PRESCREENING FOR ENVIRONMENTAL HAZARDS-A SYSTEM FOR SELECTING AND PRIORITIZING CHEMICALS

Final Phase II Report to

U.S. ENVIRONMENTAL PROTECTION AGENCY
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ASSESSMENT DIVISION
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PRESCREENING FOR ENVIRONMENTAL HAZARDS--
A SYSTEM FOR SELECTING AND PRIORITIZING CHEMICALS

by

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I.   SUMMARY

The overall objective of this program is the development for the
Environmental Protection Agency of a system 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 commer-
cial production, the recommended scheme could also be used for evaluating
the potential hazard of chemicals already in production.

The work reported here was conducted in two closely coordinated
but distinct phases. The Phase I program summarized here has been
previously documented in a final report to USEPA. Phase II
extends the conceptual system design conducted in Phase I to produce
an operational interactive computer system for estimating the distribu-
tion of a chemical in the environment.

Phase I

A number of alternatives have been explored for ranking chemicals
so that subsequent experimental research efforts may be properly focused.
The recommended method has the potential of fulfilling identified needs.
Basically, the method consists of selecting chemicals for further atten-
tion 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 method for estimating future environmental levels 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
future levels, and that overestimation is kept within reasonable bounds.
A test using available information on tolerable air concentrations indi-
cates 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.

Phase II

The basic steady-state model formulation accomplished in Phase I has been extended so that concentrations at any future time can be estimated, given current levels and knowledge of future chemical emissions. The model has been implemented as an interactive program on a commercial time-sharing service and complete user documentation, including sample cases, has been prepared.

It is recommended that the system, though operational, should first be used by the Office of Pesticides and Toxic Substances on a trial basis before actually trying to rank chemicals on a routine basis.

Additional research is needed on 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 further investigation.

II.   INTRODUCTION

A.   Purpose and Scope

The overall goal of this project is to provide the Environmental Protection Agency (EPA) with an <u>objective</u> system(s) for selecting and ranking chemicals, chemical classes and use classes for prescreening as to their environmental hazard. The study is to include an analysis and evaluation of existing systems, an evaluation and testing of the proposed system(s), and the implementation of the proposed system within the Office of Toxic Substances. The system may consist of a procedure, scheme, or mathematical model.

The Environmental Protection Agency is concerned with chemicals · in the environment which have adverse effects upon man and his living and non-living surroundings. It is the goal of the EPA to be able to predict and identify potential chemical hazards before these chemicals become widely dispersed and uncontrollable (typical examples of such chemicals are mercury and polychlorinated biphenyls). However, before attempting to initiate a testing procedure for the evaluation of hazard, it is first necessary to identify and select on the basis of minimal information those chemicals, chemical classes and use classes that are most likely to pose a hazard. It is the goal of this project to develop, implement and install an efficient system(s) to accomplish the afore-mentioned identification and ranking process.

B.   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, syner-gism, 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 when we acknowledge that the eventual distribution of substances in the environment is not easy to predict; indeed, decades may pass before we are able to estimate such distributions with sufficient accuracy so as 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 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 environment.

The 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 Institute for Occupational Safety and Health "Registry of Toxic Effects of Chemical Substances" (formerly called "The Toxic Substances List") 1978 Edition, for example, includes nearly 34,000 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 assist in determining whether or not the probable risks are "unreasonable."

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 areas, such a methodology 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 carcinogenic, teratogenic, mutagenic, chronically

toxic, etc., to humans; phytotoxic; persistent; bioac-
cumulative; synergistic, etc.).

(3) The data and resource (e.g., personnel) requirements
must be consistent with the level of confidence desired
for the screen. A highly accurate screen may be expected
to generate very significant input demands.

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 environ-
ment. 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 potentially 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 use-
fully be focused on the question of carcinogenicity.

A reasonable and defensible chemical screening system is not a
substitute for experimental and environmental monitoring data. A
screening system is nothing more than a systematic mechanism for review-
ing 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.

C.   The Data Problem

The primary rationale for an early warning or prescreening 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

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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.[*] 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.

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

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[*] 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.

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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.

D.   Project Design

1.   Phase I

The project has been conducted in two distinct phases:

● Phase I   -- System conceptualization, analysis, and
              design

● Phase II -- System development, testing, and
              implementation

Phase I was completed in April 1977 and documented in the report "Pre-screening for Environmental Hazards--A System for Selecting and Prioritizing Chemicals." EPA Office of Toxic Substances, EPA-560/1-77-002.* That report documents the conceptual development of the proposed prescreening system. Phase I encompassed the following seven 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.

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*Available from National Technical Information Service, Springfield, VA 22161 as PB 267 093.

- 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.* 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 was presented for testing the applicability and reliability of the basic system, and for evaluating the potential benefits of the more complex variations.

2.   Phase II

Phase II encompassed the following five tasks:

- Task 8 - Model Refinement and Extension - The principal effort undertaken was to extend the multiple compartment environmental model so that levels of pollution could be estimated at any

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*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.

future time (given current levels), whereas the Phase I model was limited to eventual (steady-state) concentrations under the assumption that "eventual" pollutant emission rates would be known.

- Task 9 - System Specification - An interactive (conversational) computer program specification was developed which defined the system's operational features, capabilities, inputs, and outputs.

- Task 10 - System Development - The multiple compartment environmental model was completely reprogrammed in the APL computer language.

- Task 11 - System Implementation - The model was implemented as an interactive program on a time-shared computer system. However, very considerable difficulty was experienced in locating adequately supported computer facilities. The program was transferred from National Institutes of Health facilities in Bethesda, Maryland, to EPA's National Computer Center at Research Triangle Park, North Carolina, and finally to a commercial time-sharing service (Scientific Time Sharing Corporation of Bethesda, Maryland) which has in the past provided similar services directly to EPA offices.

- Task 12 - System User Documentation - Documentation was prepared to enable EPA personnel to properly use the system.

E.   Status of System

The multiple-compartment environmental model described in this report is currently accessible via a commercial time-sharing service. The model yields temporal estimates of chemical concentrations by compartment, given the necessary physical/chemical properties of the chemical and initial concentration values. Knowledge of computer programming is not necessary to use the model. Access to the model may be gained by contacting the U.S. Environmental Protection Agency, Office of Pesticides and Toxic Substances, Assessment Division (TS-792), Washington, D.C.

The current implementation of the model is structured to process one chemical at a time--essentially it is intended to operate as a research tool. The system is not now designed to process multiple chemicals in a production mode as might be necessary in ranking a set of chemicals, although this feature may be easily added later if desirable. The computer system interacts with the user by requesting requisite input data (in specified physical units) and providing the user with various input, analytical, and reporting options.

F. Organization of this Report

Chapter III reviews the system design criteria developed in Phase I and acknowledges that paramount importance was placed upon devising a practicable system that would not generate onerous demands for input data. The twin concepts concerning

- Levels of concern versus
- Environmental levels

also developed in Phase I, are briefly summarized.

Chapter IV extends the steady-state compartmental model to the more realistic time-dependent case. The exact solution to the governing vector differential equation is presented. The chemical transport relationships among the 19 defined environmental compartments (media) are described. Next the inherent limitations of the model are summarized and suggestions given for extending the model to overcome its principal limitation, that of spatial invariance.

Chapter V describes how to use the interactive computer system that has been programmed for evaluating the environmental model. First the basic structure and data requirements of the model are summarized, including the principal assumptions and limitations inherent in its derivation. Next the prospective user is guided through all operational steps, from completing input data sheets, to executing the model, to interpreting output. Three sample problems are provided, along with actual system output, to help orient the user to the interactive nature of the system.

Appendix 1 contains the mathematical details for solving the general multiple compartment model of the environment. Two distinct analytical approaches are taken and then these are resolved. The mathematical basis for calculating via computer the matrix solution to the underlying differential equations is also presented.

Appendix 2 develops expressions for determining the rate of convective mass transfer of the chemical between phases. The presentation here is much more thorough than in the Phase I report. Several of the mass transfer expressions in the Phase I report are revised.

Appendix 3 presents methods for estimating the diffusivities of the pollutant in air and of the chemical in water. These properties are required in the model. The estimation methods in Appendix 3 are improved over those given in Appendix III of the Phase I report and somewhat easier to use.

Appendix 4 provides a brief discussion on estimation of emission rates.

Appendix 5 describes the computer program and provides a listing of the APL code.

III. OVERVIEW OF THE PRESCREENING SYSTEM

A.   System Design Criteria

In Phase I the following criteria were developed to guide the
design of a workable environmental hazard identification and prioritiza-
tion system; the criteria are presented roughly in descending order of
importance.

(1) Practicability. Recognizing that the intent of the system is
to select and rank chemicals, chemical classes and use classes for pre-
screening as to their environmental hazard, an unreasonably difficult
and resource-demanding process is not warranted. Prescreening, by im-
plication, has quite limited goals in terms of expected accuracy and
precision. As stated earlier, a reasonable and defensible chemical
prescreening system is not a substitute for experimental and environ-
mental monitoring data. The system, then, should recognize practical
limitations in terms of EPA personnel skill levels and numbers, opera-
tional cost, and response time. This issue is further discussed in the
next section.

(2) 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. More to the point, the
system should make minimal demands for data. In general, this criterion
is antithetical to the achievement of scientific credibility. For example,
if the viscosity of a material is a necessary property but is not likely
to be furnished by a manufacturer, then we may decide to circumvent the
need for an experimental measurement of viscosity by using some empirical
correlation.

(3) 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 reason-
able 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 should 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 should 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, (c) ecologically important species, and (d) presumably, then, the inanimate environment.

(4) Credibility. The system should possess demonstrable credibility in selecting and prioritizing chemical environmental hazards. The results should be statistically credible, i.e., at most a relatively 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 relatively small percentage of the chemicals ranked as highly hazardous should in fact prove to be benign.

(5) Consistency. The identification system(s) should 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.

(6) Tested Concepts. The system should utilize only proven techniques, methodologies, information sources, etc., and not attempt to incorporate hertofore 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) 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

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toxicity, inhalation toxicity, aquatic toxicity, bioaccumulation, etc. 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.

(8) Discrimination. The system must possess the ability to roughly 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.

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

(10) 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.

(11) Built-in Hierarchy. In recognition of the many potential information sources and voluminous data (not all of which are 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.

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

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(13) 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 de-
gradation of a chemical substance are unknown or very complicated, it
is unlikely that any simple identification and prioritization system
will be able to flag the potential hazards accurately.

(14) Synergism. The goal of the project is to design an objec-
tive 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 chemi-
cal substances. There is very little data on the importance of syner-
gism in the environment, and even if there were more, it would not be
easy to incorporate synergistic effects into an objective system design.
From the subjective regulatory viewpoint, the problem of synergism would
be even more difficult to deal with.

It has not been possible to satisfy all these criteria equally.
Greater success has been realized with respect to the first five
criteria than for the remainder.

B. Practicability

As noted above, paramount importance was assigned to designing
a practical and readily-operable system. For several reasons, this basic
requirement was restated as a need for inherent 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 identifi-
cation systems. Another is that to a simple or even simplistic system,
refinement and embellishments may be added as needed. Every additional

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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 and prescreening candidates.

C.   Basic Parallel System Structure

The system consists of two parallel branches, the results of which are eventually merged and used for ranking, as shown in Figure III-1. The general concept is to estimate, on the one hand, the levels of a chemical 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.

D.   Environmental Levels

The first branch of the system is shown in Figure III-2. It has as its purpose the computation of the levels of a chemical that will be attained in the environment at any time in the future, given current levels. 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 of prescreening. Closer estimation would require detailed information on the modes of emission of each product and on the distribution (geographical and temporal) of 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.

FIGURE III-1

SCHEMATIC DIAGRAM OF THE SYSTEM

Branch 1

ESTIMATION OF
FUTURE
ENVIRONMENTAL
LEVELS BY
COMPARTMENT
BASED ON DATA ON:
RELEASE
PERSISTENCE
PHYSICAL PROPERTIES
AND COMPARTMENT DATA

Branch 2

ESTIMATION OF
LEVELS OF
CONCERN BY
COMPARTMENT
BASED ON DATA ON:
CHEMICAL COMPOSITION
STRUCTURE
PHYSICAL PROPERTIES

RANKINGS
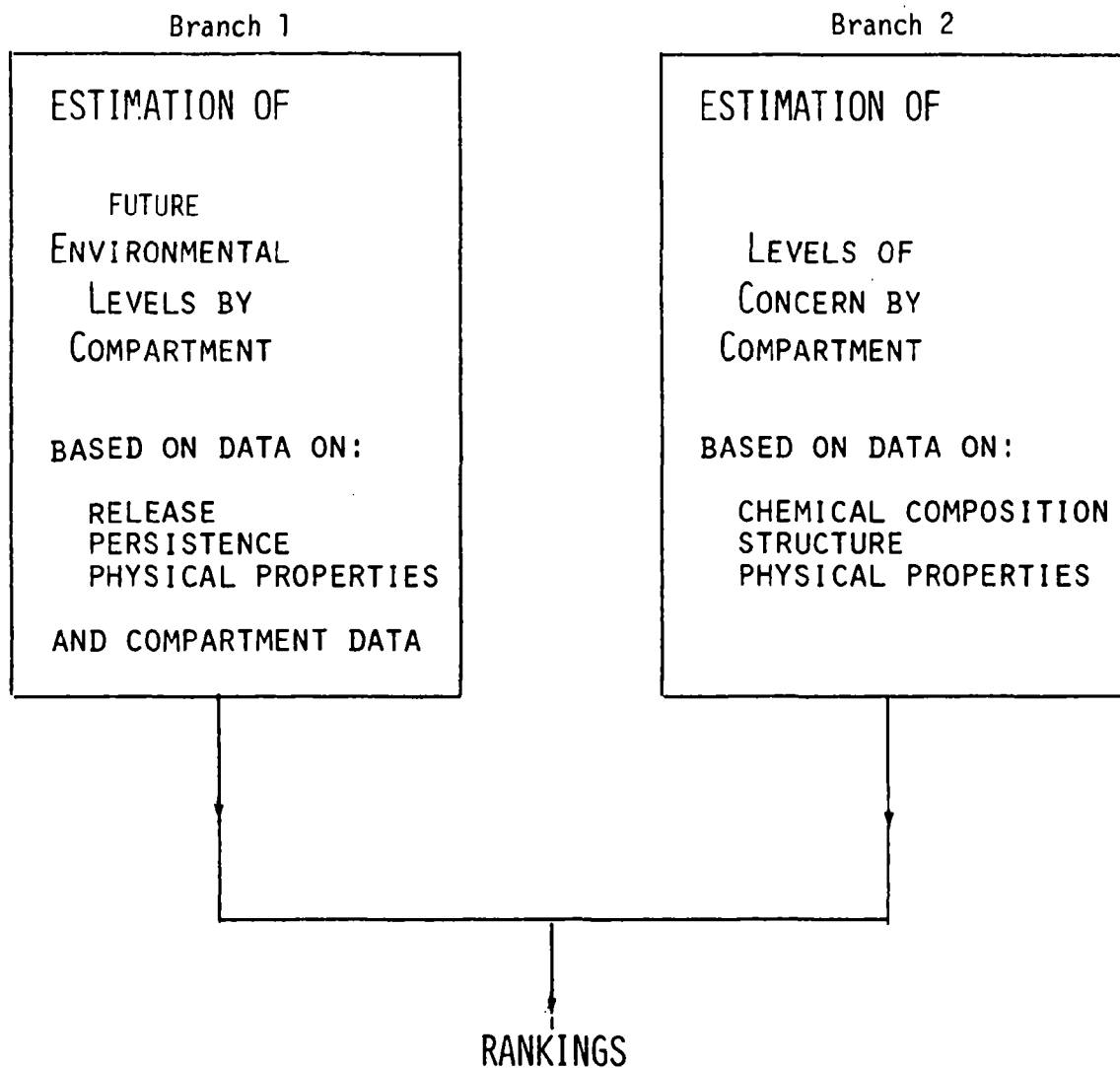
FIGURE III-2

SCHEMATIC DIAGRAM OF THE FIRST BRANCH OF THE SYSTEM
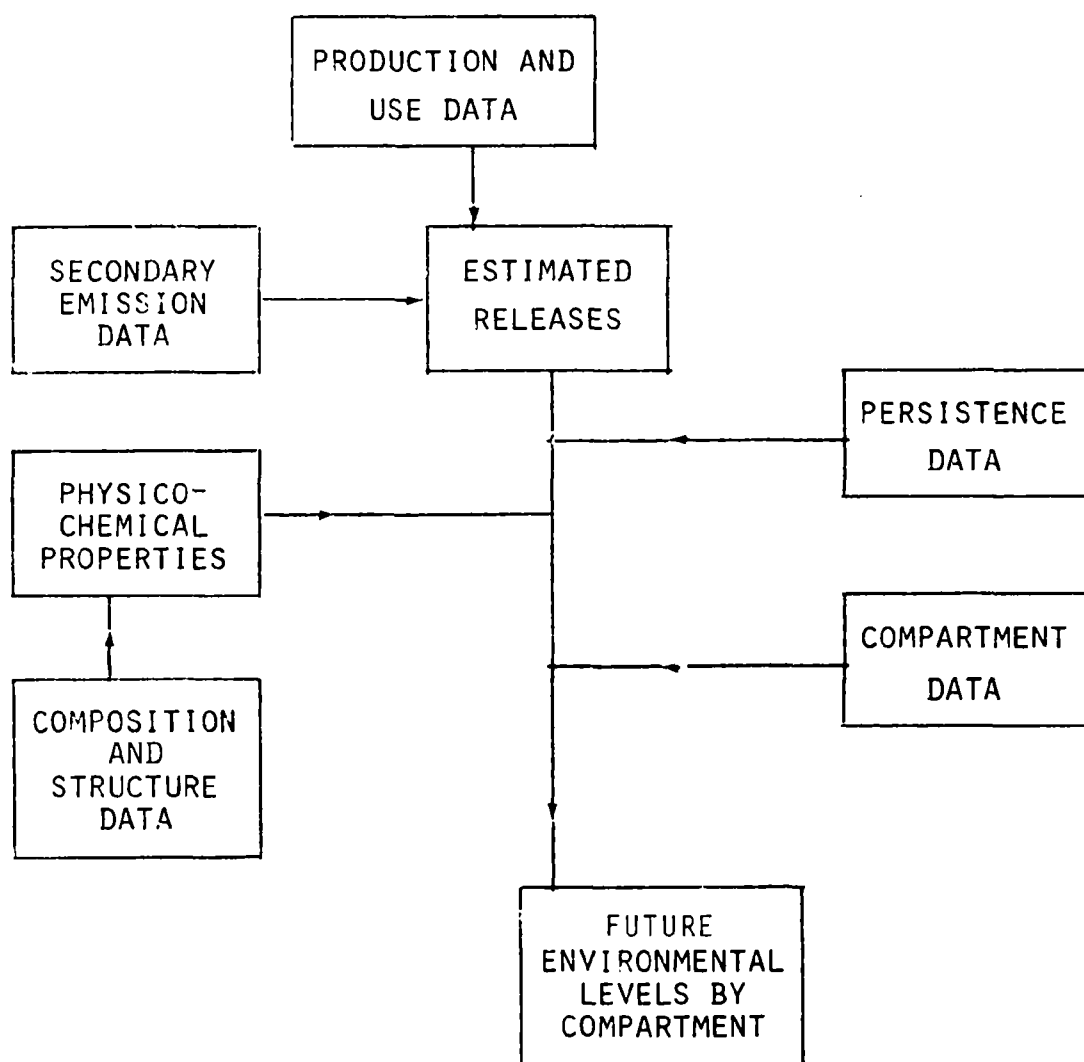
This branch of the system will include several types of data inputs:

- quantification over the time period of interest of the total industrial rate of production and allocation of this production to modes of use for various 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 final products in water and air; and

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

Based on these data and fixed data on regional water flows, the system will compute the chemical levels in various environmental compartments (e.g., air, surface water, soil, etc.) over time.

Further details regarding the multiple compartment model of the environment will be found in the next chapter.

E. Levels of Concern and Ranking

The second branch of the system is shown in Figure III-3. It has the aim of estimating the levels of the chemical 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, 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 consists of information on the presence or absence of a number of functional groups in the compound in question. Further details concerning the second branch of the prescreening system will be found in Chapter IV of the Phase I report.

Ranking of chemicals would then proceed according to the methodology described in Chapter V of the Phase I report. Five example test cases appear in Chapter VI of that report.

