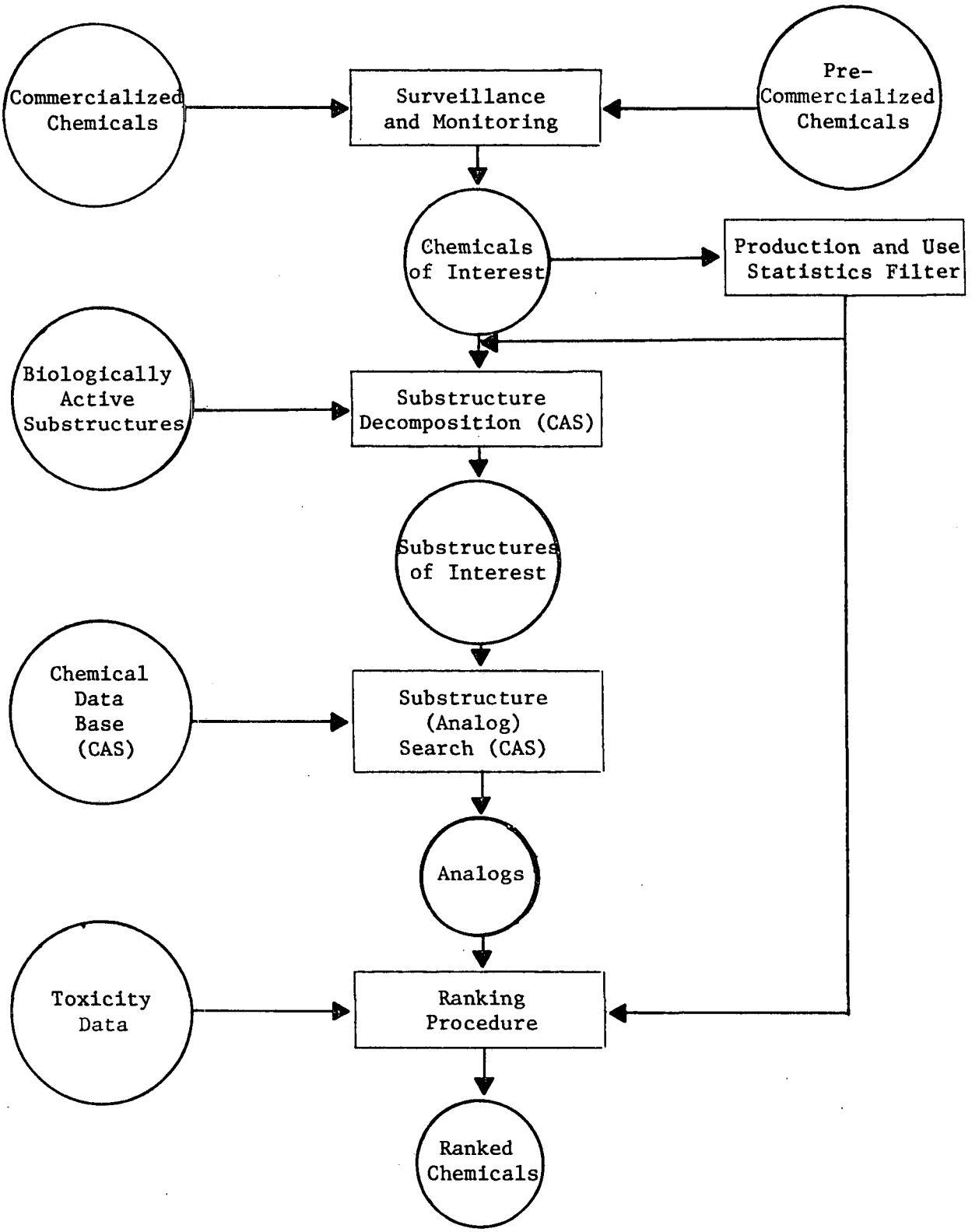


FIGURE 3

STRUCTURE/TOXICITY CORRELATION SYSTEMS

Apart from the practical difficulties of establishing structure/toxicity correlations for predictive purposes, there are also important conceptual problems. These center around the normally observed concentration dependence of toxic effects. For example, certain heavy metals, chlorinated hydrocarbons, cyanides, sulfides, etc., have been associated with health and environmental hazards of various kinds. Assessment of whether a chemical with given structural characteristics is likely to give rise to major environmental problems however, depends critically on how much of the chemical is released and how it is distributed in the environment following release. The structure/toxicity approach is deficient in not taking into account production, use and emissions.

(8) Structure/Toxicity/Release. It would be possible to modify the structure/toxicity correlations to incorporate release rates or some surrogate thereof. However, the resultant rankings might be misleading for substances of different persistences.

(9) Quantity/Toxicity. The relative hazard of a chemical with an environmental regime is sometimes evaluated as some function of the product of a quantity (or concentration) index and a toxicity index.[9] The assumption is that materials of moderate toxicity present in the environment in large quantities are comparable in hazard potential with highly toxic materials present in small quantities. This basic premise may not be entirely credible. The quantity and toxicity indices may be defined very crudely, with a severe loss in discrimination,[10] or quite precisely, with an attendant increase in data requirements.

(10) Environmental Levels/Levels of Concern. After assessing the above concepts with respect to the desired system design criteria, we developed the selection and ranking systems described in detail in the remainder of this report. From input data likely to be readily available or attainable, the system evaluates steady state concentrations of toxic substances in the atmosphere, hydrosphere, and lithosphere. Ranking is based on the ratio of eventual concentration levels in each environmental compartment to the level of concern in that compartment.

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9 *Control of Hazardous Material Spills* (R802610), Proceedings of the 1974 National Conference on Control of Hazardous Material Spills, American Institute of Chemical Engineers, New York, August 1974, p. 25. See also "Facility Test Plans," Vol. II, *Destructing Chemical Wastes in Commercial Scale Incinerators*, Environmental Protection Agency, Office of Solid Waste Management Programs, Washington, D.C., March 1975.

10 *Ibid.*

In Table I, ten system concepts summarized above are rated with respect to the systems evaluation criteria cited in section C.1. No system meets all the criteria. Except for credibility, the criteria most difficult to satisfy are short response time, minimal personnel requirements, minimal input data requirements, and adequate handling of degradation products and synergistic effects.

Credibility and reproducibility are most difficult to achieve in the area of levels of concern. For any system that is aimed at preliminary screening, especially, the "levels of concern" must be set in ways that leave much to be desired from a scientific point of view. A scientific definition such as,

> the level of concern in any compartment is the concentration in that compartment which would, under chronic exposure cause damage y per year

could be adopted, but serious problems of measurement would exist if y is small. For example, if y is 1000 excess deaths per year (a level which we would consider very high for purposes of pre-screening), the concentration which causes an increase in mortality of five per million per year would have to be established. This would require large-scale experiments of long duration. It cannot be expected that adequate data would be available for estimating the level of concern so defined for many chemicals, much less for chemicals not yet in widespread use. These problems exist whenever standards are set.

TABLE I

RELATION OF SYSTEM CONCEPTS AND CRITERIA

CRITERIA

SYSTEMS CONCEPTS	1. Objectivity	2. Reproducibility	3. Credibility	4. Specificity	5. Discrimination	6. State-of-the-Art Concepts	7. Response Time	8. Personnel Requirements	9. Expansion	10. Built-In Hierarchy	11. Gaps in Knowledge	12. Statistical Confidence	13. Input Data Needs	14. Degradation Products	15. Synergism	SUMMARY Yes	No	?
1. Clinical and Epidemiological	yes	yes	yes	yes	yes	yes	no	no	yes	no	no	yes	no	?	yes	9	5	1
2. Model Ecosystems	yes	yes	?	yes	yes	yes	no	no	yes	no	no	yes	no	yes	yes	9	5	1
3. Cost-Risk-Benefit	no	yes	yes	yes	yes	?	no	no	yes	yes	no	yes	no	?	?	7	5	3
4. Delphi	no	no	?	yes	yes	no	yes	yes	no	no	yes	no	yes	yes	yes	8	6	1
5. Hierarchical Testing	yes	?	yes	yes	yes	yes	yes	yes	yes	yes	?	no	yes	no	no	10	3	2
6. Stressor Matrix	yes	yes	yes	yes	yes	yes	no	no	yes	yes	yes	yes	no	no	no	10	5	-
7. Structure/Toxicity	yes	yes	?	yes	no	no	yes	yes	yes	yes	yes	yes	no	no	no	9	5	1
8. Structure/Toxicity Release	yes	yes	?	yes	yes	no	yes	yes	yes	yes	yes	yes	no	no	no	10	4	1
9. Quantity/Toxicity	yes	yes	?	?	?	yes	yes	yes	yes	yes	yes	yes	yes	no	no	10	2	3
10. Environmental Levels/ Levels of Concern	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	?	?	no	12	1	2

II. OVERVIEW OF THE PROPOSED SYSTEM

A. INTRODUCTION

The system consists of two parallel branches, the results of which are eventually merged and used for ranking, as shown in Figure 4. The general concept is to estimate, on the one hand, the levels of pollutant that will be encountered in the environment, and on the other, the levels which can be tolerated in the environment. A comparison of these two sets of numbers then leads to a preliminary ranking of the potential pollutants in priority order. More refined rankings are possible and will be discussed in Chapter V.

This simplified description immediately raises important questions, even on the premise that environmental levels and tolerable levels can be estimated. The primary questions are:

- How will the system predict the concentration of degradation products?
- How will the system predict the toxicity (or tolerable levels) of degradation products?
- How will the system allow for interactions and synergistic effects?

As far as interactions and synergistic effects are concerned, we have no way of handling them. Effects such as those of phosphates in water or freons in the upper atmosphere, for example, are notoriously difficult to predict, and it is unlikely that simple models could encompass enough of these situations to be worthwhile. We, therefore, do not propose a system which will attack this aspect of the problem. On the other hand, the system has the capability of handling degradation products, at least in an approximate way by estimating the environmental levels on the basis of the longest-lived degradation product and the tolerable levels on the basis of the degradation product of highest putative toxicity.

B. EVENTUAL ENVIRONMENTAL LEVELS

The first branch of the system is shown in Figure 5. It has as its purpose the computation of the levels of pollutant that will be attained in the environment. We do not expect that the computed levels will correspond closely to what would be found in the environment after decades or centuries, but we feel that estimation to within one or two orders of magnitude will go a long way toward meeting the objectives. Closer estimation would require detailed information on the modes of emission of each product and on the distribution (geographical and temporal) of

FIGURE 4

SCHEMATIC DIAGRAM OF THE PROPOSED SYSTEM

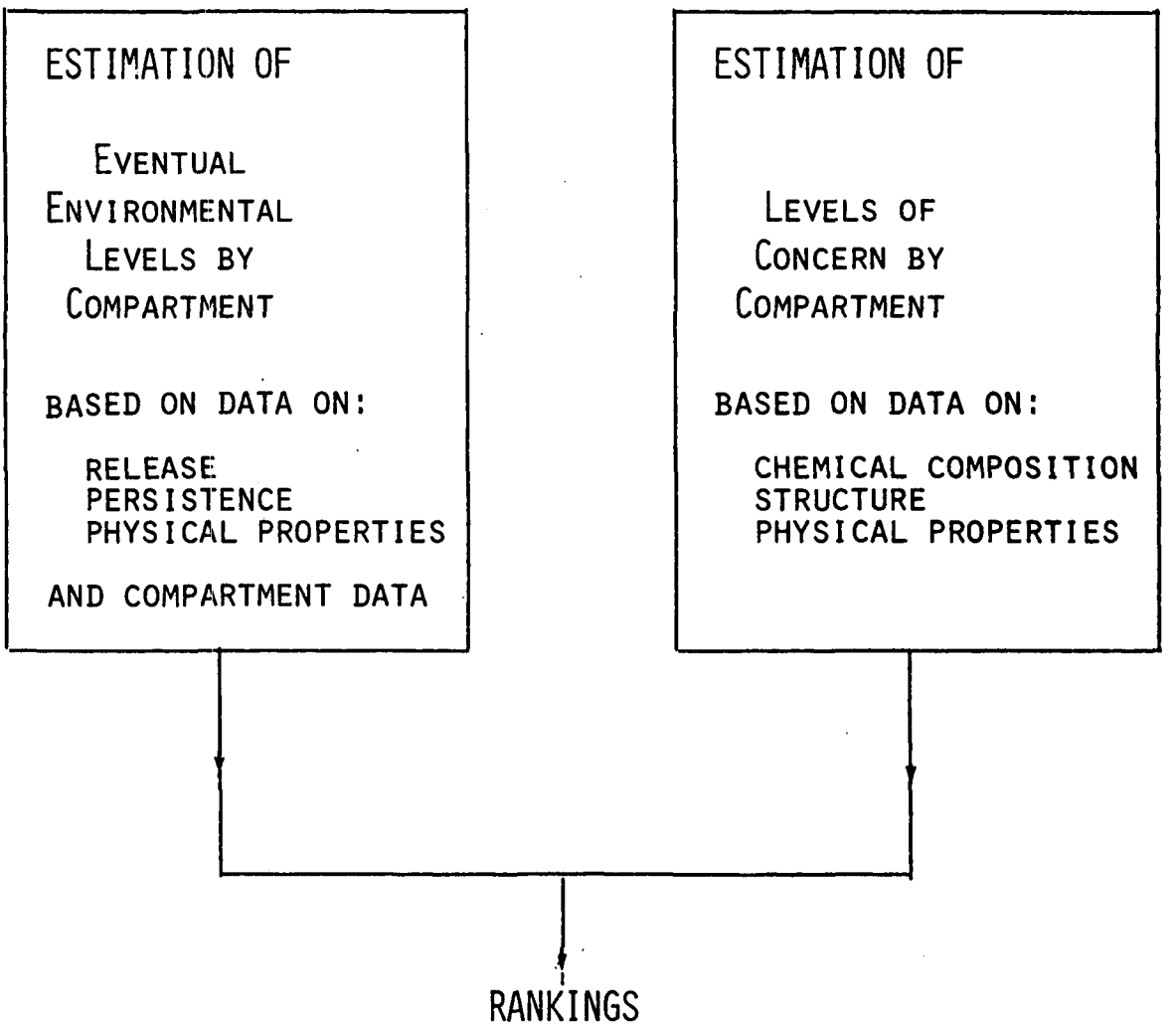
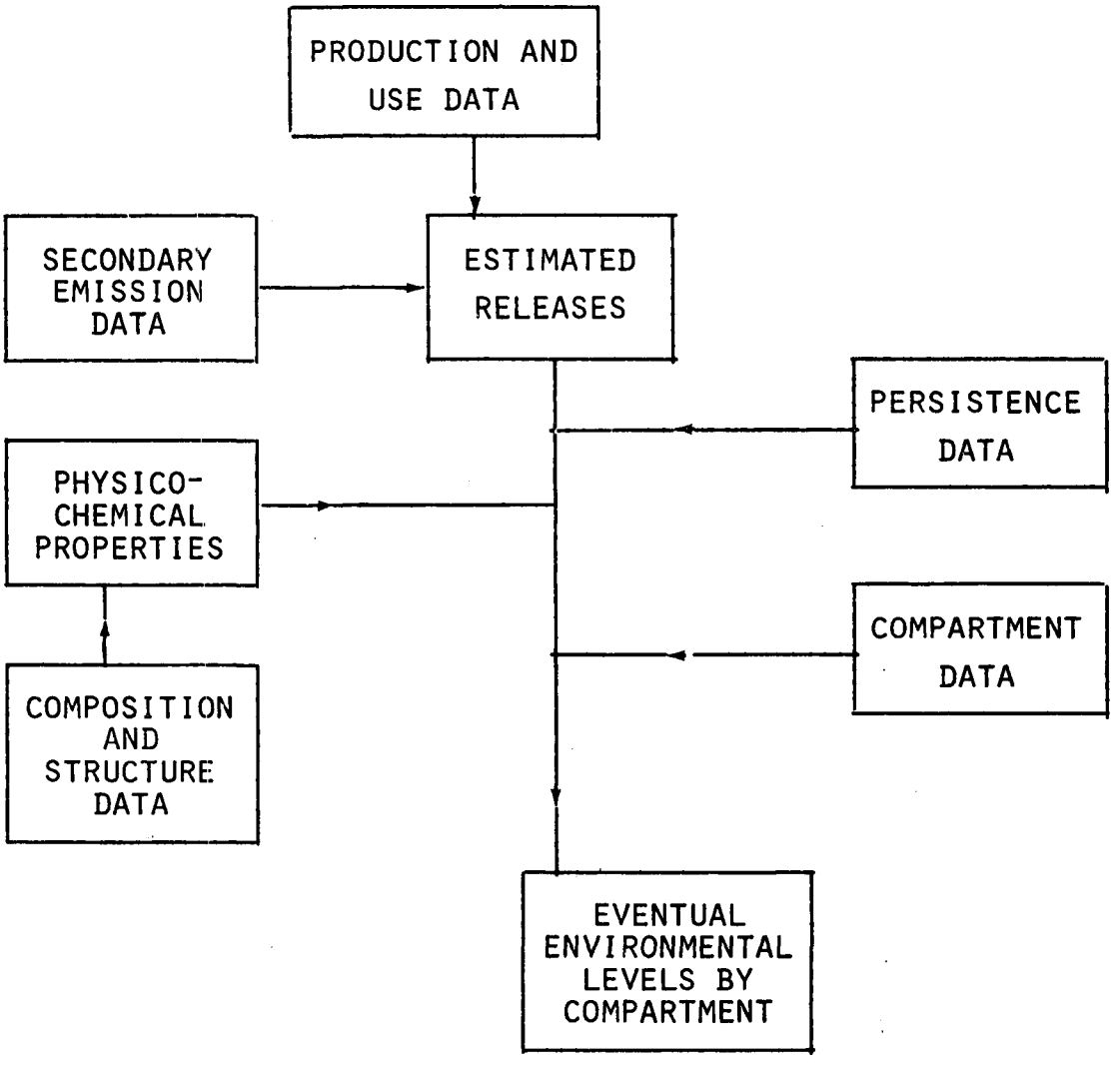


FIGURE 5

SCHEMATIC DIAGRAM OF THE FIRST BRANCH OF THE SYSTEM



these emissions, and it is unlikely that these would be known within orders of magnitude when a product is in the early stages of commercialization.

This branch of the system will include several types of data inputs:

- quantification of the total eventual industrial rate of production and allocation of this production to modes of use with three different ranges of emission;

- quantification of the emission of the product from non-industrial sources (e.g., natural production by plants, production as a result of chemical reactions of other materials in the environment, unintended or by-product emissions);

- quantification of the gross geographic distribution of the emissions;

- estimation of the half-life for degradation of the product into non-toxic final products, at least in four different ranges, in water and air; and

- quantification of basic physico-chemical constants, such as the solubility in water, the partition coefficient between fat and water, the vapor pressure, etc.

Based on these data and fixed data on regional water and air flows, the system would compute the eventual levels in various compartments (air, surface water, plants, animals).

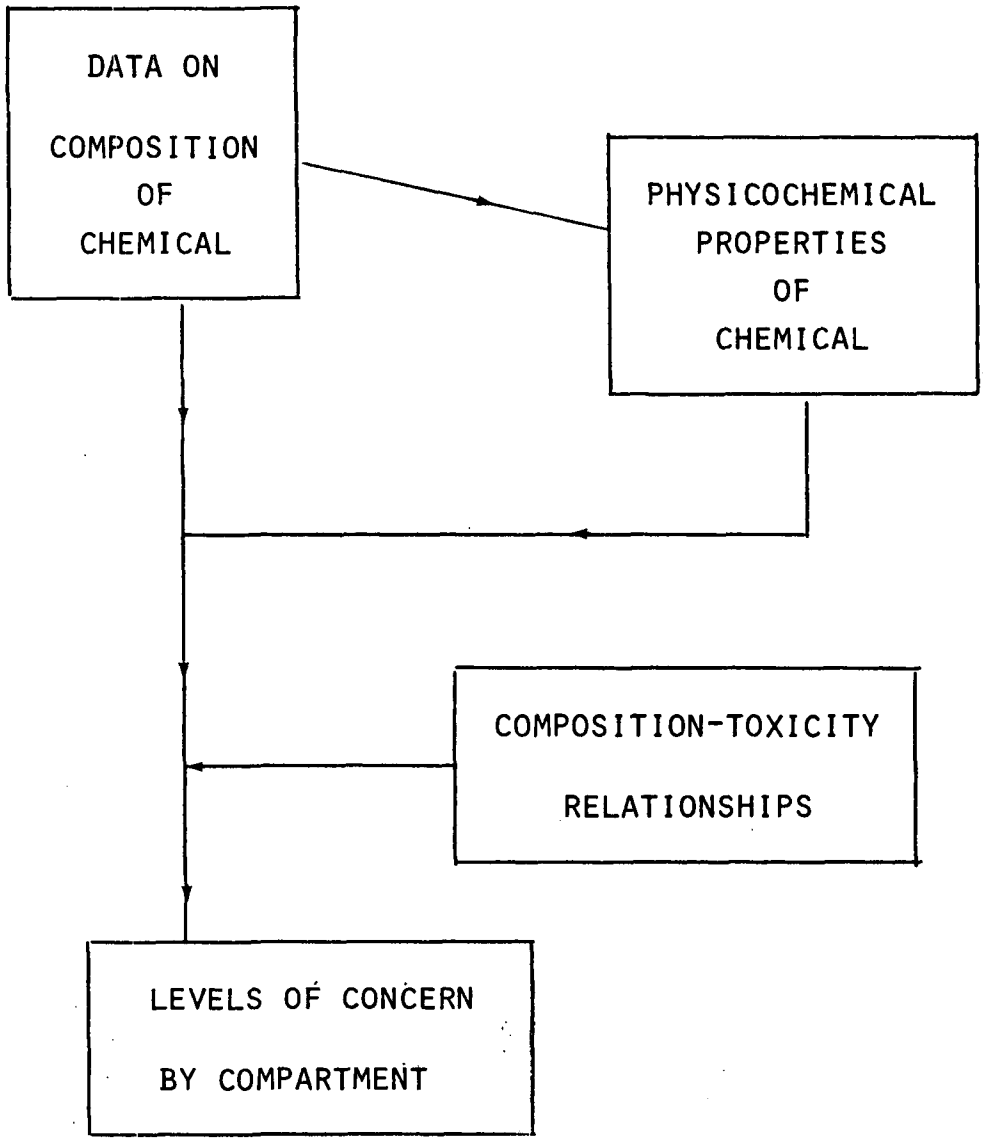
C. LEVELS OF CONCERN

The second branch of the system is shown in Figure 6. It has the aim of estimating the levels of the pollutant which are of concern. Again, we do not expect that the computed levels will correspond closely with toxicity data on any specific compound. We feel that, given the current state of the art, estimation of levels of concern which are within two or three orders of magnitude of those dictated by toxicological data would be adequate. Moreover, as shown in Chapter IV, we believe that this kind of accuracy can be achieved with relatively simple methods.

At the simple level which we propose, the input into this part of the system would consist of information on the presence or absence of a number of functional groups in the compound in question.

FIGURE 6

SCHEMATIC DIAGRAM OF THE SECOND BRANCH OF THE SYSTEM



D. RANKING METHODS

The preliminary ranking would be carried out by comparing the levels of concern with the eventual environmental levels. We currently envision estimates of environmental levels on five primary compartments: air, atmospheric moisture, surface water, ground moisture, and groundwater; and two secondary compartments: vegetable matter and flesh. The levels of concern could be developed on the basis of these compartments or in terms of combinations of these (for example, human intake could be specified in terms of air breathed, water drunk, and flesh and vegetable matter consumed).

For each compartment, the ranking system would calculate the ratio of the eventual environmental level to the level of concern. The compound would then be ranked on the basis of the highest of these ratios. In view of the requirement that the resulting ranks be conservative, we would envision any compound for which the largest ratio is of the order of 10^{-3} to be classified as definitely of concern, assuming that the predictors of levels of concern are set so as to be unbiased.

The compounds classified as being of concern would then be ranked by considering the actual ratios of eventual levels to levels of concern as well as the time horizon available for action. This time horizon is defined as the last time at which emissions could be discontinued without exceeding a threshold level (for example, one one-thousandth of the level of concern) in any compartment. The second ranking variable is important because it sets a definite limit on how long we can afford to wait for results from the research effort undertaken as a result of the ranking.

III. EVENTUAL ENVIRONMENTAL LEVELS

A. INTRODUCTION

The estimation of the levels of a pollutant that will eventually be encountered in the environment can be conducted in a number of ways. Ideally, the whole chain from release of the substance through dissolution, evaporation, sorption, transport, and degradation would be considered in detail; this would require voluminous data on physicochemical characteristics of each compound to be considered and extensive computations. At the other extreme, simple projections or guesses could be provided, but these would fail to meet a basic requirement of objectivity.

B. ESTIMATION OF EVENTUAL ENVIRONMENTAL LEVELS

We propose that a simple multiple compartment model be used. Schematically, this model is shown in Figure 7. For present purposes we do not provide a compartment for the upper atmosphere; this is neither by oversight nor because of the difficulty in dealing with this compartment: it reflects the recognition that most of the damage in this compartment is due to compounds of low molecular weight and reasonable chains of degradation products would have to be predicted and their interactions with the higher atmosphere would have to be estimated before a reasonable assessment of potential damage could be made.

Compartments for animals and vegetable matter are not shown in Figure 7. We propose to compute the eventual concentration in these by applying the octanol/water partition coefficient[11] to the average fat content as a reasonable approximation.

The quantitative model assumes that each of the compartments behaves as a completely mixed, flow reactor, with flows between compartments. In most cases, the flows are bulk flows determined by water flows and concentration in the compartment in which the flow originates. In the case of flow between ground or water and air, diffusional and convective processes are invloved as well as bulk flows (through rainfall). On this basis, as discussed more fully in Appendix I, the conditions in compartment "X" at a time "$t + \Delta t$" can be related to conditions in the system at time "t" by the equation.