FIGURE III-3

SCHEMATIC DIAGRAM OF THE SECOND BRANCH OF THE SYSTEM
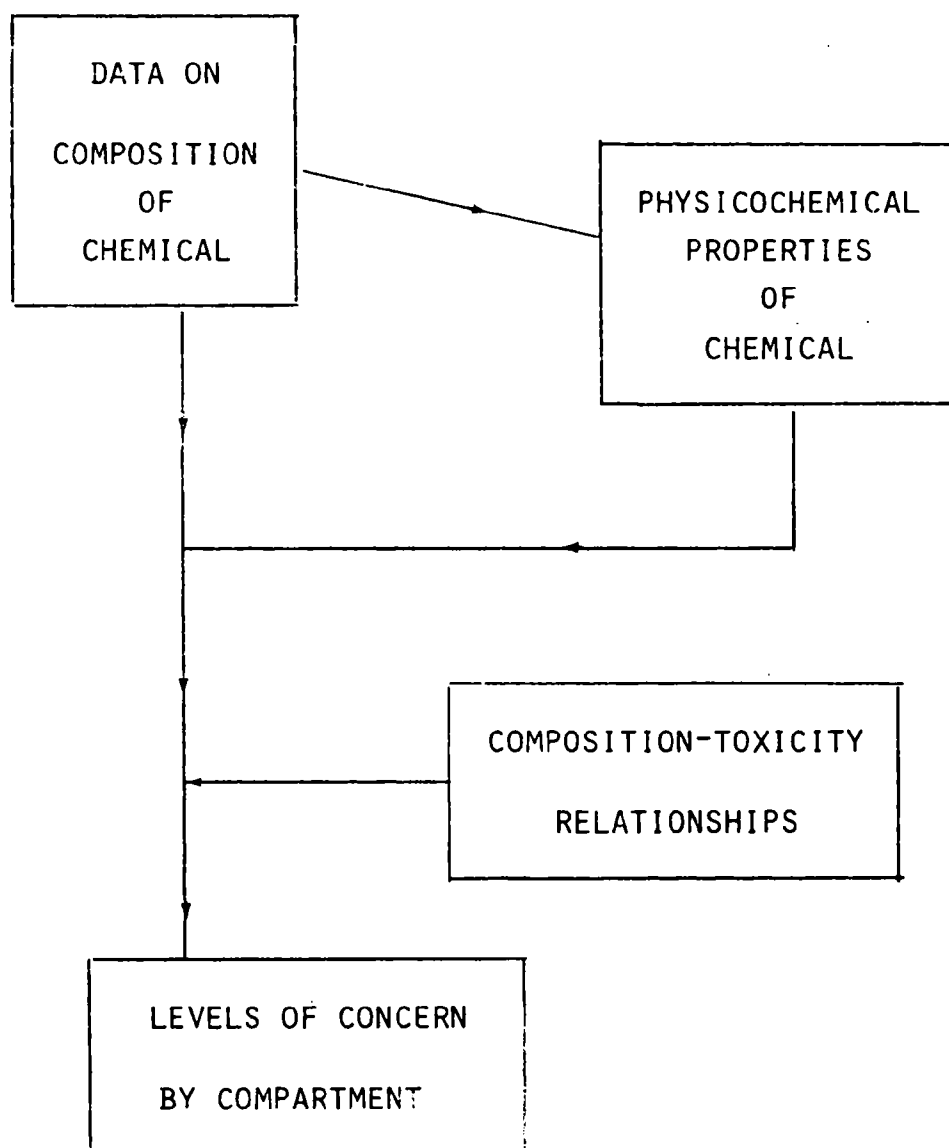
IV. ESTIMATION OF ENVIRONMENTAL LEVELS

A. Environmental Compartment Model

The Phase I report (Chapter III) documented the theoretical under-
pinnings of the proposed multiple compartment model of the environment.
Only the highlights of that work will be presented here, along with
clarification of certain aspects that were not entirely apparent in the
original model description. However, the interested reader is strongly
encouraged to also consult the Phase I report for further background
information.

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

A simple multiple compartment model of the environment is proposed,
as shown schematically in Figure IV-1. The distribution of a chemical
among the compartments of the environment is determined by the inter-
compartmental flows and compartment concentrations of the chemical.
The ocean is considered a residual compartment in which the chemical
is absorbed or decomposed so that flows back from the ocean can be
neglected. 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 recogni-
tion that most of the damage in this compartment is due to compounds
of low molecular weight; 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. Furthermore, the air compartment over the entire
United States is assumed to be finite and closed.

FIGURE IV-1

SCHEMATIC DIAGRAM OF INTERCOMPARTMENT FLOWS

OF EMITTED CHEMICAL

(man and biosphere omitted)
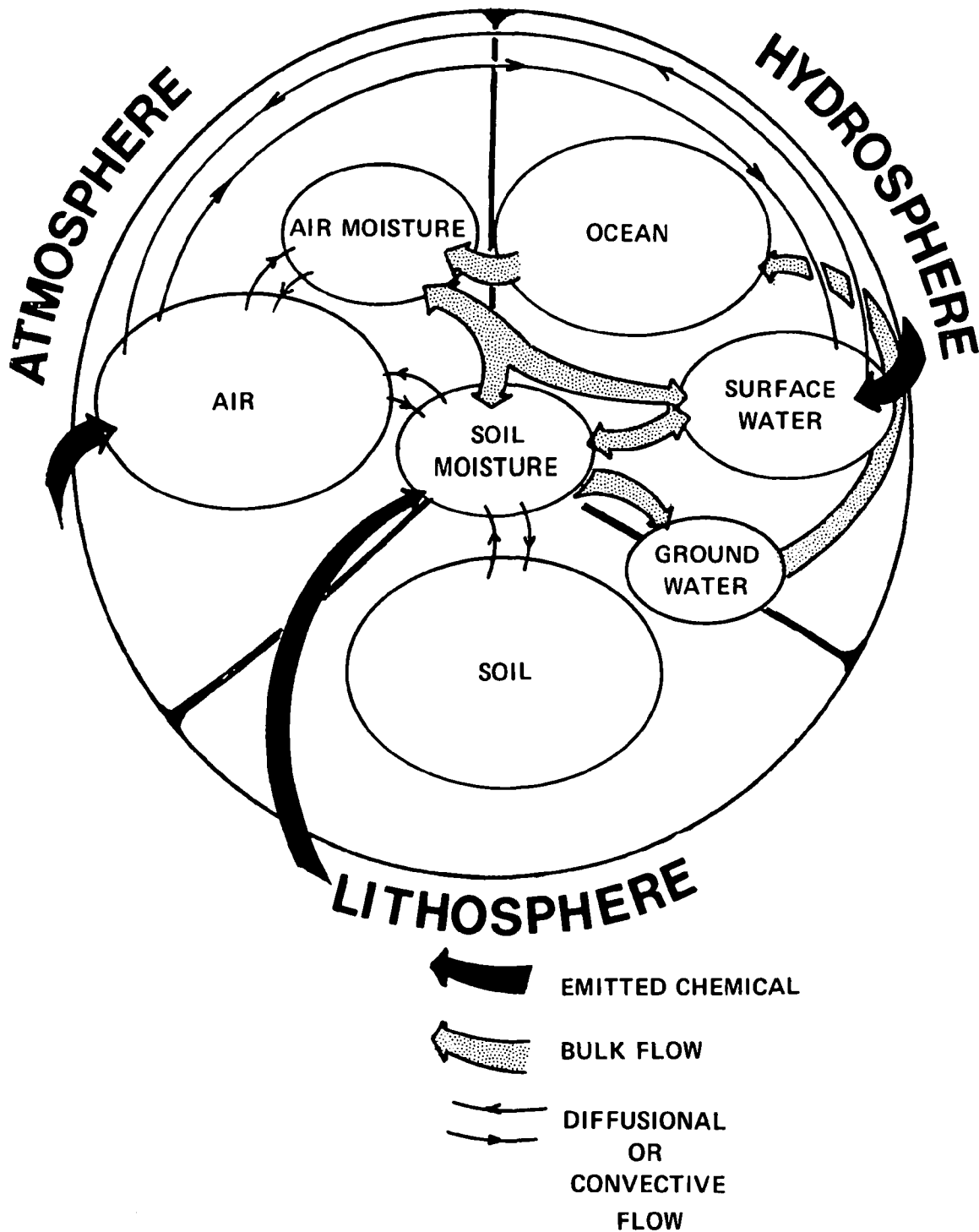
Compartments for animals and vegetable matter (biomass) are not shown in Figure IV-1. We propose to compute the concentration in these by applying the octanol/water partition coefficient[*] to the average fat content as a reasonable approximation.

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. The concentration of the chemical is assumed to be uniform everywhere within the compartment. The model does not recognize geographical variations in chemical concentration. In the case of transport between air and surface water or soil moisture, convective mass transfer processes are involved as well as bulk flows (through rainfall).

The total amount of chemical 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. The mass balance for compartment x recognizes:

(1) Bulk water flows
(2) Diffusion
(3) Convection
(4) Emissions (by industry, etc.)
(5) Reactions

Hence,

$$
W_x C_x(t + \Delta t) = W_x C_x(t) + \Delta t \left[\dot{P}_x(t) + \sum_{y \neq x} (\dot{F}_{y \to x} + r_{y \to x}) \, C_y(t) - K_x W_x C_x(t) \right.
$$

$$
\left. - C_x(t) \sum_{y \neq x} (\dot{F}_{x \to y} + r_{x \to y}) \right] \tag{1}
$$

---

[*] 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.

where

W_x = weight of compartment x, in kg,

C_x = concentration of chemical in compartment x, in kg/kg

$\dot{F}_{x \to y}$ = bulk flow rate of chemical solution from compartment x to compartment y, in kg/yr,

$r_{x \to y}$ = convective flow rate of chemical from compartment x to compartment y, in kg/yr/unit concentration,

$\dot{P}_x$ = chemical emission rate into compartment x, in kg/yr,

K_x = first order reaction constant for compartment x, in yr^{-1}

This difference equation can be converted to an ordinary differential equation by subtracting $W_x C_x(t)$ from both sides of the equation, dividing by Δt, and taking the limit as Δt approaches zero.

$$W_x \frac{d}{dt} C_x(t) = \dot{P}_x(t) + \sum_{y \neq x} (\dot{F}_{y \to x} + r_{y \to x}) \, C_y(t) - K_x W_x C_x(t)$$
$$- C_x(t) \sum_{y \neq x} (\dot{F}_{x \to y} + r_{x \to y}) \tag{2}$$

with initial conditions

$$C_x(t) = C_x(0) \text{ at } t = 0 \tag{3}$$

where for several compartments F and r may be zero or negligible. In equation (2), the first term on the right-hand side gives the emission rate into the compartment, the second term gives the flow rate into compartment x from all other compartments, the third term gives the rate of degradation of the chemical in compartment x, and the final term gives all flow rates out of compartment x into all other compartments.

As shown in Appendix 1, equations (2) and (3) may be conveniently rewritten in vector-matrix notation:

$$\frac{d\overline{C}}{dt} = \overline{M}\ \overline{C}(t) + \overline{p}(t) \tag{4}$$

with initial conditions

$$\overline{C}(t) = \overline{C}(0) \text{ at } t = 0 \tag{5}$$

where

$\overline{C}(t)$ is a column vector with elements $[C_x(t)]$

$\overline{p}(t)$ is a column vector with elements $[p_x(t)]$

$\overline{M}$ is a constant square matrix with elements $[m_{xy}]$ and

$$m_{xx} = -a_x; \quad m_{xy} = b_{yx} \quad x \neq y$$

and

$$b_{yx} = \rho_{yx}/W_x, \quad \rho_{yx} = \dot{F}_{y \to x} + r_{y \to x}, \tag{6}$$

$$a_x = K_x + W_x^{-1} \sum_{y \neq x} \rho_{xy}, \tag{7}$$

$$p_x(t) = \dot{P}_x(t)/W_x \tag{8}$$

In the notation used in writing equation (4), the new coefficients and terms have the following interpretations:

a_x = total concentration loss rate per unit concentration from compartment x, produced by chemical reactions (rate K_x), bulk flows to other compartments (rates $\dot{F}_{x \to y}/W_x$), and convective flows to other compartments (rates $r_{x \to y}/W_x$);

b_{yx} = concentration gain rate per unit concentration from compartment y to compartment x;

$p_x(t)$ = concentration gain rate from direct emissions into compartment x.

For the case of constant emission rates $\bar{p}$ over a time interval
T $[0 \le t \le T]$, the solution to the linear, first-order vector differen-
tial equation (4) is

$$\bar{C}(t) = e^{\bar{M}t}\bar{C}(0) + \left[\int_0^t e^{\bar{M}(t - \lambda)} d\lambda \right] \bar{p} \qquad 0 \le t \le T \qquad (9)$$

Suppose that the time interval t of interest can be decompcsed
into equal subintervals T so that all emission rates $\bar{p}(t)$ are constant
in each subinterval. If only the sequence of chemical concentrations
at times T, 2T, 3T, ... are of interest, then equation (9) can be
written as a recurrence formula

$$\bar{C}[(k + 1)T] = e^{\bar{M}T}\bar{C}(kT) + \bar{\Delta}\,\bar{p}(kT) \qquad k = 0, 1, 2, \ldots \qquad (10)$$

where

$$\bar{\Delta} = \int_0^T e^{\bar{M}(T - \lambda)} d\lambda \qquad (11)$$

Finally, if $\bar{p}(t)$ is constant over <u>all</u> time periods $t \ge 0$ and
T = 1 year, equation (10) becomes

$$\bar{C}(k + 1) = e^{\bar{M}}\bar{C}(k) + \bar{\Delta}\,\bar{p} \qquad k = 0, 1, 2, \ldots \qquad (12)$$

Equation (12) is particularly easy to evaluate because the matrix $e^{\bar{M}}$
and the vector $\bar{\Delta}\,\bar{p}$ are constant independent of time. The computer
methods for evaluating $e^{\bar{M}}$ and $\bar{\Delta}\,\bar{p}$ are presented in Appendix 1.

Equation (9) for incremental constant annual emission rates
(i.e., $\bar{p}(0)$, $\bar{p}(T)$, $\bar{p}(2T)$, ...) and equation (12) for constant $\bar{p}$ over
time have been programmed for computer evaluation. Finally, a third
option that has been programmed provides for a constant fractional
increase or decrease per year f_x in the chemical emission rate,
separately for each compartment. That is,

$$\bar{p}(k) = \bar{E}(k)\bar{p}(0) \qquad (13)$$

where $\bar{E}(k)$ is a diagonal matrix (e_{xy}) with

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$$e_{xx}(k) = (1 + f_x)^k; \quad e_{xy}(k) = 0 \quad x \neq y \tag{14}$$

Hence, equation (10) with T = 1 year becomes

$$\overline{C}(k + 1) = e^{\overline{M}}\overline{C}(k) + \overline{\Delta}\,\overline{E}(k)\,\overline{p}(0) \qquad k = 0, 1, 2, \ldots \tag{15}$$

In order to calculate the chemical concentrations in the various compartments at any time according to the preceding equations, the emission rate vector $\overline{p}$, coefficient matrix $\overline{M}$, and initial concentration vector $\overline{C}(0)$ must be evaluated or estimated. For compounds not previously manufactured and not existing in nature, $\overline{C}(0) = \overline{0}$. Mechanisms for estimating these data are discussed at length in Chapter III of the Phase I report. Certain of these estimation methods are explicated further in Appendix 2 of this report.

B.   Compartments

Thus far in the development of the multiple compartment environmental model, we have not defined the nature of and interrelationships among the compartments of interest. In principle, there is no restriction on the number of compartments that may be defined; however, the data requirements become quite substantial as the number of compartments increases.

In order to demonstrate the utility of the model, we have defined 19 environmental compartments, as shown in Table IV-1. That is, we assume that these 19 compartments represent an ideal abstraction of the environment of the entire contiguous United States. As noted above, each compartment is viewed as a completely mixed, flow reactor, with bulk and convective flows between compartments. Therefore, the concentration of the chemical is assumed to be uniform everywhere within the compartment. No geographical variations are permitted in any physical or chemical properties (including concentration) of the chemical or the environment within a compartment. Thus, for example, the model presumes that all lakes throughout the United States may be arithmetically combined (in terms of surface area, volume of water, flow, etc.) into a single lake compartment.

TABLE IV -1   U.S. COMPARTMENT DATA

Compartment	Mass $(10^{15}$ kg)	Effective Area $(10^{10}$ m^2)	Annual Flow $(10^{15}$ kg)
Air (1 Mile High)	16.2	-	-
Atmospheric Moisture	0.18	-	4.8*
Surface Water (Lakes)	18.8	14	0.19
(Streams)	0.05	2.5	1.86
Soil Moisture (0-1m)	0.6	769	3.1
(1-5m)	0.4	-	-
(5-10m)	0.2	-	-
(10-15m)	0.2	-	-
(15-30m)	0.2	-	-
(30-50m)	0.2	-	-
Ground Water (Shallow)	63.7	-	0.31
(Deep)	63.7	-	0.006
Ocean	50	-	-
Soil (0-1m)	15.2	-	-
(1-5m)	60.9	-	-
(5-10m)	76.1	-	-
(10-15m)	76.1	-	-
(15-30m)	228.5	-	-
(30-50m)	304.4	-	-

Note: Dash (-) denotes value not required.

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

Source: Phase I Report, page 36.

Table IV-2 gives the estimated annual bulk water flows between compartments containing water. These flows are based on Case 4 presented in Table III d and Figure 8d of the Phase I Report.

Table IV-3 identifies the basic type of first-order degradation reaction appropriate for each compartment and the nature of chemical flows between compartments. For example, R_w in the stream-stream cell indicates that the reaction rate or half-life of the chemical in water is a necessary model parameter (if no degradation in water occurs, then $R_w = 0$). The notation B in the soil moisture 10-15 meters - ground water (shallow) cell indicates that a bulk flow of chemical containing water occurs from the former to the latter compartment. The notation C-9 in the soil moisture 0-1 meter - air cell indicates that chemical mass transfer occurs from the former to the latter compartment and that transport equation (9) in Chapter III of the Phase I report governs. The notation E in the air - air moisture cell indicates that chemical transport between these two compartments is nearly instantaneous so that equilibrium conditions obtain at all times. Finally, a blank cell indicates zero flow.

C. Limitations of the Model

The principal limitation of the model is

(1) Failure to recognize spatial (geographic) variations in model parameters (e.g., chemical mass transfer rates) and chemical concentrations. This, of course, is a consequence of devising a lumped-parameter system. Again, this was an intentional limitation in order to balance data requirements and computational demands with the basic intent of prescreening. As discussed in the next section, this limitation may be readily relaxed.

Other limitations or key assumptions are:

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TABLE IV-2

BULK WATER FLOWS BETWEEN COMPARTMENTS

(in 10^{15}kg/yr)

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	.110	.000	.000	.000	.000	.000	.000	.000
5. SOIL MOISTURE 1-5M	.000	.050	.050	.010	.000	.090	.000	.000	.000	.020	.000	.000
6. SOIL MOISTURE 5-10M	.000	.020	.020	.000	.010	.000	.045	.000	.000	.020	.020	.000
7. SOIL MOISTURE 10-15M	.000	.010	.010	.000	.000	.005	.000	.012	.000	.010	.020	.000
8. SOIL MOISTURE 15-30M	.000	.005	.005	.000	.000	.000	.002	.000	.005	.000	.005	.000
9. SOIL MOISTURE 30-50M	.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

Source: Phase I Report, Page 41.

TABLE IV-3. CHEMICAL REACTIONS AND FLOWS BETWEEN COMPARTMENTS

Code

B = Bulk Flow
C = Convective flow (Number indicates governing transport equation in Phase I Report)

E = Equilibrium condition (Instantaneous flow)
R_a = Reaction in air
R_w = Reaction in water
R_s = Reaction in soil
Blank indicates zero

FROM \ TO	1 AIR	2 AIR MOISTURE	3 LAKES	4 STREAMS	5 SOIL MOISTURE 0-1M	6 SOIL MOISTURE 1-5M	7 SOIL MOISTURE 5-10M	8 SOIL MOISTURE 10-15M	9 SOIL MOISTURE 15-30M	10 SOIL MOISTURE 30-50M	11 GROUND WATER (SHALLOW)	12 GROUND WATER (DEEP)	13 OCEAN	14 SOIL 0-1M	15 SOIL 1-5M	16 SOIL 5-10M	17 SOIL 10-15M	18 SOIL 15-30M	19 SOIL 30-50M
1 AIR	R_a	E	C-7	C-8	C-10														
2 AIR MOISTURE	E	R_w	B	B	B														
3 LAKES	C-5	B	R_w	B	B	B	B	B	B	B	C								
4 STREAMS	C-6	B	B	R_w	B	B	B	B	B	B	B		B						
5 SOIL MOISTURE 0-1M	C-9	B	B	B	R_w	B								C-13					
6 SOIL MOISTURE 1-5M			B	B	B	R_w	B				B				C-13				
7 SOIL MOISTURE 5-10M			B	B		B	R_w	B			B	B				C-13			
8 SOIL MOISTURE 10-15M			B	B			B	R_w	B		B	C					C-13		
9 SOIL MOISTURE 15-30M			B	B				B	R_w	B		B						C-13	
10 SOIL MOISTURE 30-50M			B	B						R_w		B							C-13
11 GROUND WATER (SHALLOW)											R_w	B							
12 GROUND WATER (DEEP)												R_w	B						
13 OCEAN		B											R_w						
14 SOIL 0-1M					C-14									R_s					
15 SOIL 1-5M						C-14									R_s				
16 SOIL 5-10M							C-14									R_s			
17 SOIL 10-15M								C-14									R_s		
18 SOIL 15-30M									C-14									R_s	
19 SOIL 30-50M										C-14									R_s

(2)   The first limitation above arises from two assumptions:

        (a) Each environmental compartment behaves as a completely mixed, flow reactor, and

        (b) The concentration of the chemical is uniform everywhere within a given compartment.

(3)   The upper atmosphere (above one mile) is ignored.

(4)   The air compartment over the United States is finite and closed.

(5)   There is no compartment for biomass.

(6)   Prediction of chemical adsorption by soil is not well developed in the literature yet.

(7)   Knowledge of bulk water flows between compartments is imperfect.

(8)   No provision has been made to account for loss of water due to transpiration from plants.

(9)   The solute concentrations in the water and air phases at the interface are in equilibrium, such that Henry's law pertains. Generally, this implies that the solute concentrations in the bulk water and air phases are low, say, less than 0.02 mole fraction in water.

Finally, we note that at present it would be quite difficult to test the veracity of the model due to the paucity of environmental monitoring data across all compartments of interest.

D. Extensions of the Model

1. Spatial Limitation

The present mathematical formulation of the environment is commonly referred to as a lumped-parameter model, as distinct from a distributed-parameter model. The model now recognizes the spatial distribution of a chemical only to the extent that it occurs in the 19 defined environmental compartments. The model assumes that perfect mixing occurs in each compartment, so that the concentration of the chemical within that compartment is everywhere uniform. Clearly, it is not realistic to assume, as the model does, that the concentration of a chemical in, say, the air compartment is everywhere the same in the United States. This assumption of uniformity is reasonable if we seek only to estimate the relative distribution of the chemical among the various media.