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[11] See Neely, W.B., D.R. Branson and G.E. Blau, "Partition Coefficient to Measure Bioconcentration Potential of Organic Chemicals in Fish," *Environmental Science and Technology 8*, 1974, pp. 1113-1115.

$$W_x C_x (t + \Delta t) = W_x C_x(t) + \Delta t[P_x(t) + \sum_y (\dot{F}_{y \to x} + r_{y \to x}) C_y(t) - K_x W_x C_x(t) - C_x(t) \sum_y (\dot{F}_{x \to y} + r_{x \to y})] \quad (1)$$

where W_x is the weight of compartment x, in kg,

C_x is the concentration of pollutant in compartment x, in kg/kg,

$\dot{F}_{x \to y}$ is the bulk flow of pollutant solution from compartment x to compartment y in kg/yr,

$r_{x \to y}$ is the diffusional flow of pollutant from compartment x to compartment y in kg/yr/unit concentration,

$\dot{P}_x$ is the pollutant emission rate into compartment x, in kg/yr,

K_x is the first order reaction constant in compartment x in yr^{-1}

The eventual environmental levels, $C_x(\infty)$, in the various compartments can then be expressed as a rector by the equation

$$\vec{C}(\infty) = -M^{-1}\vec{P}(\infty) \quad (2)$$

so that the eventual environmental levels can be computed from the emission rates by inverting the matrix M whose elements are:

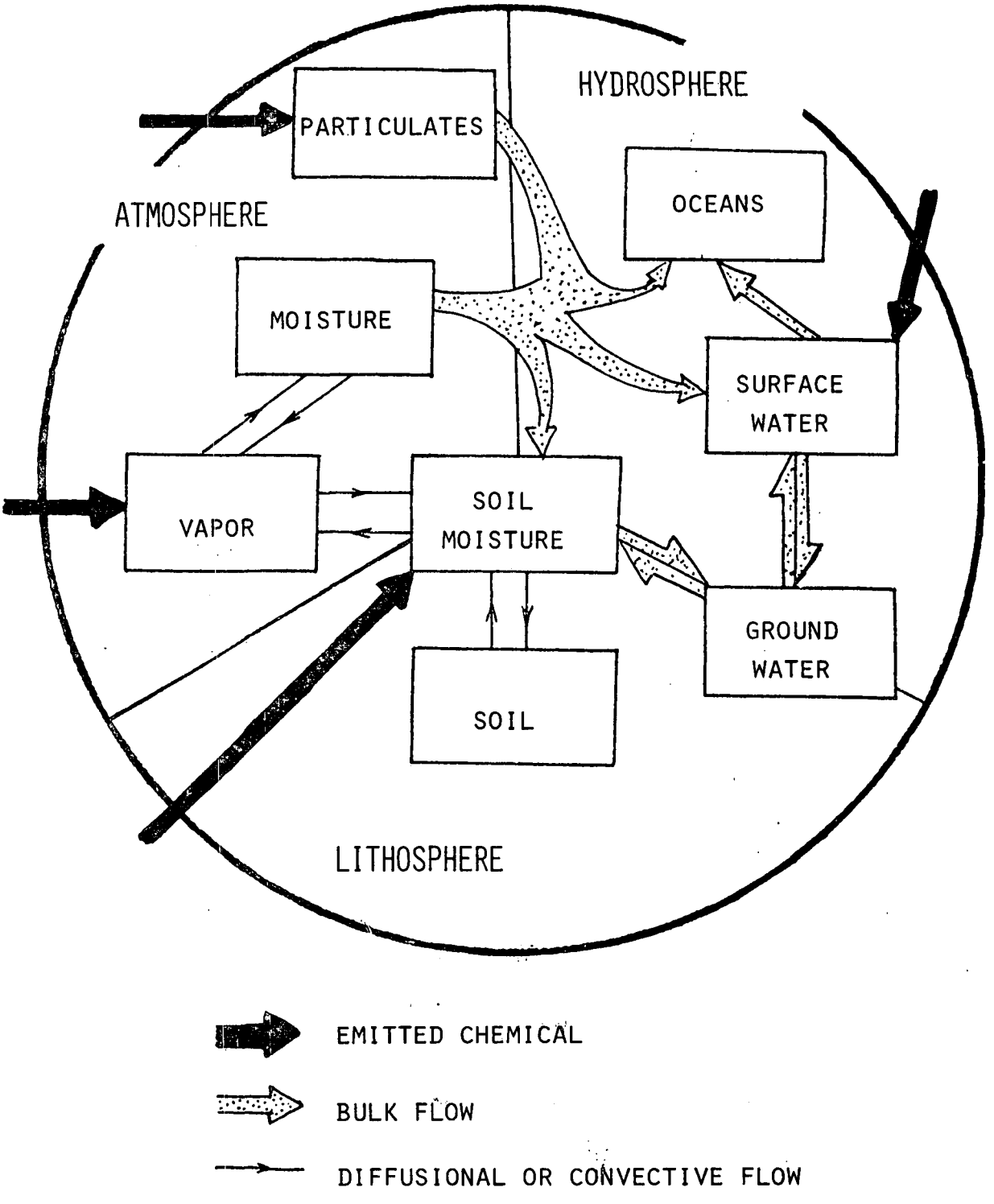
$$m_{xx} = -k_x W_x - \sum_y \dot{F}_{x \to y} - \sum_y r_{x \to y} \quad (3)$$

$$m_{xx} = \dot{F}_{y \to x} + r_{y \to x} \quad (4)$$

FIGURE 7

SCHEMATIC DIAGRAM OF INTERCOMPARTMENT FLOWS OF EMITTED CHEMICAL

(man and biosphere omitted)



The data required for the computation are:

(1) emission rates

- total emissions
- allocation to compartments

(2) compartment data

- size
- flows

(3) physicochemical data

- half life in water and air
- air/water partition coefficients
- octanol/water partition coefficients

(4) transport rates for water/air and ground/air

C. ESTIMATION OF EMISSION RATES

1. Total Emissions

At a naive level, the rate at which a substance is produced could be used as an estimator of the rate of emission of that substance into the environment, either directly or by applying a proportionality constant to it. Such a simple procedure would fail to recognize the fact that some chemicals are produced primarily for conversion to other chemicals, in which case only a small fraction will be emitted in the original form; whereas others are used in ways that are, directly or indirectly, dispersive. For example, phosgene is produced primarily as an intermediate in chemical synthesis, whereas freon is (or was) produced mainly for use in aerosols (which are directly dispersive) and for refrigeration equipment (from which it is dispersed by leaks or eventual destruction of the equipment).

A variety of ways for estimating emission rates were considered. We believe that for present purposes it is sufficient to allocate total production into three ranges of usage:

(a) Low emission uses, comprising use as chemical intermediates in the same or proximal plants. We estimate that in this type of use emissions would not exceed 5% of production. The use of a factor of 3% for purposes of estimation would lead, at most, to a 50% underestimate of emissions in extreme cases and would be highly conservative for most chemicals in this use class.

(b) Intermediate emission uses, comprising uses involving substantial handling and transportation prior to transformation of the compound. We estimate that in this type of use emissions would range from 5% to at most 50% of production. For estimation, a factor of 30% would be used; it would be about as conservative as that for low emission uses.

(c) High emission uses, comprising uses in which the compound is not modified chemically. For these, long-term production rate will make up for losses in use, so the uses may be considered to be completely dispersive. A factor of 100% will be applied to production to estimate emissions.

In the absence of specific allocation of the product to these three emission classes, the system should allocate all production to the high emission class.

In addition to these three categories of use, total "emissions" from sources other than intended production will have to be estimated. This category includes "emissions" from unintended production, such as production as a by-product, and from production occurring in the environment through natural processes or as the result of reactions between other emitted chemicals. These have to be estimated and provided to the system.

2. Allocation of Emissions

The emissions in each category, computed as outlined above, must next be allocated to the various compartments. We currently foresee only three primary compartments into which emissions would be considered:

- air
- ground
- surface water.

The input would, therefore, have to specify the fraction of compound from each class of emission that goes into each of these three compartments.

Multi-regional compartment models could be considered. At present, the development of compartment data on a regional basis is a definite bottleneck to such a refinement because data on inter-regional flows are meager. The allocation of emissions to regions could be handled by requiring

input of estimated distribution or, in the absence of specific input, by allocating the emissions to regions on the following basis:

(a) For emissions from the low emission rate class, the allocation to regions should be on the basis of concentration of industrial production.

(b) For emissions from the high emission rate class, the allocation should be on the basis of population.

(c) For emissions from the intermediate emission rate class, the allocation should be on the average of the preceding two.

D. ESTIMATION OF PHYSICOCHEMICAL PROPERTIES

The methodology for computing eventual environmental levels involves the use of a number of physicochemical properties. Principally, we are concerned with

(1) Effective first-order reaction constants in the various compartments;

(2) Air/water partition coefficients

(3) Octanol/water partition coefficients.

These properties of the compounds will have to be entered into the system or computed.

1. Effective First-Order Reaction Constants

The main purpose of the system is to rank chemicals in terms of the damage that their release may cause to the environment. Hence, a compound that disappears rapidly from the environment is still of concern if its degradation products persist and lead to damaging environmental levels. For this reason, the system requires information on the *effective* rather than actual reaction constants. Probably the easiest framework in which to think of these parameters is to discuss them in terms of the time at which one-half of the compound has degraded to basically nontoxic materials or materials that are found in nature in substantial concentrations (H_2O, CO_2, NaCl). The half-life can then be converted to an effective reaction constant by assuming first-order chemical kinetics (that is, the reaction constant would be 0.693 divided by the half life.)

We believe that a crude classification of the half-lives will be adequate for our purposes. We suggest the following classification to be provided as input:

(a) extremely reactive-- compounds with half-lives of up to one week;

(b) highly reactive--compounds with half-lives between one week and one month;

(c) moderately reactive--compounds with half-lives between one month and one year;

(d) persistent--compounds with half-lives between one year and ten years;

(e) inert--compounds with half-lives in excess of ten years;

In the absence of better data or estimates, the longest half-life of the range would be used to determine the effective reaction constant to be used,and for the last group, an effective half-life of 100 years would be assumed.

The system should, of course, be capable of taking more accurate data if this is available for any or all of the compartments.

As a step for future improvement, we recommend the development of methods for predicting effective reaction constants from the kinds of data that are generally available at the time that OTS wishes to evaluate the potential future damage. We believe that methods could be found that lead to predictions of half-lives within an order of magnitude, and these could be used to increase the objectivity of the process and reduce the burden of input preparation.

2. Air/Water Partition Coefficients

Air/water partition coefficients are needed in order to compute transport rates and equilibria at air/water interfaces. Unless better information is available on a substance, these partition coefficients will be estimated by the ratio of the vapor pressure of the substance to the water solubility; a temperature of about 15°C should be used for evaluating these properties.

3. Octanol/water Partition Coefficients

The eventual concentration in flesh is an important parameter in itself and is needed to estimate human consumption. We propose to estimate this eventual concentration by considering flesh as a mixture consisting of 50% water at the concentration in streams and 50% protein and fat at a concentration equal to the stream water concentration times the octanol/water partitioning coefficient. For vegetable matter, the same procedure would be used, but the effective fat would be assumed to be 10% of the weight.

In the absence of specific data on partitioning coefficients, the methods advocated by Leo and co-workers should be used.[12] Primarily, the method would involve the computation of the logarithm of the partitioning coefficient from additive contributions of individual substructures of the molecule of interest. This computational method would lend itself to automation, but manual operation appears preferable at least initially in view of the possible departures from additivity discussed by Leo and co-workers. Automation could be pursued at a subsequent stage when the usefulness of the system has been established.

E. TRANSPORT RATES BY DIFFUSION

1. Between Liquid and Vapor Phases

We have chosen not to rely too heavily on transport equations derived from aerodynamics, because they may be unreliable in predicting the transport from water surfaces or ground moisture to air and vice versa. As an alternative, we have opted to depend on estimates based on the rate of evaporation from water bodies and ground moisture, using the functional form of the aerodynamic formulations for extrapolation.

On this basis, the transport between surface water (sw) and the atmosphere (a) can be expressed as

$$\dot{T}_{sw \to a} = r_{sw \to a} \, C_{sw} \tag{1}$$

$$\dot{T}_{a \to sw} = r_{a \to sw} \, C_a \tag{2}$$

with

$$r_{sw \to a} = 1000 \cdot A \cdot M \cdot \left(\frac{D_c}{D_w}\right)^{2/3} \cdot 11 \; V_p/S \tag{3}$$

$$r_{a \to sw} = 1000 \cdot A \cdot M \cdot \left(\frac{D_c}{D_w}\right)^{2/3} \cdot 7 \tag{4}$$

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[12] Leo, A., Hansch, and D. Elkins, "Partition Coefficients and Their Uses," *Chemical Reviews*, 1971, Vol. 71, No. 6, pp. 525-616

where

$T_{x \to y}$ is the rate of transport from x to y in kg/yr

A is the total surface area in m^2

M is the molecular weight of the contaminant

D_{ca} is the diffusivity of the contaminant in air in m^2/sec

D_{wa} is the diffusivity of water vapor in air in m^2/sec

V_p is the vapor pressure of the contaminant in atmospheres

C_{sw} is the concentration of the contaminant in surface water (kg/kg)

C_a is the concentration of the contaminant in air (kg/kg)

Based on an effective surface area for lakes (l) and streams (s) of 1.4×10^{11} m^2 and $0.25 \times 10^{11} m^2$, respectively, we have

$$r_{l \to a} = 1.5 \times 10^{15} \cdot M \cdot \left(\frac{D_{ca}}{D_{wa}}\right)^{2/3} V_p/S \tag{5}$$

$$r_{s \to a} = 0.28 \times 10^{15} M \cdot \left(\frac{D_{ca}}{D_{wa}}\right)^{2/3} V_p \tag{6}$$

$$r_{a \to l} = 0.98 \times 10^{15} \cdot M \cdot \left(\frac{D_{ca}}{D_{wa}}\right)^{2/3} \tag{7}$$

$$r_{a \to s} = 0.18 \times 10^{15} M \left(\frac{D_{ca}}{D_{wa}}\right)^{2/3} \tag{8}$$

For the transport from ground moisture (gm) to air we have

$$r_{gm \to a} = 4.3 \times 10^{16} M \left(\frac{D_{ca}}{D_{wa}}\right)^{2/3} V_p/S \tag{9}$$

$$r_{a \to gm} = 2.7 \times 10^{16} M \left(\frac{D_{ca}}{D_{wa}}\right)^{2/3} \tag{10}$$

and

$$\dot{T}_{x \to y} = r_{x \to y} C_x \tag{11}$$

The method which we recommend for estimating diffusivities is discussed in Appendix III.

Because of the very large surface area available, the transport between air (a) and atmospheric (am) moisture is rapid and the diffusional processes may be ignored. For our purpose we will use

$$r_{am \to a} = 1.1 \times 10^{26} V_p$$

$$r_{a \to am} = 7 \times 10^{25} \qquad (12)$$

2. Between Ground Moisture and Soil

We have not found any reliable correlation which permits the prediction of soil adsorption from readily available data. The total surface area of active ingredients is equally difficult to estimate. For these reasons we recommend that the transport from ground moisture to soil be estimated as proportional to the diffusivity of the contaminant in water, D_{cw}, the fraction of organic material in the soil, f_o, and the concentration in ground moisture, C_{gm}:

$$\dot{T}_{gm \to soil} = 1.1 \times 10^{19} D_{cw} f_o C_{gm} \qquad (13)$$

while the transport from soil to ground moisture can be estimated as directly proportional to the diffusivity of the contaminant in water, inversely proportional to the octanol/water partitioning coefficient, $P_{o/w}$ and the concentration is soil C_s:

$$\dot{T}_{soil \to gm} = 1.1 \times 10^{19} D_{cw} \frac{1}{P_{o/w}} C_s \qquad (14)$$

The method for estimating D_{cw} is discussed in Appendix III.

These equations imply that at equilibrium the ratio of concentration in the organic fraction of soil to concentration in ground moisture is equal to the octanol/water partition coefficient

$$\left(\frac{C_s/f_o}{C_{gm}}\right)_e = P_{o/w} \qquad (15)$$

F. COMPARTMENT DATA

Estimates of the various compartments, in terms of size and flows, are shown in Table II. For the most part, these are based on data from the U.S. Geological Survey. In the case of air, we assumed a column one mile high and an average flow of two miles per hour through a 1000 mile front.

TABLE II

U.S. COMPARTMENT DATA

COMPARTMENT	SUB-COMPARTMENT	Effective area (m^2)	INVENTORY 10^{15}kg	ANNUAL FLOW 10^{15}kg	TIME OF RESIDENCE yr
Air (1 mile, 2 mph)		-	16.2	710	0.002
Surface Water	Lakes	1.4×10^{11}	18.8	0.19	100
	Streams	0.25×10^{11}	0.05	1.86	0.3
Ground water	Shallow	-	63.7	0.31	200
	Deep	-	63.7	0.006	
Ground Moisture	0-1 m	8×10^{11}	0.6	3.1	
	1-5 m		0.4	-	
	5-10 m		0.2	-	
	10-15 m		0.2	-	
	15-30 m		0.2	-	
	30-50 m		0.2	-	
Atmospheric Moisture		∞	0.18	4.8*	0.04
Soil	0-1 m		15.2		
	1-5 m		60.9		
	5-10 m		76.1		
	10-15 m		76.1		
	15-30 m		228.5		
	30-50 m		304.4		

* Net of short-term reevaporation of approximately 1.2×10^{15}kg per year.

We have not been able to locate adequate data for individual basins or regions except for selected flows (such as water run-off). For the contiguous States, estimates of the cross-flows of water between compartments, are given in Tables III a, b, c, d. The first two tables differ in the short-circuiting from ground moisture to ground water, the last two differ from the first two by allowing back flow from deeper to shallower soil layers. These differences are illustrated in Figures 8a, b, c, d which show schematically the flows in the four cases.

The flows from air particulates are not specified in the tables. These flows will depend largely on the size of particulates. We suggest that flows from air particulates to ground, lakes, and streams be specified as part of the input data.

TABLE IIIa

WATER FLOWS BETWEEN COMPARTMENTS

(in 10^{15}kg/yr)

CASE 1

FLOW FROM: \ TO:	1	2	3	4	5	6	7	8	9	10	11	12
1.*AIR MOISTURE*	.000	1.800	.100	2.900	.000	.000	.000	.000	.000	.000	.000	.000
2.*LAKES*	.170	.000	1.690	.080	.050	.025	.015	.010	.010	.100	.000	.000
3.*STREAMS*	.030	.160	.000	.120	.050	.015	.005	.000	.000	.100	.000	1.500
4.*SOIL MOISTURE* 0-1*M*	2.800	.100	.100	.000	.100	.000	.000	.000	.000	.000	.000	.000
5.*SOIL MOISTURE* 1-5*M*	.000	.050	.050	.000	.000	.100	.000	.000	.000	.000	.000	.000
6.*SOIL MOISTURE* 5-10*M*	.000	.020	.020	.000	.000	.000	.100	.000	.000	.000	.000	.000
7.*SOIL MOISTURE* 10-15*M*	.000	.010	.010	.000	.000	.000	.000	.100	.000	.000	.000	.000
8.*SOIL MOISTURE* 15-30*M*	.000	.005	.005	.000	.000	.000	.000	.000	.100	.000	.000	.000
9.*SOIL MOISTURE* 30-50*M*	.000	.005	.005	.000	.000	.000	.000	.000	.000	.100	.000	.000
10.*GROUND WATER(SHALLOW)*	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.100	.200
11.*GROUND WATER(DEEP)*	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.100
12.*OCEAN*	1.800	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000

TABLE IIIb

WATER FLOWS BETWEEN COMPARTMENTS

(in 10^{15}kg/yr)

CASE 2

FLOW FROM: \ TO:	1	2	3	4	5	6	7	8	9	10	11	12
1.*AIR MOISTURE*	.000	1.800	.100	2.900	.000	.000	.000	.000	.000	.000	.000	.000
2.*LAKES*	.170	.000	1.690	.080	.050	.025	.015	.010	.010	.100	.000	.000
3.*STREAMS*	.030	.160	.000	.120	.050	.015	.005	.000	.000	.100	.000	1.500
4.*SOIL MOISTURE 0-1M*	2.800	.100	.100	.000	.100	.000	.000	.000	.000	.000	.000	.000
5.*SOIL MOISTURE 1-5M*	.000	.050	.050	.000	.000	.080	.000	.000	.000	.020	.000	.000
6.*SOIL MOISTURE 5-10M*	.000	.020	.020	.000	.000	.000	.050	.000	.000	.020	.010	.000
7.*SOIL MOISTURE 10-15M*	.000	.010	.010	.000	.000	.000	.000	.020	.000	.010	.020	.000
8.*SOIL MOISTURE 15-30M*	.000	.005	.005	.000	.000	.000	.000	.000	.010	.000	.010	.000
9.*SOIL MOISTURE 30-50M*	.000	.005	.005	.000	.000	.000	.000	.000	.000	.000	.010	.000
10.*GROUND WATER(SHALLOW)*	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.250	.000
11.*GROUND WATER(DEEP)*	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.300
12.*OCEAN*	1.800	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000

TABLE IIIc

WATER FLOWS BETWEEN COMPARTMENTS

(in 10^{15}kg/yr)

CASE 3

FLOW FROM: \ TO:	1	2	3	4	5	6	7	8	9	10	11	12
1.*AIR MOISTURE*	.000	1.800	.100	2.900	.000	.000	.000	.000	.000	.000	.000	.000
2.*LAKES*	.170	.000	1.690	.080	.050	.025	.015	.010	.010	.100	.000	.000
3.*STREAMS*	.030	.160	.000	.120	.050	.015	.005	.000	.000	.100	.000	1.500
4.*SOIL MOISTURE* 0-1*M*	2.800	.100	.100	.000	.110	.000	.000	.000	.000	.000	.000	.000
5.*SOIL MOISTURE* 1-5*M*	.000	.050	.050	.010	.000	.110	.000	.000	.000	.000	.000	.000
6.*SOIL MOISTURE* 5-10*M*	.000	.020	.020	.000	.010	.000	.110	.000	.000	.000	.000	.000
7.*SOIL MOISTURE* 10-15*M*	.000	.010	.010	.000	.000	.010	.000	.110	.000	.000	.000	.000
8.*SOIL MOISTURE* 15-30*M*	.000	.005	.005	.000	.000	.000	.010	.000	.110	.000	.000	.000
9.*SOIL MOISTURE* 30-50*M*	.000	.005	.005	.000	.000	.000	.000	.010	.000	.100	.000	.000
10.*GROUND WATER(SHALLOW)*	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.100	.200
11.*GROUND WATER(DEEP)*	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.100
12.*OCEAN*	1.800	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000

TABLE IIId

WATER FLOWS BETWEEN COMPARTMENTS

(in 10^{15}kg/yr)

CASE 4

FLOW FROM: \ TO:	1	2	3	4	5	6	7	8	9	10	11	12
1.*AIR MOISTURE*	.000	1.800	.100	2.900	.000	.000	.000	.000	.000	.000	.000	.000
2.*LAKES*	.170	.000	1.690	.080	.050	.025	.015	.010	.010	.100	.000	.000
3.*STREAMS*	.030	.160	.000	.120	.050	.015	.005	.000	.000	.100	.000	1.500
4.*SOIL MOISTURE* 0-1*M*	2.800	.100	.100	.000	.110	.000	.000	.000	.000	.000	.000	.000
5.*SOIL MOISTURE* 1-5*M*	.000	.050	.050	.010	.000	.090	.000	.000	.000	.020	.000	.000
6.*SOIL MOISTURE* 5-10*M*	.000	.020	.020	.000	.010	.000	.045	.000	.000	.020	.020	.000
7.*SOIL MOISTURE* 10-15*M*	.000	.010	.010	.000	.000	.005	.000	.012	.000	.010	.020	.000
8.*SOIL MOISTURE* 15-30*M*	.000	.005	.005	.000	.000	.000	.002	.000	.005	.000	.005	.000
9.*SOIL MOISTURE* 30-50*M*	.000	.005	.005	.000	.000	.000	.000	.000	.000	.000	.005	.000
10.*GROUND WATER(SHALLOW)*	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.250	.000
11.*GROUND WATER(DEEP)*	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.300
12.*OCEAN*	1.800	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000

FIGURE 8a - SCHEMATIC DIAGRAM OF FLOWS FOR "CASE 1"

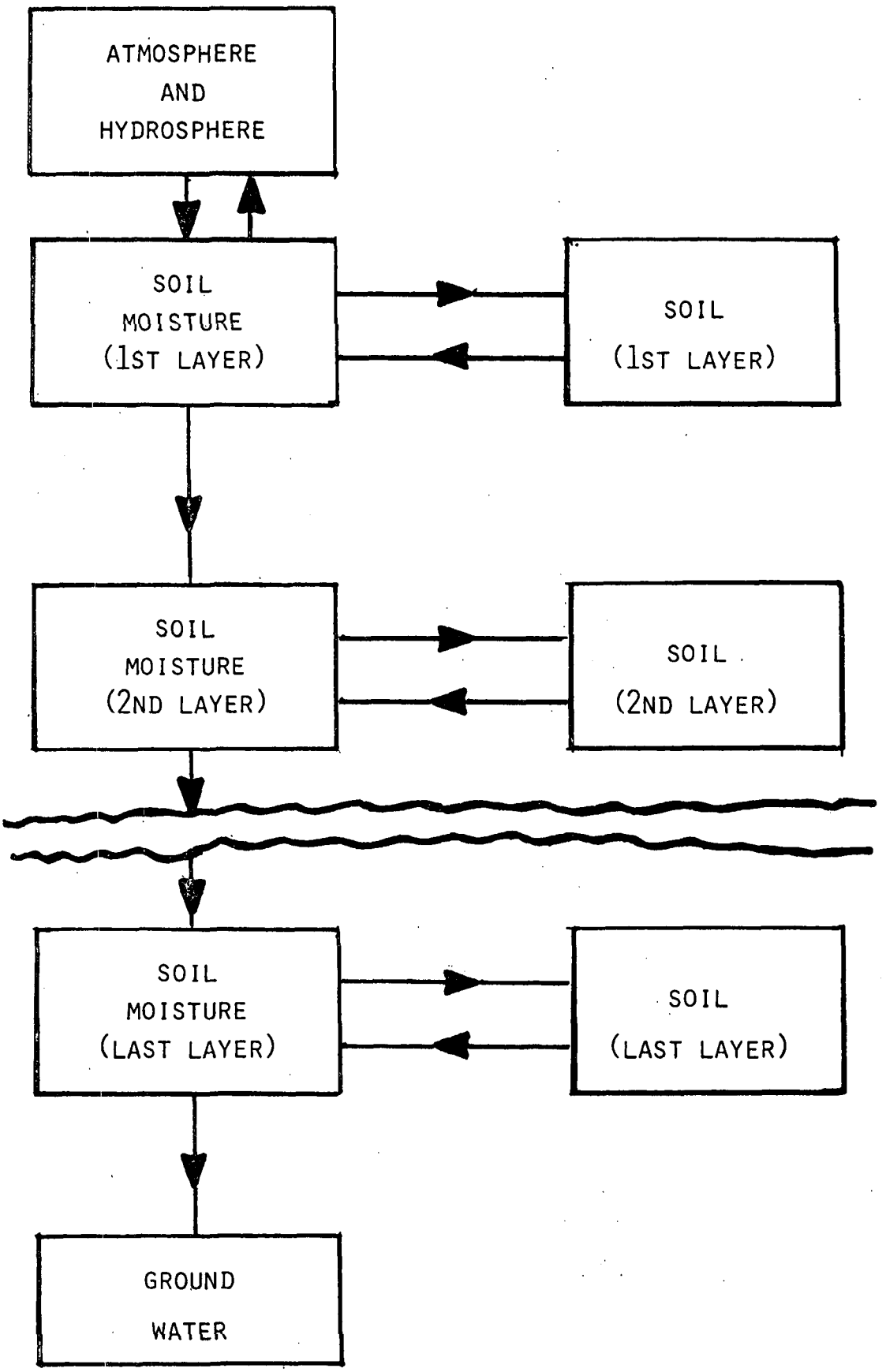


FIGURE 8b – SCHEMATIC DIAGRAM OF FLOWS FOR "CASE 2"

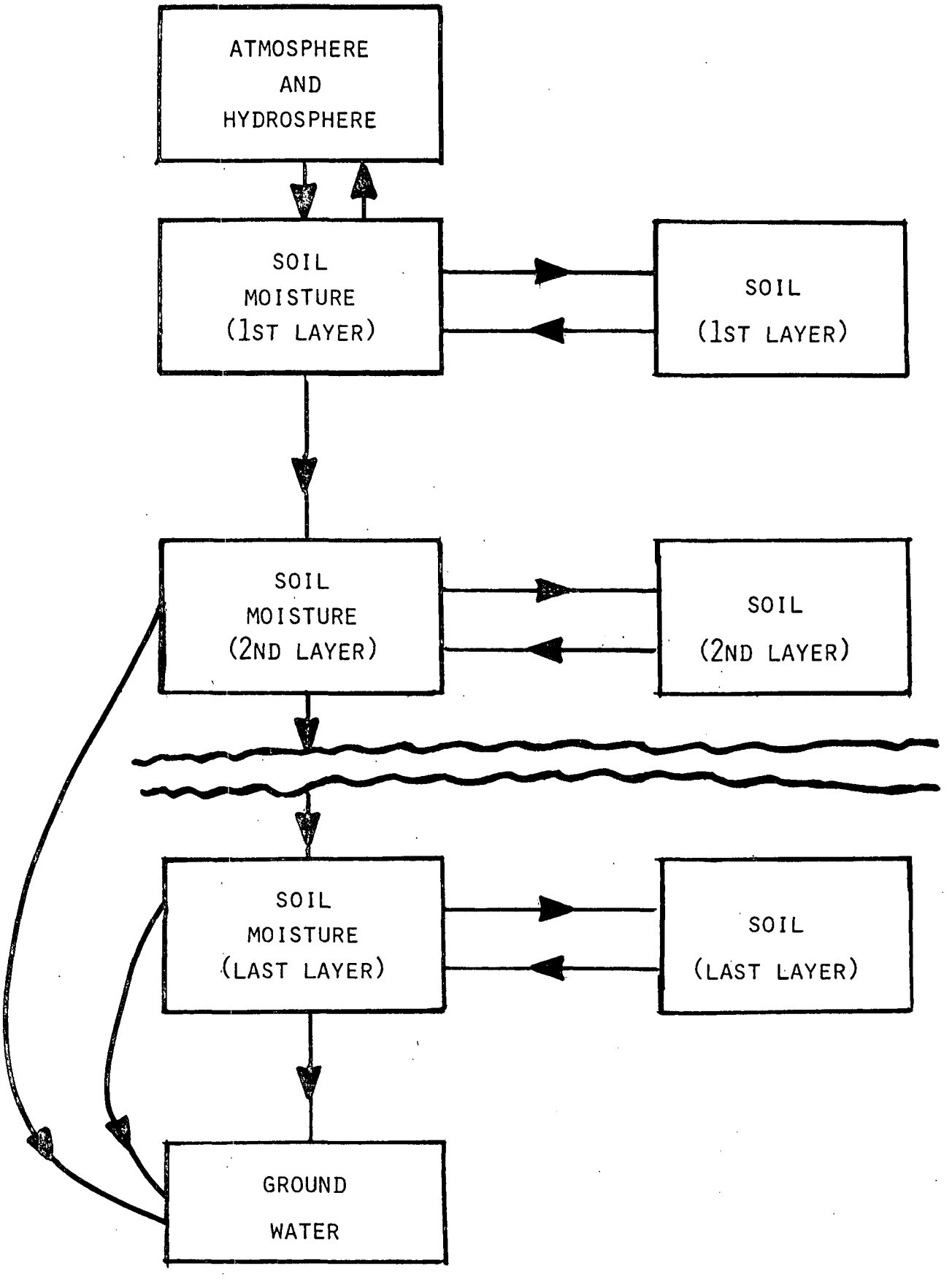


FIGURE 8c - SCHEMATIC DIAGRAM OF FLOWS FOR "CASE 3"

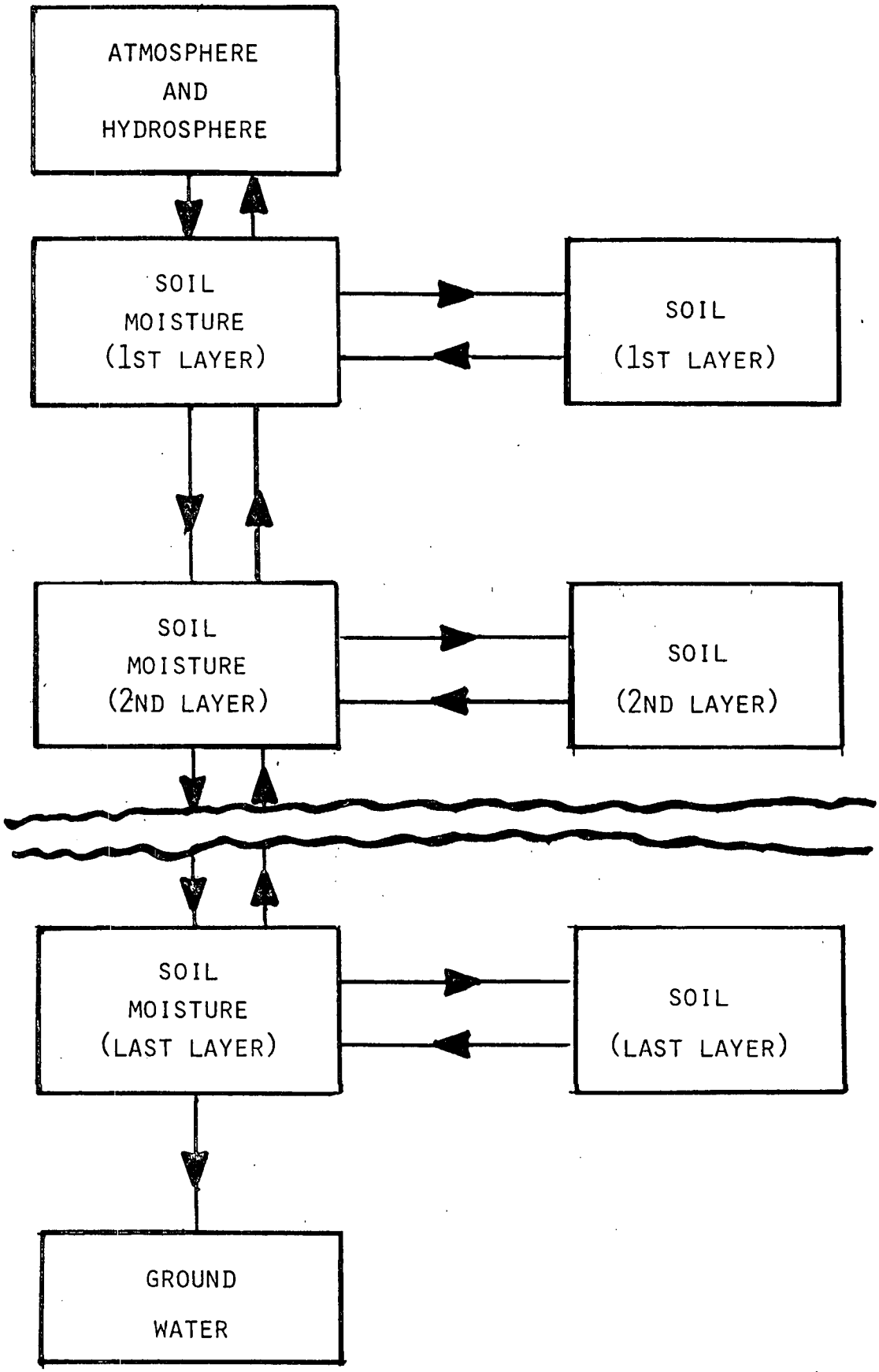
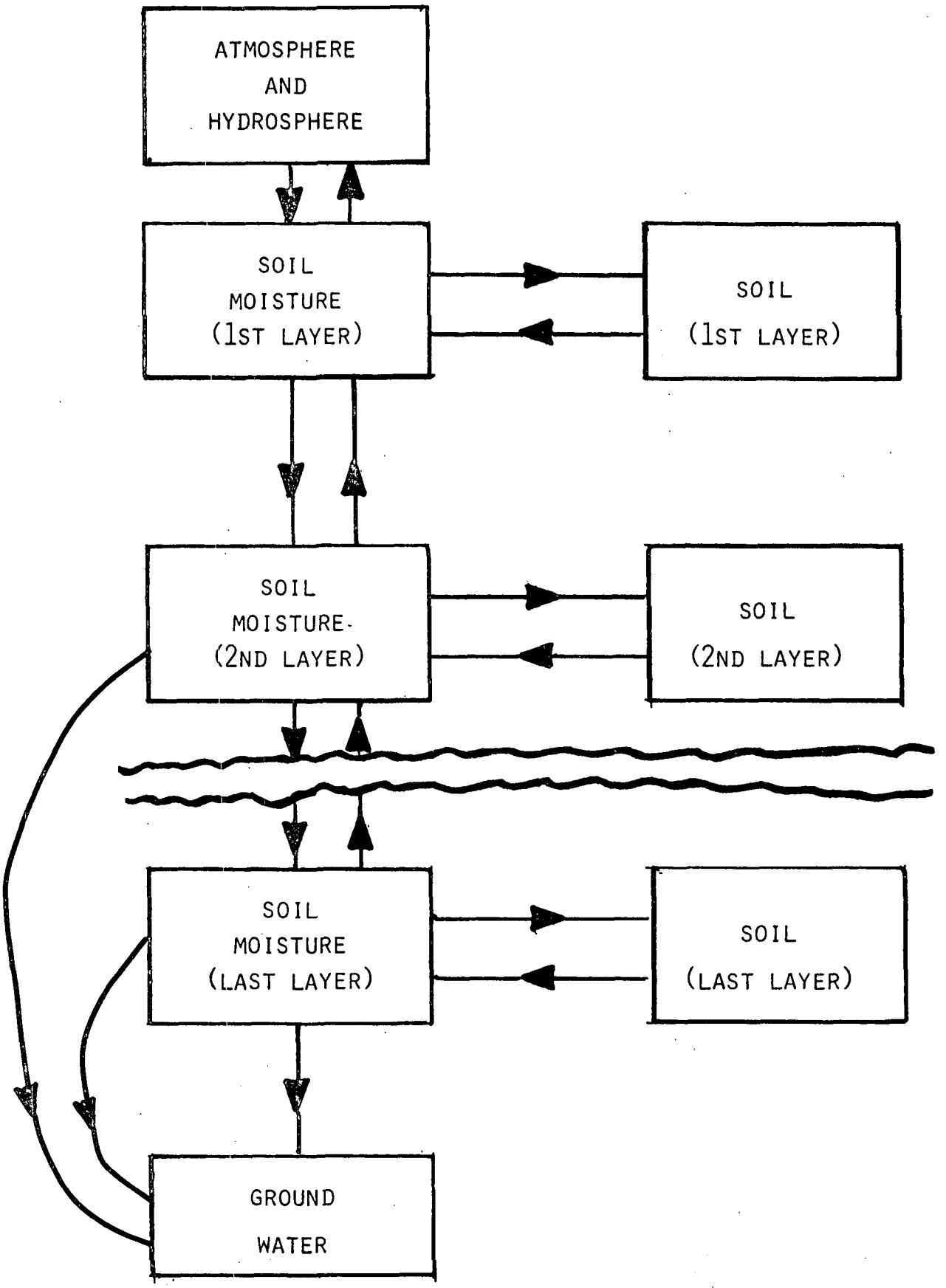


FIGURE 8d - SCHEMATIC DIAGRAM OF FLOWS FOR "CASE 4"



IV. LEVELS OF CONCERN

The second "branch" of the proposed system must calculate the levels of a contaminant that are of concern. In principle, the system can cope with a variety of levels of concern. For example, levels of concern for surface water, air,and flesh might be specified as concentrations, and a level of concern for total human intake (specified in terms of human intake of water, air, and flesh) might be specified in terms of the amount taken in. The various levels of concern need not be consistent across compartments,[13] as long as the disparities are known and can be adjusted for in the ranking process.

Ideally, the levels of concern should be set on the basis of potential damage caused by chronic exposure. For example, the level of concern could be defined as the concentration or intake of the compound which causes an excess mortality of 10^{-9} per person year (one excess death every five years at current population levels) due to chronic exposure. Unfortunately such data are unavailable (and unobtainable).

Alternatives which readily present themselves, such as use of acute LD_{50} or chronic levels which produce substantial excess in mortality, are far from the ideal because dose-response curves of different compounds may intersect, as shown in Figure 9. The main interest is in preventing even low levels of excess mortality and the ranking should, as far as possible, reflect this interest; if the intersection represented in Figure 8 is at 50% mortality, the compounds should be assigned the same level of concern.

On a practical level it was necessary to establish whether any kind of toxicity levels could be predicted to within two or three orders of magnitude on the basis of simple information such as chemical formula. Our main emphasis has been in resolving this issue as a prelude for more refined methods based on more definitive data. Appendix II discusses the methods by which we attempted to develop crude predictors of toxicity.

Because of the tentative nature of the work, we did not look for the most comprehensive sets of data on the most relevant levels of concern. Most of our work was done using the "allowable levels" of air concentration for compounds on the "toxic substances list." In summary, we found that crude methods exist which could "narrow" the spread of "allowable levels" for a given calculated level to a ratio (of highest to lowest "allowable level") of 10^4 (Figure 10). The geometric mean between these

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[13] Though obviously they should be consistent across compounds being considered.

FIGURE 9

SCHEMATIC REPRESENTATION OF INTERSECTING DOSE-RESPONSE CURVES

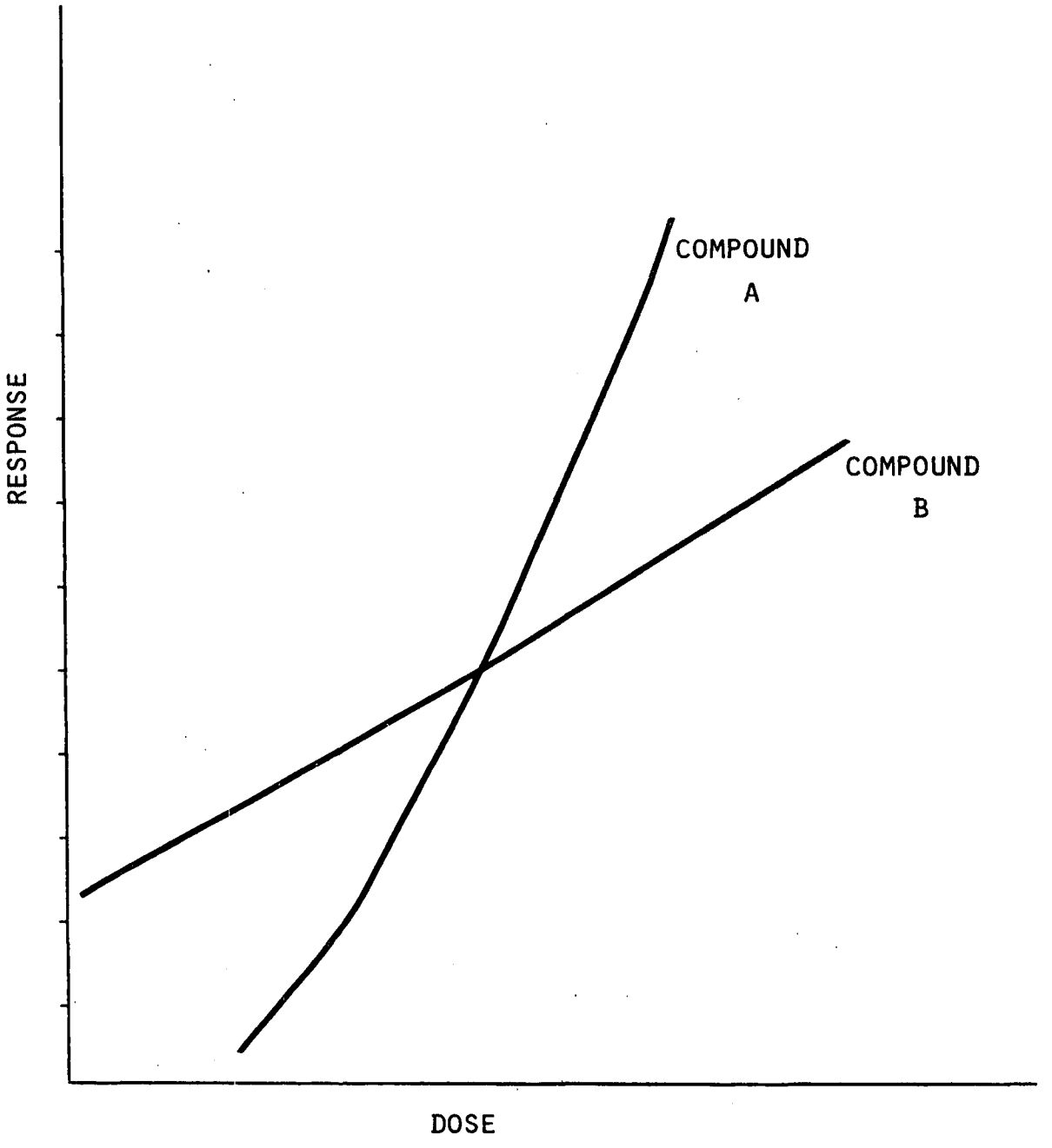
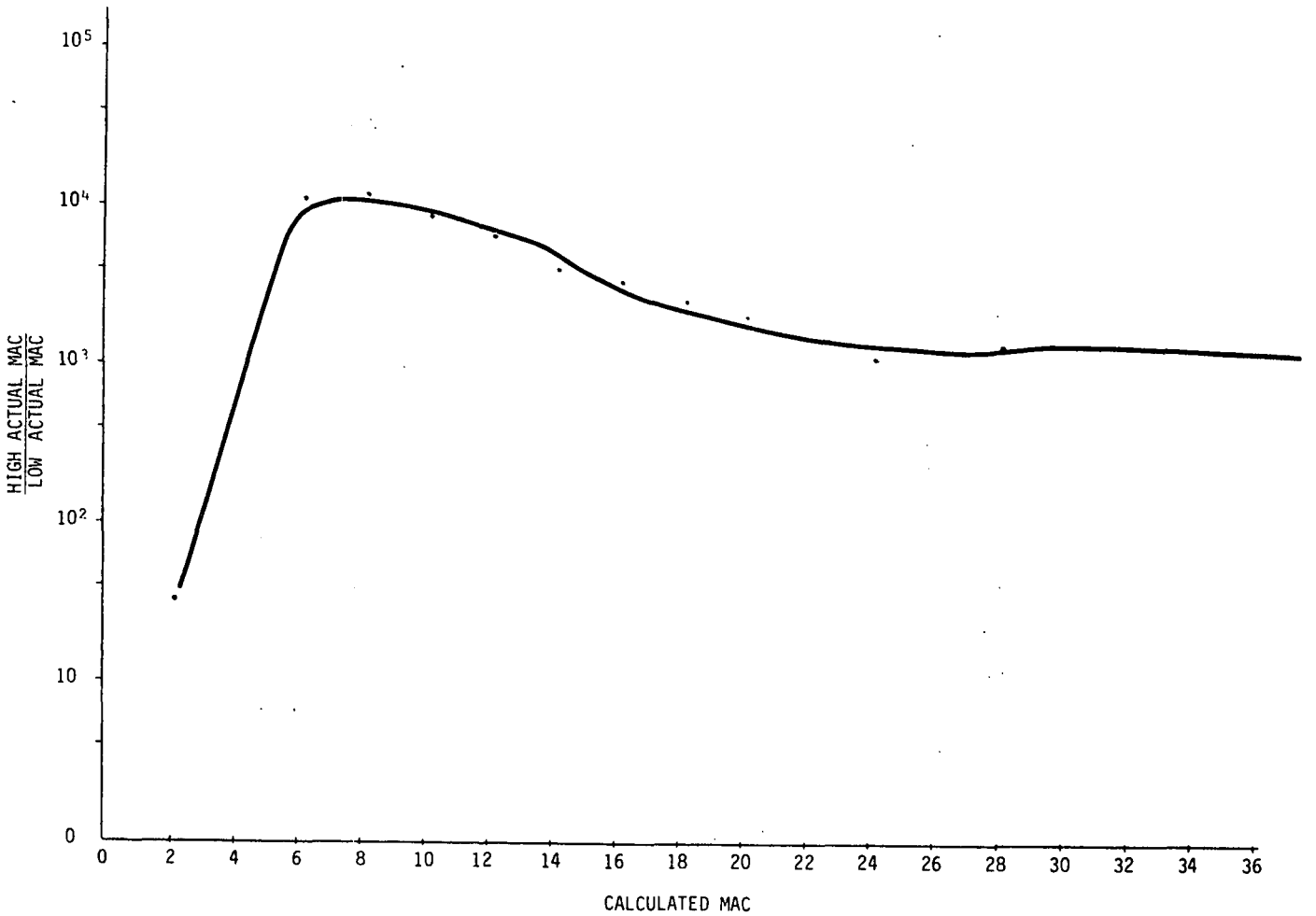


FIGURE 10

RANGE OF ACTUAL MAXIMUM ALLOWABLE CONCENTRATION RELATED TO CALCULATED VALUES



two limits will generally be within a factor of 100 of the "allowable level," and in the majority of cases it should do considerably better. The use of formal statistical methods would reduce the dispersion between empirical "allowable levels" at a given calculated level, but it was not considered effective to develop better estimators until the conceptual design of the system had been reviewed.

Based on these findings, it appears feasible to develop relatively simple methods of predicting levels of concern from data which are generally available when a product goes into commercial production. In refining the crude methods developed in this phase, several alternatives are possible.

One alternative is to rely on the same form of relationship that we used in our crude work, namely

$$\text{Level of Concern} = f\{\frac{1}{L}\} \tag{15}$$

where the L is the sum of contributions, ℓ_i, of the different functional groups of the compound. The refinement would arise from improved values of the functional group contributions which would give better predictions than the crude values we assigned. This methodology could be used for levels of concern in various compartments if empirical data are available.

Another alternative is to use Equation (15) to predict the level of concern for the basic members of each homologous series and use Hansch approaches, which rely on octanol/water partition coefficients to extrapolate to other members of the series. Since the octanol/water partition coefficient is used in the estimation of eventual environmental level, no additional data requirements are needed in the operation of the system.

Other approaches, based on extrapolating from the substance of known level of concern whose chemical structure most resembles that of the compound in question could also be developed.

The ultimate choice between approaches should be based on three considerations:

(1) The cost of developing and operating the system;

(2) The dispersion of empirical values about the predicted values; and

(3) The relationship between the predicted levels of concern for a compound and the sum of the predicted levels for degradation products.

On this basis we believe that the development of improved values for functional group contributions (shown in Equation 15) is the best choice.

V. RANKINGS

A. SUBSTANCES OF CONCERN

The levels of concern and the eventual environmental levels will be compared to classify substances as "substances of concern" and others.

The classification will be in terms of the ratio of the eventual environmental level (or function of eventual environmental levels) to the corresponding level of concern. These ratios will be computed for each level of concern (e.g., for each compartment, or for human consumption, etc.) which has been specified or estimated. A number of classification methods could be considered, but we feel that for this initial classification it is sufficient to use the highest of the ratios. For example, if a substance has ratios of 10^{-5} for water, 10^{-3} for air, and 10^{-4} for human consumption, the classification would be based on the ratio for air (10^{-3}) which is the highest.