There are two possible approaches to extending the model to deal with geographic variation. First, we could convert the lumped-parameter ordinary differential equations to distributed-parameter partial differential equations. However, the resulting set of partial differential equations would be most difficult and expensive to solve via computer. Second, and more practical, we can add a new geographic region dimension to the set of environmental compartments.

There are two practical cases to be faced:

Case 1. The objective may be to estimate the concentration of a chemical within a single geographic region (say, a given river basin) or

Case 2. The objective may be to estimate the concentration of the chemical throughout the United States. These two problems are very closely related but different.

2. First Case

For the selected region of interest, we will make the reasonable assumption that the concentration of the chemical is uniform within each of the 19 environmental compartments. (If this assumption were not valid, then it would be necessary to subdivide the given geographic region into a number of sub-regions for which the assumption would be true. This would be Case 2.) In the case of the single geographic region, the current model is immediately applicable with only modest programming changes. One technical hurdle, however, is finding some way to express chemical flows between the exogenous world and the 19 regional compartments. It would be necessary to estimate the size of each of the 19 compartments in the region as well as the annual water flows between compartments as we have already done when the region is defined to be the entire United States. No particular difficulty is foreseen in estimating these necessary environmental compartment data for a specified region using such sources as the U.S. Geological Survey.

3. Second Case

Here we are concerned with estimating the concentration of a chemical throughout the United States while recognizing the effect of geography (which is ignored in the present model). This can be accomplished in a fairly straightforward manner by subdividing the United States into a number of distinct geographical regions chosen so that the concentration of a chemical in a given environmental compartment in a specified region may be assumed uniform.

To make this idea clearer, suppose we decide to subdivide the United States into 10 distinct regions. For each of these regions, then, we will define 19 environmental compartments; in any given environmental compartment in any region the concentration of the chemical may be assumed uniform. In total there are now 190 environmental compartments whose linkages must be specified. For example, transport of the chemical can in principle occur between any two compartments in contiguous regions. For each of the regions we would have to estimate the sizes of its 19 environmental compartments and the water flows

between them, as well as the water flows across the geographic region boundary into an adjoining environmental compartment.

In principle, there is no great difficulty in modifying the existing mathematical model to recognize interconnected regions. The compartmental data requirements, of course, will be increased by a factor roughly equal to the number of regions.

We believe that the present mathematical environmental compartment model can be extended rather easily to handle multiple geographic regions. The closed-form matrix exponential solution to the coupled set of ordinary differential equations remains the same but the size of the matrix of coefficients will be greatly enlarged; no doubt the cost of computer time would be fairly high compared to present costs. Because the basic structure of the mathematical model of the environment is not changed by extending it to geographic regions, we do not foresee any conceptual difficulties. As always, the difficult problem will be to collect all the descriptive geographical region compartment data, but that task is definitely feasible using published U.S. Geological Survey data and need be done but once.

A good regional subdivision of the entire conterminous United States is that currently used by the Water Resources Council, which is well-documented in the First National Assessment of Water Resources.[*] The 17 water resource regions are (1) North Atlantic, (2) South Atlantic-Gulf, (3) Great Lakes, (4) Ohio, (5) Tennessee, (6) Upper Mississippi, (7) Lower Mississippi, (8) Souris-Red-Rainy, (9) Missouri, (10) Arkansas-White-Red, (11) Texas-Gulf, (12) Rio Grande, (13) Upper Colorado, (14) Lower Colorado, (15) Great Basin, (16) Columbia-North Pacific, (17) California.

[*] The Nation's Water Resources, Water Resources Council, Washington, D.C., 1968.

V. USING THE MODEL

A.   Computer Program

The basic multiple compartment environmental model described in the
preceding chapter has been implemented in a time-shared computer environment
in order to facilitate user interaction in directing the course of the com-
putations. The program has been coded in machine-independent APL because
this language is particularly adept at handling matrix manipulations; the
APL code appears in Appendix 5.   However, in order to operate the system
no knowledge whatsoever of APL by the user is necessary. The interested
potential user should contact the U.S. Environmental Protection Agency,
Office of Pesticides and Toxic Substances, Assessment Division (TS-792),
Washington, D.C., to determine the operational status of the system.

The system has been intentionally designed to be easy to learn and
use and to make minimal demands for data.

B.   Basic Steps to Use the System

1. The user should first familiarize himself/herself with the
overall purpose and structure of the model as described in both
this and the Phase I reports. The importance cannot be over-
stressed of having a thorough understanding of the limitations
and basic assumptions inherent in the model.

2. The user should next formulate a clear statement of the
environmental issue to be certain that the multimedia model offered
here is truly appropriate.

3. The user should next refer to the data sheets in Figure V-1
to determine the basic data requirements imposed by the model.
The user must decide whether the default values provided auto-
matically by the system, Table V-1, are adequate for the problem
at hand or whether they should be replaced.

4. The user should next complete the data sheets, as described
in Section V.E.

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5. The user should next access the system via his/her terminal, following the directions provided in Section V.F. The system will then automatically prompt the user to enter data and output instructions, as described in Section V.G.

6. The user should then review the results obtained for reasonability to guard against the possibility of inadvertently inputing incorrect data.

C. Review of the Model

The proposed model represents the air-land-water environments of the United States as a closed system of interconnected compartments, each containing a specified chemical at some compartment-average concentration which varies with time. The distribution of the chemical among the various compartments, which behave individually as completely-mixed, flow reactors, is determined by the level of direct emissions and inter-compartmental convective mass transfer and bulk water flows containing the chemical as solute. The 19 environmental compartments are described in Table IV-1.

Some of the more important assumptions and limitations inherent in the model to be borne in mind are the following:

- The concentration of chemical is uniform everywhere within a compartment and does not vary geographically.

- There is no spatial (geographic) variation in model parameters.

- Note that the use of compartment-average concentrations may lead to substantial underestimates in some locales and overestimates in others.
- The upper atmosphere (above 1 mile) is ignored.

- The air compartment over the United States is finite and closed.

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● There is no compartment for biomass.

● Chemical concentrations are presumed low in all compartments (e.g., less than 0.02 mole fraction in water).

The model computes the exact solution to Equation (2) -- that is, the time-varying and steady-state chemical concentrations and percentage of the total mass of chemical (distribution) in each compartment -- given the input data specified below. The model also reports, as a user option, the magnitude of the intercompartmental chemical flows and the matrix of coefficients $\overline{M}$ [see equations (6-8)].

As presently programmed, the user cannot change (1) the bulk water flows between compartments specified in Table IV-2, and (2) the basic compartmental linkages described in Table IV-3.

D. Data Requirements for Using Model

1. Physico-chemical Properties of Chemical

The following data must be available in order to use the model:

a. Molecular weight

b. Vapor pressure*, atm

c. Solubility in water*, kg of chemical/kg of aqueous solution

d. Soil/water partition coefficient for organic fraction of soil*

†e. Diffusion coefficient in air at 1 atm*, meters^2/sec.

†f. Diffusion coefficient in water*, meters^2/sec.

g. Reaction rate* or half-life* in

- Air

- Water

- Adsorbed to soil

---

*Temperature-dependent property.

†These properties will be estimated by the system on request; see Appendix 3.

2. Initial Concentrations of Chemical

The concentration of the chemical in kg/kg at time t = 0 must be provided for each of the 19 compartments. If the material does not presently exist in the environment, the initial concentration in each compartment is zero.

3. Chemical Emission Rates

The annual emission rate (kg/yr) of the chemical from all sources (e.g., production, use, nature, etc.) into the following four compartments must be provided over the future time period of interest:

- Air
- Lakes
- Streams
- Soil moisture 0-1 meter

4. Compartment Data

The following data are automatically incorporated in the model but may be overridden with user-supplied data if desired.

a. Mass of Compartment

Table IV-1 gives the estimated mass (in 10^{15} kg) for each of the 19 compartments.

b. Surface Area

The total surface area (in 10^{10} meter^2) for convective mass transfer is also given in Table IV-1 for the three compartments lakes, streams, and soil moisture 0-1 meter.

c. Fraction of Organic Material In Soil

The estimated fraction of organic material in the six soil compartments, f_o, are given below:

Soil Layer, Meters	f_o
0-1	0.10
1-5	0.05
5-10	0.03
10-15	0.03
15-30	0.03
30-50	0.03

E.   Completing the Data Sheets

1.   Types of Data Sheets

There are three data sheets (Figure V-1), one each for

(1) Physico-chemical data

(2) Initial concentrations and emission rates

(3) Compartment data

The physico-chemical data, initial chemical concentrations, and emission-related data may change from computer run to computer run, but the basic compartment data are general to the model and will change infrequently if at all.

2.   First Data Sheet

The chemical name and run descriptor may not exceed forty characters each (including spaces). The run descriptor is included to differentiate between runs of the same chemical, or to provide the user with a place to make comments. The descriptor appears in terminal display and report output. The physico-chemical data are entered as indicated. For temperature-dependent properties, values at 20°C are recommended. All properties must be entered only in the units indicated on the data sheets.

Enter the soil/water partition coefficient pertaining to the organic fraction of the soil. If this is not avaiable, the octanol/water partition coefficient may be substituted.

FIGURE V-1

PHYSICO-CHEMICAL DATA

CHEMICAL NAME: _____

RUN DESCRIPTOR: _____

PHYSICO-CHEMICAL PROPERTIES

MOLECULAR WEIGHT _____

VAPOR PRESSURE _____ ATM

SOLUBILITY IN WATER _____ KG/KG OF SOLUTION

SOIL/WATER PARTITION COEFFICIENT FOR ORGANIC FRACTION
   OF SOIL _____

DIFFUSION COEFFICIENT IN AIR _____ METERS^2/SEC

   NORMAL BOILING POINT _____ KELVIN

   MOLAL VOLUME (AT NORMAL BOILING POINT) _____ CM^3/GRAM MOLE

DIFFUSION COEFFICIENT IN WATER _____ METERS^2/SEC

   MOLAL VOLUME (AT NORMAL BOILING POINT) _____ CM^3/GRAM MOLE

COMPARTMENT TYPE	EXTREME	HIGH	MODERATE	PERSISTENT	INERT	B. HALF-LIFE	C. REACTION CONSTANT
AIR	_____	___	_____	_____	___	_____ YRS	_____ /YR
WATER	_____	___	_____	_____	___	_____ YRS	_____ /YR
ADSORBED TO SOIL	_____	___	_____	_____	___	_____ YRS	_____ /YR

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FIGURE V-1 (Cont.)

CHEMICAL INITIAL CONCENTRATIONS (KG/KG)

AIR	AM	LAKES	STREAMS	SM 0-1	SM 1-5	SM 5-10	SM 10-15	SM 15-30	SM 30-50

GRND WATER SHALLOW	GRND WATER DEEP	OCEAN	SOIL 0-1	SOIL 1-5	SOIL 5-10	SOIL 10-15	SOIL 15-30	SOIL 30-50

EMISSION DATA

EMISSION RATE TYPE

		EMISSION RATE TIME PERIODS					
		#1	#2	#3	#4	#5	#6
_____ (1) CONSTANT EMISSION RATES:	YEARS OF INTEREST	___	___	___	___	___	___
_____ (2) CONSTANT PERCENT CHANGE:	YEARS OF INTEREST	___	___	___	___	___	___
_____ (3) INCREMENTAL EMISSION RATES:	DURATION IN YEARS PER EMISSION RATE	___	___	___	___	___	___

COMPARTMENT	PERCENT CHANGE (FOR TYPE 2)	EMISSION RATES (KG/YEAR)				
		RATE 1	RATE 2	RATE 3	RATE 4	RATE 5
AIR	_____	___	___	___	___	___
LAKES	_____	___	___	___	___	___
STREAMS	_____	___	___	___	___	___
SOIL MOISTURE 0-1 M	_____	___	___	___	___	___

FIGURE V-1 (Cont.)

COMPARTMENT DATA

COMPARTMENT	FRACTION ORGANIC	WEIGHT (KG)	SURFACE AREA (SQ. METERS)
AIR		_____	
AIR MOISTURE		_____	
LAKES		_____	_____
STREAMS		_____	_____
SOIL MOISTURE 0-1M		_____	_____
SOIL MOISTURE 1-5M		_____	
SOIL MOISTURE 5-10M		_____	
SOIL MOISTURE 10-15M		_____	
SOIL MOISTURE 15-30M		_____	
SOIL MOISTURE 30-50M		_____	
GROUND WATER (SHALLOW)		_____	
GROUND WATER (DEEP)		_____	
OCEAN		_____	
SOIL 0-1M	_____	_____	
SOIL 1-5M	_____	_____	
SOIL 5-10M	_____	_____	
SOIL 10-15M	_____	_____	
SOIL 15-30M	_____	_____	
SOIL 30-50M	_____	_____	

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The diffusion coefficients should be entered if known; otherwise they can be calculated by the model based on the estimation methods in Appendix 3. In this case, to compute the diffusion coefficient pertaining to air mixtures or to aqueous solutions, the user must supply the chemical's molal volume at its normal boiling point. Alternatively, the user may choose to utilize methods described in Appendix III of the Phase I Report. As a last resort, when no other method is available, order-of-magnitude values may be used: set the diffusion coefficient for air at 1×10^{-5} meters^2/sec and the diffusion coefficient for water at 1×10^{-9} meters^2/sec.

The user must provide either the <u>effective</u> first-order reaction rate constant pertaining to air, water, and soil media or sufficient information from which the reaction rate constant may be determined. If the half-life is specified, then the computer will evaluate the reaction rate constant as ln2 divided by the half-life. If the reactivity is known only in a qualitative sense, then the following approximate classification is used:

Reactivity	Half-Life, Years	Reaction Rate Constant, per Year
Extreme	0.01 (~ week)	69.3
High	0.1 (~ month)	6.93
Moderate	1	0.693
Persistant	10	0.0693
Inert	100	0.00693

If in doubt concerning the reactivity, a conservative (long-half life) guess would be best.

If the reaction rate constants in <u>all</u> media are exactly zero, there will be no steady-state solution (this situation is not recommended). Finally, if all the reaction rate constants are <u>near</u> zero, the steady-state solution may not be computable. These conditions will not impede the time-varying solutions.

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3. Second Data Sheet

a. Chemical Initial Concentrations

Enter the initial concentration (at time zero) of the chemical in each compartment in kg/kg. Some useful concentration conversion factors are given in Table V-1. The default concentration value is zero for all compartments, so that it is necessary to enter only the nonzero initial concentrations.

b. Emission Rate Data

The chemical emission rate* (kg/year) may be expressed in three ways: (1) constant emission rate for all years, (2) base emission rate with constant percent annual change, and (3) emission rates which change incrementally for specified years. The same method must be used for all compartments (but not necessarily the same emission rate). According to the model, the chemical may be emitted only to four compartments: air, lakes, streams, and the first (shallowest) soil moisture layer.

First, check the emission rate type desired. Then on the same row as the rate type, specify the time period information (maximum of six entries). For the first two types, constant emission rate and constant percent change, the time information consists of the years** of interest (the years for which the user wishes to examine the model output). For incremental emission rates, enter the duration in years* that the specified emission rate persists.

----

* See Appendix 4 for a brief discussion on estimation of emission rates.
** Only integral values are permitted.

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TABLE V-1

CONCENTRATION CONVERSION FACTORS TO YIELD

UNITS OF KG OF CHEMICAL/KG OF MEDIUM

Medium	Original Concentration Unit	Multiply by
Air	$\mu g/1000m^3$	$0.833 \times 10^{-12*}$
Water	$\mu g/l$	10^{-9}
	ng/l	10^{-12}
Soil	$\mu g/kg$	10^{-9}
	ng/kg	10^{-12}

---

* Density of dry air at $20^{\circ}C$ and 1 atm taken as 1.20 g/l.

Finally, enter the emission rates themselves. For emission rate types (1) and (2), only a single rate should be entered in the column "RATE 1." For emission rate type (2), also enter the percent change (positive or negative) that is to be applied to each of the four compartments each year. For emission rate type (3), enter up to five emission rates corresponding to the time periods specified previously. Only one reaction rate method may be used for each medium, but the same method need not be used for all three media. Examples of completed data sheets are provided in Section V.H.

4. Third Data Sheet

The compartment data sheet need be completed only if the user wishes to deviate from the default values built into the system. The default values are shown in Table V-2. For any individual data items, the default values may still be used even though other data items are changed. To use specific default values, make no entry on the data sheet, i.e., it is necessary to enter data only for those items that change. The organic fraction is required only for the six soil compartments. Transport surface areas are required only for the lakes, streams, and shallowest soil moisture compartments.

F. Accessing the System

After signing on, the computer model is activated by typing:
)LOAD MODEL
After the computer prints the time and date that data were last saved, the user is prompted for a variety of options concerning input, running the model, and display. The eight options are:

TABLE V-2

COMPARTMENT DATA

(DEFAULT VALUES)

COMPARTMENT	F-ORGANIC	WEIGHT (KG)	SURFACE AREA (SQ. METERS)
AIR		16.2E15	
AIR MOISTURE		.18E15	
LAKES		18.8E15	14E10
STREAMS		.05E15	2.5E10
SOIL MOISTURE 0-1M		.60E15	769E10
SOIL MOISTURE 1-5M		.40E15	
SOIL MOISTURE 5-10M		.20E15	
SOIL MOISTURE 10-15M		.20E15	
SOIL MOISTURE 15-30M		.20E15	
SOIL MOISTURE 30-50M		.20E15	
GROUND WATER (SHALLOW)		63.7E15	
GROUND WATER (DEEP)		63.7E15	
OCEAN		50E15	
SOIL 0-1M	.10	15.2E15	
SOIL 1-5M	.05	60.9E15	
SOIL 5-10M	.03	76.1E15	
SOIL 10-15M	.03	76.1E15	
SOIL 15-30M	.03	228.5E15	
SOIL 30-50M	.03	304.4E15	

```
0 =  Exit from model
1 =  Input all data
2 =  Input only physico-chemical data
3 =  Input only emission-related data
4 =  Print current data
5 =  Print intermediate data
6 =  Run model based on current data
7 =  Examine last outputs
```

The usual sequence of operations involves entering new data and performing a computer run. The input is divided into three sections: chemical data, compartment data, and emission-related data. All input in specified units is prompted. Compartment data need not be entered or displayed if default values are acceptable. Following input of data, the user has various options for displaying the data entered, and if necessary all or part of the data may be re-entered. If the data are acceptable, the model is executed and the resulting chemical concentrations are printed. After completing a run, any or all subsections of the model may be executed selectively. Upon exiting the model, the input data may be saved by typing:

)SAVE

which overwrites the old data. Then, to end a session, type:

)OFF

G.   Executing the Model

1.   Input Process

After completing the data sheets, the user enters the data into the model. The input routine takes the user through the data sheets in much the same manner as they were filled out.

The user is specifically prompted for each item of data by the system. The physical units of the data are also specified. Internal program checks are made to verify that the input is in the correct form with regard to number of characters and numeric range. A message is

printed if an error is encountered, and the user is requested to re-enter the input. Most of the data for the model are numeric and such input is indicated in APL by a ⬜:. There is no strict convention for literal (also known as alphanumeric) data, but a colon at the end of a prompt has been adopted here. The chemical name and run descriptor are examples of literal data. Procedural input which requires a yes/no response is indicated by a question mark. Procedural input to select among options asks the user to type an option number (e.g., the form of the emission rates).

An effort has been made to simplify the data entry process. Data items that require more than one number, such as compartment-based information and the time periods, are entered all at once in vector form—as numbers separated by spaces. The prompts will indicate how many values are needed. Zeros are entered when there are no data for a given compartment.

The entire compartment data section may be skipped by answering "YES" to the question: "DO YOU WISH TO USE DEFAULT VALUES FOR ALL COMPARTMENT DATA?" For the compartment data (when entered individually) and for the initial concentrations, the user may enter "DEFAULT" which causes the default values to be used for those data items.

After the input process is completed, the user has the option of printing out the data as entered: "WOULD YOU LIKE TO PRINT THE INPUTS?" This input summary may include, at the user's option, the compartment data: "INCLUDING COMPARTMENT DATA?" The input summary is one computer page in size or less, even with the compartment data included.

The intermediate calculated results may be displayed after the input display section: "WOULD YOU LIKE TO PRINT THE INTERMEDIATE RESULTS?" The intermediate results are the intercompartmental chemical flows, both due to convection (r_{xy}) and bulk transport (F_{xy}), and the matrix $\overline{M}$ [in equations (6-7)].

At this point the user is queried: "ARE ALL INPUTS OK?" If so, the model proceeds to the run output section. If the data are in error, the user can transfer to the beginning of the data input process or only to the emission-related data. To get to the latter point, answer "YES" to the question: "ARE THE CHEMICAL AND COMPARTMENT DATA OK?" If the answer is "NO", then the entire input process (and the model) begins again.

The final section executes the model based on the data resident and prints the output. The output consists of the final calculated results from the model, i.e., the chemical concentrations in the various compartments at the time periods indicated by the emission-related data. For the special case of constant emission rates, the output also includes the steady-state concentrations.

After printing the outputs, the seven model options are listed again and the user proceeds as desired. At this point, the user may wish to view the emission rates, especially if the percent change type emission rates were used. To do so, enter option 3, display current data; the emission rates at all time periods will be shown. This fact highlights a difference between display and output — output involves calculation while display does not.

2. Input in the APL Environment

Numbers are entered much the same as on a calculator. Only the minimum form is necessary to enter a number. In other words, decimal points are not needed for integers and neither are trailing zeros after the decimal point. Negative numbers are indicated by a high minus sign $(^-)$, not by the middle minus (-) which is used for the operational symbols of subtraction and negation.