The threshold which would divide the "substances of concern" from others can be set at a very low level to ensure, as far as possible, that no potentially harmful compounds are missed. Based on the uncertainties inherent in the calculations, we believe that the threshold ratio should be no higher than 10^{-2}. Lower ratios could be used and would be justifiable if a ratio of the order of 10^{-2} to 10^{-3} results in a substantial fraction of compounds being ranked as not of concern.

B. PRIORITY ORDERING

Compounds which are classified as substances of concern can be ordered into priority ranks in a variety of ways which require little or no additional effort other than computation. From the point of view that the output of this system is intended to guide research activities, it would appear fruitful to use the framework developed for estimating the eventual environmental levels to estimate the time scale available for such research activities.

To tie in closely with the potential for meaningful action, the system could compute the "action date," the latest date at which the emission of the compound could stop without driving the eventual environmental levels above a threshold related to the levels of concern. The action date could then be used alone, or in conjunction with the ratio of eventual level to level of concern, to create a priority list.

VI. SOME EXAMPLES

A. INTRODUCTION

In order to examine the behavior of the proposed system we are presenting some examples. The substances we have chosen for illustrative purposes are: benzene, bis (2-chloroisopropyl) ether, chlorodifluoromethane, methyl chloroform, and trichloromethane. The level of concern desired as discussed in Chapter IV and Appendix II will be used for all compartments.

For all these cases we have assumed that particulates have a half life of about eight months in the atmosphere. Also, we have assumed that the six soil layers have organic fractions of 10%, 5%, 3%, 3%, 3%, and 3%, respectively.

Sensitivity analyses are presented for the case of benzene.

B. DATA ON THE COMPOUNDS

The necessary data was collected using the forms shown in Tables IVa and b. The information sheets for the five compounds are reproduced in Appendix IV. Most of the data were obtained from reports published by the Office of Toxic Substances. In general, production data may be obtained from the U.S. Tariff Commission reports or from the SRI directory of manufactured chemicals. The user and percentage of distribution to each use would ordinarily have to be provided by the manufacturer. Some judgment is required with respect to whether a use should be classified as low, intermediate or high emission. Emissions from sources other than manufacturer and use of the manufactured chemical are difficult to identify. In the case of benzene, for example, the major emission source is motor vehicle exhaust. Unless this were known from other studies, as it was for this example, it might have been overlooked. The probable distribution of emissions to air, ground and surface water was estimated on the basis of the uses and volatility of the compounds. This distribution will ordinarily involve some judgment, and a range of possible distributions should be used to check the sensitivity of the results to these estimates.

Vapor pressure at room temperature, solubility in water, and the octanol/water partition coefficient were obtained from a variety of published and unpublished sources. First-order reaction constants were estimated if enough information was available; otherwise judgment was used to classify the compounds by reactivity and the method outlined in Chapter III was used.

TABLE IVa. DATA SHEET NO. 1

Chemical:

Emission Data:

Production Rate kg/yr.
Natural Production kg/yr.

Uses	% of Prod.	% Emission	Emission Rate kg/yr.
I. Low Emission			
• Production	100%	3%	
•		3%	
•		3%	
•		3%	
II. Intermediate Emission			
•		30%	
•		30%	
•		30%	
•		30%	
III. High Emission			
•		100%	
•		100%	
•		100%	
•		100%	
IV. Natural Sources		100%	
Total			_____

Distribution of Emissions

To Air kg/yr

To Air Particulates kg/yr

To Lakes kg/yr

To Streams kg/yr

To Ground kg/yr

TABLE IVb. DATA SHEET NO. 2

Chemical:

Basic Data:

Molecular Weight	_____	
Molar Refractivity	_____	
Vapor Pressure*	_____	atm
Water Solubility*	_____	gm/gm
Octanol/Water Partition Coeff.*	_____	

* at 20°C

Reaction Constants

Compartment Type	Reactivity					Half Life	Reaction Rate
	Extreme	High	Moderate	Persistent	Inert		
Air							
Particulate							
Air Moisture							
Water							
Adsorbed to Soil							

C. RESULTS

The eventual environmental levels are shown in Tables V a, b, c, d, e. These tables give, for each compound, the computed eventual environmental levels in various compartments. For air and particulates, the concentration is in kilograms of compound per billion kilograms of dry air. For air moisture it is in kilograms of compound per billion kilograms of moisture. For lakes, streams, ground water, and soil moisture the concentration is in kilograms of compound per billion kilograms of water in the corresponding compartment. For the soil compartments the concentration is per billion kilograms of soil in the compartment.

Each table shows four "cases," corresponding to the four matrices of bulk flows presented in Tables III a, b, c, d. It is clear that the differences in bulk flow affect the eventual levels only to a minor degree in most compartments; the concentrations in deep ground water are a factor of two higher when short-circuiting into deep ground water is allowed (cases 2 and 4).

1. Benzene

The eventual environmental levels are about 2400 parts per billion in the air (including vapor and particulate) and about 6 ppb in air moisture and surface waters. Using the method outlined in Chapter IV and Appendix II, the MAC for benzene is 8 mg/m^3 or 7000 ppb. Using a safety factor of 100 to arrive at a level of concern we obtain 70 ppb. This level is exceeded for the respirable air. The levels in meat (about 400 parts per billion) and vegetable matter (about 90 parts per billion) are substantial.

2. Bis (2-chloroisopropyl) ether

Because of the low emission rate, bis (2-chloroisopropyl) ether is not expected to reach one part per billion in any compartment. The MAC obtained by the method of Chapter IV is about 500 parts per billion; if we use a safety factor of 100, the level of concern would be 5 ppb, much higher than the estimated environmental levels even if the octanol/water partition coefficient is applied.

3. Chlorodifluoromethane

For this compound the MAC is about 3000 ppb, so the level of concern is 30 ppb. The eventual concentration in air is 24 ppb, quite close to the level of concern, hence, the geographic distribution of emission would be important.

TABLE Va: *STEADY-STATE CONCENTRATIONS OF BENZENE*

MOL. WT.:78
ML. VOL.:26.2
VAP. PRESS.:0.1
WATER SOL. :0.0018
OCT/WAT PART.:135
BULK RATE FLOW FROM PART. TO LAKES :0.01
STREAMS:0.01
SOIL :0.98

		ASSUMED VALUES		*STEADY-STATE CONCENTRATIONS (PPB)*			
COMPARTMENT	*REACTION CONSTANT*	*EMISSION RATE(E6)*	*F-ORG*	*CASE 1*	*CASE 2*	*CASE 3*	*CASE 4*
AIR	0.01380	520.00000	0.00000	2395.672	2395.463	2395.634	2395.411
AIR MOISTURE	0.01380	0.00000	0.00000	6.341	6.341	6.341	6.341
PARTICULATE	0.06930	48.80000	0.00000	22.990	22.990	22.990	22.990
LAKES	0.06930	8.00000	0.00000	6.510	6.510	6.510	6.510
STREAMS	0.06930	2.00000	0.00000	6.406	6.406	6.406	6.406
SOIL MOISTURE 0-1*M*	0.06930	0.00000	0.00000	6.257	6.257	6.257	6.256
SOIL MOISTURE 1-5*M*	0.06930	0.00000	0.00000	5.117	5.117	5.139	5.136
SOIL MOISTURE 5-10*M*	0.06930	0.00000	0.00000	4.548	4.472	4.555	4.491
SOIL MOISTURE 10-15*M*	0.06930	0.00000	0.00000	3.912	3.553	3.881	3.467
SOIL MOISTURE 15-30*M*	0.06930	0.00000	0.00000	2.675	1.504	2.678	1.293
SOIL MOISTURE 30-50*M*	0.06930	0.00000	0.00000	1.787	0.834	1.834	0.785
GROUND WATER(SHALLOW)	0.06930	0.00000	0.00000	0.312	0.326	0.313	0.326
GROUND WATER(DEEP)	0.06930	0.00000	0.00000	0.007	0.047	0.007	0.053
OCEAN	0.06930	0.00000	0.00000	1.837	1.828	1.837	1.828
SOIL 0-1*M*	0.06931	0.00000	0.10000	0.062	0.062	0.062	0.062
SOIL 1-5*M*	0.03466	0.00000	0.05000	0.050	0.050	0.051	0.051
SOIL 5-10*M*	0.02079	0.00000	0.03000	0.045	0.044	0.045	0.044
SOIL 10-15*M*	0.02079	0.00000	0.03000	0.038	0.035	0.038	0.034
SOIL 15-30*M*	0.02079	0.00000	0.03000	0.026	0.015	0.026	0.013
SOIL 30-50*M*	0.02079	0.00000	0.03000	0.018	0.008	0.018	0.008

TABLE Vb: *STEADY-STATE CONCENTRATIONS OF BIS-(2-CHLOROISOPROPYL) ETHER*

MOL. WT.:171
ML. VOL.:41.3
VAP. PRESS.:0.001
WATER SOL. :0.0017
OCT/WAT PART.:5.899999976
BULK RATE FLOW FROM PART. TO LAKES :0.01
STREAMS:0.01
SOIL :0.98

COMPARTMENT	REACTION CONSTANT	ASSUMED VALUES EMISSION RATE(E6)	F-ORG	STEADY-STATE CONCENTRATIONS (PPB) CASE 1	CASE 2	CASE 3	CASE 4
AIR	0.00690	0.01000	0.00000	0.706	0.705	0.706	0.705
AIR MOISTURE	0.00690	0.00000	0.00000	0.081	0.080	0.081	0.080
PARTICULATE	0.06930	0.00000	0.00000	0.000	0.000	0.000	0.000
LAKES	0.06930	0.15000	0.00000	0.083	0.083	0.083	0.083
STREAMS	0.06930	0.14000	0.00000	0.082	0.082	0.082	0.081
SOIL MOISTURE 0-1M	0.06930	0.00000	0.00000	0.079	0.079	0.079	0.079
SOIL MOISTURE 1-5M	0.06930	0.00000	0.00000	0.066	0.066	0.066	0.066
SOIL MOISTURE 5-10M	0.06930	0.00000	0.00000	0.060	0.059	0.060	0.059
SOIL MOISTURE 10-15M	0.06930	0.00000	0.00000	0.052	0.048	0.052	0.047
SOIL MOISTURE 15-30M	0.06930	0.00000	0.00000	0.038	0.022	0.038	0.019
SOIL MOISTURE 30-50M	0.06930	0.00000	0.00000	0.027	0.013	0.027	0.012
GROUND WATER(SHALLOW)	0.06930	0.00000	0.00000	0.004	0.004	0.004	0.004
GROUND WATER(DEEP)	0.06930	0.00000	0.00000	0.000	0.001	0.000	0.001
OCEAN	0.06930	0.00000	0.00000	0.023	0.023	0.023	0.023
SOIL 0-1M	0.06931	0.00000	0.10000	0.001	0.001	0.001	0.001
SOIL 1-5M	0.03466	0.00000	0.05000	0.001	0.001	0.001	0.001
SOIL 5-10M	0.02079	0.00000	0.03000	0.000	0.000	0.000	0.000
SOIL 10-15M	0.02079	0.00000	0.03000	0.000	0.000	0.000	0.000
SOIL 15-30M	0.02079	0.00000	0.03000	0.000	0.000	0.000	0.000
SOIL 30-50M	0.02079	0.00000	0.03000	0.000	0.000	0.000	0.000

TABLE Vc: *STEADY-STATE CONCENTRATIONS OF CHLORODIFLUOROMETHANE*

MOL. WT.:86.5
ML. VOL.:12.5
VAP. PRESS.:9.5
WATER SOL. :0.003
OCT/WAT PART.:12
BULK RATE FLOW FROM PART. TO LAKES :0.01
STREAMS:0.01
SOIL :0.98

COMPARTMENT	REACTION CONSTANT	ASSUMED VALUES EMISSION RATE(E6)	F-ORG	STEADY-STATE CONCENTRATIONS (PPB) CASE 1	CASE 2	CASE 3	CASE 4
AIR	0.03470	13.20000	0.00000	23.481	23.481	23.481	23.481
AIR MOISTURE	0.03470	0.00000	0.00000	0.001	0.001	0.001	0.001
PARTICULATE	0.03470	0.00000	0.00000	0.000	0.000	0.000	0.000
LAKES	0.00500	0.00000	0.00000	0.001	0.001	0.001	0.001
STREAMS	0.00500	0.00000	0.00000	0.001	0.001	0.001	0.001
SOIL MOISTURE 0-1M	0.00500	0.00000	0.00000	0.001	0.001	0.001	0.001
SOIL MOISTURE 1-5M	0.00500	0.00000	0.00000	0.001	0.001	0.001	0.001
SOIL MOISTURE 5-10M	0.00500	0.00000	0.00000	0.001	0.001	0.001	0.001
SOIL MOISTURE 10-15M	0.00500	0.00000	0.00000	0.001	0.001	0.001	0.001
SOIL MOISTURE 15-30M	0.00500	0.00000	0.00000	0.001	0.001	0.001	0.001
SOIL MOISTURE 30-50M	0.00500	0.00000	0.00000	0.001	0.000	0.001	0.000
GROUND WATER(SHALLOW)	0.00500	0.00000	0.00000	0.000	0.000	0.000	0.000
GROUND WATER(DEEP)	0.00500	0.00000	0.00000	0.000	0.000	0.000	0.000
OCEAN	0.00500	0.00000	0.00000	0.001	0.001	0.001	0.001
SOIL 0-1M	0.00070	0.00000	0.10000	0.001	0.001	0.001	0.001
SOIL 1-5M	0.00035	0.00000	0.05000	0.000	0.000	0.000	0.000
SOIL 5-10M	0.00021	0.00000	0.03000	0.000	0.000	0.000	0.000
SOIL 10-15M	0.00021	0.00000	0.03000	0.000	0.000	0.000	0.000
SOIL 15-30M	0.00021	0.00000	0.03000	0.000	0.000	0.000	0.000
SOIL 30-50M	0.00021	0.00000	0.03000	0.000	0.000	0.000	0.000

TABLE Vd: *STEADY-STATE CONCENTRATIONS OF METHYL CHLOROFORM*

MOL. WT.:133
ML. VOL.:26.3
VAP. PRESS.:0.13
WATER SOL. :0.0044
OCT/WAT PART.:310
BULK RATE FLOW FROM PART. TO LAKES :0.01
STREAMS:0.01
SOIL :0.98

COMPARTMENT	REACTION CONSTANT	ASSUMED VALUES EMISSION RATE(E6)	F-ORG	STEADY-STATE CONCENTRATIONS (PPB) CASE 1	CASE 2	CASE 3	CASE 4
AIR	0.06930	185.00000	0.00000	168.027	168.015	168.026	168.015
AIR MOISTURE	0.06930	0.00000	0.00000	0.492	0.492	0.492	0.492
PARTICULATE	0.06930	1.00000	0.00000	0.471	0.471	0.471	0.471
LAKES	0.00690	1.00000	0.00000	0.505	0.505	0.505	0.505
STREAMS	0.00690	0.50000	0.00000	0.497	0.497	0.497	0.497
SOIL MOISTURE 0-1M	0.00690	2.00000	0.00000	0.485	0.485	0.485	0.485
SOIL MOISTURE 1-5M	0.00690	0.00000	0.00000	0.444	0.443	0.444	0.444
SOIL MOISTURE 5-10M	0.00690	0.00000	0.00000	0.414	0.410	0.414	0.410
SOIL MOISTURE 10-15M	0.00690	0.00000	0.00000	0.380	0.358	0.376	0.349
SOIL MOISTURE 15-30M	0.00690	0.00000	0.00000	0.280	0.166	0.279	0.141
SOIL MOISTURE 30-50M	0.00690	0.00000	0.00000	0.197	0.086	0.201	0.079
GROUND WATER(SHALLOW)	0.00690	0.00000	0.00000	0.162	0.175	0.163	0.175
GROUND WATER(DEEP)	0.00690	0.00000	0.00000	0.030	0.078	0.030	0.081
OCEAN	0.00690	0.00000	0.00000	0.364	0.358	0.364	0.359
SOIL 0-1M	0.00069	0.00000	0.10000	0.465	0.465	0.465	0.465
SOIL 1-5M	0.00035	0.00000	0.05000	0.412	0.412	0.413	0.412
SOIL 5-10M	0.00021	0.00000	0.03000	0.370	0.366	0.370	0.367
SOIL 10-15M	0.00021	0.00000	0.03000	0.340	0.320	0.336	0.312
SOIL 15-30M	0.00021	0.00000	0.03000	0.250	0.148	0.249	0.126
SOIL 30-50M	0.00021	0.00000	0.03000	0.176	0.077	0.180	0.071

TABLE Ve: *STEADY-STATE CONCENTRATIONS OF TRICHLOROFLUOROMETHANE*

MOL. WT.:137
ML. VOL.:21.9
VAP. PRESS.:1
WATER SOL. :0.0011
OCT/WAT PART.:340
BULK RATE FLOW FROM PART. TO LAKES :0.01
STREAMS:0.01
SOIL :0.98

	ASSUMED VALUES			*STEADY-STATE CONCENTRATIONS (PPB)*			
COMPARTMENT	*REACTION CONSTANT*	*EMISSION RATE(E6)*	*F-ORG*	*CASE 1*	*CASE 2*	*CASE 3*	*CASE 4*
AIR	0.03470	99.80000	0.00000	217.907	217.906	217.907	217.906
AIR MOISTURE	0.03470	0.00000	0.00000	0.020	0.020	0.020	0.020
PARTICULATE	0.03470	11.10000	0.00000	7.106	7.106	7.106	7.106
LAKES	0.00510	5.00000	0.00000	0.021	0.021	0.021	0.021
STREAMS	0.00510	7.60000	0.00000	0.020	0.020	0.020	0.020
SOIL MOISTURE 0-1*M*	0.00510	3.00000	0.00000	0.020	0.020	0.020	0.020
SOIL MOISTURE 1-5*M*	0.00510	0.00000	0.00000	0.018	0.018	0.018	0.018
SOIL MOISTURE 5-10*M*	0.00510	0.00000	0.00000	0.017	0.017	0.017	0.017
SOIL MOISTURE 10-15*M*	0.00510	0.00000	0.00000	0.015	0.014	0.015	0.014
SOIL MOISTURE 15-30*M*	0.00510	0.00000	0.00000	0.011	0.006	0.011	0.005
SOIL MOISTURE 30-50*M*	0.00510	0.00000	0.00000	0.008	0.003	0.008	0.003
GROUND WATER(SHALLOW)	0.00510	0.00000	0.00000	0.008	0.009	0.008	0.009
GROUND WATER(DEEP)	0.00510	0.00000	0.00000	0.002	0.004	0.002	0.004
OCEAN	0.00510	0.00000	0.00000	0.016	0.015	0.016	0.015
SOIL 0-1*M*	0.00069	0.00000	0.10000	0.021	0.021	0.021	0.021
SOIL 1-5*M*	0.00035	0.00000	0.05000	0.018	0.018	0.018	0.018
SOIL 5-10*M*	0.00021	0.00000	0.03000	0.016	0.016	0.016	0.016
SOIL 10-15*M*	0.00021	0.00000	0.03000	0.015	0.014	0.015	0.014
SOIL 15-30*M*	0.00021	0.00000	0.03000	0.011	0.006	0.011	0.005
SOIL 30-50*M*	0.00021	0.00000	0.03000	0.007	0.003	0.008	0.003

4. Methyl Chloroform

For methyl chloroform the level of concern is 70 ppb. The air concentration is nearly 170 ppb, so the substance is of concern.

5. Trichlorofluoromethane

The level of concern of 30 ppb is exceeded in the air compartment by a factor of 7, thus it is a substance of substantial concern.

D. RELATIVE PRIORITY

Based on the computation benzene and trichlorofluoromethane would be ranked as of most concern since eventual levels exceed the levels of concern by substantial margins. Methyl chloroform would also be of direct concern. Chlorodifluoromethane would be of concern if its major source of emission where concentrated. Bis (2-chloroisopropyl) ether would be considered of little concern.

E. SENSITIVITY ANALYSIS

The sensitivity of the eventual environmental levels to the elements of the matrix of bulk flows was assessed by using four matrices. As mentioned earlier, only the eventual levels in deep ground water are affected to a major extent. It follows that the flows need not be specified with great accuracy except when there is concern about deep ground water.

The sensitivity of the eventual environmental levels to other parameters was explored for the case of benzene.

- Decreasing the emission into air from 520 to 320 million kilograms per year (Table VIa) caused a nearly proportional change in eventual levels in air and water compartments. Particulate levels were not affected.

- Increasing the reaction rate in all water compartments tenfold (Table VIb) led to an 13% reduction in eventual levels in the water compartments and in the vapor phase. There was no effect on particulates.

Table VIa. *STEADY-STATE CONCENTRATIONS OF BENZENE*

MOL. WT.:78
MOL. VOL.:26.2
VAP. PRESS.:0.1
WATER SOL. :0.0018
OCT/WAT PART.:135
BULK RATE FLOW FROM PART. TO LAKES :0.01
STREAMS:0.01
SOIL :0.98

COMPARTMENT	REACTION CONSTANT	ASSUMED VALUES EMISSION RATE(E6)	F-ORG	STEADY-STATE CONCENTRATIONS (PPB) CASE 1	CASE 2	CASE 3	CASE 4
AIR	.01380	320.00000	.00000	1602.474	1602.334	1602.449	1602.299
AIR MOISTURE	.06900	.00000	.00000	4.242	4.241	4.242	4.241
PARTICULATE	.01380	48.80000	.00000	39.884	39.884	39.884	39.884
LAKES	.06900	8.00000	.00000	4.355	4.355	4.355	4.354
STREAMS	.06900	2.00000	.00000	4.285	4.285	4.285	4.285
SOIL MOISTURE 0-1M	.06900	.00000	.00000	4.185	4.185	4.185	4.185
SOIL MOISTURE 1-5M	.06900	.00000	.00000	3.425	3.424	3.439	3.437
SOIL MOISTURE 5-10M	.06900	.00000	.00000	3.044	2.993	3.049	3.006
SOIL MOISTURE 10-15M	.06900	.00000	.00000	2.619	2.379	2.599	2.322
SOIL MOISTURE 15-30M	.06900	.00000	.00000	1.792	1.007	1.794	.866
SOIL MOISTURE 30-50M	.06900	.00000	.00000	1.197	.558	1.228	.526
GROUND WATER(SHALLOW)	.06900	.00000	.00000	.210	.219	.210	.219
GROUND WATER(DEEP)	.06900	.00000	.00000	.005	.031	.005	.036
OCEAN	.06900	.00000	.00000	1.232	1.226	1.232	1.226
SOIL 0-1M	.06900	.00000	.10000	.041	.041	.041	.041
SOIL 1-5M	.03450	.00000	.05000	.034	.034	.034	.034
SOIL 5-10M	.02070	.00000	.03000	.030	.030	.030	.030
SOIL 10-15M	.02070	.00000	.03000	.026	.024	.026	.023
SOIL 15-30M	.02070	.00000	.03000	.018	.010	.018	.009
SOIL 30-50M	.02070	.00000	.03000	.012	.006	.012	.005

Table VIb: *STEADY-STATE CONCENTRATIONS OF BENZENE*

MOL. WT.:78
MOL. VOL.:26.2
VAP. PRESS.:0.1
WATER SOL. :0.0018
OCT/WAT PART.:135
BULK RATE FLOW FROM PART. TO LAKES :0.01
STREAMS:0.01
SOIL :0.98

COMPARTMENT	*REACTION CONSTANT*	*ASSUMED VALUES EMISSION RATE(E6)*	*F-ORG*	*STEADY-STATE CONCENTRATIONS (PPB) CASE 1*	*CASE 2*	*CASE 3*	*CASE 4*
AIR	.01380	520.00000	.00000	2150.722	2150.693	2150.624	2150.591
AIR MOISTURE	.06900	.00000	.00000	5.693	5.693	5.693	5.693
PARTICULATE	.01380	48.80000	.00000	39.884	39.884	39.884	39.884
LAKES	.69000	8.00000	.00000	5.844	5.844	5.843	5.843
STREAMS	.69000	2.00000	.00000	5.751	5.751	5.751	5.751
SOIL MOISTURE 0-1*M*	.69000	.00000	.00000	5.617	5.617	5.617	5.617
SOIL MOISTURE 1-5*M*	.69000	.00000	.00000	2.298	2.298	2.348	2.347
SOIL MOISTURE 5-10*M*	.69000	.00000	.00000	1.574	1.521	1.597	1.552
SOIL MOISTURE 10-15*M*	.69000	.00000	.00000	1.001	.861	1.014	.847
SOIL MOISTURE 15-30*M*	.69000	.00000	.00000	.538	.352	.552	.332
SOIL MOISTURE 30-50*M*	.69000	.00000	.00000	.362	.281	.372	.279
GROUND WATER(SHALLOW)	.69000	.00000	.00000	.027	.028	.027	.028
GROUND WATER(DEEP)	.69000	.00000	.00000	.000	.001	.000	.001
OCEAN	.69000	.00000	.00000	.238	.238	.238	.238
SOIL 0-1*M*	.06900	.00000	.10000	.056	.056	.056	.056
SOIL 1-5*M*	.03450	.00000	.05000	.023	.023	.023	.023
SOIL 5-10*M*	.02070	.00000	.03000	.016	.015	.016	.015
SOIL 10-15*M*	.02070	.00000	.03000	.010	.009	.010	.008
SOIL 15-30*M*	.02070	.00000	.03000	.005	.003	.005	.003
SOIL 30-50*M*	.02070	.00000	.03000	.004	.003	.004	.003

- Increasing the reaction rate for air moisture by a factor of 10 (Table VIc) led to very small reductions of the concentration in most compartments.

- Reducing the octanol/water partition coefficient to practically zero (and thereby eliminating adsorption into soil) had practically no impact on eventual levels in water and air. (Table VId)

- Reducing the rate of precipitation of particulates by 50% (Table VIe) nearly doubled the concentration of particulates in air. Doubling the rate (Table VIf) almost halved the concentration. Only minor effects were seen in other compartments.

- Increasing the vapor pressure by a factor of 5 lead to a 3% increase in the concentration of vapor in air and an 80% reduction in the water compartments (Table VIg). Decreasing the vapor pressure by 50% reduced the concentration of vapor in air and nearly doubled the concentration in water compartments by 3% (Table VIh).

In view of these results it appears that the eventual levels are not sensitive to soil adsorption characteristics and relatively insensitive to reaction rates. This is fortunate because these parameters are relatively difficult to obtain with any accuracy. Adsorption parameters need not be refined further, reaction rate constants should be within one order of magnitude in order to be useful.

Table VIc: *STEADY-STATE CONCENTRATIONS OF BENZENE*

MOL. WT.:78
MOL. VOL.:26.2
VAP. PRESS.:0.1
WATER SOL. :0.0018
OCT/WAT PART.:135
BULK RATE FLOW FROM PART. TO LAKES :0.01
STREAMS:0.01
SOIL :0.98

COMPARTMENT	*REACTION CONSTANT*	*ASSUMED VALUES EMISSION RATE(E6)*	*F-ORG*	*STEADY-STATE CONCENTRATIONS (PPB) CASE 1*	*CASE 2*	*CASE 3*	*CASE 4*
AIR	.01380	520.00000	.00000	2465.858	2465.642	2465.819	2465.588
AIR MOISTURE	.69000	.00000	.00000	6.527	6.527	6.527	6.526
PARTICULATE	.01380	48.80000	.00000	39.884	39.884	39.884	39.884
LAKES	.06900	8.00000	.00000	6.701	6.701	6.701	6.700
STREAMS	.06900	2.00000	.00000	6.594	6.593	6.594	6.593
SOIL MOISTURE 0-1*M*	.06900	.00000	.00000	6.440	6.440	6.440	6.440
SOIL MOISTURE 1-5*M*	.06900	.00000	.00000	5.270	5.269	5.292	5.289
SOIL MOISTURE 5-10*M*	.06900	.00000	.00000	4.685	4.606	4.692	4.625
SOIL MOISTURE 10-15*M*	.06900	.00000	.00000	4.030	3.661	3.999	3.573
SOIL MOISTURE 15-30*M*	.06900	.00000	.00000	2.757	1.550	2.760	1.332
SOIL MOISTURE 30-50*M*	.06900	.00000	.00000	1.842	.859	1.890	.809
GROUND WATER(SHALLOW)	.06900	.00000	.00000	.322	.337	.323	.337
GROUND WATER(DEEP)	.06900	.00000	.00000	.007	.048	.007	.055
OCEAN	.06900	.00000	.00000	1.896	1.887	1.896	1.887
SOIL 0-1*M*	.06900	.00000	.10000	.064	.064	.064	.064
SOIL 1-5*M*	.03450	.00000	.05000	.052	.052	.052	.052
SOIL 5-10*M*	.02070	.00000	.03000	.046	.046	.046	.046
SOIL 10-15*M*	.02070	.00000	.03000	.040	.036	.040	.035
SOIL 15-30*M*	.02070	.00000	.03000	.027	.015	.027	.013
SOIL 30-50*M*	.02070	.00000	.03000	.018	.008	.019	.008

Table VId: *STEADY-STATE CONCENTRATIONS OF BENZENE*

MOL. WT.:78
MOL. VOL.:26.2
VAP. PRESS.:0.1
WATER SOL. :0.0018
OCT/WAT PART.:1E-6
BULK RATE FLOW FROM PART. TO LAKES :0.01
STREAMS:0.01
SOIL :0.98

COMPARTMENT	ASSUMED VALUES REACTION CONSTANT	EMISSION RATE(E6)	F-ORG	STEADY-STATE CONCENTRATIONS (PPB) CASE 1	CASE 2	CASE 3	CASE 4
AIR	.01380	520.00000	.00000	2469.882	2469.677	2469.863	2469.633
AIR MOISTURE	.06900	.00000	.00000	6.538	6.537	6.538	6.537
PARTICULATE	.01380	48.80000	.00000	39.884	39.884	39.884	39.884
LAKES	.06900	8.00000	.00000	6.712	6.712	6.712	6.711
STREAMS	.06900	2.00000	.00000	6.605	6.604	6.605	6.604
SOIL MOISTURE 0-1M	.06900	.00000	.00000	6.451	6.450	6.451	6.450
SOIL MOISTURE 1-5M	.06900	.00000	.00000	5.760	5.759	5.777	5.775
SOIL MOISTURE 5-10M	.06900	.00000	.00000	5.480	5.438	5.485	5.446
SOIL MOISTURE 10-15M	.06900	.00000	.00000	5.095	4.840	5.096	4.774
SOIL MOISTURE 15-30M	.06900	.00000	.00000	4.658	3.742	4.666	3.475
SOIL MOISTURE 30-50M	.06900	.00000	.00000	4.305	3.093	4.338	2.934
GROUND WATER(SHALLOW)	.06900	.00000	.00000	.375	.345	.376	.345
GROUND WATER(DEEP)	.06900	.00000	.00000	.008	.065	.008	.069
OCEAN	.06900	.00000	.00000	1.902	1.891	1.902	1.891
SOIL 0-1M	.06900	.00000	.10000	.000	.000	.000	.000
SOIL 1-5M	.03450	.00000	.05000	.000	.000	.000	.000
SOIL 5-10M	.02070	.00000	.03000	.000	.000	.000	.000
SOIL 10-15M	.02070	.00000	.03000	.000	.000	.000	.000
SOIL 15-30M	.02070	.00000	.03000	.000	.000	.000	.000
SOIL 30-50M	.02070	.00000	.03000	.000	.000	.000	.000

Table VIe: *STEADY-STATE CONCENTRATIONS OF BENZENE*

MOL. WT.:78
MOL. VOL.:26.2
VAP. PRESS.:0.1
WATER SOL. :0.0018
OCT/WAT PART.:135
BULK RATE FLOW FROM PART. TO LAKES :0.005
STREAMS:0.005
SOIL :0.49

COMPARTMENT	REACTION CONSTANT	ASSUMED VALUES EMISSION RATE(E6)	F-ORG	STEADY-STATE CONCENTRATIONS (PPB) CASE 1	CASE 2	CASE 3	CASE 4
AIR	.01380	520.00000	.00000	2442.257	2442.043	2442.218	2441.990
AIR MOISTURE	.06900	.00000	.00000	6.465	6.464	6.465	6.464
PARTICULATE	.01380	48.80000	.00000	67.444	67.444	67.444	67.444
LAKES	.06900	8.00000	.00000	6.637	6.637	6.637	6.636
STREAMS	.06900	2.00000	.00000	6.531	6.530	6.531	6.530
SOIL MOISTURE 0-1M	.06900	.00000	.00000	6.379	6.378	6.379	6.378
SOIL MOISTURE 1-5M	.06900	.00000	.00000	5.219	5.219	5.241	5.238
SOIL MOISTURE 5-10M	.06900	.00000	.00000	4.640	4.562	4.647	4.581
SOIL MOISTURE 10-15M	.06900	.00000	.00000	3.991	3.626	3.960	3.539
SOIL MOISTURE 15-30M	.06900	.00000	.00000	2.730	1.535	2.734	1.319
SOIL MOISTURE 30-50M	.06900	.00000	.00000	1.824	.851	1.872	.801
GROUND WATER(SHALLOW)	.06900	.00000	.00000	.319	.333	.320	.333
GROUND WATER(DEEP)	.06900	.00000	.00000	.007	.048	.007	.055
OCEAN	.06900	.00000	.00000	1.878	1.869	1.878	1.869
SOIL 0-1M	.06900	.00000	.10000	.063	.063	.063	.063
SOIL 1-5M	.03450	.00000	.05000	.052	.052	.052	.052
SOIL 5-10M	.02070	.00000	.03000	.046	.045	.046	.045
SOIL 10-15M	.02070	.00000	.03000	.039	.036	.039	.035
SOIL 15-30M	.02070	.00000	.03000	.027	.015	.027	.013
SOIL 30-50M	.02070	.00000	.03000	.018	.008	.018	.008

Table VIf: *STEADY-STATE CONCENTRATIONS OF BENZENE*

MOL. WT.:78
MOL. VOL.:26.2
VAP. PRESS.:0.1
WATER SOL. :0.0018
OCT/WAT PART.:135
BULK RATE FLOW FROM PART. TO LAKES :0.02
STREAMS:0.02
SOIL :1.96

COMPARTMENT	ASSUMED VALUES REACTION CONSTANT	EMISSION RATE(E6)	F-ORG	STEADY-STATE CONCENTRATIONS (PPB) CASE 1	CASE 2	CASE 3	CASE 4
AIR	.01380	520.00000	.00000	2486.323	2486.106	2486.284	2486.051
AIR MOISTURE	.06900	.00000	.00000	6.581	6.581	6.581	6.581
PARTICULATE	.01380	48.80000	.00000	21.947	21.947	21.947	21.947
LAKES	.06900	8.00000	.00000	6.757	6.756	6.757	6.756
STREAMS	.06900	2.00000	.00000	6.649	6.648	6.649	6.648
SOIL MOISTURE 0-1M	.06900	.00000	.00000	6.494	6.493	6.494	6.493
SOIL MOISTURE 1-5M	.06900	.00000	.00000	5.313	5.313	5.335	5.332
SOIL MOISTURE 5-10M	.06900	.00000	.00000	4.723	4.644	4.731	4.664
SOIL MOISTURE 10-15M	.06900	.00000	.00000	4.063	3.691	4.032	3.602
SOIL MOISTURE 15-30M	.06900	.00000	.00000	2.780	1.562	2.783	1.343
SOIL MOISTURE 30-50M	.06900	.00000	.00000	1.857	.866	1.906	.816
GROUND WATER(SHALLOW)	.06900	.00000	.00000	.325	.339	.326	.339
GROUND WATER(DEEP)	.06900	.00000	.00000	.007	.049	.007	.056
OCEAN	.06900	.00000	.00000	1.912	1.902	1.912	1.903
SOIL 0-1M	.06900	.00000	.10000	.064	.064	.064	.064
SOIL 1-5M	.03450	.00000	.05000	.053	.053	.053	.053
SOIL 5-10M	.02070	.00000	.03000	.047	.046	.047	.046
SOIL 10-15M	.02070	.00000	.03000	.040	.036	.040	.036
SOIL 15-30M	.02070	.00000	.03000	.027	.015	.027	.013
SOIL 30-50M	.02070	.00000	.03000	.018	.009	.019	.008

TABLE VIg: *STEADY-STATE CONCENTRATIONS OF BENZENE*

MOL. WT.:78
MOL. VOL.:26.2
VAP. PRESS.:0.5
WATER SOL. :0.0018
OCT/WAT PART.:135
BULK RATE FLOW FROM PART. TO LAKES :0.01
STREAMS:0.01
SOIL :0.98

COMPARTMENT	*REACTION CONSTANT*	*ASSUMED VALUES EMISSION RATE(E6)*	*F-ORG*	*STEADY-STATE CONCENTRATIONS (PPB) CASE 1*	*CASE 2*	*CASE 3*	*CASE 4*
AIR	.01380	520.00000	.00000	2532.815	2532.770	2532.807	2532.759
AIR MOISTURE	.06900	.00000	.00000	1.341	1.341	1.341	1.341
PARTICULATE	.01380	48.80000	.00000	39.884	39.884	39.884	39.884
LAKES	.06900	8.00000	.00000	1.377	1.377	1.377	1.377
STREAMS	.06900	2.00000	.00000	1.355	1.355	1.355	1.355
SOIL MOISTURE 0-1M	.06900	.00000	.00000	1.323	1.323	1.323	1.323
SOIL MOISTURE 1-5M	.06900	.00000	.00000	1.083	1.083	1.087	1.087
SOIL MOISTURE 5-10M	.06900	.00000	.00000	.962	.946	.964	.950
SOIL MOISTURE 10-15M	.06900	.00000	.00000	.828	.752	.821	.734
SOIL MOISTURE 15-30M	.06900	.00000	.00000	.566	.318	.567	.274
SOIL MOISTURE 30-50M	.06900	.00000	.00000	.378	.176	.388	.166
GROUND WATER(SHALLOW)	.06900	.00000	.00000	.066	.069	.066	.069
GROUND WATER(DEEP)	.06900	.00000	.00000	.001	.010	.001	.011
OCEAN	.06900	.00000	.00000	.390	.388	.390	.388
SOIL 0-1M	.06900	.00000	.10000	.013	.013	.013	.013
SOIL 1-5M	.03450	.00000	.05000	.011	.011	.011	.011
SOIL 5-10M	.02070	.00000	.03000	.010	.009	.010	.009
SOIL 10-15M	.02070	.00000	.03000	.008	.007	.008	.007
SOIL 15-30M	.02070	.00000	.03000	.006	.003	.006	.003
SOIL 30-50M	.02070	.00000	.03000	.004	.002	.004	.002

TABLE VIh: *STEADY-STATE CONCENTRATIONS OF BENZENE*

MOL. WT.:78
MOL. VOL.:26.2
VAP. PRESS.:0.05
WATER SOL. :0.0018
OCT/WAT PART.:135
BULK RATE FLOW FROM PART. TO LAKES :0.01
STREAMS:0.01
SOIL :0.98

COMPARTMENT	ASSUMED VALUES REACTION CONSTANT	EMISSION RATE(E6)	F-ORG	STEADY-STATE CONCENTRATIONS (PPB) CASE 1	CASE 2	CASE 3	CASE 4
AIR	.01380	520.00000	.00000	2393.525	2393.119	2393.451	2393.017
AIR MOISTURE	.06900	.00000	.00000	12.671	12.669	12.671	12.669
PARTICULATE	.01380	48.80000	.00000	39.884	39.884	39.884	39.884
LAKES	.06900	8.00000	.00000	13.009	13.007	13.009	13.006
STREAMS	.06900	2.00000	.00000	12.801	12.799	12.801	12.798
SOIL MOISTURE 0-1M	.06900	.00000	.00000	12.503	12.501	12.503	12.500
SOIL MOISTURE 1-5M	.06900	.00000	.00000	10.230	10.228	10.272	10.266
SOIL MOISTURE 5-10M	.06900	.00000	.00000	9.094	8.941	9.108	8.973
SOIL MOISTURE 10-15M	.06900	.00000	.00000	7.824	7.106	7.762	6.935
SOIL MOISTURE 15-30M	.06900	.00000	.00000	5.352	3.008	5.358	2.585
SOIL MOISTURE 30-50M	.06900	.00000	.00000	3.576	1.667	3.670	1.570
GROUND WATER(SHALLOW)	.06900	.00000	.00000	.626	.653	.628	.653
GROUND WATER(DEEP)	.06900	.00000	.00000	.014	.094	.014	.107
OCEAN	.06900	.00000	.00000	3.682	3.662	3.682	3.663
SOIL 0-1M	.06900	.00000	.10000	.124	.124	.124	.124
SOIL 1-5M	.03450	.00000	.05000	.101	.101	.102	.101
SOIL 5-10M	.02070	.00000	.03000	.090	.088	.090	.083
SOIL 10-15M	.02070	.00000	.03000	.077	.070	.077	.069
SOIL 15-30M	.02070	.00000	.03000	.053	.030	.053	.026
SOIL 30-50M	.02070	.00000	.03000	.035	.016	.036	.016

VII. RECOMMENDATIONS

The subsystem used to compute eventual levels is ready for implementation. The data requirements for this subsystem are quite manageable, and the results are relatively insensitive to data which may not be available.

The area which may require additional effort is the development of a more definitive matrix of bulk flows and of similar matrices that can be used for a "worst case" analysis or for regional analyses. Since these matrices constitute fixed data for the system, they may be modified at any time that better information becomes available.

The refinement of soil adsorption relationships is of low priority because of the relative insensitivity of the results to this relation. The subsystem used to compute levels of concern requires refinement and expansion to compartments other than air. One possible approach is to base the levels of concern on the amount taken in by humans. This amount can be approximated from the eventual levels by a linear transformation:

$$\text{Daily Human Uptake} = B(C_{air} + C_{part} + C_{moisture}\frac{W_{moist}}{W_{air}})$$

$$+ D\,C_{water} + M(.5\,C_{water} + .5\,P_{o/w}C_{water})$$

$$+ V(.9\,C_{soil\ moisture} + .1\,P_{o/w}C_{soil\ moisture})$$

where B is the kg/day of air breathed

D is the kg/day of water drunk

M is the kg/day of meat consumed

V is the kg/day of vegetable matter consumed

and C_{water} is a suitable average of the concentration in lakes and streams.

This would provide a useful summary index.

It is essential, however, that regardless of the indices chosen the level of concern be based on the concentrations that are likely to impose undue risk to health and environment under chronic exposure conditions rather than on concentrations that cause easily measurable damage: if the damage is easily measurable the risks are intolerable.

Inasmuch as the system must be able to cope with new chemicals, the most attractive alternative would be based on correlating structure with damage measured by epidemiologic methods under actual conditions. While this would provide a valid and defensible beginning, we believe that the

available information would not be sufficient to establish a correlation between structure and effect. Delphi methods and experimentation could be used separately or jointly to provide a reasonable relation between structure and effect; if the substances to be used in the assessments are selected on the basis of their contribution to the analysis, such an effort could yield a useful tool for screening at a reasonable cost. Such an approach should be considered. Other approaches, which the Office of Toxic Substances is already pursuing are providing useful results for measurable damage. Methods for extrapolating from these approaches would be useful.

Appendix I

Distribution of a Pollutant in the Environment

APPENDIX I

DISTRIBUTION OF A POLLUTANT IN THE ENVIRONMENT

The distribution of a pollutant among the compartments of the environment is determined by intercompartment flows and compartment concentrations. For purposes of the present analysis, it appears adequate to divide the environment into five primary compartments. The ocean is considered a residual compartment in which the pollutant is absorbed or decomposed so that flows back from the ocean can be neglected. A schematic diagram of the flows is given in Figure I-1, which is identical to Figure 7 in the text of the report. The total amount of material in a compartment at time $t + \Delta t$ must be equal to the amount in that compartment at time t plus the amount created in or flowing into the compartment in time Δt minus the amount degraded in or flowing out of the compartment in time Δt. From these considerations it is possible to write equations for each compartment. For example, for streams we have

$$\begin{aligned} W_s C_s(T+\Delta t) &= W_s C_s(t) \\ &+ [\dot{P}_s + \dot{F}_{gm\to s} C_{gm}(t) + \dot{F}_{gw} C_{gw}(t) + \dot{F}_{l\to s} C_l(t) \\ &\quad + \dot{F}_{am\to s} C_{am}(t) + r_{a\to s} C_a(t)]\Delta t \\ &- [\dot{F}_{s\to o} + \dot{F}_{s\to l} + r_{s\to a}] C_s(t) \end{aligned} \qquad \text{(I-1)}$$

where W_x is the weight of water in compartment x, in kg,

C_x is the concentration of pollutant in compartment x, in kg/kg,

$\dot{F}_{x\to y}$ is the bulk flow of pollutant solution from compartment x to compartment y in kg/yr,

$r_{x\to y}$ is the diffusional flow of pollutant from compartment x to compartment y in kg/yr/unit concentration,

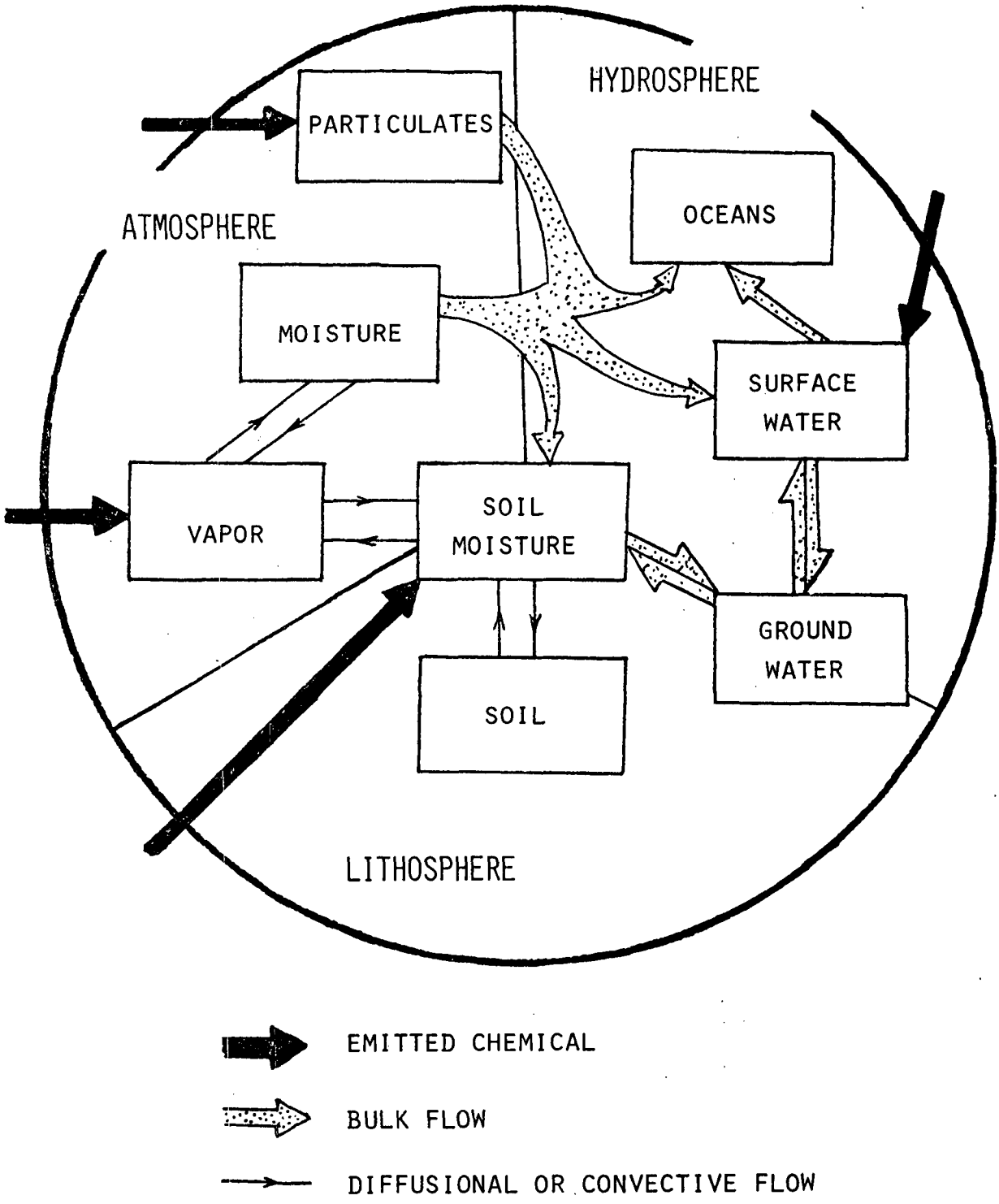
$\dot{P}_x$ is the pollutant emission rate into compartment x, in kg/yr,

k_x is the first order reaction constant in water, in kg/kg/yr,

FIGURE I-1

SCHEMATIC DIAGRAM OF INTERCOMPARTMENT FLOWS OF EMITTED CHEMICAL

(man and biosphere omitted)



and the subscripts are

l	for lakes
s	for streams
gm	for ground moisture
gw	for ground water
a	for air
am	for atmospheric moisture
o	for ocean

Considering all compartments, the equations corresponding to Equation I-1 can be summarized by

$$\begin{aligned} W_x C_x(t+\Delta t) &= W_x C_x(t) + \Delta t [P_x(t) \\ &\quad + \sum_y (\dot{F}_{y\to x} + r_{y\to x})\, C_y(t) - k_x W_x C_x(t) \\ &\quad - C_x(t) \sum_y (\dot{F}_{x\to y} + r_{x\to y})] \end{aligned} \qquad \text{(I-2)}$$

where in many cases $\dot{F}$ and r are zero or negligible. Defining the variable

$$Z_x = W_x C_x(t+\Delta t) - W_x C_x(t) - P_x(t)\Delta t$$

the above equation can be expressed as

$$\begin{aligned} Z_x &= \Delta t [\sum_y (\dot{F}_{y\to x} + r_{y\to x})\, C_y(t) - k_x W_x C_x(t) \\ &\quad - C_x(t) \sum_y (\dot{F}_{x\to y} + r_{x\to y})] \end{aligned} \qquad \text{(I-3)}$$

or, in matrix form:

$$\vec{Z} = (\Delta t) \cdot M \cdot \vec{C} \qquad \text{(I-4)}$$

where M is a matrix of coefficients.

At steady state $C_x(t+\Delta t) = C_x(t)$, so that

$$Z_x = -P_x(\infty)\,\Delta t \qquad \text{(I-5)}$$

where $P_x(\infty)$ is the eventual (steady state) rate of emissions into compartment x. Under these conditions Equation I-4 becomes

$$\vec{P}(\infty) = -M \cdot \vec{C}(\infty) \qquad \text{(I-6)}$$

and the vector of steady state concentrations becomes

$$\vec{C}(\infty) = -M^{-1}\,\vec{P}(\infty) \qquad \text{(I-7)}$$

so that the eventual environmental levels can be computed from Equation I-7 by inverting the matrix M.

The elements of the matrix M can be computed as follows:

$$m_{xx} = -k_x W_x - \sum_y \dot{F}_{x\to y} - \sum_y r_{x\to y}$$

$$m_{xy} = \dot{F}_{y\to x} + r_{y\to x}$$

where

- k_x is the first order effective reaction constant for compartment x
- $\dot{F}_{x\to y}$ is the bulk flow rate of solution from compartment x to compartment y
- $r_{x\to y}$ is the diffusional flow rate for the pollutant from compartment x to compartment y per unit concentration in compartment x

The values of $\dot{F}_{x\to y}$ and $r_{x\to y}$ for compartment pairs for which they are not negligible are given in the text of the report.