Given the scale and mathematical nature of this model, the use of scientific notation is desirable. What would be written in mathematics as

$$2.6 \times 10^{15} \text{ and } -320 \times 10^{-5}$$

are written in APL as

        2.6E15 and ¯320E¯5

or as

        26E14 and ¯3.2E¯3, etc.

The E means "times ten to the power of ..." or exponent. It is recommended that the user utilize the APL style of scientific notation to facilitate the computer input process. This form also requires less space.

In APL input, strings of numbers (such as the compartment data and initial concentrations) are separated by spaces. More than one space is permitted between the numbers, but no spaces may be imbedded within the number itself. Incorrect input of this sort results in an APL syntax error, which must be corrected. Press carriage return to end a line of input. If an error is discovered, backspace to that point in the line and press linefeed or attention (depending on the type of terminal being used). This causes everything to the right of the attention to be deleted. Then continue the line from that point on and end as usual with a carriage return.

H.   Sample Session Involving All Three Types of Emission Rates

        The sample session on the computer is described via:

    1.   The set of five data sheets that describe the runs. The estimates of initial environmental compartmental loadings and emission rates for benzene are taken from a 1980 draft document "Exposure Assessments of Priority Pollutants: Benzene" prepared by Arthur D. Little, Inc. for USEPA. The reaction rate data for benzene are not valid, having been chosen for demonstration purposes only. Literature reaction rate data indicate that benzene undergoes fairly rapid degradation in the air and water environments, so that the true steady-state in these phases is achieved quickly.

    2.   Annotations that help interpret the interactive session that follows. (Page 79)

    3.   The terminal-printed record of the session, with comment codes provided.

PHYSICO-CHEMICAL DATA

CHEMICAL NAME: BENZENE

RUN DESCRIPTOR: BASE CASE

PHYSICO-CHEMICAL PROPERTIES

MOLECULAR WEIGHT	78	
VAPOR PRESSURE	.1	ATM
SOLUBILITY IN WATER	.0018	KG/KG OF SOLUTION
SOIL/WATER PARTITION COEFFICIENT FOR ORGANIC FRACTION OF SOIL	135	
DIFFUSION COEFFICIENT IN AIR		$METERS^2/SEC$
NORMAL BOILING POINT	353	KELVIN
MOLAL VOLUME (AT NORMAL BOILING POINT)	96.0	$CM^3/GRAM$ MOLE
DIFFUSION COEFFICIENT IN WATER		$METERS^2/SEC$
MOLAL VOLUME (AT NORMAL BOILING POINT)	96.0	$CM^3/GRAM$ MOLE

COMPARTMENT TYPE	EXTREME	HIGH	MODERATE	PERSISTENT	INERT	B. HALF-LIFE	C. REACTION CONSTANT
AIR						50 YRS	/YR
WATER			X			YRS	39 /YR
ADSORBED TO SOIL			X			YRS	/YR

CHEMICAL INITIAL CONCENTRATIONS (KG/KG)

AIR	AM	LAKES	STREAMS	SM 0-1	SM 1-5	SM 5-10	SM 10-15	SM 15-30	SM 30-50
3E-9	0	1E-8	1E-8	0	0	0	0	0	0

GRND WATER SHALLOW	GRND WATER DEEP	OCEAN	SOIL 0-1	SOIL 1-5	SOIL 5-10	SOIL 10-15	SOIL 15-30	SOIL 30-50
0	0	0	0	0	0	0	0	0

EMISSION DATA

EMISSION RATE TYPE

	EMISSION RATE TIME PERIODS					
	#1	#2	#3	#4	#5	#6
__X__ (1) CONSTANT EMISSION RATES: YEARS OF INTEREST	1	5	10			
_____ (2) CONSTANT PERCENT CHANGE: YEARS OF INTEREST						
_____ (3) INCREMENTAL EMISSION RATES: DURATION IN YEARS PER EMISSION RATE						

COMPARTMENT	PERCENT CHANGE (FOR TYPE 2)	EMISSION RATES (KG/YEAR) RATE 1	RATE 2	RATE 3	RATE 4	RATE 5
AIR		230E6				
LAKES		2.1E6				
STREAMS		0.53E6				
SOIL MOISTURE 0-1 M		230E6				

RUN 1

COMPARTMENT DATA

COMPARTMENT	F-ORGANIC	WEIGHT (KG)	SURFACE AREA (SQ. METERS)
AIR		Default	
AIR MOISTURE			
LAKES			Default
STREAMS			
SOIL MOISTURE 0-1M			
SOIL MOISTURE 1-5M			
SOIL MOISTURE 5-10M			
SOIL MOISTURE 10-15M			
SOIL MOISTURE 15-30M			
SOIL MOISTURE 30-50M			
GROUND WATER (SHALLOW)			
GROUND WATER (DEEP)			
OCEAN			
SOIL 0-1M	Default		
SOIL 1-5M			
SOIL 5-10M			
SOIL 10-15M			
SOIL 15-30M			
SOIL 30-50M			

CHEMICAL INITIAL CONCENTRATIONS (KG/KG)

AIR	AM	LAKES	STREAMS	SM 0-1	SM 1-5	SM 5-10	SM 10-15	SM 15-30	SM 30-50
3E-9	0	1E-8	1E-8	0	0	0	0	0	0

GRND WATER SHALLOW	GRND WATER DEEP	OCEAN	SOIL 0-1	SOIL 1-5	SOIL 5-10	SOIL 10-15	SOIL 15-30	SOIL 30-50
0	0	0	0	0	0	0	0	0

EMISSION DATA

EMISSION RATE TYPE

		EMISSION RATE TIME PERIODS					
		#1	#2	#3	#4	#5	#6
_____ (1) CONSTANT EMISSION RATES:	YEARS OF INTEREST	___	___	___	___	___	___
__X__ (2) CONSTANT PERCENT CHANGE:	YEARS OF INTEREST	1	5	10	25	___	___
_____ (3) INCREMENTAL EMISSION RATES:	DURATION IN YEARS PER EMISSION RATE	___	___	___	___	___	___

COMPARTMENT	PERCENT CHANGE (FOR TYPE 2)	EMISSION RATES (KG/YEAR)				
		RATE 1	RATE 2	RATE 3	RATE 4	RATE 5
AIR	5	230E6				
LAKES	5	2.1E6				
STREAMS	5	0.53E6				
SOIL MOISTURE 0-1 M	0	230E6				

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RUN 2

CHEMICAL INITIAL CONCENTRATIONS (KG/KG)

AIR	AM	LAKES	STREAMS	SM 0-1	SM 1-5	SM 5-10	SM 10-15	SM 15-30	SM 30-50
3E-9	0	1E-8	1E-8	0	0	0	0	0	0

GRND WATER SHALLOW	GRND WATER DEEP	OCEAN	SOIL 0-1	SOIL 1-5	SOIL 5-10	SOIL 10-15	SOIL 15-30	SOIL 30-5
0	0	0	0	0	0	0	0	0

EMISSION DATA

EMISSION RATE TYPE

		EMISSION RATE TIME PERIODS					
		#1	#2	#3	#4	#5	#6
_____	(1) CONSTANT EMISSION RATES: YEARS OF INTEREST	___	___	___	___	___	___
_____	(2) CONSTANT PERCENT CHANGE: YEARS OF INTEREST	___	___	___	___	___	___
X	(3) INCREMENTAL EMISSION RATES: DURATION IN YEARS PER EMISSION RATE	5	5	5	10	___	___

COMPARTMENT	PERCENT CHANGE (FOR TYPE 2)	EMISSION RATES (KG/YEAR)				
		RATE 1	RATE 2	RATE 3	RATE 4	RATE 5
AIR	_____	230E6	250E6	300E6	270E6	_____
LAKES	_____	2.1E6	4E6	6E6	5E6	_____
STREAMS	_____	0.53E6	1E6	1.5E6	1.3E6	_____
SOIL MOISTURE 0-1 M	_____	230E6	250E6	300E6	270E6	_____

EXAMPLE OF TYPE 1 EMISSION RATE INCLUDING PRINTING OF

COMPARTMENT DATA AND INTERMEDIATE RESULTS


```
        )LOAD MODEL                                                        (a)
SAVED 15:36:59 10/01/80
wSSIZE IS 691896

OPTIONS ARE:
0 - EXIT FROM MODEL
1 - INPUT ALL DATA
2 - INPUT ONLY PHYSICO-CHEMICAL DATA
3 - INPUT ONLY EMISSION-RELATED DATA
4 - PRINT CURRENT DATA
5 - PRINT INTERMEDIATE RESULTS
6 - RUN MODEL BASED ON CURRENT DATA
7 - EXAMINE LAST OUTPUTS
ENTER OPTION NUMBER
L:                                                                         (b)
        1


PHYSICO-CHEMICAL DATA


ENTER CHEMICAL NAME: BENZENE
ENTER RUN DESCRIPTOR: BASE CASE
ENTER MOLECULAR WEIGHT:
L:
        78
ENTER VAPOR PRESSURE (ATM.):
U:
        .1
ENTER SOLUBILITY IN WATER (KG/KG):
U:
        .0018
ENTER SOIL/WATER PARTITION COEFFICIENT FOR ORGANIC FRACTION OF SOIL:
L:

        135
DO YOU HAVE THE DIFFUSIVITY IN AIR? NO
ENTER NORMAL BOILING POINT (°K):
U:
        353
ENTER MOLAL VOLUME AT NORMAL BOILING PT. (CM*3/G-MOL):                     (c)
U:
        96
DO YOU HAVE THE DIFFUSIVITY IN WATER? NO
DIFFUSIVITY IN WATER HAS BEEN CALCULATED


DO YOU HAVE THE REACTION RATE CONSTANT IN AIR? NO
DO YOU HAVE THE HALF-LIFE IN AIR? Y                                        (d)
ENTER HALF-LIFE (YEARS):
U:
        50
```

DO YOU HAVE THE REACTION RATE CONSTANT IN WATER? NO
DO YOU HAVE THE HALF-LIFE IN WATER? N
ENTER I=INERT, P=PERSISTANT, M=MODERATE, H=HIGH, E=EXTREME
ENTER THE LETTER FOR THE CHEMICAL'S GENERAL LEVEL OF REACTIVITY IN WATER: M

DO YOU HAVE THE REACTION RATE CONSTANT IN SOIL? N
DO YOU HAVE THE HALF-LIFE IN SOIL? N
ENTER I=INERT, P=PERSISTANT, M=MODERATE, H=HIGH, E=EXTREME
ENTER THE LETTER FOR THE CHEMICAL'S GENERAL LEVEL OF REACTIVITY IN SOIL: M

DO YOU WISH TO USE DEFAULT VALUES FOR ALL COMPARTMENT DATA? YES   (e)

EMISSION RELATED DATA

ENTER 19 INITIAL CONCENTRATIONS:
□:
        $3E^-9$ 0 $1E^-8$ $1E^-8$ 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0   (f)

FROM NOW ON, 'DEFAULT' IS NO LONGER A VALID INPUT
ENTER 1 FOR CONSTANT EMISSION RATES
ENTER 2 FOR CONSTANT PERCENT INCREASE
ENTER 3 FOR INCREMENTAL EMISSION RATES
ENTER OPTION NUMBER:
□:
        1
ENTER EMISSION RATES FOR AIR, LAKES, STREAMS, SOIL MOISTURE (KG./YEAR):
□:
        230E6 2.1E6 .53E6 230E6
ENTER YEARS OF INTEREST:
□:
        1 5 10

WOULD YOU LIKE TO PRINT THE INPUTS? Y
INCLUDING COMPARTMENT DATA? Y

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BENZENE   *(BASE CASE)*

```
MOLECULAR WEIGHT:        78
VAPOR PRESSURE:          0.1 (ATM.)
SOLUBILITY IN WATER:     0.0018 (KG/KG)
SOIL/WATER COEF:         135
NORMAL BOILING POINT:    353 (°K)
MOLAL VOLUME:            96 (CM*3/G-MOL)
DIFFUSIVITY IN AIR:      9.3607E⁻06 (M*2/SEC)
               WATER:    8.9949E⁻10 (M*2/SEC)
```

g

```
REACTION RATE CONSTANT (PER YEAR)
AIR:     .01386
WATER:   .69315
SOIL:    .69315
```

h

COMPARTMENT	F-ORGANIC	WEIGHT (KG.)	AREA (M*2)
AIR		1.620E16	0.000E0
AIR MOISTURE		1.800E14	0.000E0
LAKES		1.880E16	1.400E11
STREAMS		5.000E13	2.500E10
SOIL MOISTURE 0-1 M		6.000E14	7.690E11
SOIL MOISTURE 1-5 M		4.000E14	0.000E0
SOIL MOISTURE 5-10M		2.000E14	0.000E0
SOIL MOISTURE 10-15M		2.000E14	0.000E0
SOIL MOISTURE 15-30M		2.000E14	0.000E0
SOIL MOISTURE 30-50M		2.000E14	0.000E0
GROUND WATER (SHALLOW)		6.370E16	0.000E0
GROUND WATER (DEEP)		6.370E16	0.000E0
OCEAN		5.000E16	0.000E0
SOIL 0-1M	0.1	1.520E16	0.000E0
SOIL 1-5M	0.05	6.090E16	0.000E0
SOIL 5-10M	0.03	7.610E16	0.000E0
SOIL 10-15M	0.03	7.610E16	0.000E0
SOIL 15-30M	0.03	2.285E17	0.000E0
SOIL 30-50M	0.03	3.044E17	0.000E0

i

COMPARTMENT	CO	EMISSION RATES (KG/YR)		
		YEAR 1	YEAR 5	YEAR 10

COMPARTMENT			
AIR	3.0E⁻9	2.3E8	
AIR MOISTURE	0.0E0	0.0E0	
LAKES	1.0E⁻8	2.1E6	
STREAMS	1.0E⁻8	5.3E5	
SOIL MOISTURE 0-1 M	0.0E0	2.3E8	
SOIL MOISTURE 1-5 M	0.0E0	0.0E0	
SOIL MOISTURE 5-10M	0.0E0	0.0E0	
SOIL MOISTURE 10-15M	0.0E0	0.0E0	
SOIL MOISTURE 15-30M	0.0E0	0.0E0	
SOIL MOISTURE 30-50M	0.0E0	0.0E0	
GROUND WATER (SHALLOW)	0.0E0	0.0E0	
GROUND WATER (DEEP)	0.0E0	0.0E0	
OCEAN	0.0E0	0.0E0	
SOIL 0-1M	0.0E0	0.0E0	
SOIL 1-5M	0.0E0	0.0E0	
SOIL 5-10M	0.0E0	0.0E0	
SOIL 10-15M	0.0E0	0.0E0	
SOIL 15-30M	0.0E0	0.0E0	
SOIL 30-50M	0.0E0	0.0E0	

WOULD YOU LIKE TO PRINT THE INTERMEDIATE RESULTS? Y

CONVECTIVE FLOWS PER UNIT CONCENTRATION (KG./YR.)

COMPARTMENT FROM\TO	AIR	AM	LAKES	STREAMS	SM 1	SM 2	SM 3	SM 4	SM 5	SM 6
AIR	0.0E00	7.0E25	2.3E16	4.0E15	1.2E17	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
AIR MOISTURE	6.1E27	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
LAKES	3.4E18	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
STREAMS	6.0E17	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL MOISTURE 0-1 M	1.9E19	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL MOISTURE 1-5 M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL MOISTURE 5-10M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL MOISTURE 10-15M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL MOISTURE 15-30M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL MOISTURE 30-50M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
GROUND WATER (SHALLOW)	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
GROUND WATER (DEEP)	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
OCEAN	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL 0-1M	0.0E00	0.0E00	0.0E00	0.0E00	7.3E07	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL 1-5M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	2.9E08	0.0E00	0.0E00	0.0E00	0.0E00
SOIL 5-10M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	3.7E08	0.0E00	0.0E00	0.0E00
SOIL 10-15M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	3.7E08	0.0E00	0.0E00
SOIL 15-30M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	1.1E09	0.0E00
SOIL 30-50M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	1.5E09

COMPARTMENT FROM\TO	GW 1	GW 2	OCEAN	SOIL 1	SOIL 2	SOIL 3	SOIL 4	SOIL 5	SOIL 6
AIR	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
AIR MOISTURE	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
LAKES	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
STREAMS	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL MOISTURE 0-1 M	0.0E00	0.0E00	0.0E00	9.9E08	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL MOISTURE 1-5 M	0.0E00	0.0E00	0.0E00	0.0E00	2.0E09	0.0E00	0.0E00	0.0E00	0.0E00
SOIL MOISTURE 5-10M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	1.5E09	0.0E00	0.0E00	0.0E00
SOIL MOISTURE 10-15M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	1.5E09	0.0E00	0.0E00
SOIL MOISTURE 15-30M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	4.5E09	0.0E00
SOIL MOISTURE 30-50M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	5.9E09
GROUND WATER (SHALLOW)	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
GROUND WATER (DEEP)	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
OCEAN	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL 0-1M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL 1-5M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL 5-10M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL 10-15M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL 15-30M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL 30-50M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00

BULK WATER FLOWS (KG./YR.)   ①

COMPARTMENT FROM\TO	AM	LAKES	STREAMS	SM 1	SM 2	SM 3	SM 4	SM 5	SM 6	GW 1	GW 2	OCEAN
AIR MOISTURE	0.0E00	1.8E15	1.0E14	2.9E15	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
LAKES	1.7E14	0.0E00	1.7E15	8.0E13	5.0E13	2.5E13	1.5E13	1.0E13	1.0E13	1.0E14	0.0E00	0.0E00
STREAMS	3.0E13	1.6E14	0.0E00	1.2E14	5.0E13	1.5E13	5.0E12	0.0E00	0.0E00	1.0E14	0.0E00	1.5E15
SOIL MOISTURE 0-1 M	2.8E15	1.0E14	1.0E14	0.0E00	1.1E14	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL MOISTURE 1-5 M	0.0E00	5.0E13	5.0E13	1.0E13	0.0E00	9.0E13	0.0E00	0.0E00	0.0E00	2.0E13	0.0E00	0.0E00
SOIL MOISTURE 5-10M	0.0E00	2.0E13	2.0E13	0.0E00	1.0E13	0.0E00	4.5E13	0.0E00	0.0E00	2.0E13	2.0E13	0.0E00
SOIL MOISTURE 10-15M	0.0E00	1.0E13	1.0E13	0.0E00	0.0E00	5.0E12	0.0E00	1.2E13	0.0E00	1.0E13	2.0E13	0.0E00
SOIL MOISTURE 15-30M	0.0E00	5.0E12	5.0E12	0.0E00	0.0E00	0.0E00	2.0E12	0.0E00	5.0E12	0.0E00	5.0E12	0.0E00
SOIL MOISTURE 30-50M	0.0E00	5.0E12	5.0E12	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	5.0E12	0.0E00
GROUND WATER (SHALLOW)	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	2.5E14	0.0E00
GROUND WATER (DEEP)	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	3.0E14
OCEAN	1.8E15	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00

M. MATRIX OF COEFFICIENTS (PER YEAR)

COMPARTMENT TO\FROM	AM	LAKES	STREAMS	SM 1	SM 2	SM 3	SM 4	SM 5	SM 6
AIR MOISTURE	-9.4E00	2.1E02	3.7E01	1.2E03	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
LAKES	1.2E00	-1.8E02	8.5E-03	5.3E-03	2.7E-03	1.1E-03	5.3E-04	2.7E-04	2.7E-04
STREAMS	8.1E01	3.4E01	-1.2E04	2.0E00	1.0E00	4.0E-01	2.0E-01	1.0E-01	1.0E-01
SOIL MOISTURE 0-1 M	2.1E02	1.3E-01	2.0E-01	-3.1E04	1.7E-02	0.0E00	0.0E00	0.0E00	0.0E00
SOIL MOISTURE 1-5 M	0.0E00	1.3E-01	1.3E-01	2.8E-01	-1.2E00	2.5E-02	0.0E00	0.0E00	0.0E00
SOIL MOISTURE 5-10M	0.0E00	1.3E-01	7.5E-02	0.0E00	4.5E-01	-1.4E00	2.5E-02	0.0E00	0.0E00
SOIL MOISTURE 10-15M	0.0E00	7.5E-02	2.5E-02	0.0E00	0.0E00	2.2E-01	-1.0E00	1.0E-02	0.0E00
SOIL MOISTURE 15-30M	0.0E00	5.0E-02	0.0E00	0.0E00	0.0E00	0.0E00	6.0E-02	-8.0E-01	0.0E00
SOIL MOISTURE 30-50M	0.0E00	5.0E-02	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	2.5E-02	-7.7E-01
GROUND WATER (SHALLOW)	0.0E00	1.6E-03	1.6E-03	0.0E00	3.1E-04	3.1E-04	1.6E-04	0.0E00	0.0E00
GROUND WATER (DEEP)	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	3.1E-04	3.1E-04	7.8E-05	7.8E-05
OCEAN	0.0E00	0.0E00	3.0E-02	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL 0-1M	0.0E00	0.0E00	0.0E00	6.5E-08	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL 1-5M	0.0E00	0.0E00	0.0E00	0.0E00	3.2E-08	0.0E00	0.0E00	0.0E00	0.0E00
SOIL 5-10M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	2.0E-08	0.0E00	0.0E00	0.0E00
SOIL 10-15M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	2.0E-08	0.0E00	0.0E00
SOIL 15-30M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	1.9E-08	0.0E00
SOIL 30-50M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	2.0E-08

COMPARTMENT TO/FROM	GW 1	GW 2	OCEAN	SOIL 1	SOIL 2	SOIL 3	SOIL 4	SOIL 5	SOIL 6
AIR MOISTURE	0.0E00	0.0E00	9.9E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
LAKES	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
STREAMS	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL MOISTURE 0-1 M	0.0E00	0.0E00	0.0E00	1.2E-07	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL MOISTURE 1-5 M	0.0E00	0.0E00	0.0E00	0.0E00	7.3E-07	0.0E00	0.0E00	0.0E00	0.0E00
SOIL MOISTURE 5-10M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	1.8E-06	0.0E00	0.0E00	0.0E00
SOIL MOISTURE 10-15M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	1.8E-06	0.0E00	0.0E00
SOIL MOISTURE 15-30M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	5.5E-06	0.0E00
SOIL MOISTURE 30-50M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	7.3E-06
GROUND WATER (SHALLOW)	-7.0E-01	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
GROUND WATER (DEEP)	3.9E-03	-7.0E-01	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
OCEAN	0.0E00	6.0E-03	-7.3E-01	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL 0-1M	0.0E00	0.0E00	0.0E00	-6.9E-01	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00
SOIL 1-5M	0.0E00	0.0E00	0.0E00	0.0E00	-6.9E-01	0.0E00	0.0E00	0.0E00	0.0E00
SOIL 5-10M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	-6.9E-01	0.0E00	0.0E00	0.0E00
SOIL 10-15M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	-6.9E-01	0.0E00	0.0E00
SOIL 15-30M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	-6.9E-01	0.0E00
SOIL 30-50M	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	0.0E00	-6.9E-01

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ARE ALL INPUTS OK? Y
ALIGN PAPER AND PRESS CARRIAGE RETURN ⓝ

BENZENE (*BASE CASE*)

CONCENTRATION DISTRIBUTION
(KG./KG.)