Appendix II

Chemical Classes with Potential for Causing Biological Damage

APPENDIX II

CHEMICAL CLASSES WITH POTENTIAL FOR CAUSING BIOLOGICAL DAMAGE

A. INTRODUCTION

Anyone with a background in chemistry recognizes that some chemical classes are more hazardous than others. The student in freshman chemistry laboratory, for example, will handle strong mineral acids with far more circumspection than metal oxides or organic solvents. Still, systematic correlation of biotic hazard with chemical type has defied many excellent scientists, whose attempts have proved expensive and unsatisfying.

If we are to protect the biota of the environment including man from chemical risk, we must either (1) exhaustively test *all* chemicals for potential environmental damage -- a prohibitively expensive alternative, or (2) devise some sort of screening methodology which will enable us to restrict our precautionary investigations only to suspect chemicals. The necessary condition for the development of any sort of screening methodology is that there be a workable and defensible correlation between chemical class and environmental damage. One such correlation is presented below.

B. DOSAGE

All chemical substances are toxic. *All* chemical substances can damage the environment. With respect to chemical substances found in the natural environment, damage to the biosphere can result from either low concentration levels (boron deficiencies in many U.S. soils) or excessive levels (mercury pollution of Minamata Bay). That is to say, the dose-response curve is *not* a monotonically increasing function passing through the origin: it will, for many naturally occurring substances, have at least one point at which the first derivative is zero. The complicated relation of dose level to effect is frequently cited as a reason for the hopelessness of trying to relate environmental harm to chemical class. While it is a real difficulty, it is not insurmountable, since all organisms tend to have the same basic biochemistry. Thus, the dosage problem can be avoided in part by restricting comparisons to the same species or by normalizing for body mass. Persistence, biodegradation, and biomagnification are further complicating factors. These difficulties do not preclude the possibility of workable screening, but they should serve as a warning that no screening system can be perfectly reliable and that any screening system should always be applied with its limitations strongly in mind.

C. SELECTION RULES

One possible screening methodology is to promulgate "selection rules;" i.e., a list of chemical substituents which, when present, make a chemical suspect. The following group of selection rules has been developed and evaluated:

A chemical compound may damage the biosphere if it contains or reacts with water to form compounds containing:

(1) Be, B, P, and/or any element of atomic number greater than 22 (except Br^- and I^- salts and "noble" gases);

(2) A covalently bound halogen;

(3) A proton with large K_a;

(4) A base with large K_b;

(5) An -O-O- linkage;

(6) >C=O, >C-OH, -C-O-C- groups, but not -C(O-)=O

(7) R'-S-R and R'-S-S-R groups where R and R' can be the same or different and where R and/or R' is or contains any element of atomic number less than 22;

(8) N bonded to N (except for N_2), O, S, and/or C;

(9) R-C=C and/or R-C≡C- groups where R is not -C- (note that this rule includes aromatics); and

(10) A heterocyclic ring (saturated and/or unsaturated).

Application of these selection rules screens out all the hazardous chemicals on the OTS's Appendix I list except for Al, silicones, $CaCl_2$, and ethyl acetate, and the inclusion of these on the list, it should be noted, is questionable. Spot application testing indicates that these rules are capable of catching 80%-90% of the chemicals in the much longer CHRIS list; again, it is questionable whether those chemicals this screening misses (acetic acid, ammonium nitrate and sulfate, amyl acetate, butane, etc.) are really of major environmental concern. These tests indicate that the selection rules proposed are effective at screening out hazardous substances. For the screen to be useful, however, it must pass a high percentage "innocent" chemicals.

To test the "fineness" of the screen, the selection rules were applied to a "neutral" chemical list; i.e., a general list of chemicals not specifically hazardous. When applied to 47 inorganic chemicals (every 20th compound on pp. 528-620, 44th ed. of the *Chemical Rubber Handbook)*, the selection rules passed only 7, yet it seemed to be working well. When every 100th organic chemical on pp. 770-862 was checked, only 1 out of 17 passed. Again, the screen seemed to be working well. It is clear there are few "innocent" chemicals. Applied to the *Chemical and Engineering News* (June 2, 1975, p. 32) list of 50 biggest volume chemicals (Table II-1) 18 out of 50 passed and the selection rules seemed to be working; i.e., those that passed would probably be judged "innocent" by most experts. It should be noticed in this instance, where the list is not one specifically of hazardous substance, that a substantial fraction (about 36%) of the chemicals listed passed the screen. Of those that did not some are already under investigation (e.g., vinyl chloride, styrene, dimethyl, terephthalate), and others could very well prove to be problems in the future (e.g., cumene, vinyl acetate).

A workable screening should, of course, err on the side of being too conservative. The inconvenience of having to examine further "innocent" compounds caught by the screen is far less worrisome than major leakage of hazardous substances through the screen. However, if a screen were too indiscriminate, it would obviously be worthless. Lists of "innocent" chemicals are relatively hard to come by. One such listing is the GRAS ("generally recognized as safe") food additive list. Examination and application of the above selection rules to this list is rather unsettling, since many of these substances do *not* pass the screening. Many flavoring substances, for example, contain $\succeq$C=O, H$\succeq$C=O, or -C-OH groups turpenes, heterocyclic rings, and even phenolic groups. Some of these may, in fact, merit reinvestigation. On the other hand, sugars fail rules 6 and 10, and proteins fail 6, 7, 8, and 9. In fact, there is a very large class of substances of biological origin which would fail the screening. There are two possible approaches to this problem:

(1) Some kind of specification of dosage level, and

(2) Restricting the applicability of selection rules 6, 7, 8, and 9 (and 10 where the heterocyclic element is *not* oxygen) to compounds of molecular weight under 150-200 (exclusive of any elements of At. No. greater than 22).

TABLE II-1

SELECTION RULES APPLIED TO 50 TOP CHEMICALS

Rank 1974	Rank 1973		PRODUCTION (Billions of lb) 1974	PRODUCTION (Billions of lb) 1973	SELECTION RULE FAILED
1	1	Sulfuric acid	64.71	63.45	3
2	2	Lime, except refractory dolomite	40.75	39.76	
3	3	Oxygen, high and low purity	32.12	32.45	
4	4	Ammonia, synthetic anhydrous	31.40	30.19	4
5	5	Ethylene	23.52	22.33	
6	6	Sodium hydroxide, 100% liquid	21.73	21.44	4
7	7	Chlorine, gas	21.24	20.80	2
8	9	Nitrogen, high and low purity	17.17	16.52	
9	8	Nitric acid	16.37	26.88	3
10	10	Sodium carbonate, synthetic and natural	15.10	15.04	
11	11	Ammonium nitrate, original solution	15.09	14.31	
12	12	Phosphoric acid	14.26	13.70	3
13	13	Benzene	11.07	10.65	9
14	14	Propylene	9.82	9.88	
15	15	Ethylene dichloride	7.70	9.29	2
16	18	Toluene	7.49	6.94	9
17	16	Urea, primary solution	7.40	7.27	6,8
18	17	Methanol, synthetic	6.86	7.06	6
19	20	Styrene	5.94	5.98	9
20	19	Formaldehyde, 37% by weight	5.85	6.42	6
21	11	Xylenes	5.79	5.66	9
22	21	Ethylbenzene	5.70	5.69	9
23	23	Vinyl chloride	5.60	5.35	2
24	24	Hydrochloric acid	4.81	5.03	3
25	25	Ethylene oxide	3.89	4.17	6
26	26	Ammonium sulfate	3.88	3.97	
27	27	Butadiene (1,3-), rubber grade	3.66	3.64	9
28	30	Terephthalic acid, crude	3.43	3.20	9
29	28	Carbon black	3.35	3.49	
30	29	Ethylene glycol	3.11	3.28	6
31	31	Carbon dioxide, all forms	2.91	3.14	
32	32	Cumene	2.87	2.67	9
33	33	Sodium sulfate, high and low purity	2.75	2.61	
34	34	Dimethyl terephthalate	2.74	2.56	9
35	37	p-Xylene	2.68	2.33	9
36	40	Cyclohexane	2.34	2.12	
37	38	Phenol	2.32	2.28	3,9
38	35	Aluminum sulfate, commercial	2.32	2.50	
39	36	Acetic acid	2.26	2.43	
40	41	Acetone	2.06	1.99	6
41	39	Calcium chloride, solid and liquid	2.00	2.16	
42	44	Isopropanol	1.91	1.84	6
43	42	Ethanol, synthetic	1.90	1.96	6
44	43	Sodium tripolyphosphate	1.87	1.92	1
45	45	Propylene oxide	1.74	1.75	6
46	46	Acetic anhydride	1.71	1.67	
47	47	Titanium dioxide	1.58	1.57	1
48	50	Sodium silicate	1.54	1.45	
49	47	Adipic acid	1.51	1.57	
50	49	Vinyl acetate	1.40	1.50	9

D. TLV'S, LD_{50}'s AND CHEMICAL TYPE

In order to quantize possible correlations between toxicity and chemical type, TLV's in ppm were compared to molecular weight within types of compounds such as aliphatic alcohols, aldehydes, and monochlorides. Two difficulties were immediately evident: (1) there are not enough TLV's quoted for members of a homologous series so that any trends can be traced further than the first two or three members of the series, and (2) TLV's are *not* empirical numbers but rather represent a rather arbitrary and unhappy attempt to quantize judgmental assessments of toxic levels.

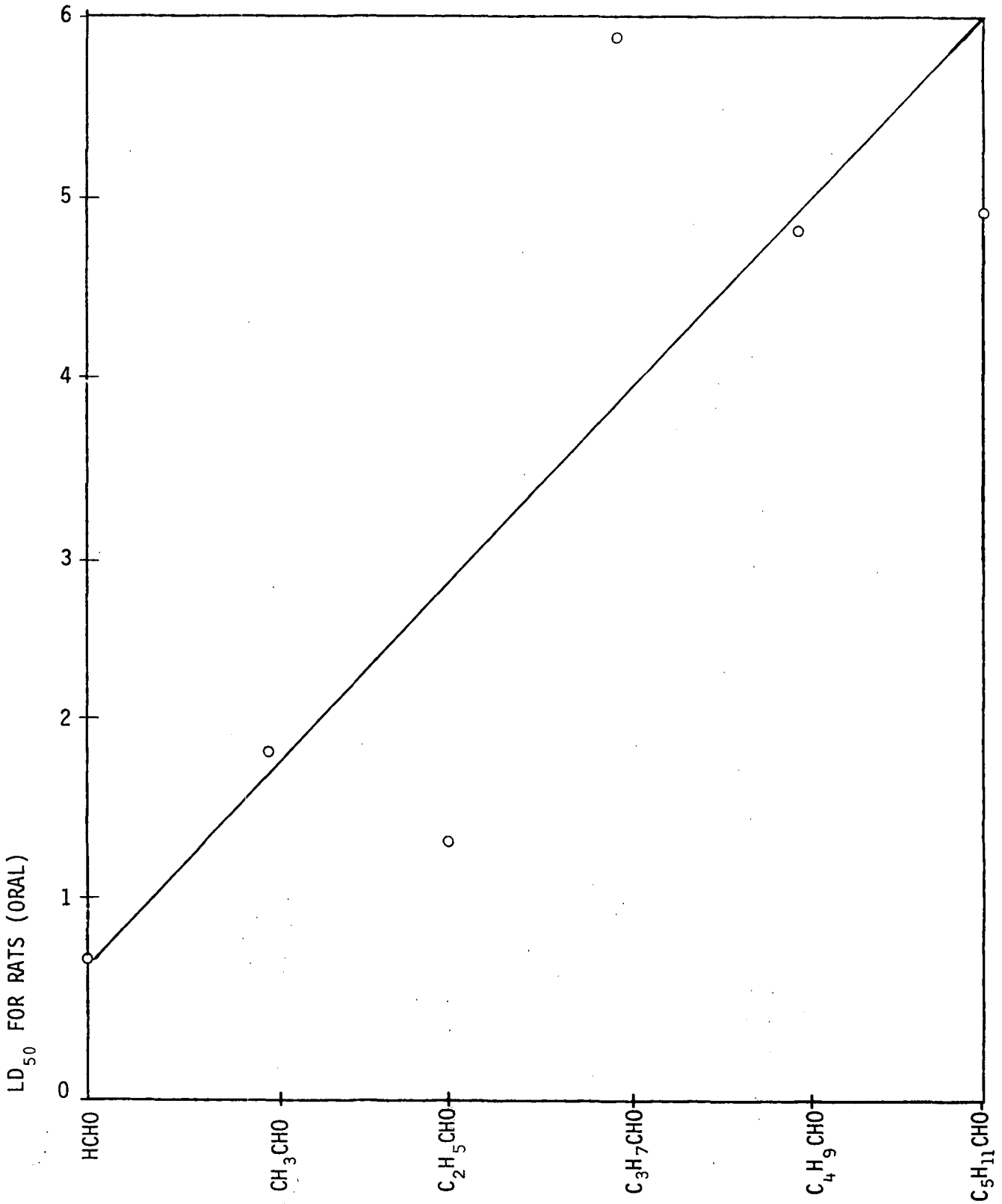
LD_{50} values were also examined for a possible quantitative correlation. Because of the importance of body mass (really a dilution factor) comparisons were made only for the same organism. Oral values were used since that seemed the most probable route of exposure in real environmental situations. However, since oral values encompass transport through biomembranes as well as specifically toxic biochemical effects, one could argue that injection values might be preferable. The results (Figure II-1 is one example) are not very compelling, but do illustrate that with many important exceptions, toxicity tends to decrease with increasing chain length in a homologous series of aldehydes. Another disquieting observation is that the LD_{50} values for organic compounds all tend to be similar, suggesting that what one is looking at is not real biochemical toxicity, but simply the limits of the liber to accommodate these substances.

E. THE 1974 TOXIC SUBSTANCES LIST AND CHEMICAL TYPE

In order to correlate toxicity with chemical class an extensive list of substances is needed with some quantitative measure of toxicity. Such a list is Table G-1, Appendix I, in the 1974 "The Toxic Substances List" *(Federal Register 37*, No. 202, October 18, 1972) which tabulates about 400 chemicals. This list, for all its difficulties, at least seems to boast some sort of official imprimatur. Chief among the difficulties is the fact that it is an air pollution list, giving maximum respiration exposure levels in mg/m^3. As a consequence the hazard of heavy metals, particularly if they are in the form of fine powder or dusts, and of substances which have been notorious causes of respiratory attack in past industrial settings, are given a very magnified (and from the standpoint of water pollution, distorted) prominence. We find that silver metal, copper, and even carbon black, calcium oxide, and mineral oil appear as much more hazardous than cyanide, benzoyl peroxide, nitric and hydrochloric acids, sulfur dioxide, Malathion, pyridine, and phenol. Data in the EPA's *Water Quality Criteria Book* should be more relevant but it is too sketchy for the present purposes. Data are not given for many different chemical classes, and those data that are given are for different species. The "toxicity factors" and "harmful quantities" listed in the Batelle Memorial Institute study on penalties for hazardous

FIGURE II-1

TOXICITY VS CHAIN LENGTH FOR ALIPHATIC ALDEHYDES



spills, might be used but the orientation of the study is largely economic. To demonstrate a methodology for estimating environmental levels of concern, we have based our initial work on the air standards listing.

A matrix was formed with the approximately 400 toxic substances listed in the left-hand column in order of increasing allowable level (ranging from 0.001 mg/m^3 for soluble rhodium salts to 9,000 mg/m^3 for carbon dioxide. Across the top were ranged chemical types) based on the selection rules. (The key to Figure II-2.)

One or more entries were checked for the chemical types exemplified by each substance. The resulting completed matrix was examined to see if chemical types tended to cluster in certain MAC ranges. Sophisticated, rigorous techniques are available for quantitatively establishing non-randomness but their application here did not appear to be warranted. Figure II-2 is a highly abbreviated representation of the results. The matrix clearly evinced the tendency of some classes of chemicals to cluster in a characteristic acceptable level range and it provided tangible, semi-quantitative evidence to support the existence of certain toxicity trends.

1. Toxic Heavy Metals

Heavy metals and their compounds, both soluble and insoluble, especially if they are in finely divided form such as dusts or mists, are very injurious when inhaled, with the majority falling in the range of 0.001 mg/m^3 (for soluble Rh salts) to 1 mg/m^3 (for Yttrium). Metals with less stringent allowable levels include tin (2 mg/m^3); tantalum, manganese, soluble compounds of molybdenum, ZnO fume, and zirconium compounds (all with 5 mg/m^3); iron oxide fume (10 mg/m^3); and TiO_2, MgO fume, and molybdenum (all with 15 mg/m^3).

2. Strong Acids and Bases

Sulfuric, oxalic, and phosphoric acids all have an allowable level of 1 mg/m^3 but otherwise strong acids and bases show little tendency to cluster.

3. Isocyanates

Isocyanates appear to be highly toxic substances but not many examples are included in the list. They range from 0.05 mg/m^3 for methyl isocyanate down to 0.2 mg/m^3 for methylene biphenyl isocyanate.

FIGURE II-2

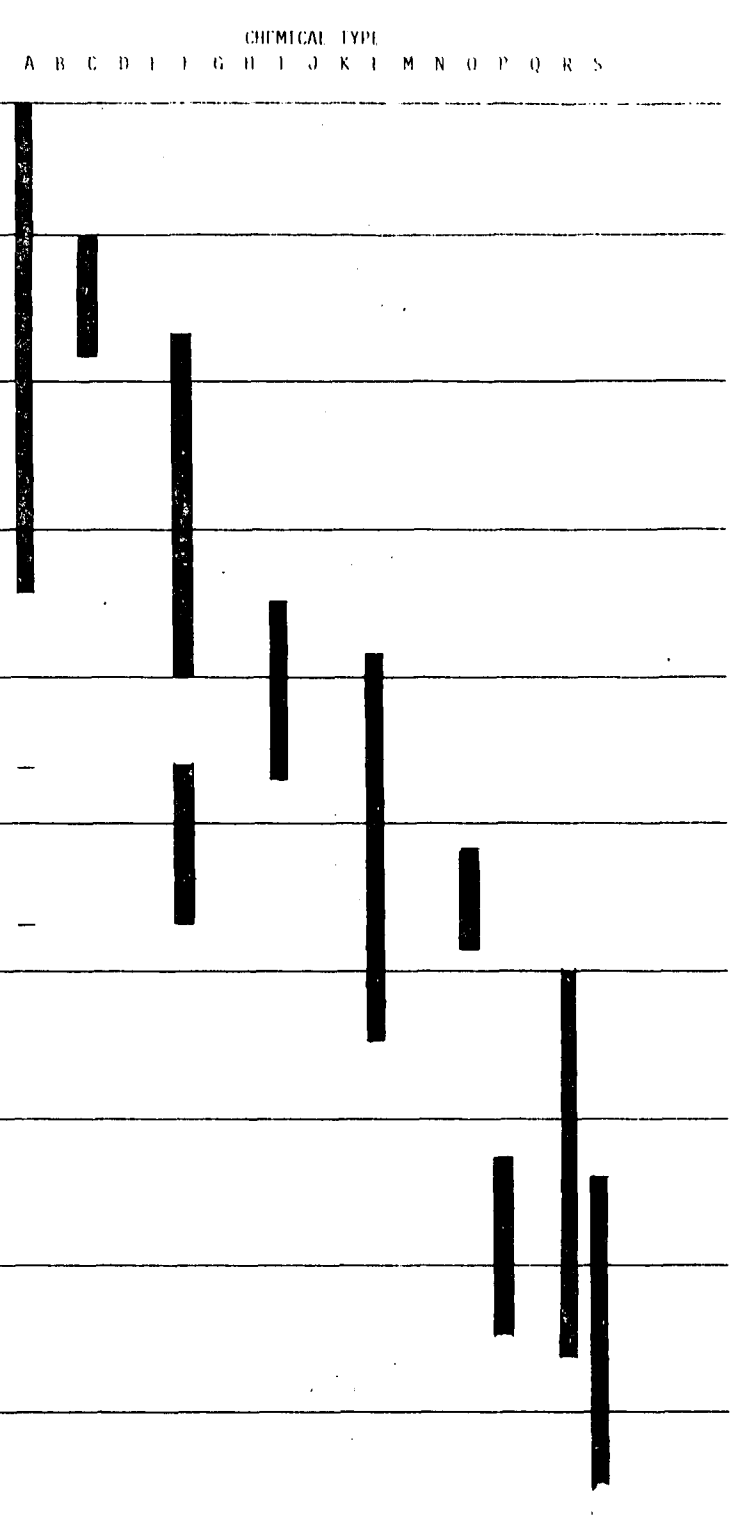
CHEMICAL TYPE KEY

A	Heavy metals
B	Stong acids and
C	-N=C=O
D	Organic phosphorus
E	Phenols
F	P-S-O-N-halides
G	Halogenated hydrocarbons
H	-N , -N=N-, $-\overset{\overset{O}{\|}}{C}-N<$
I	$R-NO_2$
J	Ø-R
K	
L	-CN
M	
N	R-O-R', R-O-O-R'
O	R-S-S-, RSH, R-S-K
P	>C=O (but not -COO)
Q	$Cl-\overset{\overset{\|}{O}}{}-COOR(H)$, $=\overset{\overset{\|}{C}}{}-COOR(H)$
R	$\overset{\overset{\|}{ROH}}{}$
S	$R-\overset{\overset{O}{\|}}{C}-OR$

FIGURE II-2

TOXICITY-CHEMICAL TYPE MATRIX

ACCEPTABLE LIMIT RANGE	SOME EXAMPLE SUBSTANCES
0.1	Sol. Rh salts (0.001) Nickel carbonyl (0.007) Methyl isocyanate (0.05) Tetraethyl lead (0.075)
>0.5	Endrin (0.1) Org. Sn compds. (0.1) Strychnine(0.15) Arsine (0.2)
>1.0	Hafnium (0.5) Chlorodane(0.5) Sb and compds. (0.5) Bromine (0.8)
>5	Sulfuric acid (1) DDT (1) Hydrzine (1.3) Allyl chloride (3)
>10	Benzoyl peroxide (5) Nitric acid (9) p-Nitrogniline (6) Nitrogen dioxide (9)
>50	Methyl amine (12) Sulfur dioxide (13) Phenol (19) Ammonia (39)
>100	Naphthalene (50) Carbon monoxide (55) Acetonitrile (70) Ethylene oxide (90)
>500	Ethyl acrylate (100) Ethyl butyl ketone(230) Methanol (260) Dioxane (360)
>1000	Propyl alcohol (500) Turpentine(560) 1,2-Dichlorethane (790) t-Butyl acetate (950)
>5000	Ethyl ether (1,200) Ethanol (1,900) n-Heptane (2,000)



4. Organic Phosphorus Compounds

Phosphings and organic phosphorus compounds also appear to be highly toxic with the substances listed tending to "cluster" a bit diffusely between 0.1 mg/m^3 for triorthocresyl phosphate and 0.4 mg/m^3 for phosphings. Of course, it should be noted that organic substances can exemplify more than one suspect chemical class.

5. Phenols

Phenolic substances range over a broad spectrum of maximum allowable limits with phenol itself being at 19 mg/m^3.

6. P-S-O-N-halide

Compounds with covalent bonds among P,S,O,N, and halides can be very dangerous. They tend to concentrate between 0.2 mg/m^3 (for ozone) and 3 mg/m^3 (for chlorine gas). A second clustering appears to occur between 6 mg/m^3 (for sulfur monochloride) and 30 mg/m^3 (for nitric oxide). Particularly toxic is oxygen difluoride (0.1 mg/m^3).

7. Halogenated Hydrocarbons

Halogenated hydrocarbons, which includes many pesticides, rather to our surprise do not seem to tend to cluster but are widely scattered throughout the entire allowable level range from 0.1 mg/m^3 for Endrin to 7,600 mg/m^3 for 1,1,2-trichloro, 1,2,2-trifluoroethane. Some interesting trends are evident, however. Bromination is less troublesome than chlorination and fluorination markedly reduces toxicity even when heavier halogens remain in the compound. While not noted in the matrix, we might observe in passing that aliphatic hydrocarbons are not very toxic and do not start to make their appearance until quite high allowable levels.

8. Amine, Azo, and Amide Compounds

Some of these N-compounds are quite dangerous; p-phenylene diamine, for example, appears at 0.1 mg/m^3. Most of the compounds do not start to appear in what might be called a "diffuse cluster," until about 1 mg/m^3 (for ethylene imine). They then continue to occur with some frequency until triethylamine at 100 mg/m^3.

9. Nitro-Compounds

Nitro-compounds appear to tend to cluster between 1.5 mg/m^3 (for trinitrotoluene) to 6 mg/m^3 (for p-nitroaniline) but examples can be found both above or below this range: picric acide at 0.1 mg/m^3 and nitrotoluene at 30 mg/m^3.

10. Phenyl-benzyl Compounds

Unless halogenated or containing some other active groups, phenyl-, benzyl-, toluene, and related compounds are not among the most dangerous substances. They begin to appear with allowable levels at about 1 mg/m^3 and continue to reappear down to about 500 mg/m^3 in a diffuse "cluster."

11. Heterocyclic Nitrogen

These substances appear to be thinly scattered throughout a wide range from strychnine (0.15 mg/m^3) to N-ethylmorpholine (94 mg/m^3) with pyridine at 15 mg/m^3. It should be noted that this listing does not include many exceedingly deadly compounds of biological origin probably because of their non-volatility and relative rarity.

12. Cyanide-Nitriles

Cyanides, rather surprisingly, do not fall high on the list. They form a somewhat thinly populated cluster ranging from 3 to 70 mg/m^3.

13. Fused Rings

Fused ring compounds range thinly over the list and cluster about 50 mg/m^3. Those few high on the list are there because of some active group such as a halogen. Naphthalene is at the bottom of this range at 50 mg/m^3.