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COMPARTMENT	YEAR 0	YEAR 1	YEAR 5	YEAR 10	STEADY ST
AIR	$3.0E^-9$	$4.0E^-8$	$1.2E^-7$	$1.9E^-7$	$3.3E^-7$
AIR MOISTURE	$0.0E0$	$2.7E^-10$	$8.3E^-10$	$1.3E^-9$	$2.2E^-9$
LAKES	$1.0E^-8$	$2.7E^-10$	$8.3E^-10$	$1.3E^-9$	$2.2E^-9$
STREAMS	$1.0E^-8$	$2.7E^-10$	$8.3E^-10$	$1.3E^-9$	$2.2E^-9$
SOIL MOISTURE 0-1 M	$0.0E0$	$2.8E^-10$	$8.4E^-10$	$1.3E^-9$	$2.2E^-9$
SOIL MOISTURE 1-5 M	$0.0E0$	$6.5E^-11$	$3.1E^-10$	$5.3E^-10$	$9.3E^-10$
SOIL MOISTURE 5-10M	$0.0E0$	$3.4E^-11$	$2.0E^-10$	$3.5E^-10$	$6.3E^-10$
SOIL MOISTURE 10-15M	$0.0E0$	$1.7E^-11$	$1.0E^-10$	$1.9E^-10$	$3.5E^-10$
SOIL MOISTURE 15-30M	$0.0E0$	$8.4E^-12$	$4.7E^-11$	$8.7E^-11$	$1.6E^-10$
SOIL MOISTURE 30-50M	$0.0E0$	$8.1E^-12$	$4.4E^-11$	$8.0E^-11$	$1.5E^-10$
GROUND WATER (SHALLOW)	$0.0E0$	$5.0E^-13$	$3.1E^-12$	$5.7E^-12$	$1.1E^-11$
GROUND WATER (DEEP)	$0.0E0$	$8.3E^-15$	$1.2E^-13$	$2.6E^-13$	$5.4E^-13$
OCEAN	$0.0E0$	$4.2E^-12$	$2.7E^-11$	$4.9E^-11$	$9.0E^-11$
SOIL 0-1M	$0.0E0$	$3.7E^-18$	$6.1E^-17$	$1.1E^-16$	$2.1E^-16$
SOIL 1-5M	$0.0E0$	$8.8E^-19$	$1.1E^-17$	$2.2E^-17$	$4.4E^-17$
SOIL 5-10M	$0.0E0$	$2.8E^-19$	$4.0E^-18$	$8.7E^-18$	$1.8E^-17$
SOIL 10-15M	$0.0E0$	$1.5E^-19$	$2.1E^-18$	$4.7E^-18$	$9.9E^-18$
SOIL 15-30M	$0.0E0$	$7.7E^-20$	$9.4E^-19$	$2.2E^-18$	$4.5E^-18$
SOIL 30-50M	$0.0E0$	$7.5E^-20$	$8.9E^-19$	$2.0E^-18$	$4.1E^-18$

MASS DISTRIBUTION
(º/º)

COMPARTMENT	YEAR 0	YEAR 1	YEAR 5	YEAR 10	STEADY ST
AIR	13.0	97.0	96.8	96.8	96.7
AIR MOISTURE		0.6	0.6	0.6	0.6
LAKES	43.5	0.6	0.6	0.6	0.6
STREAMS	43.5	0.7	0.6	0.6	0.6
SOIL MOISTURE 0-1 M		0.7	0.7	0.7	0.7
SOIL MOISTURE 1-5 M		0.2	0.2	0.3	0.3
SOIL MOISTURE 5-10M		0.1	0.2	0.2	0.2
SOIL MOISTURE 10-15M			0.1	0.1	0.1
SOIL MOISTURE 15-30M					
SOIL MOISTURE 30-50M					
GROUND WATER (SHALLOW)					
GROUND WATER (DEEP)					
OCEAN					
SOIL 0-1M					
SOIL 1-5M					
SOIL 5-10M					
SOIL 10-15M					
SOIL 15-30M					
SOIL 30-50M					
	100.0	100.0	100.0	100.0	100.0

RUN 2

EXAMPLE OF TYPE 2 EMISSION RATE

```
OPTIONS ARE:
0 - EXIT FROM MODEL
1 - INPUT ALL DATA
2 - INPUT ONLY PHYSICO-CHEMICAL DATA
3 - INPUT ONLY EMISSION-RELATED DATA
4 - PRINT CURRENT DATA
5 - PRINT INTERMEDIATE RESULTS
6 - RUN MODEL BASED ON CURRENT DATA
7 - EXAMINE LAST OUTPUTS
ENTER OPTION NUMBER
⊔:
     3
```

(P)

(q)

```
EMISSION RELATED DATA

ENTER 19 INITIAL CONCENTRATIONS:
⊔:
     3E⁻9 0 1E⁻8 1E⁻8 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0

FROM NOW ON, 'DEFAULT' IS NO LONGER A VALID INPUT
ENTER 1  FOR CONSTANT EMISSION RATES
ENTER 2  FOR CONSTANT PERCENT INCREASE
ENTER 3  FOR INCREMENTAL EMISSION RATES
ENTER OPTION NUMBER:
⊔:
     2
ENTER EMISSION RATES FOR AIR, LAKES, STREAMS, SOIL MOISTURE (KG./YEAR):
⊔:
     230E6 2.1E6 .53E6 230E6
ENTER THE ANNUAL PERCENT GROWTH FOR AIR, LAKES, STREAMS, SOIL MOISTURE:
⊔:
     5 5 5 0
ENTER THE YEARS OF INTEREST
⊔:
     1 5 10 25
```

(r)

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WOULD YOU LIKE TO PRINT THE INPUTS? Y
INCLUDING COMPARTMENT DATA? N
```

BENZENE   (BASE CASE)

MOLECULAR WEIGHT: 78
VAPOR PRESSURE: 0.1 (ATM.)
SOLUBILITY IN WATER: 0.0018 (KG/KG)
SOIL/WATER COEF: 135
NORMAL BOILING POINT: 353 (°K)
MOLAL VOLUME: 96 (CM*3/G-MOL)
DIFFUSIVITY IN AIR: 9.3607E-06 (M*2/SEC)
              WATER: 8.9949E-10 (M*2/SEC)

REACTION RATE CONSTANT (PER YEAR)
AIR: .01386
WATER: .69315
SOIL: .69315

COMPARTMENT	CO	PERCENT	EM RATE (KG/YR) YEAR 0
AIR	3.0E-9	5.0	2.3E8
AIR MOISTURE	0.0E0		0.0E0
LAKES	1.0E-8	5.0	2.1E6
STREAMS	1.0E-8	5.0	5.3E5
SOIL MOISTURE 0-1 M	0.0E0		2.3E8
SOIL MOISTURE 1-5 M	0.0E0		0.0E0
SOIL MOISTURE 5-10M	0.0E0		0.0E0
SOIL MOISTURE 10-15M	0.0E0		0.0E0
SOIL MOISTURE 15-30M	0.0E0		0.0E0
SOIL MOISTURE 30-50M	0.0E0		0.0E0
GROUND WATER (SHALLOW)	0.0E0		0.0E0
GROUND WATER (DEEP)	0.0E0		0.0E0
OCEAN	0.0E0		0.0E0
SOIL 0-1M	0.0E0		0.0E0
SOIL 1-5M	0.0E0		0.0E0
SOIL 5-10M	0.0E0		0.0E0
SOIL 10-15M	0.0E0		0.0E0
SOIL 15-30M	0.0E0		0.0E0
SOIL 30-50M	0.0E0		0.0E0

WOULD YOU LIKE TO PRINT THE INTERMEDIATE RESULTS? N
ARE ALL INPUTS OK? Y
ALIGN PAPER AND PRESS CARRIAGE RETURN

BENZENE   (BASE CASE)

CONCENTRATION DISTRIBUTION
(KG./KG.)

COMPARTMENT	YEAR 0	YEAR 1	YEAR 5	YEAR 10	YEAR 25
AIR	$3.0E^{-9}$	$4.0E^{-8}$	$1.4E^{-7}$	$2.5E^{-7}$	$6.7E^{-7}$
AIR MOISTURE	$0.0E0$	$2.7E^{-10}$	$9.2E^{-10}$	$1.7E^{-9}$	$4.5E^{-9}$
LAKES	$1.0E^{-8}$	$2.7E^{-10}$	$9.1E^{-10}$	$1.7E^{-9}$	$4.4E^{-9}$
STREAMS	$1.0E^{-8}$	$2.7E^{-10}$	$9.2E^{-10}$	$1.7E^{-9}$	$4.5E^{-9}$
SOIL MOISTURE 0-1 M	$0.0E0$	$2.8E^{-10}$	$8.9E^{-10}$	$1.6E^{-9}$	$4.1E^{-9}$
SOIL MOISTURE 1-5 M	$0.0E0$	$6.5E^{-11}$	$3.3E^{-10}$	$6.4E^{-10}$	$1.7E^{-9}$
SOIL MOISTURE 5-10M	$0.0E0$	$3.4E^{-11}$	$2.1E^{-10}$	$4.2E^{-10}$	$1.2E^{-9}$
SOIL MOISTURE 10-15M	$0.0E0$	$1.7E^{-11}$	$1.1E^{-10}$	$2.3E^{-10}$	$6.3E^{-10}$
SOIL MOISTURE 15-30M	$0.0E0$	$8.4E^{-12}$	$5.0E^{-11}$	$1.0E^{-10}$	$2.9E^{-10}$
SOIL MOISTURE 30-50M	$0.0E0$	$8.1E^{-12}$	$4.6E^{-11}$	$9.6E^{-11}$	$2.6E^{-10}$
GROUND WATER (SHALLOW)	$0.0E0$	$5.0E^{-13}$	$3.2E^{-12}$	$6.8E^{-12}$	$1.9E^{-11}$
GROUND WATER (DEEP)	$0.0E0$	$8.3E^{-15}$	$1.2E^{-13}$	$3.0E^{-13}$	$9.1E^{-13}$
OCEAN	$0.0E0$	$4.2E^{-12}$	$2.8E^{-11}$	$5.9E^{-11}$	$1.6E^{-10}$
SOIL 0-1M	$0.0E0$	$9.7E^{-18}$	$6.5E^{-17}$	$1.3E^{-16}$	$3.7E^{-16}$
SOIL 1-5M	$0.0E0$	$8.8E^{-19}$	$1.1E^{-17}$	$2.6E^{-17}$	$7.6E^{-17}$
SOIL 5-10M	$0.0E0$	$2.8E^{-19}$	$4.2E^{-18}$	$1.0E^{-17}$	$3.0E^{-17}$
SOIL 10-15M	$0.0E0$	$1.5E^{-19}$	$2.1E^{-18}$	$5.5E^{-18}$	$1.7E^{-17}$
SOIL 15-30M	$0.0E0$	$7.7E^{-20}$	$9.8E^{-19}$	$2.5E^{-18}$	$7.6E^{-18}$
SOIL 30-50M	$0.0E0$	$7.5E^{-20}$	$9.2E^{-19}$	$2.3E^{-18}$	$7.0E^{-18}$

MASS DISTRIBUTION
(°/°)

COMPARTMENT	YEAR 0	YEAR 1	YEAR 5	YEAR 10	YEAR 25
AIR	13.0	97.0	96.9	96.8	96.9
AIR MOISTURE		0.6	0.6	0.6	0.6
LAKES	43.5	0.6	0.6	0.6	0.6
STREAMS	43.5	0.7	0.6	0.6	0.6
SOIL MOISTURE 0-1 M		0.7	0.6	0.6	0.6
SOIL MOISTURE 1-5 M		0.2	0.2	0.2	0.3
SOIL MOISTURE 5-10M		0.1	0.1	0.2	0.2
SOIL MOISTURE 10-15M			0.1	0.1	0.1
SOIL MOISTURE 15-30M					
SOIL MOISTURE 30-50M					
GROUND WATER (SHALLOW)					
GROUND WATER (DEEP)					
OCEAN					
SOIL 0-1M					
SOIL 1-5M					
SOIL 5-10M					
SOIL 10-15M					
SOIL 15-30M					
SOIL 30-50M					
	100.0	100.0	100.0	100.0	100.0

```
OPTIONS ARE:
0 - EXIT FROM MODEL
1 - INPUT ALL DATA
2 - INPUT ONLY PHYSICO-CHEMICAL DATA
3 - INPUT ONLY EMISSION-RELATED DATA
4 - PRINT CURRENT DATA
5 - PRINT INTERMEDIATE RESULTS
6 - RUN MODEL BASED ON CURRENT DATA
7 - EXAMINE LAST OUTPUTS
ENTER OPTION NUMBER
 :
      4
INCLUDING COMPARTMENT DATA? N
```

(t)

BENZENE   (BASE CASE)

MOLECULAR WEIGHT: 78
VAPOR PRESSURE: 0.1 (ATM.)
SOLUBILITY IN WATER: 0.0018   (KG/KG)
SOIL/WATER COEF: 135
NORMAL BOILING POINT: 353 (°K)
MOLAL VOLUME: 96 (CM*3/G-MOL)
DIFFUSIVITY IN AIR: 9.3607E$^-$06 (M*2/SEC)
                 WATER: 8.9949E$^-$10 (M*2/SEC)

REACTION RATE CONSTANT (PER YEAR)
AIR: .01386
WATER: .69315
SOIL: .69315

COMPARTMENT	CO	PERCENT	EMISSION RATES (KG/YR)				
			YEAR 0	YEAR 1	YEAR 5	YEAR 10	YEAR 25
AIR	3.0E$^-$9	5.0	2.3E8	2.3E8	2.8E8	3.6E8	7.4E8
AIR MOISTURE	0.0E0		0.0E0	0.0E0	0.0E3	0.0E0	0.0E0
LAKES	1.0E$^-$8	5.0	2.1E6	2.1E6	2.6E6	3.3E6	6.8E6
STREAMS	1.0E$^-$8	5.0	5.3E5	5.3E5	6.4E5	8.2E5	1.7E6
SOIL MOISTURE 0-1 M	0.0E0		2.3E8	2.3E8	2.3E8	2.3E8	2.3E8
SOIL MOISTURE 1-5 M	0.0E0		0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
SOIL MOISTURE 5-10M	0.0E0		0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
SOIL MOISTURE 10-15M	0.0E0		0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
SOIL MOISTURE 15-30M	0.0E0		0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
SOIL MOISTURE 30-50M	0.0E0		0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
GROUND WATER (SHALLOW)	0.0E0		0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
GROUND WATER (DEEP)	0.0E0		0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
OCEAN	0.0E0		0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
SOIL 0-1M	0.0E0		0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
SOIL 1-5M	0.0E0		0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
SOIL 5-10M	0.0E0		0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
SOIL 10-15M	0.0E0		0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
SOIL 15-30M	0.0E0		0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
SOIL 30-50M	0.0E0		0.0E0	0.0E0	0.0E0	0.0E0	0.0E0

RUN 2

RUN 3

EXAMPLE OF TYPE 3 EMISSION RATE

```
OPTIONS ARE:
0 - EXIT FROM MODEL
1 - INPUT ALL DATA
2 - INPUT ONLY PHYSICO-CHEMICAL DATA
3 - INPUT ONLY EMISSION-RELATED DATA
4 - PRINT CURRENT DATA
5 - PRINT INTERMEDIATE RESULTS
6 - RUN MODEL BASED ON CURRENT DATA
7 - EXAMINE LAST OUTPUTS
ENTER OPTION NUMBER
⊔:
        3


EMISSION RELATED DATA


ENTER 19 INITIAL CONCENTRATIONS:
⊔:
        3E⁻9 0 1E⁻8 1E⁻8 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
ENTER 19 NUMBERS
ENTER 19 INITIAL CONCENTRATIONS:
⊔:
        3E⁻9 0 1E⁻8 1E⁻8 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
```

```
FROM NOW ON, 'DEFAULT' IS NO LONGER A VALID INPUT
ENTER 1   FOR CONSTANT EMISSION RATES
ENTER 2   FOR CONSTANT PERCENT INCREASE
ENTER 3   FOR INCREMENTAL EMISSION RATES
ENTER OPTION NUMBER:
⊔:
        3
HOW MANY INCREMENTS?
⊔:
        4
ENTER THE 4 INCREMENTAL TIME PERIODS:
⊔:
        5 5 5 10
```

```
ENTER EMISSION RATES FOR AIR, LAKES, STREAMS, SOIL MOISTURE FOR TIME PERIOD 1 (KG./YR.):
⊔:
        230E6 2.1E6 .53E6 230E6
ENTER EMISSION RATES FOR TIME PERIOD 2 (KG./YR.):
⊔:
        250E6  4E6 1E6 250E6
ENTER EMISSION RATES FOR TIME PERIOD 3 (KG./YR.):
⊔:
        300E6 6E6 1.5E6 300E6
ENTER EMISSION RATES FOR TIME PERIOD 4 (KG./YR.):
⊔:
        270E6 5E6 1.3E6 270E6


WOULD YOU LIKE TO PRINT THE INPUTS? Y
INCLUDING COMPARTMENT DATA? N
```

BENZENE   (BASE CASE)

MOLECULAR WEIGHT: 78
VAPOR PRESSURE: 0.1 (ATM.)
SOLUBILITY IN WATER: 0.0018 (KG/KG)
SOIL/WATER COEF: 135
NORMAL BOILING POINT: 353 (°K)
MOLAL VOLUME: 96 (CM*3/G-MOL)
DIFFUSIVITY IN AIR: 9.3607E⁻06 (M*2/SEC)
              WATER: 8.9949E⁻10 (M*2/SEC)

REACTION RATE CONSTANT (PER YEAR)
AIR: .01386
WATER: .69315
SOIL: .69315

COMPARTMENT	C0	EMISSION RATES (KG/YR)			
		YEAR 5	YEAR 10	YEAR 15	YEAR 25
AIR	3.0E⁻9	2.3E8	2.5E8	3.0E8	2.7E8
AIR MOISTURE	0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
LAKES	1.0E⁻8	2.1E6	4.0E6	6.0E6	5.0E6
STREAMS	1.0E⁻8	5.3E5	1.0E6	1.5E6	1.3E6
SOIL MOISTURE 0-1 M	0.0E0	2.3E8	2.5E8	3.0E8	2.7E8
SOIL MOISTURE 1-5 M	0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
SOIL MOISTURE 5-10M	0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
SOIL MOISTURE 10-15M	0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
SOIL MOISTURE 15-30M	0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
SOIL MOISTURE 30-50M	0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
GROUND WATER (SHALLOW)	0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
GROUND WATER (DEEP)	0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
OCEAN	0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
SOIL 0-1M	0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
SOIL 1-5M	0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
SOIL 5-10M	0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
SOIL 10-15M	0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
SOIL 15-30M	0.0E0	0.0E0	0.0E0	0.0E0	0.0E0
SOIL 30-50M	0.0E0	0.0E0	0.0E0	0.0E0	0.0E0

WOULD YOU LIKE TO PRINT THE INTERMEDIATE RESULTS? N
ARE ALL INPUTS OK? Y
ALIGN PAPER AND PRESS CARRIAGE RETURN

BENZENE   *(BASE CASE)*

CONCENTRATION DISTRIBUTION
(KG./KG.)

COMPARTMENT	YEAR 0	YEAR 5	YEAR 10	YEAR 15	YEAR 25
AIR	$3.0E^-9$	$1.2E^-7$	$2.1E^-7$	$2.8E^-7$	$3.4E^-7$
AIR MOISTURE	$0.0E0$	$8.3E^-10$	$1.4E^-9$	$1.9E^-9$	$2.3E^-9$
LAKES	$1.0E^-8$	$8.3E^-10$	$1.4E^-9$	$1.9E^-9$	$2.3E^-9$
STREAMS	$1.0E^-8$	$8.3E^-10$	$1.4E^-9$	$1.9E^-9$	$2.3E^-9$
SOIL MOISTURE 0-1 M	$0.0E0$	$8.4E^-10$	$1.4E^-9$	$1.9E^-9$	$2.3E^-9$
SOIL MOISTURE 1-5 M	$0.0E0$	$3.1E^-10$	$5.6E^-10$	$7.8E^-10$	$9.7E^-10$
SOIL MOISTURE 5-10M	$0.0E0$	$2.0E^-10$	$3.7E^-10$	$5.2E^-10$	$6.5E^-10$
SOIL MOISTURE 10-15M	$0.0E0$	$1.0E^-10$	$2.0E^-10$	$2.8E^-10$	$3.6E^-10$
SOIL MOISTURE 15-30M	$0.0E0$	$4.7E^-11$	$9.1E^-11$	$1.3E^-10$	$1.7E^-10$
SOIL MOISTURE 30-50M	$0.0E0$	$4.4E^-11$	$8.3E^-11$	$1.2E^-10$	$1.5E^-10$
GROUND WATER (SHALLOW)	$0.0E0$	$3.1E^-12$	$5.9E^-12$	$8.5E^-12$	$1.1E^-11$
GROUND WATER (DEEP)	$0.0E0$	$1.2E^-13$	$2.7E^-13$	$4.0E^-13$	$5.4E^-13$
OCEAN	$0.0E0$	$2.7E^-11$	$5.1E^-11$	$7.3E^-11$	$9.3E^-11$
SOIL 0-1M	$0.0E0$	$6.1E^-17$	$1.2E^-16$	$1.7E^-16$	$2.1E^-16$
SOIL 1-5M	$0.0E0$	$1.1E^-17$	$2.3E^-17$	$3.4E^-17$	$4.5E^-17$
SOIL 5-10M	$0.0E0$	$4.0E^-18$	$9.1E^-18$	$1.3E^-17$	$1.8E^-17$
SOIL 10-15M	$0.0E0$	$2.1E^-18$	$4.9E^-18$	$7.3E^-98$	$1.0E^-17$
SOIL 15-30M	$0.0E0$	$9.4E^-19$	$2.2E^-18$	$3.4E^-18$	$4.6E^-18$
SOIL 30-50M	$0.0E0$	$8.9E^-19$	$2.1E^-18$	$3.1E^-18$	$4.2E^-18$

MASS DISTRIBUTION
(o/o)

COMPARTMENT	YEAR 0	YEAR 5	YEAR 10	YEAR 15	YEAR 25
AIR	13.0	96.8	96.8	96.8	96.7
AIR MOISTURE		0.6	0.6	0.6	0.6
LAKES	43.5	0.6	0.6	0.6	0.6
STREAMS	43.5	0.6	0.6	0.6	0.6
SOIL MOISTURE 0-1 M		0.7	0.7	0.7	0.7
SOIL MOISTURE 1-5 M		0.2	0.3	0.3	0.3
SOIL MOISTURE 5-10M		0.2	0.2	0.2	0.2
SOIL MOISTURE 10-15M		0.1	0.1	0.1	0.1
SOIL MOISTURE 15-30M					
SOIL MOISTURE 30-50M					
GROUND WATER (SHALLOW)					
GROUND WATER (DEEP)					
OCEAN					
SOIL 0-1M					
SOIL 1-5M					
SOIL 5-10M					
SOIL 10-15M					
SOIL 15-30M					
SOIL 30-50M					
	100.0	100.0	100.0	100.0	100.0

```
OPTIONS ARE:
0 - EXIT FROM MODEL
1 - INPUT ALL DATA
2 - INPUT ONLY PHYSICO-CHEMICAL DATA
3 - INPUT ONLY EMISSION-RELATED DATA
4 - PRINT CURRENT DATA
5 - PRINT INTERMEDIATE RESULTS
6 - RUN MODEL BASED ON CURRENT DATA
7 - EXAMINE LAST OUTPUTS
ENTER OPTION NUMBER
□:
        0
```

(x)

```
     )SAVE
15:36:59 09/30/80 MODEL
     )OFF
```

(y)

(z)

Comments

a The load command prints the last time the workspace (the model and data) was saved.

b ☐: is an APL notation for indicating numeric input.

c cm^3/g - mol in APL symbols.

d Only the first letter is necessary for a YES/NO response.

e No compartment data explicitly entered, since default values are used.

f Example of vector input and scientific notation in APL.

g The boiling point and molal volume are printed when applicable.

h Undistributed reaction rate constants.

i The default compartment data

j For display purposes, the emission rates are <u>not</u> repeated for each year.

k Convective flows (calculated).

l Bulk flows (constant)

m Matrix of coefficients (calculated).

n A carriage return was entered here to start the printing process.

o The steady-state is included on Type 1 when it can be calculated.

p At the end of run the options are listed again.

q Option 3 is chosen to begin another run using different emission rates.

r The soil moisture emission rate is constant.

s Year 0 is the base or initial rate. This base rate also applies to year one.

t Option 4 is chosen so that the emission rates for each year after applying the growth rate can be viewed, since they are calculated along with the concentrations.
Note that when a printing option (i.e., four or five) is chosen, the options are presented again, which allows the user to view the current data without necessarily running the model.

u   An example of incorrect input: too many numbers were entered.

v   This means that the duration for the first emission rate is
5 years; the second 5 years; the third 5 years; and the fourth
10 years.

w   The compartment data does not change during the three runs shown
here and so are displayed only during the first run.

x   Run the model again after an exit, enter the word MODEL.

y   Since only one run may be stored at a time, data is not saved
automatically and the user has the option of filing data through
the use of the)SAVE command. This can be done at any point
outside the model (i.e., after the exit option).

z   The sign-off message has not been included here.

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APPENDIX 1

MATHEMATICAL ANALYSIS

A. General Time-Dependent Solution of Multiple Compartment Model of the Environment

1. Laplace Transform Approach

The distribution of a chemical among the compartments of the environment is given by the solution to the set of simultaneous, first-order, linear, ordinary differential equations defined in Section IV. A. Equation (2) can be written in the form:

$$\dot{C}_x(t) + a_x C_x(t) = p_x(t) + \sum_{y \neq x} b_{yx} C_y(t), \tag{1}$$

where
$$b_{yx} = \rho_{yx}/W_x, \quad \rho_{yx} = F_{y \to x} + r_{y \to x}, \tag{2}$$

$$a_x = K_x + (1/W_x) \sum_{y \neq x} r_{xy}, \tag{3}$$

and
$$p_x(t) = P_x(t)/W_x \tag{4}$$

In the notation used in writing equation (1) the new coefficients and terms have the following interpretations:

a_x = total concentration loss rate per unit concentration from compartment x, produced by chemical reactions (rate K_x), bulk flows to other compartments (rates $F_{x \to y}/W_x$), and diffusional flows to other compartments (rates $r_{x \to y}/W_x$);

b_{yx} = concentration gain rate per unit concentration from compartment y to compartment x;

$p_x(t)$ = concentration gain rate from direct emissions into compartment x.

For a given index x, the index y runs over the residual set of indices. Writing equation (1) for x = 1, 2, ..., n we have a set of n linear differential equations in n unknown functions. This set of equations can be solved by taking Laplace transforms, solving the set of linear equations in the transforms, and taking inverse transforms. Let

$$\tilde{C}_x(s) = \int_0^\infty C_x(t)\exp(-st)dt. \tag{5}$$

Multiplying equation (1) by exp(-st) and integrating, we have

$$(s + a_x)\tilde{C}_x(s) - \sum_y b_{yx}\tilde{C}_y(s) = Q_x(s), \tag{6}$$

where

$$Q_x(s) = \tilde{p}_x(s) + C_x(0^+) \tag{7}$$

We now solve the set of linear equations (6) with x = 1, 2, ..., n to obtain $\tilde{C}_x(s)$, x = 1, 2, ..., n and then invert these functions to obtain $C_x(t)$, x = 1, 2, ..., n.

2. Constant Emission Rates

The solution is relatively easy to obtain when the emission rates are constant. Then

$$p_x(t) = p_x(0) = \text{constant (designated by } p_x), \tag{8}$$

and

$$Q_x(s) = (p_x/s) + c_x, \quad c_x = C_x(0^+). \tag{9}$$

When $Q_x(s)$ is substituted in (6), the solution for $\tilde{C}_x(s)$ is a quotient of polynomials, and the inverse transforms are sums of exponential functions.

To illustrate the procedure we use n = 3. The set of equations (6) becomes

$$(s + a_1)\tilde{C}_1(s) - b_{21}\tilde{C}_2(s) - b_{31}\tilde{C}_3(s) = (p_1/s) + c_1$$

$$- b_{12}\tilde{C}_1(s) + (s + a_2)\tilde{C}_2(s) - b_{32}\tilde{C}_3(s) = (p_2/s) + c_2$$

$$- b_{13}\tilde{C}_1(s) - b_{23}\tilde{C}_2(s) + (s + a_3)\tilde{C}_3(s) = (p_3/s) + c_3 \; .$$

The determinant of the coefficients of the variables is

$$D(s) = (s - s_1)\,(s - s_2)(s - s_3),$$

where s_1, s_2, s_3 are the roots of the characteristic equation, $D(s) = 0$.
Then the solution for $\tilde{C}_1(s)$ is

$$\tilde{C}_1(s) = \frac{\begin{vmatrix} p_1 + c_1 s & -b_{21} & -b_{31} \\ p_2 + c_2 s & s + a_2 & -b_{32} \\ p_3 + c_3 s & -b_{23} & s + a_3 \end{vmatrix}}{s(s - s_1)(s - s_2)(s - s_3)}$$

$$= \frac{A_{10}}{s} + \frac{A_{11}}{s-s_1} + \frac{A_{12}}{s-s_2} + \frac{A_{13}}{s-s_3} \; .$$

Taking the inverse transform of $\tilde{C}_1(s)$ the solution $C_1(t)$ is

$$C_1(t) = A_{10} + A_{11}\, e^{s_1 t} + A_{12}\, e^{s_2 t} + A_{13}\, e^{s_3 t}.$$

In general, the solution will have the form

$$C_x(t) = A_{x0} + \sum_{j=1}^{n} A_{xj}\, \exp(s_j t), \tag{10}$$

where s_1, s_2, $\ldots s_n$ are the roots of $D(s) = 0$, and

$$D(s) = \begin{vmatrix} s + a_1 & - b_{21} & \cdots & - b_{n1} \\ - b_{12} & s + a_2 & \cdots & - b_{n2} \\ - b_{13} & - b_{23} & \cdots & \\ \vdots & \vdots & & \\ - b_{1n} & - b_{2n} & \cdots & s + a_n \end{vmatrix} \tag{11}$$

It can be shown that $D(s) > 0$ for $s \geq 0$, and therefore there are no real roots that are non-negative, except for the unlikely case that the reaction rates $K_i = 0$, $i = 1, 2, \ldots, n$. The proof is based on the fact that

$$a_i = K_i + \sum_j B_{ij}, \quad B_{ij} = b_{ij} W_j / W_i,$$

from which $D(s)$ can be expanded into a sum of products of the factors $(s + K_i)$, with positive coefficients. For $n = 2$,

$$D(s) = (s + K_1)(s + K_2) + B_{21}(s + K_1) + B_{12}(s + K_2).$$

For $n = 3$,

$$D(s) = \prod_{i=1}^{3} (s + K_i)$$

$$+ (B_{31} + B_{32})(s + K_1)(s + K_2) + \ldots$$

$$+ (B_{23}B_{31} + B_{32}B_{21} + B_{21}B_{31})(s + K_1) + \ldots \quad (12)$$

If the reaction rates are not all zero, the roots $s_1, s_2, \ldots, s_n$ are real negative roots or complex roots (occurring in conjugate pairs) having negative real parts. The sum of the terms for a pair of conjugate complex roots is a sum of exponentially-damped sine and cosine terms. Hence, A_{x0} is the steady-state solution.

To find the solution (10) we find the roots $s_1, s_2, \ldots, s_n$ of $D(s) = 0$ with $\tilde{D}(s)$ from (11). The solution for $\tilde{C}_x(s)$ is

$$\tilde{C}_x(s) = N_x(s)/s \prod_{j=1}^{n} (s - s_j) \quad (13)$$

where $N_x(s)$ is the determinant obtained by replacing the xth column of $D(s)$ by the column consisting of the elements $p_1 + c_1 s, p_2 + c_2 s, \ldots, p_n + c_n s$. The A_{xj} coefficients are

$$A_{x0} = N_x(0)/ \prod_{j=1}^{n} (- s_j), \quad (14)$$

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$$A_{x1} = N_x(s_1)/s_1 \prod_{\substack{j=1 \\ j \neq i}}^{n} (s_i - s_j), \quad i = 1, 2, \ldots, n. \tag{15}$$

It is easy to show that $N_x(0) > 0$, and it is obvious that $\prod_{k=1}^{n} (-s_k) > 0$ since the roots are negative or complex-conjugate pairs. Hence, the concentration approaches a steady-state solution A_{x0} that is positive, in agreement with our intuition.

The solution is obtained by substituting the values of the roots and A_{xj} from (14) and (15) into equation (10). The operations involved are elementary but tedious. The difficult step is to find the solutions of $D(s) = 0$, particularly when some of the roots are complex. The remainder of the operations can be programmed easily for machine computation.

3. Increasing Emission Rates

Now assume that the emission rates increase with time t. We will treat the case for which

$$\dot{P}_x(t) = \alpha_x t^{k_x}, \quad k_x > 0, \tag{16}$$

which should be general enough for most purposes, since it is unlikely that the emission rate for any pollutant will increase at a faster rate than a power function of t.

We start with the case $k_x = k$, independent of x. The variation from compartment to compartment is described solely by the coefficient α_x. From (4) and (7) we obtain

$$Q_x(s) = g_x/s^{k+1} + c_x, \quad g_x = \alpha_x \Gamma(k+1)/W_x. \tag{17}$$

The solution of the set of equations (6) for $x = 1, 2, \ldots, n$ is

$$\hat{C}_x(s) = N_x(s)/s^{k+1} D(s), \tag{18}$$

where $D(s)$ is given by (11) and $N_x(s)$ is the determinant obtained from $D(s)$ by replacing the xth column by a column in which the jth element is $g_j + c_j s^{k+1}$. We now must find the inverse Laplace transform of (18) to obtain $C_x(t)$.

If k is a positive integer, we can expand $\tilde{C}_x(s)$ into partial fractions,

$$\tilde{C}_x(s) = \sum_{i=1}^{n} A_{xi}/(s - s_i) + \sum_{j=0}^{k} B_{xj}/s^{j+1}. \tag{19}$$

Inverting (19) the solution is

$$C_x(t) = \sum_{i=1}^{n} A_{xi} \exp(s_i t) + \sum_{j=0}^{k} B_{xj} t^j/j! \tag{20}$$

The $n+k+1$ coefficients A_{xi} and B_{xj} are obtained from the same number of linear equations obtained by equating (18) and (19). The A_{xi} coefficients are

$$A_{xi} = N_x(s_i)/s_i^{k+1} \prod_{\substack{j=1 \\ j \neq i}}^{n} (s_i - s_j), \quad i = 1, 2, \ldots, n. \tag{21}$$

Also,

$$B_{xk} = N_x(0)/ \prod_{i=1}^{n} (- s_i). \tag{22}$$

The other B_{xj} coefficients can be obtained by expanding $N_x(s)$.

The dominant term in the solution $C_x(t)$ for large t is $B_{xk} t^k/k!$, which has a positive coefficient by the argument used in the previous section. Hence, $C_x(t)$ increases indefinitely as a power function t^k, the same type function as the emission-rate function, as t increases indefinitely.

It is not likely that the emission rates will increase as fast as t^k with k a positive integer. Values of k in the range $0 < k < 1$ are more likely. Assume that k is a rational number, $k = h/m$, where h and m are positive integers. Put $r = s^{1/m}$. Then $\tilde{C}_x(s)$ in (18) becomes

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$$N_x(r^m)/r^{h+m} \; D(r^m),$$

which is a quotient of two polynomials in r. We expand into partial fractions and then replace r by $s^{1/m}$. When this has been done and the terms involving roots of $D(r^m) = 0$ are collected, $\tilde{C}_x(s)$ can be written in the form

$$\tilde{C}_x(s) = \sum_{i=1}^{n} A_{xi}/(s - s_i) + \sum_{j=0}^{m+h} B_{xj}/s^{j/m}, \qquad (23)$$

where the A_{xi} and B_{xj} coefficients are determined from the expansion. Inverting (23) the solution is

$$C_x(t) = \sum_{i=1}^{n} A_{xi} \exp(s_i t) + \sum_{j=0}^{m+h} B_{xj} t^{(j-m)/m}/\Gamma(j/m). \qquad (24)$$

The dominant term in $C_x(t)$ for large t is the term involving $t^{h/m}(=t^k)$ with a positive coefficient. Again, we conclude that $C_x(t)$ increases indefinitely (in the form t^k) as t increases indefinitely.

The problem is more complicated, but not essentially more difficult, when k_x is not the same for all compartments. The solution can be obtained by the method described above for rational values of k_x. The dominant term in $C_x(t)$ for large t is a term involving t^{k_x}, if the flow rates into compartment x from compartments having higher k-values are negligible; and it is a term involving t^{k_y}, where k_y is k_x or the largest k-value with a non-negligible flow rate into compartment x, whichever is larger.

4. Decreasing Emission Rates

First, assume that

$$\dot{P}_x(t) = \alpha_x t^{-k}, \quad 0 < k < 1. \qquad (25.)$$

Then

$$Q_x(s) = g_x/s^{1-k} + c_x, \quad g_x = (\alpha_x/W_x)\Gamma(1 - k). \qquad (26)$$

Put $k = h/m$. By the method used above, $C_x(t)$ has the form (24) except that the upper limit in the second sum is m-h, instead of m+h. The dominant term in $C_x(t)$ for large t is a term involving t^{-k}. Hence, the steady-state solution is zero.

The solution for the case in which k in (25) is replaced by k_x can be obtained in a similar way. Again, the steady-state solution is zero.

Second, assume that

$$\dot{P}_x(t) = \alpha_x \exp(-h_x t), \quad h_x > 0. \tag{27}$$

Then

$$Q_x(s) = g_x/(s + h_x) + c_x, \quad g_x = \alpha_x/W_x; \tag{28}$$

and

$$\tilde{C}_x(s) = \sum_{i=1}^{n} A_{xi}/(s - s_i) + \sum_{j=1}^{n} B_{xj}/(s + h_j), \tag{29}$$

where the coefficients are obtained from the expansion into partial fractions. Then

$$C_x(t) = \sum_{j=1}^{n} A_{xi} \exp(s_i t) + \sum_{j=1}^{n} B_{xj} \exp(-h_j t). \tag{30}$$

Since the roots s_i, $i = 1, 2, \ldots, n$ are negative or have negative real parts, the solution $C_x(t)$ decreases exponentially towards the steady-state zero solution.

5.   Step-wise Increasing or Decreasing Emission Rates

For step-wise increasing or decreasing emission rates, the time
interval t, $[0 \leq t < \infty]$ can be decomposed into subintervals for which
all emission rates $p_x(t)$ are constant in each subinterval. The solution
for this case, given in Section A.2 above, can be applied to each sub-
interval, starting with the initial values $C_x(0)$ for the first subinterval
and using the values $C_x(t_1)$ at the end t_1 of the first subinterval as
the initial values for the second subinterval, etc.

In each subinterval the solution will have the form of equation (10),
but the coefficients A_{xj} (j = 0, 1, ...n) will change from subinterval to
subinterval as some of the p_x values change. However, if there are no
changes in the reaction rates K_x or in the transition rates b_{xy} with time,
the values of the roots s_j will be the same for all the subintervals.

6.   Steady-state Solution

From equations (10) and (14) the steady-state solution for compart-
ment x is

$$C_x(\infty) = A_{x0} = N_x(0) / \prod_{j=1}^{n} (-s_j) = N_x(0)/D(0). \qquad (31)$$

This follows since $D(s) = (s - s_1)(s - s_2) \ldots (s - s_n)$. The last member
of (31) displays the fact that the steady-state solution can be obtained
without finding the roots of the characteristic equation.

7.   Multiple Roots

Thus far in the analysis we have assumed implicitly that each root
s_j of $D(s) = 0$ occurs but once. In the general case multiple roots may
occur, making the computations more difficult. For simplicity we omit
the compartment index x. It is understood that a separate set of compu-
tations must be made for each compartment.

Assume that there is one multiple root s_1 of multiplicity k. The
concentration C(t) is the inverse Laplace transform of $\tilde{C}(s)$, where

$$\tilde{C}(s) = \frac{N(s)}{s\,D(s)} = \frac{N(s)}{s(s - s_1)^k \displaystyle\prod_{j=k+1}^{n} (s - s_j)} \tag{32}$$

The partial-fraction expansion of $\tilde{C}(s)$ is

$$\tilde{C}(s) = \frac{A_0}{s} + \frac{A_1}{(s - s_1)^k} + \frac{A_2}{(s - s_1)^{k-1}} + \cdots + \frac{A_k}{s - s_1} + \sum_{j=k+1}^{n} \frac{A_j}{(s - s_j)} \tag{33}$$

The functions in (32) and (33) must be identical. Multiplying by the least common denominator we obtain the identity

$$N(s) \equiv \left[A_0 (s - s_1)^k + s \sum_{h=1}^{k} A_h (s - s_1)^{h-1} \right] \Pi(s)$$

$$+ s(s - s_1)^k \sum_{j=k+1}^{n} A_j \, \Pi_j'(s), \tag{34}$$

where

$$\Pi(s) = \prod_{m=k+1}^{n} (s - s_m), \quad \Pi_j'(s) = \Pi(s)/(s - s_j) \tag{35}$$

Putting $s = 0$, $s = s_1$, $s = s_{k+1}$, $\ldots$, $s = s_n$ in (3) we obtain

$$A_0 = N(0)/(-s_1)^k \prod_{j=k+1}^{n} (-s_j) \tag{36}$$

$$A_1 = N(s_1)/s_1 \prod_{j=k+1}^{n} (s_1 - s_j) \tag{37}$$

$$A_j = N(s_j)/s_j (s_j - s_1)^k \, \Pi_j'(s_j), \quad j = k+1, \ldots, n \tag{38}$$

These equations are modifications of equation (15) for unequal roots.

To obtain the values of A_2, A_3, ... A_k we can substitute other particular (and arbitrary) values of s into the identity (34) to obtain simultaneous linear equations to solve. A second method is to equate coefficients of like powers of s from both sides of identity (34). A third method is to differentiate (34) successively k-1 times and put $s = s_1$ in the derivatives. Although the third method yields the missing coefficients by explicit equations in terms of the derivatives of N(s) evaluated at $s = s_1$, it is not a practical solution. Hence, we use the first two methods.

We can obtain an explicit equation for A_k by the second method when we equate coefficients of s^n. In this way we obtain

$$A_k = c_x - A_0 - \sum_{j=k+1}^{n} A_j, \tag{39}$$

where c_x is the concentration in compartment x at $t = 0$. A possible objection to (39) is that it accumulates errors in A_0, A_{k+1}, ..., A_n. But this objection can be raised to the first method also.

Perhaps the best compromise is to use (39) to obtain A_k -- which completes the computations for a double root -- and then use $k - 2$ arbitrary values of s to obtain $k - 2$ simultaneous equations in A_2, A_3, ..., A_{k-1}.

Multiple roots are not likely to occur in practical applications. And roots of multiplicity 3 or more are much less likely to occur than roots of multiplicity 2. Hence, equations (36), (37), (38), and (39) will suffice for almost all cases.

The case of two double roots can be treated in a similar way. Let s_1 and s_2 be the double roots. Then $\tilde{C}(s)$ can be expanded in the form

$$\tilde{C}(s) = \frac{A_0}{s} + \frac{A_1}{(s - s_1)^2} + \frac{A_2}{(s - s_1)} + \frac{A_3}{(s - s_2)^2} + \frac{A_4}{(s - s_2)} + \sum_{j=5}^{n} \frac{A_j}{(s - s_j)} \tag{40}$$

Putting $s = 0$, $s = s_1$, $s = 2_2$, $s = s_5$, ..., $s = s_n$ in the identity corresponding to (34) we obtain

$$A_0 = N(0)/(-s_1)^2(-s_2)^2 \prod_{j=5}^{n}(-s_j) \qquad (41)$$

$$A_1 = N(s_1)/s_1(s_1 - s_2)^2 \prod_{j=5}^{n}(s_1 - s_j) \qquad (42)$$

$$A_2 = N(s_2)/s_2(s_2 - s_1)^2 \prod_{j=5}^{n}(s_2 - s_j) \qquad (43)$$

$$A_j = N(s_j)/s_j(s_j - s_1)^2(s_j - S_2)^2 \prod_j'(s_j), \quad j = 5, \ldots, n. \qquad (44)$$

The equation corresponding to (39) is

$$c_x = A_0 + A_2 + A_4 + \sum_{j=5}^{n} A_j. \qquad (45)$$

Use an arbitrary value, not equal to a root, to obtain a second equation to solve simultaneously with (45) to obtain A_2 and A_4.

This completes the solution for the coefficients for two double roots. However, it is very unlikely that cases of this type will occur in practice.

The inverse Laplace transforms of $\tilde{C}(s)$ in (33) and (40) can be obtained easily from the simple transform

$$\int_0^{\infty} e^{s_1 t} e^{-st} \, dt = 1/(s - s_1). \qquad (46)$$

Differentiating $(k-1)$ times with respect to s_1 we obtain

$$\int_0^{\infty} (t^h e^{s_1 t}/h!) e^{-st} \, dt = 1/(s - s_1)^{h+1}, \quad h = 1, \ldots, k-1 \qquad (47)$$

The inverse transform of (33) becomes

$$C(t) = A_0 + e^{s_1 t} \sum_{h=1}^{k} A_h \frac{t^{k-h}}{(k-h)!} + \sum_{j=k+1}^{n} A_j e^{s_j t} \qquad (48)$$

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The inverse transform of (40) becomes

$$C(t) = A_0 + e^{s_1 t}(A_1 t + A_2) + e^{s_2 t}(A_3 t + A_4) + \sum_{j=5}^{n} A_j e^{s_j t} \tag{49}$$

8. Complex Roots

Thus far in Appendix 1, the analysis applies to real or complex roots. The only differences between the case in which all roots are real and the case in which some (or all) of the roots are complex are (1) the computation of the A_j coefficients, whether or not there are multiple roots, will require arithmetical operations with complex numbers, and (2) the exponential functions of complex exponents in $C(t)$ must be expanded into real and imaginary components to obtain a form for $C(t)$ that involves only real-valued functions of real numbers. The fact that this expansion yields real-valued functions depends on well-known properties of rational functions.

First, the Fundamental Theorem of Algebra states that the polynomial equation, $D(s) = 0$, of degree n has exactly n roots (when multiplicities are counted) that are in the complex field, of which the real field is a part. Then it is easy to show that complex roots (if any) occur in conjugate pairs, if the coefficients of $D(s)$ are real. Hence, if $s_1 = r + iq$, $i = \sqrt{-1}$, is a root, then $s_2 = r - iq$ also is a root. The proof follows directly from the fact that s_1^j and s_2^j are conjugates for integral values of j.

First, assume that s_1 is a single root. Hence, s_2 is a single root. Let A_1 and A_2 be the corresponding coefficients of $1/(s - s_1)$ and $1/(s - s_2)$ in the expansion of $\hat{C}(s)$. Then

$$A_1 = \frac{N(s_1)}{(s_1 - s_2)M(s_1)}, A_2 = \frac{N(s_2)}{(s_2 - s_1)M(s_2)}, \tag{50}$$

where

$$M(s) = s \prod_{j=3}^{n} (s - s_j) \tag{51}$$

Since $N(s)$ and $M(s)$ are polynomials having real coefficients, $N(s_1)$ and $N(s_2)$ are conjugates, and $M(s_1)$ and $M(s_2)$ are conjugates. Then

it is easy to show that A_1 and A_2 in (50) are conjugate, using the fact that $s_1 - s_2 = 2$ iq. The details are elementary and are left as an exercise.

Now write A_1 and A_2 in complex form,

$$A_1 = R + iQ, \quad A_2 = R - iQ \tag{52}$$

and expand $e^{s_1 t}$ and $e^{s_2 t}$ as follows:

$$e^{s_1 t} = e^{rt}(\cos qt + i \sin qt), \quad e^{s_2 t} = e^{rt}(\cos qt - i \sin qt) \tag{53}$$

Then

$$A_1 e^{s_1 t} + A_2 e^{s_2 t} = 2e^{rt} (R \cos qt - Q \sin qt), \tag{54}$$

which is a real-valued function of real variables.

Similarly, if $s_1 = r + iq$ is a double root, then $s_2 = r - iq$ is a double root. In $C(t)$ shown in (49) A_1 and A_3 are conjugates, while A_2 and A_4 are conjugates. Then again the sum of the involved terms is a real-valued function including terms of the form (54) and these terms multipled by t.

The real-valued functions could have been used in the inverse transform $C(t)$ and their coefficients determined directly. However, it is much easier to use the exponential form to obtain the coefficients and then expand by (53) to obtain the real-valued functions. The exponential function of a complex variable is easier to use and manipulate than are the damped exponential functions of real variables.

B. Matrix Representation[*]

1. General Solution

It will be convenient to express the governing set of ordinary differential equations (1) in matrix notation:

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[*]A working knowledge of matrix analysis is assumed. Of many suitable references on the subject, two are Bellman, R., Introduction to Matrix Analysis, McGraw-Hill Book Company, Inc., New York, 1960, and Ogata, K., State Space Analysis of Control Systems, Prentice-Hall, Inc., Englewood Cliffs, NJ, 1967.

$$\frac{d\overline{C}}{dt} = \overline{M}\overline{C} + \overline{p}(t) \qquad\qquad (55)$$

with initial conditions $\overline{C} = \overline{C}(0) = \overline{C}_o$ (56)

where $\overline{C} = \overline{C}(t)$, $\overline{C}_o$, and $\overline{p}(t)$ are column vectors and $\overline{M}$ is a square matrix (m_{xy}) with

$$m_{xx} = -a_x; \; m_{xy} = b_{yx} \qquad x \neq y \qquad\qquad (57)^*$$

The complete solution to the linear dynamic equations (55) and (56) is

$$\overline{C}(t) = e^{\overline{M}t}\overline{C}_o + \int_0^t e^{\overline{M}(t - \lambda)}\overline{p}(\lambda) \, d\lambda \qquad\qquad (58)$$

2.   Constant Emission Rates

The matrix integration above may be readily carried out if $\overline{M}$ is assumed to be nonsingular and the emission rates are assumed constant. In Section A.2, $\overline{M}$ has been shown to be nonsingular unless <u>all</u> the reaction rate constants K_i are exactly zero, that is, the chemical undergoes no reactions in any of the environmental compartments. Under this assumption and for the case that $\overline{p}$ is held constant over time, equation (58) becomes

$$\overline{C}(t) = e^{\overline{M}t}\overline{C}_o - \overline{M}^{-1}(I - e^{\overline{M}t}) \, \overline{p} \qquad \det \overline{M} \neq 0 \qquad\qquad (59)$$

where $\overline{M}^{-1}$ denotes the inverse of $\overline{M}$ and I is the identity matrix.

3.   Step-wise Increasing or Decreasing Emission Rates

Now consider that the integration in equation (58) is to be performed only over a time interval T and that over this interval the emission rates $\overline{p}(t)$ are to be maintained constant at their values $\overline{p}(0)$; that is, the time interval t $[0 \leq t < \infty]$ can be decomposed into subintervals for which all emission rates $p_x(t)$ are constant in each subinterval. Thus, $\overline{p}(t) = \overline{p}(0)$ for $0 \leq t \leq T$. On this basis, equation (58) can be written as