14. Ethers, Oxides, and Peroxides

Carbon chains and rings interrupted by one or two oxygens range widely from about 0.1 to 740 mg/m^3 with a noticeable increase in frequency at around 100 mg/m^3. Again, those high on the list are there by virtue of other active substituents such as chlorine. There also does appear to be some discernable tendency for peroxy-compounds to fall higher than oxy-compounds and for oxygen containing heterocyclic rings to fall higher than simple ethers.

15. Organic Sulfur Compounds

Of the five organic S-compounds examined on the list, four fell between 12 and 35 mg/m^3. The only substance above this range, perchloromethyl mercaptan (0.8 mg/m^3) is chlorinated.

16. Carbonyl Compounds (ketones, aldehydes, etc.)

With several important exceptions, carbonyl compounds do not appear very dangerous and for the most part are concentrated in the 100-800 mg/m^3 range.

17. Carboxylic Groups with Substituents on the Alpha Carbon

No significant tendencies are evident from the matrix for these substances.

18. Alcohols

With few exceptions, alcohols begin to appear on the matrix list at 50 mg/m^3 and they recur with considerable frequency down to 750 mg/m^3. Ethanol is at 1,900 mg/m^3.

19. Esters

Simple aliphatic esters begin to appear as a cluster at 250 mg/m^3 with a particularly dense concentration in the matrix at 525-900 mg/m^3.

Aliphatic hydrocarbons were not included in the matrix, but, as noted earlier, it is apparent that they are relatively innocent, not beginning to appear until about 1000 mg/m^3.

In conclusion, the foregoing matrix analysis does show semi-quantitatively that there are important correlations between chemical types and structure and that certain chemical types tend to cluster in certain allowable level ranges.

F. OTHER SCREENS

The methodologies discussed above by no means exhaust the methodologies for pre-screening potentially environmentally damaging chemical substances.

Inasmuch as the biosphere has responded to subtances present in the natural environment, a screen could be formulated on the basis of naturally occurring substances. That is, any chemical in ested into the natural environment in excess of levels found in the natural unpolluted environment could be considered suspect. Such a screen would immediately preclude man-made chemicals not found in the environment. This type of screen has the advantage of a built-in level specification and it would probably be well accepted by the environmentalists. It does have one particularly serious difficulty, however. This is that some chemical substances occur in the unpolluted natural environment at very injurious levels. These include mercury, fluoride, turpenes, and a host of toxins of biological origin.

A second screen might be based on whether a candidate compound is structurally analogous to a compound known to be biologically active. Any effective drug or medication would be suspect, for example. (In this connection it is most surprising that aspirin, so effective, appears to be so relatively harmless.) Substances which resemble a biosubstance are particularly troublesome, since the biochemistry of the organism may fail to distinguish them from their analogues. Still, they cannot perform the analogous biological function and, thus, can be most disruptive. A screen of this type would be most useful for preliminary assessment of the relative safety of complex organic compounds which are possible candidates as food additives, drugs, etc.

G. ASSESSMENT OF SOVIET WORK AND A NEW METHODOLOGY

For some years now Soviet scientists have apparently invested considerable effort in the problem of relating biological activity, specifically toxicity, to chemical structure. A recent summary of this work by Ljublina and Filov[1] has attracted attention in the United States. For calculating indices of toxicity these authors present three methodologies:

(1) Zaeva (1964)

(2) Zahradnik (1962)

(3) Ljublina (1965-1967)

In the Zaeva equation maximum allowable concentration (MAC) in mg/m^3 for organic substances are calculated by the expression:

(1) $MAC = 1000M/\Sigma \ell i$

where M is the molecular weight and $\Sigma \ell i$ is the sum of "biological activity values" which have been assigned to various chemical bonds. The Zahradnik equation is useful only for estimating the relative toxicity of members of a homologous series and is not applicable for comparisons among widely different chemical types of organic compounds -- our present concern.

Ljublina and co-workers at the Leningrad Institute of Industrial Hygiene and Occupational Diseases developed several empirical relationships correlating physiochemical properties, such as molecular weight, density, refractive index, and melting point with toxicity indices. The approach is a statistical one and it is unclear, even *a posteri*, why these

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[1] Ljublina, E.I. and V.A. Filov, *Methods Used in the USSR for Establishing Biological Safe Levels of Toxic Substances*, World Health Organization, Geneva, 1975.

correlations might be obtained. Furthermore, a large correction factor must be applied to the computation; this correction factor depends on chemical type, and thus the whole approach tends to bring us back thereby to the concepts underlying the Zaeva equation.

We have applied the Zaeva equation to the calculation of the MAC's for the air inhalation toxic substance list. While there may be some slight correlation, the results are not very satisfying (Figure II-3). There are several difficulties in applying the Zaeva equation. For example, in what is an apparent misprint in the text they list two different values by ℓi for the -C-C- bond: 15.4 and 173.7. Which does one use? The circle-points in Figure II-3 are based on one value, the square products on the other. We found the correlation is improved if one deliberately misuses the Zaeva equation, counting a bond which appears n-times in a compound only once rather than n-times (Figure II-4). We did find it sometimes possible to obtain an impressive correlation *within a homologous series*. Another problem is that there is not necessarily a relationship between Soviet MAC's and U.S. MAC's, both being judgmentally based.

Next we used the Zaeva equation, but substituted for Zaeva's "biological activity values," which we had found ambiguous in application, ℓ_i's based up the matrix we generated earlier (Figure II-2). Since in Figure II-2 the MAC level at which clustering occurs can easily be arranged according to types of substituents and/or bonds, so as to regulatory decrease, ℓ_i's can be assigned. Although the decreasing clusters of MAC's in the matrix (Figure II-2) make it clear that correlation is possible, the correlation obtained was only slightly improved over the original Zaeva equation (Figure II-5A). After examining the results, however, it became apparent that the presence of the molecular weight in the numerator of expression (1) in effect nullifies the additive toxicities in the denominator. Accordingly, we formulated a new expression:

$$(2) \quad MAC = 100/\Sigma\ell i$$

where, based on the matrix (Figure II-2), the following ℓi values are used:

ℓi = 10	-N=C=O
9	ϕ-Cl, $-C(Cl)=O$
8	ϕ-OH, ϕ-CH_3, ϕ-, R-Cl, fused rings (sat. or unsat.), P-S, -N=N=
7	ϕ-NO_2, R-NO_4 C-SH, $C(N)=O$, -N, -O-O-, $=C(=C)-C=O$
6	-C≡N, N-O, heterocyclic N- and O- rings
5	R-OH, R-Br, C-O-C, C≡C

FIGURE II-3

THE ZAEVA FORMULA

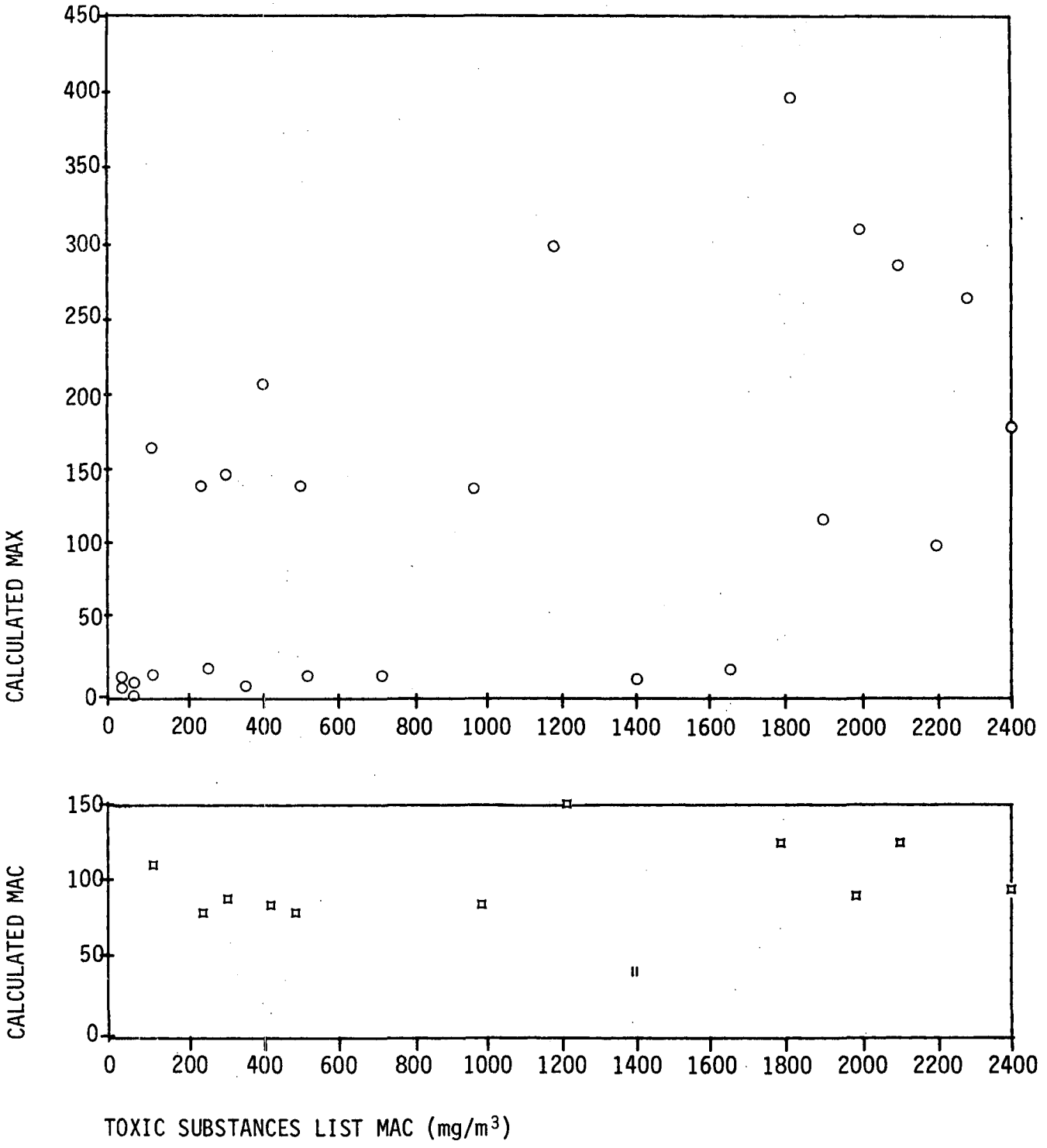


FIGURE II-4

MODIFIED ZAEVA FORMULA CORRELATION

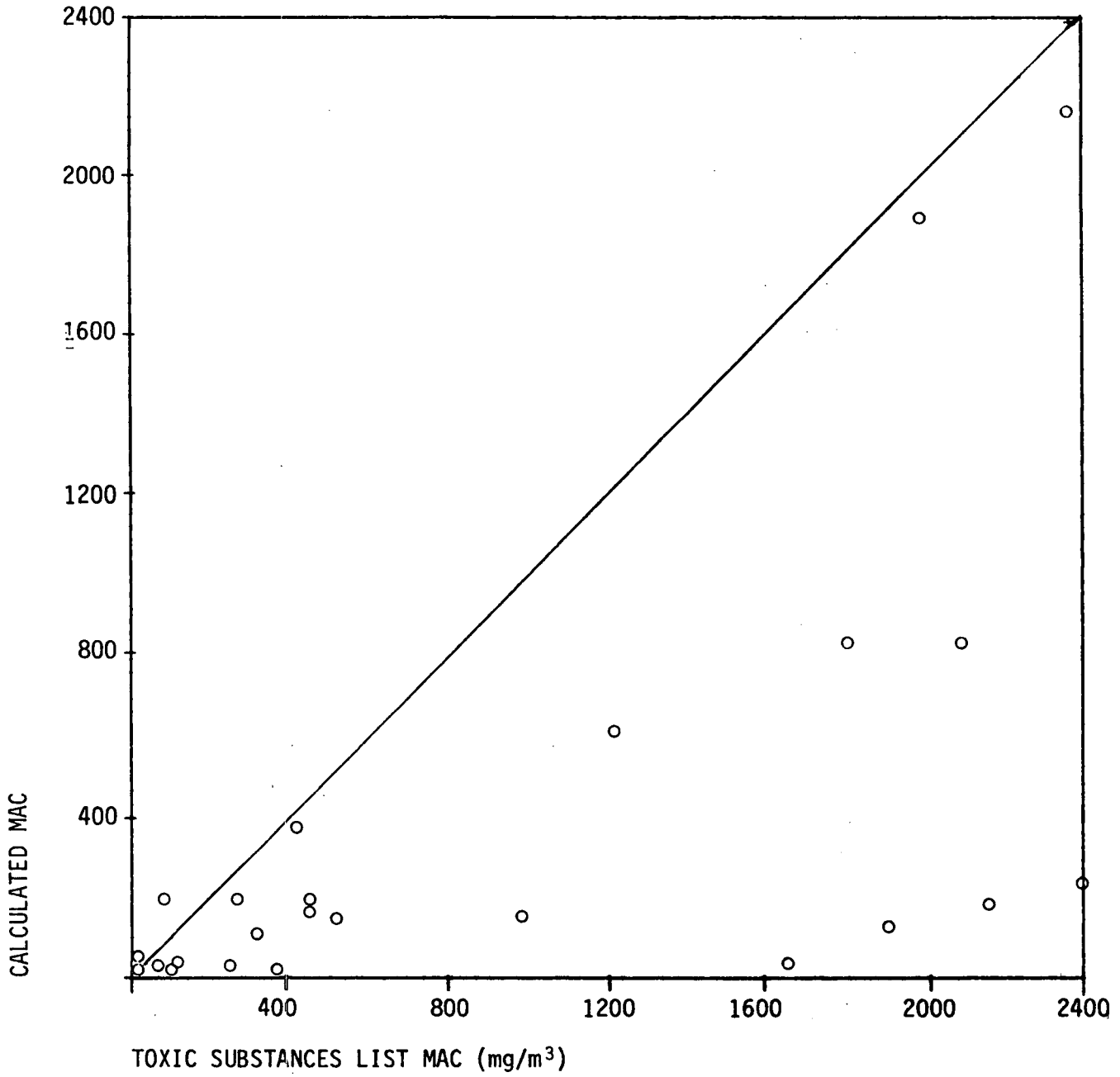
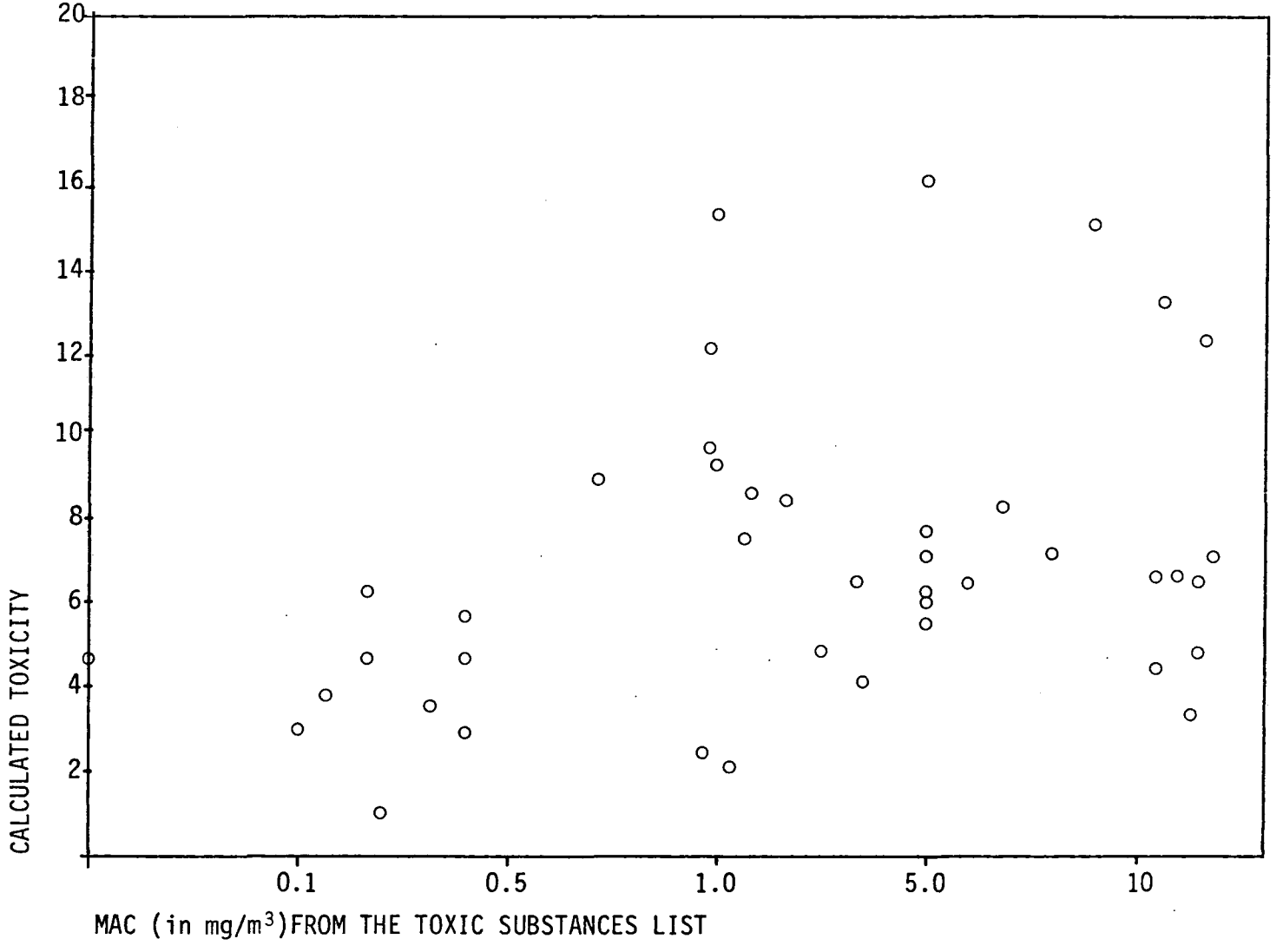


FIGURE II-5A

FIRST CORRELATION



4	$R{=}O^{O-H}$, C=C (non-aromatic
3	$R{-}C^{R}{=}O$, $C^{O-H}{=}O$
2	$C^{O-R}{=}O$, R-F

Where: ϕ = aromatic (benzene) ring

R = aliphatic HC backbone

This approach immediately gave much more promising results (Figure II-5B) and so was applied to 100 substances from the toxic substances list (Figure II-6). A number of features of this approach should be noted:

1. Since we were simply exploring, trying to find a basis for correlation, the analysis was done in an "eye balling" fashion. The whole procedure, however, is readily amenable to rigorous mathematical analysis.

2. The list used is a peculiar one, highly distorted by virtue of being an *air* pollution list. The scatter can be due to the list as well as the calculation.

3. The scatter envelope is narrowest in the most critical region -- i.e., for the more highly toxic substances.

4. There are many ways open for refining and sharpening up equation (2) and its application.

Finally, it should be noted in Figure II-6 that we were only looking for a correlation; thus, the value of MAC is not equal to the value of MAC from the toxic substances list. This can be readily accomplished by introducing a logarithmic term and a normalization constant.

FIGURE II-5B

INITIAL SECOND CORRELATION

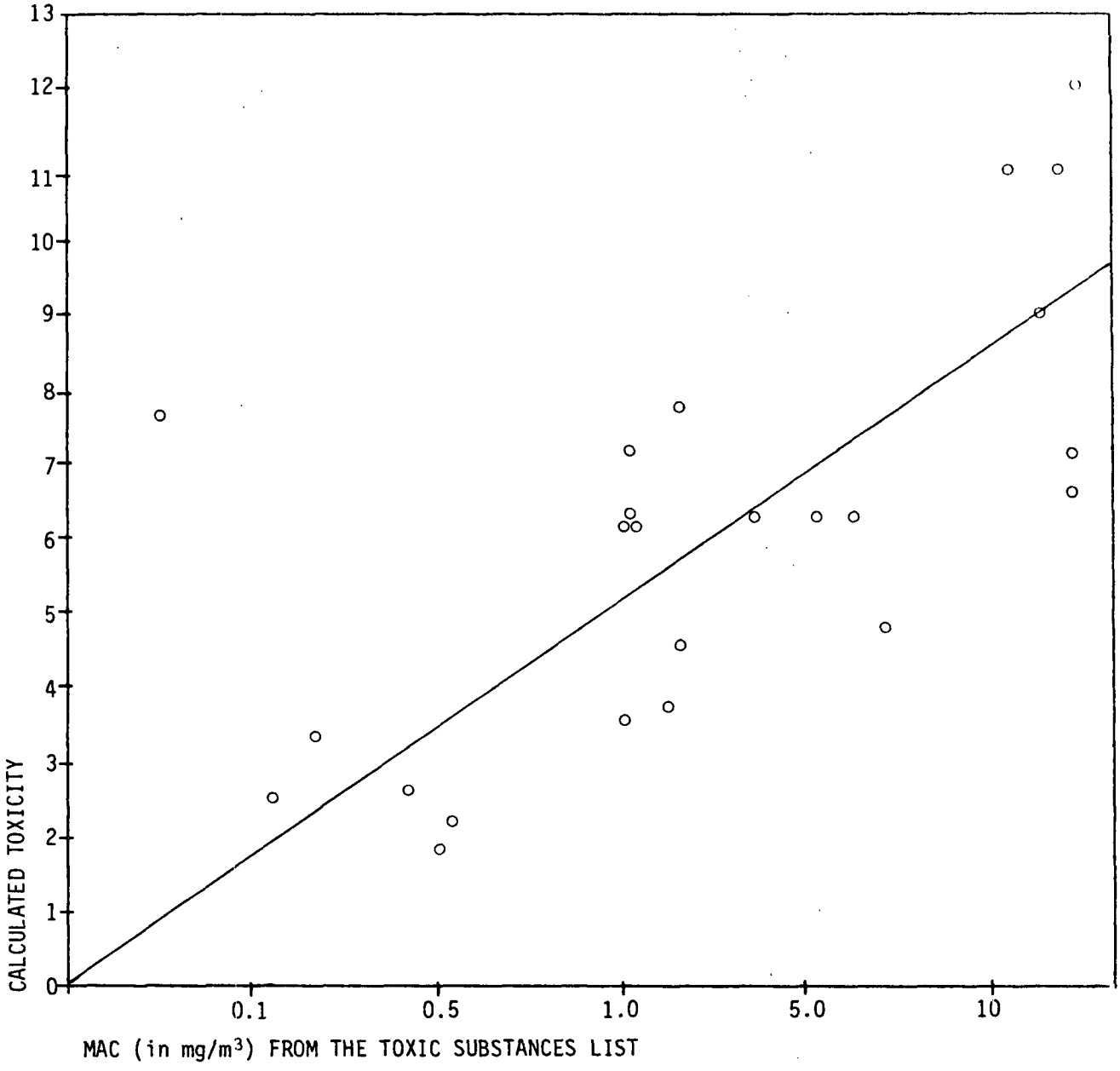
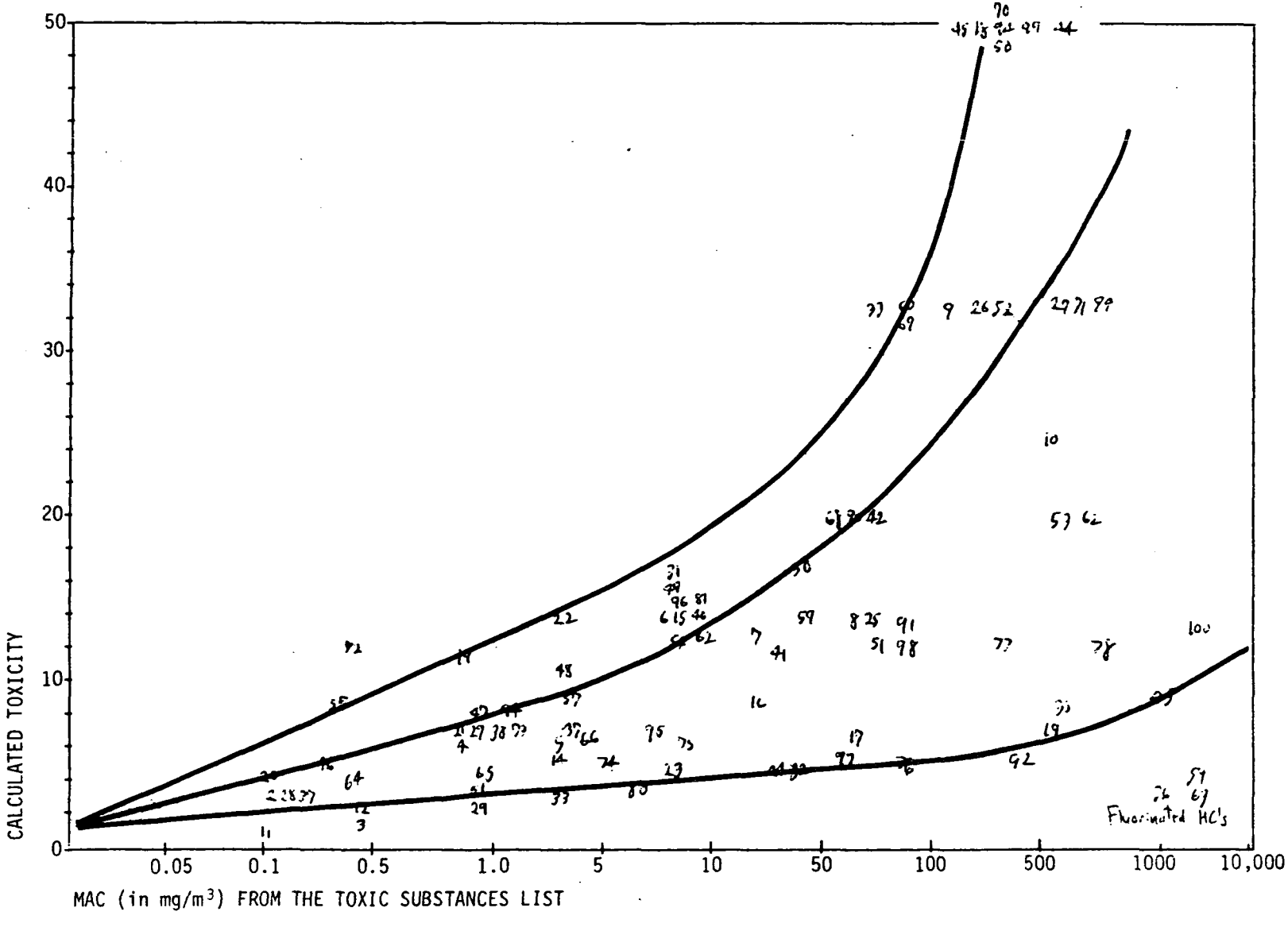


FIGURE II-6

SECOND CORRELATION



Appendix III

Estimation of Diffusivities

APPENDIX III

ESTIMATION OF DIFFUSIVITIES

A. INTRODUCTION

A variety of methods have been proposed for the estimation of diffusivities. These have been reviewed by Reid and Sherwood.[1] The better methods depend on the estimation of molecular volumes or of Lennard-Jones parameters. Boiling points and specific volumes at the normal boiling point can be used in these estimations. Since boiling points may not be available, especially for organic compounds of higher molecular weights, alternatives appeared necessary. We have found that methods based on the molar refractivity are adequate for most practical purposes.

The molar refractivity depends on the refractive index, molecular weight, and density of the substance, properties which are relatively easy to measure. When it cannot or has not been determined experimentally, it can also be derived from the chemical formula by using tables of additive values for various atoms and bonds. Finally, the molar refractivity enters into the estimation as a cube root, and for compounds of high refractive index this is not a strong function of the index; hence, for compounds of very high molecular weight, only small errors are introduced by assuming a refractive index of 1.7.

B. DIFFUSIVITY IN WATER

The diffusivity in water solution may be estimated from the following empirical relationship:

$$D_{cw} = \frac{6 \times 10^{-10}\ T}{\mu_{soln}\ (R - 0.855)} \qquad \text{(III-1)}$$

where T is the temperature in °K

μ_{soln} is the viscosity of the solution, in poises

R is the molar refractivity of the solute to the $1/3$ power

$$= \left(\frac{n^2-1}{n^2+2}\ \frac{M}{\rho}\right)^{1/3}$$

n is the refractive index

M is the molecule weight

ρ is the density

---

[1] Reid, R.C. and T.K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill, New York, 1958.

The data on which the relationship is based is given in Table III-1. For very dilute solutions soln may be replaced by the viscosity of water.

A sample of substances not included in the development of the empirical equation is given in Table III-2. For these substances the refractivity was computed as follows: for low molecular weight R was computed by adding the element refractivities; for high molecular weights it was computed by assuming an index of refraction of 1.7. The correspondence is generally good, considering the range of extrapolation involved.

C. DIFFUSIVITY IN AIR

The best method of estimating the diffusivity of gases and vapors in air is based on the relation presented by Hirschfelder:[2]

$$D_{ca} = 0.0002628 \sqrt{\frac{T^3(M_1 + M_2)/2M_1M_2}{P\sigma_{12}^1 \quad \Omega^{(1,1)}}} \qquad \text{(III-2)}$$

where T is the absolute temperature, °K

M_1 is the molecular weight of the gas or vapor

M_2 is the molecular weight of air

P is the pressure in atmospheres

σ_{12} is the arithmetic average of the Lennard-Jones distance parameter for air and gas or vapor

$\Omega^{(1,1)}$ is a function of $T^* = \frac{kT}{\sqrt{\varepsilon_1 \varepsilon_2}}$

ε_1 is the Lennard-Jones energy parameter for the gas or vapor

ε_2 is the Lennard-Jones energy parameter for air.

Although this expression is quite accurate, Lennard-Jones parameters are not readily available; therefore, the equation cannot be used directly. The expression is, nonetheless, very useful since σ_1 and ε_1 can be estimated by a number of methods. Our approach has been to rely on the observations that:

- $\Omega^{(1,1)}$ can be approximated by a reasonable function

[2] Hirschfelder, J.O., C.F. Curtis and R.B. Bird, *Molecular Theory of Gases and Liquids*, John Wiley and Sons, New York, 1954.

TABLE III-1

DIFFUSION PARAMETER AND REFRACTIVE RADIUS OF SELECTED SUBSTANCES

	$\frac{T}{D\mu_w} \times 10^7$	R
Acetamide	278	2.36
Acetic Acid	257	2.35
Allyl Alcohol	281	2.57
Bromine	256	2.63
n-Butyl Alcohol	328	2.81
Carbon Dioxide	161	1.89
Chlorine	165	2.26
Deuterium Oxide	107	1.55
Ethanol	253	2.35
Glycerol	344	2.74
Hydrogen	99	1.25
Methanol	197	2.02
Nitrogen	152	1.64
Nitrous Oxide	169	1.98
Oxygen	128	1.59
Propanol	290	2.60
Tartaric Acid	414	2.98
Urea	233	2.36

TABLE III-2

COMPARISON OF CALCULATED AND EXPERIMENTAL DIFFUSIVITIES IN WATER

Substance	R	T	$D \times 10^5 (cm^2/sec)$ Calc.	Exp.
Ammonia	1.79[a]	293.2	1.87	1.76
1,2-Propanediol	2.63	288.2	0.85	0.76
Resorcinol	3.01	293.2	0.81	0.80
Phenol	3.02	293.2	0.81	0.84
Pyrogallol	3.03	293.2	0.80	0.70
Hydroquinone	3.07	293.2	0.79	0.77
Pentaerythritol	3.15	293.2	0.76	0.69
Nicotene	3.66	283.2	0.46	0.49
Lactalbumen	20.80	293.2	0.088	0.106
Lactoglobulin	27.45	293.2	0.066	0.073
Serum Albumen	33.11	293.2	0.054	0.061
Serum Globulin	44.33	293.2	0.043	0.040
Urease	62.84	293.2	0.028	0.035

(a) from average polarizability, α; $R = (\frac{4}{3}\pi\alpha N)^{1/3}$

- $\Omega^{(1,1)}$ is a slowly varying function of T* so even a crude approximation to ε_1 will give useful values[3]

- both σ_1 and ε_1 are correlated with the molar refractivity radius R, as shown in Figures III-1a and III-1b. Note that substances with deviations on the high side of Figure III-1a have deviations on the low side in Figure III-1b (and vice versa), so the errors are partly compensating.

After appropriate substitutions we find

$$D_{ca} \approx 0.00289 \frac{T^{1.5}}{P} \frac{\sqrt{\frac{1}{M_1} + \frac{1}{29}}}{(R+2.75)^2 \cdot \emptyset} \qquad \text{(III-3)}$$

with $\emptyset = 0.81 - 0.066 \ln(y) + 0.62(y)^{-0.88}$

$$y = \frac{T}{122 \sqrt{R - .75}} \qquad \text{(III-4)}$$

The diffusivities for a number of gases and vapors in air are given in Table III-3.

Since the relations between R and the Lennard-Jones parameters were not derived from the diffusivities, the errors shown in Table III-3 are representative of estimation errors.

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[3] A 100% error in ε_1 will affect $\Omega^{(1,1)}$ and hence D_{12} by about 20%.

FIGURE III-1a

LENNARD - JONES PARAMETER σ (Å)

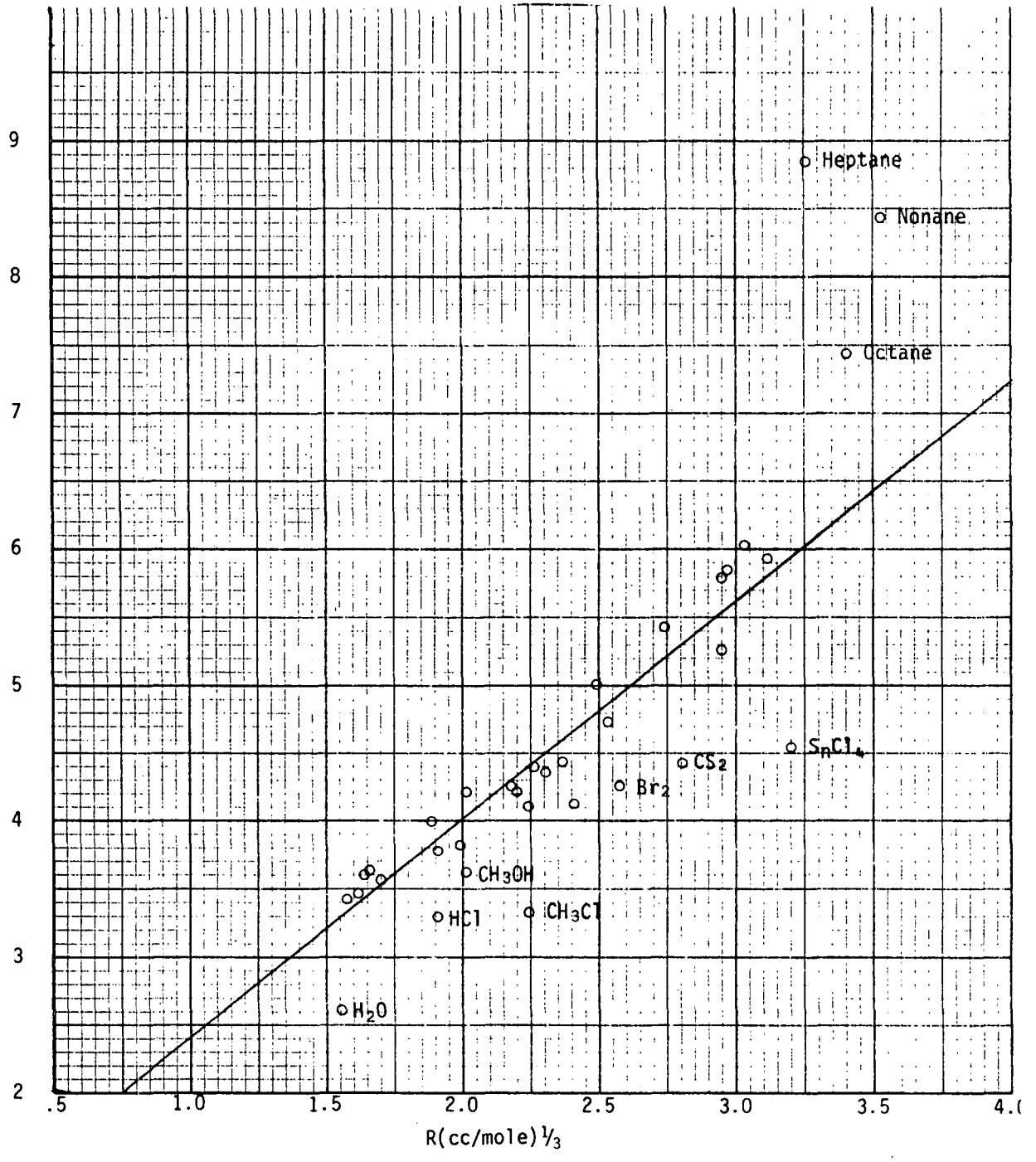

FIGURE III-1b

LENNARD - JONES PARAMETER ε/k (°K)

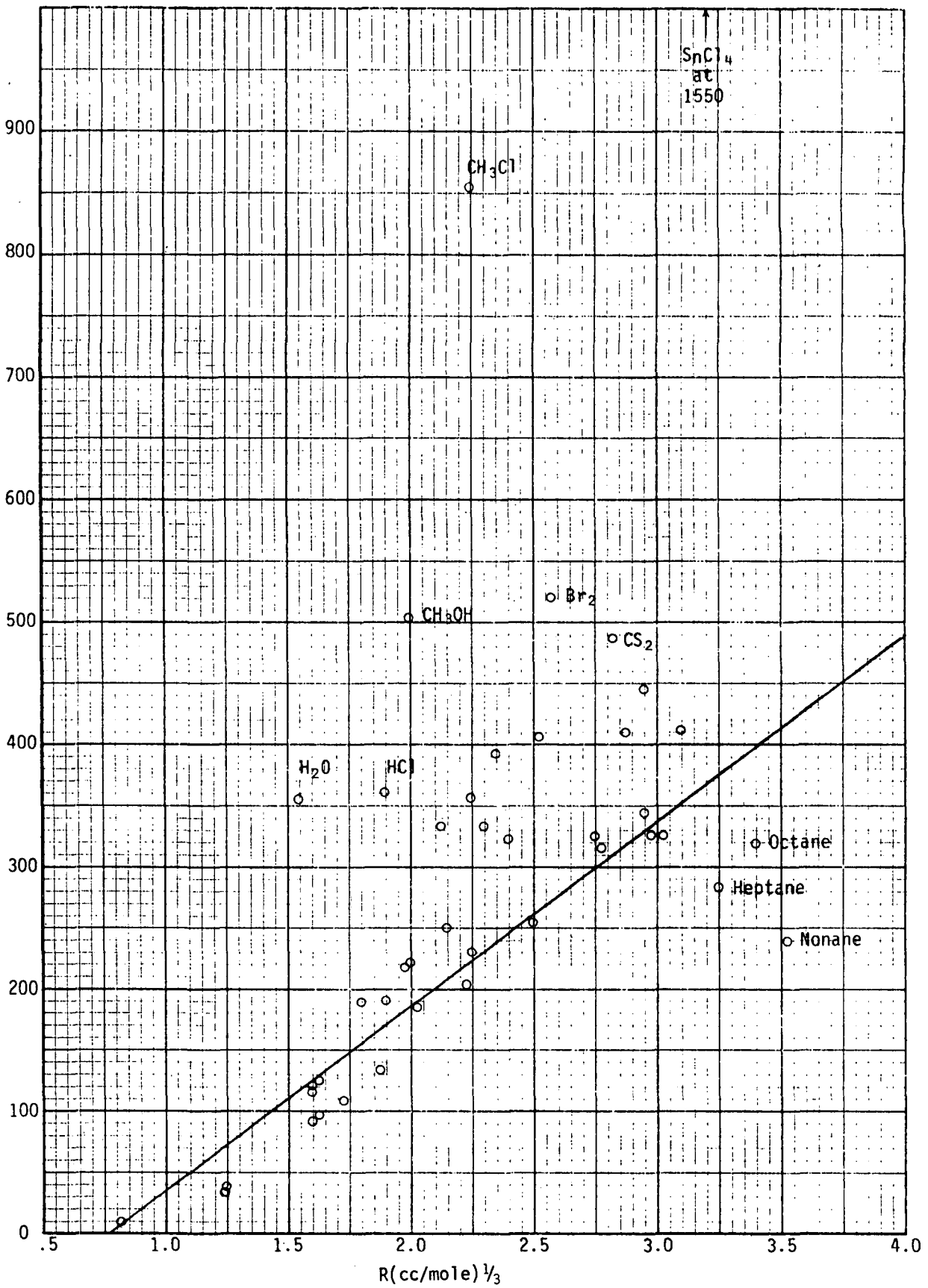

TABLE III-3

CALCULATED AND OBSERVED DIFFUSIVITIES IN AIR

Substance	M	R	T	D(cm²/sec) Calc.	Obs.
Acetic Acid	60	2.35	298	0.124	0.133
Ammonia	17	1.79	273	0.192	0.198
Ammonia	17	1.79	298	0.224	0.236
Aniline	93	3.13	298	0.082	0.073
Benzene	76	2.97	298	0.090	0.096
Bromine	160	2.57	293	0.096	0.091
Carbon Dioxide	44	1.89	273	0.142	0.136
Carbon Dioxide	44	1.89	293	0.152	0.151
Carbon Dioxide	44	1.89	298	0.166	0.164
Carbon Dioxide	44	1.89	400	0.265	0.273
Carbon Dioxide	44	1.89	600	0.538	0.555
Carbon Dioxide	44	1.89	800	0.882	0.915
Carbon Dioxide	44	1.89	1000	1.289	1.32
Carbon Dioxide	44	1.89	1300	2.007	1.97
Carbon Dioxide	44	1.89	1500	2.552	2.45
Carbon Disulphide	76	2.81	273	0.082	0.088
Chlorine	76	2.26	273	0.106	0.124
Diethylamine	73	2.89	293	0.093	0.105
Diphenyl	154	3.74	491	0.152	0.160
Ethanol	46	2.35	298	0.130	0.132
Ethyl Acetate	88	2.80	273	0.081	0.071
Ethyl Butyrate	116	3.16	273	0.067	0.057
Ethyl Ether	74	2.82	293	0.094	0.090
Helium	4	0.81	273	0.757	0.641[b]
Hydrogen	2	1.25	273	0.655	0.674[a]
Hydrogen	2	1.25	293	0.741	0.760[a]
Methanol	32	2.02	298	0.166	0.162
Naphthalene	128	3.34	298	0.073	0.061
Nitrobenzen	123	3.20	298	0.077	0.089
n-Octane	170	3.40	298	0.070	0.060
Oxygen	32	1.59	273	0.182	0.175
Oxygen	32	1.59	298	0.213	0.206
Pentane	88	2.99	298	0.087	0.070
Propanol	60	2.60	298	0.109	0.100
Propyl Acetate	102	3.00	315	0.095	0.092
Sulphur Dioxide	64	2.17	273	0.114	0.122
Toluene	92	3.15	298	0.082	0.084
Valeric Acid	102	2.99	298	0.086	0.070
Water	18	1.56	298	0.253	0.260
Water	18	1.56	373	0.359	0.353
Water	18	1.56	573	0.742	0.849
Water	18	1.56	773	1.260	1.556
Water	18	1.56	923	1.701	2.190
Water	18	1.56	1073	2.192	2.626
Water	18	1.56	1273	2.920	3.250
Water	18	1.56	1372	3.314	3.940
Water	18	1.56	1463	3.684	4.480
Water	18	1.56	1493	3.811	4.490

a) in nitrogen

b) in argon

Appendix IV

Sample Compound Data

Chemical: Benzene (C_6H_6)

Emission Data:

Production Rate	3810×10^6	kg/yr.
Natural Production		kg/yr.

Uses	% of Prod.	% Emission	Emission Rate kg/yr.
I. Low Emission			
• Production & Intermediate	100%	3%	114.3×10^6
•		3%	
•		3%	
•		3%	
II. Intermediate Emission			
•		30%	
•		30%	
•		30%	
•		30%	
III. High Emission			
• Spills		100%	10×10^6
• Vehicle Exhaust		100%	454.5×10^6
•		100%	
•		100%	
IV. Natural Sources		100%	
Total			578.8×10^6

Distribution of Emissions

To Air	520×10^6	kg/yr
To Air Particulates	48.8×10^6	kg/yr
To Lakes	8×10^6	kg/yr
To Streams	2×10^6	kg/yr
To Ground		kg/yr

Chemical: Bis (2-chloroisopropyl) ether $(Cl\text{-}CH_2\text{-}\underset{\underset{CH_3}{|}}{C}H)_2O$

Emission Data:

Production Rate as byproduct 11×10^6 kg/yr.
Natural Production kg/yr.

Uses	% of Prod.	% Emission	Emission Rate kg/yr.
I. Low Emission			
• Production	100%	3%	3×10^5
•		3%	
•		3%	
•		3%	
II. Intermediate Emission			
•		30%	
•		30%	
•		30%	
•		30%	
III. High Emission			
•		100%	
•		100%	
•		100%	
•		100%	
IV. Natural Sources		100%	
Total			3×10^5

Distribution of Emissions

To Air	0.1×10^5	kg/yr
To Air Particulates		kg/yr
To Lakes	1.5×10^5	kg/yr
To Streams	1.4×10^5	kg/yr
To Ground		kg/yr

Chemical: Chlorodifluoromethane ($CHClF_2$)

Emission Data:

Production Rate	40×10^6	kg/yr.
Natural Production		kg/yr.

Uses	% of Prod.	% Emission	Emission Rate kg/yr.
I. Low Emission			
• Production	100%	3%	1.2×10^6
•		3%	
•		3%	
•		3%	
II. Intermediate Emission			
• Refrigerant	100%	30%	12.0×10^6
•		30%	
•		30%	
•		30%	
III. High Emission			
•		100%	
•		100%	
•		100%	
•		100%	
IV. Natural Sources		100%	
Total			13.2×10^6

Distribution of Emissions

To Air	13.2×10^6	kg/yr
To Air Particulates		kg/yr
To Lakes		kg/yr
To Streams		kg/yr
To Ground		kg/yr

Chemical: Methyl Chloroform (CH_3CCl_3)

Emission Data:

Production Rate	245×10^6	kg/yr.
Natural Production		kg/yr.

Uses	% of Prod.	% Emission	Emission Rate kg/yr.
I. Low Emission			
• Production	100%	3%	7.3×10^6
• Vinylidene Chloride	9%	3%	0.7×10^6
•		3%	
•		3%	
II. Intermediate Emission			
• Exports	13%	30%	9.5×10^6
• Miscellaneous	11%	30%	8.0×10^6
•		30%	
•		30%	
III. High Emission			
• Solvent	67%	100%	164×10^6
•		100%	
•		100%	
•		100%	
IV. Natural Sources		100%	
Total			189.5×10^6

Distribution of Emissions

To Air	185×10^6	kg/yr
To Air Particulates	1×10^6	kg/yr
To Lakes	1×10^6	kg/yr
To Streams	0.5×10^6	kg/yr
To Ground	2×10^6	kg/yr

Chemical: Trichlorofluoromethane (CCl_3F)

Emission Data:

Production Rate	140×10^6	kg/yr.
Natural Production		kg/yr.

Uses	% of Prod.	% Emission	Emission Rate kg/yr.
I. Low Emission			
• Production	100%	3%	4.1×10^6
•		3%	
•		3%	
•		3%	
II. Intermediate Emission			
• Refrigerant	3%	30%	1.3×10^6
• Foaming Agent	15%	30%	6.3×10^6
•		30%	
•		30%	
III. High Emission			
• Aerosol Propellant	82%	100%	114.8×10^6
•		100%	
•		100%	
•		100%	
IV. Natural Sources		100%	
Total			126.5×10^6

Distribution of Emissions

To Air	99.8×10^6	kg/yr
To Air Particulates	11.1×10^6	kg/yr
To Lakes	5×10^6	kg/yr
To Streams	7.6×10^6	kg/yr
To Ground	3×10^6	kg/yr

TABLE IVb. DATA SHEET NO. 2

Chemical: Benzene (C_6H_6)

Basic Data:

Molecular Weight	78	
Molar Refractivity	26.2	
Vapor Pressure*	0.1	atm
Water Solubility*	0.0018	gm/gm
Octanol/Water Partition Coeff.*	135	

* at 20°C

Reaction Constants

Compartment Type	Reactivity: Extreme	High	Moderate	Persistent	Inert	Half Life	Reaction Rate
Air						50	0.0138
Particulate						50	0.0138
Air Moisture			✓			10	0.069
Water			✓			10	0.069
Adsorbed to Soil		✓				1	0.69

TABLE IVb. DATA SHEET NO. 2

Chemical: Bis (2-Chloroisopropyl) ether $(Cl\ C_3H_6)_2\ O$

Basic Data:

Molecular Weight	171	
Molar Refractivity	41.3	
Vapor Pressure*	0.0010	atm
Water Solubility*	0.0017	gm/gm
Octanol/Water Partition Coeff.*	5.9	

* at 20°C

Reaction Constants

Compartment Type	Reactivity: Extreme	High	Moderate	Persistent	Inert	Half Life	Reaction Rate
Air				✓		100	0.0069
Particulate				✓		100	0.0069
Air Moisture			✓			10	0.069
Water			✓			10	0.069
Adsorbed to Soil		✓				1	0.69

TABLE IVb. DATA SHEET NO. 2

Chemical: Chlorodifluoromethane ($CHCl\ F_2$)

Basic Data:

Molecular Weight	86.5	
Molar Refractivity	12.5	
Vapor Pressure*	9.5	atm
Water Solubility*	0.003	gm/gm
Octanol/Water Partition Coeff.*	12	

* at 20°C

Reaction Constants

Compartment Type	Reactivity: Extreme	High	Moderate	Persistent	Inert	Half Life	Reaction Rate
Air						20	0.03
Particulate						20	0.03
Air Moisture						20	0.03
Water						137	0.005
Adsorbed to Soil				✓		1000	0.001

TABLE IVb. DATA SHEET NO. 2

Chemical: Methyl Chloroform ($CH_3C\ Cl_3$)

Basic Data:

Molecular Weight	133	
Molar Refractivity	26.3	
Vapor Pressure*	0.13	atm
Water Solubility*	0.0044	gm/gm
Octanol/Water Partition Coeff.*	310	

* at 20°C

Reaction Constants

Compartment Type	Reactivity Extreme	High	Moderate	Persistent	Inert	Half Life	Reaction Rate
Air			✓			10	0.069
Particulate			✓			10	0.069
Air Moisture			✓			10	0.069
Water				✓		100	0.0069
Adsorbed to Soil				✓		100	0.0069

TABLE IVb. DATA SHEET NO. 2

Chemical: Trichlorofluoromethane (CCl_3F)

Basic Data:

Molecular Weight	137	
Molar Refractivity	21.9	
Vapor Pressure*	1	atm
Water Solubility*	0.0011	gm/gm
Octanol/Water Partition Coeff.*	340	

* at 20°C

Reaction Constants

Compartment Type	Reactivity: Extreme	High	Moderate	Persistent	Inert	Half Life	Reaction Rate
Air						20	0.03
Particulate						20	0.03
Air Moisture						20	0.03
Water						137	0.005
Adsorbed to Soil				✓		1000	0.001

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

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16. ABSTRACT

A number of alternatives for pre-screening chemicals for their potential to inflict environmental hazards were considered. A system design concept which takes into account both the toxicity of the chemical and the eventual levels which it can be expected to reach in the environment was selected for further analysis. Although neither toxicity nor eventual levels can be predicted with great accuracy, the accuracy attainable by simple methods appeared adequate for selecting and prioritizing chemicals for additional investigation. A specific design which relies on data which is usually available was developed to the point of testing the feasibility of collecting the necessary data and performing the required computations on five chemicals.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

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