$$\overline{C}(t) = e^{\overline{M}t}\overline{C}_o - \overline{M}^{-1}(I - e^{\overline{M}t}) \, \overline{p}(0) \qquad \det \overline{M} \neq 0 \quad 0 \leq t \leq T \qquad (60)$$

*Note that from equation (11) D(0) = -det $\overline{M}$. Also, no relationship is implied between $\overline{M}$ and M(s) in equation (51).

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If only the sequence of constant time periods T, 2T, 3T, ... is involved, equation (60) may also be written in the recurrence form

$$\overline{C}[(k+1)T] = e^{\overline{M}T}\overline{C}(kT) - \overline{M}^{-1}(I - e^{\overline{M}T})\,\overline{p}(kT) \qquad k = 0, 1, 2,... \qquad (61)$$

For example, if T = 1 year, then

$$\overline{C}(k+1) = e^{\overline{M}}\overline{C}(k) - \overline{M}^{-1}(I - e^{\overline{M}})\,\overline{p}(k) \qquad k = 0, 1, 2,... \qquad (62)$$

This is particularly easy to evaluate because the matrices $e^{\overline{M}}$ and $\overline{M}^{-1}(I - e^{\overline{M}})$ are constant independent of k.

4. Steady-state Solution

The steady-state solution in the case of constant emission rates $\overline{p}$ and for nonsingular $\overline{M}$ is obtained from equation (55) by setting $\frac{d\overline{C}}{dt} = 0$.

$$\overline{C}(\infty) = -\overline{M}^{-1}\overline{p} \qquad\qquad \det \overline{M} \neq 0 \qquad\qquad (63)$$

As expected, the steady-state compartment concentrations do not depend upon the initial conditions $\overline{C}(0)$. We next demonstrate that equations (31) and (63) are equivalent.

Let the inverse of $\overline{M}$ be the matrix $\overline{U} = (u_{xy})$. From the equation

$$\overline{M}\overline{U} = \overline{I}, \qquad\qquad (64)$$

where I is the identity matrix, the elements of the inverse matrix are

$$u_{xy} = -\gamma_{yx}/D(0), \qquad\qquad (65)$$

where γ_{yx} is the cofactor of the element in the yth row and x^{th} column of the determinant D(s) in equation (11). The solution (65) is obtained by solving n sets of n equations each, obtained by equating elements in (64).

From equations (63) and (65), $\overline{C}(\infty)$ is the column vector having the element in the xth row equal to

$$(p_1\gamma_{1x} + p_2\gamma_{2x} + \ldots + p_n\gamma_{nx})/D(0) = N_x(0)/D(0),$$

in agreement with (31). Hence, (31) and (63) are equivalent. The matrix inversion required in (63) has been performed in (31), which requires only the evaluation of determinants.

5. Solutions of the Characteristic Equation

The solutions of the characteristic equation are the "eigenvalues" of the matrix $\overline{M} = (m_{xy})$. That is, the roots s_1, s_2, $\ldots$ s_n are the solutions of the equation

$$\overline{M} - s\overline{I} = \overline{0}. \tag{66}$$

Hence, if a computer program is available for the computation of the eigenvalues of a matrix, it can be applied to $\overline{M}$ to find the roots.

If the transfer rates $b_{xy} = 0$ for all pairs (x, y), it is evident that the roots are $-K_1$, $-K_2$, $\ldots$, $-K_n$. Hence, if the transfer rates are small relative to the reaction rates, the roots will be close to the negatives of the reaction rates, which then can be used as the first approximates in estimating the roots by a numerical method, such as Newton's method.

We consider it likely that all the roots of the characteristic equation are real and negative, but have found no proof.

C. Numerical Solution

1. Matrix Approach

At this point, it should be fairly evident that the general Laplace Transform time-dependent solution presented in Section A would be profoundly difficult to implement on a computer, although the steady-state solution of equation (31) would be quite straightforward to achieve. There are three principal difficulties to overcome:

(1) The occurrence of multiple characteristic roots, though probably unlikely in practice, severely complicates construction of the solution.

(2) Computer programs to calculate the complex eigenvalues
(characteristic roots) of a matrix are not widely available.
Whether they can cope with multiple complex roots is moot.

(3) Exponential functions of complex variables must be
manipulated by computer to yield exponential functions
of real variables (i.e., sines and cosines).

In view of these problems, the matrix formulation offers very
significant computational advantages, as will be seen below. We will
assume in the following development that the emission rates $\bar{p}$ are
constant over a time interval T (i.e., the emission rates are step-wise
increasing or decreasing). For constant $\bar{p}$ over the interval $[0 \leq t \leq T]$,
equation (58) can be rewritten

$$\bar{C}(t) = e^{\bar{M}t}\bar{C}_o + \int_0^t e^{\bar{M}(t - \lambda)}\bar{p}\, d\lambda \qquad\qquad 0 \leq t \leq T \qquad\qquad (67)$$

where $\bar{C}(t)$, $\bar{C}_o$, and $\bar{p}$ are (n x 1) column vectors and $\bar{M}$ is an (n x n)
square matrix defined in equation (57).

Next we will show how $e^{\bar{M}t}$ and the definite integral in equation
(67) may be computed simultaneously. We define

$$\bar{N} = \left[\begin{array}{c|c} \bar{M} & \bar{p} \\ \hline \bar{0} & 0 \end{array} \right] \qquad\qquad (68)$$

where $\bar{N}$ is a constant (n + 1) x (n + 1) matrix. Then it folllows that

$$e^{\bar{N}t} = \left[\begin{array}{c|c} e^{\bar{M}t} & \int_0^T e^{\bar{M}(t - \lambda)}\bar{p}\, d\lambda \\ \hline \bar{0} & 1 \end{array} \right] \qquad\qquad (69)$$

where $\bar{0}$ is a (1 x n) row vector, each of whose elements is zero.

We can prove equation (69) as follows. By definition

$$e^{\overline{N}t} = \sum_{k=0}^{\infty} \frac{t^k \overline{N}^k}{k!} = \overline{I} + \sum_{k=1}^{\infty} \frac{t^k}{k!} \left[\begin{array}{c|c} \overline{M}^k & \overline{M}^{k-1}\overline{p} \\ \hline \overline{0} & 0 \end{array} \right] \tag{70}$$

Continuing to simplify equation (70), we obtain

$$e^{\overline{N}t} = \left[\begin{array}{c|c} \sum\limits_{k=0}^{\infty} \frac{t^k \overline{M}^k}{k!} & \sum\limits_{k=0}^{\infty} \frac{t^{k+1} \overline{M}^k \overline{p}}{(k+1)!} \\ \hline \overline{0} & 1 \end{array} \right] \tag{71}$$

Now consider the following integral

$$\int_0^t e^{\overline{M}(t-\lambda)} \, \overline{p} \, d\lambda = -\int_t^0 e^{\overline{M}s} \, \overline{p} \, ds = \int_0^t e^{\overline{M}s} \, \overline{p} \, ds \tag{72}$$

where $s = t - \lambda$.

$$\int_0^t e^{\overline{M}s} \, \overline{p} \, ds = \int_0^t \left[\sum_{k=0}^{\infty} \frac{(\overline{M}s)^k}{k!} \, \overline{p} \right] ds = \sum_{k=0}^{\infty} \int_0^t \frac{(\overline{M}s)^k}{k!} \, \overline{p} \, ds$$

$$= \sum_{k=0}^{\infty} \frac{\overline{M}^k}{k!} \frac{t^{k+1}}{k+1} \, \overline{p} = \sum_{k=0}^{\infty} \frac{t^{k+1} \overline{M}^k}{(k+1)!} \, \overline{p} \tag{73}$$

Comparing the final result of equation (73) with equation (71), we see that equation (69) is proven.

2. Computation of $e^{\overline{N}t}$

We see from equation (69) that the computation of the matrix exponential defined by

$$e^{\overline{N}t} = \sum_{r=0}^{\infty} \frac{(\overline{N}t)^r}{r!} \qquad (74)$$

will permit the calculation of $\overline{C}(t)$ from equation (67). Note that the solution (67) also holds when $\overline{M}$ is singular.

The algorithm we used for computing the exponential of a matrix [equation (74) is not efficient for this purpose] is based upon diagonal Padé table rational approximations.[*] The basic steps for computing $e^{\overline{L}}$, where $\overline{L}$ is an (n x n) matrix, are as follows:

1. Scale down by

    (a) forming $\overline{L}' = \overline{L} - [\mathrm{tr}(\overline{L})/n]\overline{I}$ where $\mathrm{tr}(\overline{L})$, the trace of $\overline{L}$, is the sum of the elements on the main diagonal of $\overline{L}$ and $\overline{I}$ is the identity matrix;

    (b) determining $\|\,\overline{L}'\,\|$, the norm of $\overline{L}'$, which is the largest of the absolute sum of the elements of each column;

    (c) calculating b equal to the larger of 1 and the logarithm to the base 2 of $\|\,\overline{L}'\,\|$, rounded up to the nearest integer; and

    (d) computing $\overline{L}'' = \overline{L}'\,2^{-b}$.

2. Calculate the exponential of the scaled down matrix, $\overline{L}''$, by

    (a) computing $Q(\overline{L}'')$ and $Q(-\overline{L}'')$ where $Q(\overline{L}'') = \overline{P} + \overline{N}$ and

    $$\overline{P} = \overline{I} + c_2\overline{L}''^2 + c_4\overline{L}''^4 + c_6\overline{L}''^6$$

---

[*] R. C. Ward, Numerical Computation of the Matrix Exponential with Accuracy Estimate, SIAM J. Numer. Anal, 14 (Sept. 1977), pp. 600-610.

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$$\overline{N} = c_1 \overline{L}" + c_3 \overline{L}" + c_3 \overline{L}"^3 + c_5 L"^5$$

and the (c_i) are those shown in Table 1.

(b) computing $e^{L"} = Q^{-1}(-\overline{L}") \; Q \; (\overline{L}")$

3. Scale the matrix up by

(a) calculating $e^{\overline{L}'} = (e^{\overline{L}"})^{2^b}$, i.e., square $e^{\overline{L}"}$ b times;

(b) calculating $e^{\overline{L}} = e^{tr(\overline{L})/n} e^{\overline{L}'}$

Table 1

Coefficients for the $\overline{P}$ and $\overline{N}$ Polynomial Forms

i	c_i
1	1/2
2	5/44
3	1/66
4	1/792
5	1/15840
6	1/665280

APPENDIX 2

CONVECTIVE MASS TRANSFER

A.   Transport Between Liquid and Vapor Phases

In order to obtain the solution to equation (2) in Section IV.A,
we must first evaluate the convective transport of the chemical between
the liquid and vapor phases. In particular, we need to estimate the
following transport rates:

$T_{sw \rightarrow a}$ = convective transport rate from surface water to air, kg/yr

$T_{a \rightarrow sw}$ = convective transport rate from air to surface water, kg/yr

$T_{gm \rightarrow a}$ = convective transport rate from ground (soil) moisture to air, kg/yr

$T_{a \rightarrow gm}$ = convective transport rate from air to ground (soil) moisture, kg/yr

The rate of mass transfer across a phase boundary can be expressed
in terms of an overall mass-transfer coefficient multiplied by a
concentration difference:

$$N_{net} = k_y (y^* - y) \tag{1}$$

In this equation N_{net} is the net molal flux of chemical from surface
water to air expressed as kg moles/yr/meter^2. The quantity y^* represents
the mole fraction of chemical in air at the interface which would be in
equilibrium with the actual composition of the surface water containing
the chemical. The quantity y is the mole fraction of chemical at some
point within the uniformly-mixed air compartment. Thus, $(y^* - y)$
represents the overall driving force for mass transfer between the
water-air phases. The mass-transfer coefficient k_y is expressed in the
units kg moles/yr/meter^2. The subscript y signifies that it applies to
the gas phase and must be used in conjunction with a driving force
expressed in terms of mole fraction in the gas phase.

Equilibrium between the gas and liquid phases at the interface is assumed to follow Henry's law,* such that

$$y^* P = (C_{sw}/S) V_p \qquad \text{for } C_{sw} \leq S$$

$$= V_p \qquad \text{for } C_{sw} \geq S \tag{2}$$

where

P = atmospheric pressure = 1 atm

C_{sw} = concentration of chemical in surface water as weight fraction, kg of chemical/kg of solution

S = solubility of chemical in water as weight fraction, kg of chemical/kg of solution

V_p = vapor pressure of chemical at ambient temperature, atm

Equation (2) may now be used to eliminate y^* from equation (1):

$$N_{net} = k_y (V_p C_{sw}/SP - y) \tag{3}$$

For dilute mixtures of chemical in air

$$y = (M_a/M) C_a \tag{4}$$

where

M_a = molecular weight of air (28.97)

M = molecular weight of chemical

_____

*Valid for low-solubility compounds. See Mackay, D., Wolkoff, A.W., Environ. Sci. Technol. 7, 1973, pp. 611 - 614.

Equation (3) can be rewritten in terms of a net convective transport rate $\dot{T}_{net}$ between water and air:

$$\dot{T}_{net} = k_y A \left(\frac{MV_p}{SP} C_{sw} - M_a C_a \right) \tag{5}$$

where $\dot{T}_{net}$ has units of kg/yr and A is the interfacial area across which transport occurs, expressed in meter^2.

We now define

$$\dot{T}_{sw \rightarrow a} = \left(k_y MA V_p / SP \right) C_{sw} \tag{6}$$

and

$$\dot{T}_{a \rightarrow sw} = k_y M_a A C_a \tag{7}$$

then

$$\dot{T}_{net} = \dot{T}_{sw \rightarrow a} - \dot{T}_{a \rightarrow sw} \tag{8}$$

which is consistent with equation (2) in Section IV.A.

In equation (5) only k_y is presumed to be unknown at this point.

On both theoretical and experimental grounds for mass transfer with laminar or turbulent flow, it has been shown that[*]

$$Sh = \alpha(Re)^{\beta}(Sc)^{\gamma} \tag{9}$$

where

Sh = dimensionless Sherwood number = $kM_a L/\rho_a D_{ca}$

Re = dimensionless Reynolds number = $Lv_a \rho_a /\mu_a$

Sc = dimensionless Schmidt number = $\mu_a /\rho_a D_{ca}$

M_a = molecular weight of air

L = characteristic path length of convective transport, meters

ρ_a = density of air, kg/meter^3

D_{ca} = diffusivity of chemical through air, meter^2/sec.

v_a = velocity of air, meter/sec.

μ_a = viscosity of air, kg/meter/sec.

α, β, γ = constants

We next determine the convective transport (evaporation) of <u>water</u> across the same boundary layer that the chemical traverses. Equation (9) also holds in this case with the substitution of k_w for k and D_{wa} for D_{ca}, where

k_w = mass-transfer coefficient of water,
kg moles of water/yr-meter^2

D_{wa} = diffusivity of water vapor through air,
meter^2/sec. (2.60 x 10^{-5} meter^2/sec at 25°C)

Hence,

$$\frac{k/D_{ca}}{k_w/D_{wa}} = (D_{wa}/D_{ca})^{\gamma} \tag{10}$$

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[*] See for example, Bennett, C.O. and Myers, J.E., <u>Momentum, Heat, and Mass Transfer</u>, McGraw-Hill Book Company, Inc., New York, 1962.

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For many situations of practical interest (e.g., laminar flow)

$$\gamma = 1/3 \tag{11}$$

so that

$$k = k_w (D_{ca}/D_{wa})^{2/3} \tag{12}$$

Under the reasonable assumption that D_{ca} is a known physical property or can be estimated,* we must still find a means to estimate k_w. We will estimate k_w based upon measured rates of evaporation of water throughout the United States. According to equation (6) the rate of evaporation of water from lakes and streams may be expressed as

$$\dot{T}_w = \left(k_w M_w A \ V_{pw} \middle/ S_w P \right) C_w \tag{13}$$

where

M_w = molecular weight of water (18.0)

V_{pw} = vapor pressure of water at ambient temperature, atm

S_w = solubility of water, kg/kg (1.0)

P = atmospheric pressure (1.0 atm)

C_w = weight fraction of water, kg/kg (1.0)

Thus,

$$k_w = \dot{T}_w / M_w A \ V_{pw} \tag{14}$$

---

* See Appendix 3

$\dot{T}_w$ may be calculated from the average U.S. annual evaporation rate measured in meters, d

$$\dot{T}_w = dA\rho_w \qquad (15)$$

Combining equations (9) and (10), we obtain

$$k_w = d\rho_w / M_w V_{pw} \qquad (16)$$

The rate of evaporation from lakes throughout the United States ranges from 20-90 inches per year.[*]   We will use an average value of 70 inches at 6°C. Then with

$$d = 70 \text{ inches/yr} = 1.78 \text{ meter/yr}$$
$$\rho_w = 1000 \text{ kg/meter}^3$$
$$M_w = 18.0$$

and

$$V_{pw} = 0.0092 \text{ atm. at } 6°C,$$

$$k_w = 11 \times 10^3 \text{ kg moles/yr/meter}^2$$

Hence equation (6) becomes

$$\dot{T}_{sw \to a} = \left[11 \times 10^3 \, M \, A \, (D_{ca}/D_{wa})^{2/3} V_p / SP \right] C_{sw} \qquad (17)$$

which is identical to equation (3) in the Phase I report.

Similarly, equation (7) becomes

$$\dot{T}_{a \to sw} = \left[11 \times 10^3 \, M_a A \, (D_{ca}/D_{wa})^{2/3} \right] C_a \qquad (18)$$

_____

[*]   U.S. Weather Bureau, for period 1946-55.

Equation (18) differs somewhat from equation (4) in the Phase I report.

The expression for the rate of transport from ground (soil) moisture to air, $\dot{T}_{gm \to a}$, is identical to equation (17) and the expression for the reverse rate from air to ground moisture, $\dot{T}_{a \to gm}$, is identical to equation (18).

B.   Transport Between Air and Air Moisture

Because of the very large surface area available, the mass transfer of chemical between air (a) and atmospheric moisture (am) is very rapid; in effect the chemical is in equilibrium between the two compartments, Thus,

$$\dot{T}_{am \to a} = \dot{T}_{a \to am} \tag{19}$$

or

$$r_{am \to a} C_{am} = r_{a \to am} C_a \tag{20}$$

Again applying Henry's law, we obtain

$$\frac{r_{am \to a}}{r_{a \to am}} = \frac{C_a}{C_{am}} = MV_p/M_a SP = 1/J \tag{21}$$

where J is a constant.

Equation (21) indicates that the chemical concentrations in the air and air moisture compartments are not independent. Therefore, one of these two compartments should be eliminated from the set of equations (1) - (4) in Appendix 1. Suppose we eliminate the redundant air moisture compartment. Then it is easy to show that for the remaining set of 18 differential equations, the new coefficients are given by

$$a'_a = [(a_a - b_{a,am}) + J(a_{am} - b_{am,a})] (1 + J)^{-1} \tag{22}$$

$$b'_{y,a} = (b_{y,a} + b_{y,am})(1 + J)^{-1} \qquad y \neq a, am \tag{23}$$

$$p_a'(t) = [p_a(t) + p_{am}(t)](1 + J)^{-1} \qquad (24)$$

and $\quad b_{a,y}' = b_{a,n} + J \, b_{am,y} \qquad\qquad y \neq a, am \qquad (25)$

All other terms a_x, $b_{y,x}$, $b_{x,y}$, and $p_x(t)$ for $x,y \neq a$ or am are unchanged from equations (2) – (4) in Appendix 1.

Furthermore, by expanding the expression for a_a' in equation (22), it can be shown that a_a' is independent of both $r_{am \rightarrow a}$ and $r_{a \rightarrow am}$. Hence, there is no need to evaluate either of these in order to use the model.

Once the differential equations are solved for the air and other 17 compartments, we can calculate

$$C_{am} = J C_a . \qquad (26)$$

APPENDIX 3

ESTIMATION OF DIFFUSION COEFFICIENTS

A.   Diffusion Coefficient for Chemical in Air

There are several empirical correlations reported in the literature
for estimating the diffusion coefficient (diffusivity) for a binary gas
system at low pressure. This physical property is required in order to
evaluate the rate of convective mass transfer of the chemical between
aqueous and air phases. It is also required to estimate the rate of
transport between soil moisture and air. It should be noted, however,
that an experimentally measured value of the diffusivity will always be
preferred to an estimate based on empirical methods.

The method of Wilke-Lee* has been found to be slightly more reliable
than other equations for predicting the diffusion coefficient in air
at ambient conditions. This method is accurate to perhaps 5-10 percent
of observed values.

The empirical correlation (suggested from the solution of the
Boltzmann equation) is

$$D_{ca} = \frac{B \; T^{3/2} \; M_r^{1/2}}{P \, \sigma_{ca}^2 \; \Omega} \qquad \text{Meters}^2/\text{Sec}$$

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*Reid, R. C., Prausnitz, J. M. , and Sherwood, T. K., The Properties of
Gases and Liquids, Third Edition, McGraw-Hill Book Company, Inc., New
York, 1977, pp. 553-560.

where

$$B = 10^{-7} \left(2.17 - 0.50\ M_r^{1/2} \right)$$

$$M_r = \left(\frac{1}{28.97} + \frac{1}{M_c} \right)$$

M_c = Molecular Weight of Chemical

T = Absolute Temperature   (293 $^{\circ}$K)

P = Atmospheric Pressure (1.0 atm)

$$\sigma_{ca} = \left(3.711 + 1.18\ v_c^{1/3} \right)/2 \quad \text{Å}$$

v_c = Molal volume at normal boiling point of chemical, cm^3/mole, estimated by the additive-volume increment method of Le Bas, using Table A3-1.

$$\Omega = A(T^*)^{-B} + C\ exp(-DT^*) + E\ exp\ (-FT^*) + G\ exp\ (-HT^*)$$

with

A	=	1.06036	E	=	1.03587
B	=	0.15610	F	=	1.52996
C	=	0.19300	G	=	1.76474
D	=	0.47635	H	=	3.89411

and

$$T^* = \frac{T}{\sqrt{(78.6)\ (1.15\ T_b)}}$$

TABLE A3-1

ADDITIVE-VOLUME INCREMENTS FOR THE CALCULATION OF MOLAL

VOLUMES v_b AT THE NORMAL BOILING POINT

BY METHOD OF LE BAS[*]

Increment, cm^3/g-mol[**]

	Increment, cm^3/g-mol
Carbon	14.8
Hydrogen	3.7
Oxygen (except as noted below)	7.4
In methyl esters and ethers	9.1
In ethyl esters and ethers	9.9
In higher esters and ethers	11.0
In acids	12.0
Joined to S, P, N	8.3
Nitrogen	
Doubly bonded	15.6
In primary amines	10.5
In secondary amines	12.0
Bromine	27
Chlorine	24.6
Fluorine	8.7
Iodine	37
Sulfur	25.6
Ring, three-membered	-6.0
Four-membered	-8.5
Five-membered	-11.5
Six-membered	-15.0
Naphthalene	-30.0
Anthracene	-47.5

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[*]Ibid, pp. 57-60.

[**]The additive-volume procedure should not be used for simple molecules. The following approximate values are employed in estimating diffusion coefficients: H_2, 14.3; O_2, 25.6; N_2, 31.2; air, 29.9; CO, 30.7; CO_2, 34.0; SO_2, 44.8; NO, 23.6; N_2O, 36.4; NH_3, 25.8; H_2O, 18.9; H_2S, 32.9; COS, 51.5; Cl_2, 48.4; Br_2, 53.2; I_2, 71.5.

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$$T_b = \text{Normal boiling point, } {}^{\circ}K$$

The variables above to be provided on input are M_c, v_c, and T_b.

B. Diffusion Coefficient for Chemical in Water

The diffusivity of the chemical in a dilute aqueous solution is required in order to estimate the chemical transport rate between ground (soil) moisture and soil, equations (13) and (14) in the Phase I report. One of the best methods for estimating infinite dilution diffusion coefficients of nonelectrolytes in water is the correlation of Hayduk and Laudie:[*]

$$D^{\circ}_{cw} = 13.26 \times 10^{-9} \eta_w^{-1.14} v_c^{-0.589}$$

where

D°_{cw} = binary diffusion coefficient at infinite dilution, meters^2/sec

η_w = viscosity of water, cP (1.002 cP at 20°C)

v_c = solute (chemical) molal volume at normal boiling point, cm^3/g-mol

v_c may be estimated by the additive-volume increment method of Le Bas using Table A3-1. The average estimation error for this method is about 4 percent.

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[*] Ibid, pp. 567-578. N.B. Exponent of η_w in reference is incorrect and should be -1.14.

APPENDIX 4

ESTIMATION OF EMISSION RATES

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% will 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 addition to these three categories of use, total "emissions" from
sources other than intended production will have to estimated. This
category includes "emissions" from unintended production, such as pro-
duction 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 also have to be estimated and provided to
the model.

The emissions in each category, computed as outlined above, must
next be allocated to the following compartments:

- Air

- Surface Water (Lakes and Streams)

- Soil Moisture (0 - 1 Meter)

APPENDIX 5

PROGRAM DESCRIPTION

COMPUTER MODEL OVERVIEW

The computer model is divided into five major sections:

Model Options	Section	Description
1,2,3	I	Data input
6	II	Intermediate calculation
4,5	III	Display of section I and II (optional)
6	IV	Final calculations
7	V	Final output from section

The programs are called in a sequential fashion upon executing option one. Options two and three also start this process, but skip one half of the data input.

MODEL

I.
- INPUT
  - *CALCΔDCA
  - *CALCΔDCW
- INPÙTE

II.
- FORMΔR
- FORMΔM
  - CTYPE

III.
- *PΔINP
- *PΔINT
  - PRINTR
  - PRINTF
  - PRINTM

IV.
- RUN
  - RUN1
  - RUN2   All of these call MEXP IDEN
  - RUN3

V.
- OUTPUT

* Will be called at user option.

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DESCRIPTION OF PROGRAMS

MODEL	The main program is automatically called upon entering the workspace, but it can be explicitly executed as well.
INPUT	Input program for physico-chemical data and compartment data
CALCΔDCA CALCΔDCW	These programs calculate the diffusivity of the chemical in air and water respectively. They are called only if the diffusivities are not available.
INPUTE	Input program for all emission-related data.
FORMΔR	Forms the convective flow matrix by applying the physico-chemical and compartment data.
FORMΔM	Forms the matrix of coefficients using reaction rates and the bulk and convective flows.
CTYPE	The compartment type 1 = air, 2 = water, 3 = soil; used for assigning reaction rates to compartments.
PΔINP	Prints the physical chemical data and emission data with the option to display compartment data.
PΔINT	Prints intermediate results by sequentially calling the following three subprograms:
PRINTR	For the convective flows
PRINTF	For the bulk flows
PRINTM	For the matrix of coefficients
RUN	Calls appropriate module for the specified emission type either 1, 2, or 3.
OUTPUT	Displays the final results: concentration in kg/kg and as a percent by compartment for each year.

Note all other programs are general APL utilities to aid in formatting, etc. Three programs are independent of the model:

DET   A stand-alone program for calculating matrix determinant.

WSDOC   For printing out an entire workspace of functions. This calls ALP, which alphabetizes a character matrix.

TABS   For invoking tabular output on an AJ832 terminal.

```
      )WSID
IS MODEL
         LWA
644840
         LLX
MODEL
      )FNS
ALP        CALCΔDCA                          CALCΔDCW          CENTER   COLNAMES          CTYPE    D         DET       FORMΔM   FORMΔR
IDEN       INPUT      INPUTE    LIP   LIP2    MEXP     MODEL    NIP      OUTPUT   PRINTF   PRINTM   PRINTR    PΔINP     PΔINT    RJUST
RUN        RUN1       RUN2      RUN3  SQ      TABS     VTM      WSDOC    YN       ΔFMT
      )VARS
AX         BASEYR     COMP      COMPA CR      CX       CXO      DCA      DCW      FDOT     FORG     IIID      K         KX       LEN
LF         MA         MBAR      MW    NAME    NO       NUM      PDOT     PER      R        RHO      S         SOL       TB       TYPE
VARS       VARSI      VARS2     VC    VP      WPC      WX       YRS      ΔC       ΔCW      ΔDEPTH   ΔMAX


      ∇ Z←ALP X;A
[1]    A←' ABCDEFGHIJKLMNOPQRSTUVWXYZΔABCDEFGHIJKLMNOPQRSTUVWXYZΔ0123456789|}'
[2]    Z←XLΔ(1+ρA)⌊QA⍳X;]
      ∇


      ∇ Z←CALCΔDCA X;B;MC;MR;O;P;S;T;T;VC
[1]    ⍝CALCULATES THE DIFFUSIVITY IN AIR (M*2/SEC.)
[2]    MC←X[1] ◇ TB←X[2] ◇ VC←X[3]
[3]    T←293 ◇ P←1
[4]    O← 1.06036 0.193 1.03587 1.76474 , 0.1561 0.47635 1.52996 3.89411
[5]    MR←÷/MA,MC
[6]    B←1E¯7×(2.17-(MR*÷2)÷2)
[7]    S←(3.711+1.18×VC*÷3)÷2
[8]    T←T÷(78.6×1.15×TB)*÷2 ◇ O←+/O[⍳4]÷(T*O[5]),*T×O[5+⍳3]
[9]    Z←(B×(T*3÷2)×(MR*÷2))÷P×(S*2)×O
      ∇


      ∇ Z←CALCΔDCW VC;NW
[1]    ⍝CALCULATES DIFFUSION COEFFICIENT OF THE SUBSTANCE IN WATER
[2]    NW←1.002 ⍝VISCOSITY OF WATER AT 20 DEG. CENT.
[3]    Z←13.26×(10*¯9)×(NW*¯1.14)×VC*¯0.589
      ∇


      ∇ Z←W CENTER X
[1]    Z←W↑(-⌊0.5×W+ρ,X)↑X
      ∇
```

```
      ∇ Z←FWS COLNAMES LV;BV;LOC;LEN;MAX
[1]   Z←'' ◇ →(0=ρFWS←,FWS)ρ0
[2]   BV←LV=1↑LV←,LV ◇ MAX←⌈/FWS)⌈⌈/LEN←(1↓LOC,1+ρLV)-1+LOC←BV/ιρLV
[3]   Z←(,LEN∘.≥⌽ιMAX)\(~BV)/LV ◇ →(1=ρFWS)ρEND2
[4]   Z←(,FWS∘.≥ιMAX)/Z ◇ →0
[5]   END2:Z←,((ρLEN),-FWS)↑((ρLEN),MAX)ρZ
      ∇


      ∇ Z←CTYPE
[1]   ⍝COMPARTMENT TYPE (1=AIR, 2=WATER, 3=SOIL)
[2]   Z← 1 2 ,(11ρ2),6ρ3
      ∇


      ∇ Z←X D Y
[1]   ⍝DIVISION BY ZERO
[2]   Z←(0≠Y)×∧÷Y+0=Y
      ∇


      ∇ Z←DET A;B;P;I
[1]   ⍝EVALUATES A DETERMINANT
[2]   ⍝BASED ON PGM FROM IBM APL LANG REF MANUAL P. 87
[3]   I←⎕IO ◇ Z←1
[4]   L1:P←(|A[;I])ι⌈/|A[;I]
[5]   →(P=I)/L2
[6]   A[I,P;]←A[P,I;]
[7]   Z←-Z
[8]   L2:B←A[I;I] ◇ Z←B×Z
[9]   →((Z=0)∨1=(ρA)[1])/0
[10]  A← 1 1 ↓A-(A[;I]÷B)∘.×A[I;]
[11]  →L1
      ∇


      ∇ FORMM;A;B;HO
[1]   ⍝FORMS 'M' MATRIX
[2]   ⍝ΔC=1 → COMBINE AIR AND AIR MOISTURE FOR CALCULATIONS
[3]   RHO←R+(2ρΔCH)↑(0 1 ,11ρ1)\(0 1 ,11ρ1)\FDOT
[4]   ⍱ΔC/'RHO[1 2;1 2]←0'
[5]   B←⍉RHO D(ρRHO)ρWX
[6]   KX←(5↑K)[CTYPE]
[7]   A←KX+(+/RHO)÷WX
[8]   ⍝DIAGONAL INSERT OF AX IN M
[9]   MBAR←(-0,ι¯1+ΔCH)⌽(-A), 0 1 ↓(0,ι¯1+ΔCH)⌽B
[10]  →(~ΔC)ρ0
[11]  CR←(MA×S)÷MW×VP ⍝ CONCENTRATIONS RATIO OR 'K'
[12]  MBAR[;2]←MBAR[;2]×CR
[13]  MBAR[;2]←+/MBAR[; 1 2]
[14]  MBAR[2;]←(+/MBAR[1 2 ;])÷1+CR
[15]  MBAR← 1 1 ↓MBAR
      ∇
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     ∇ FORMAR;A;DR;DWA;EQ13;EQ14
[1]   ⍝EQUATIONS NOS. REFER TO PHASE 1 REPORT
[2]   ⍝INDICIES ARE COMPARTMENT NOS. (X→Y)
[3]   ⍝SET UP FOR ORIGINAL SYSTEM OF 20 COMPARTMENTS
[4]    R← 20 20 ρ0
[5]   ⍝A IS THE 20 COMPARTMENT VERSION OF AREA, 'Aλ'
[6]    A←0,AX
[7]   ⍝DIFFUSIVITY OF WATER IN AIR
[8]    DWA←2.6×10*¯5
[9]   ⍝DIFFUSIVITIES RATIO
[10]   DR←(DCA÷DWA)*2÷3
[11]  ⍝FORMERLY CONVERTED GM./GM. TO MOLES/MOLE.
[12]   S←SOL
[13]  ⍝12B 12A
[14]   R[1;2]←7E25 ◊ R[2;1]←11×1E25×VP÷S
[15]  ⍝7 A→L
[16]   R[1; 4 5 6]←11000×A[4 5 6]×MA×DR
[17]  ⍝3 SW→A   GENERAL FORM OF 5 6 9
[18]   R[4 5 6 ;1]←11×1000×A[4 5 6]×MW×DR×VP÷S
[19]  ⍝13 GM→SOIL
[20]   EQ13←ΔDEPTH×1.1×(10*19)×DCW×FORG
[21]   R[6;15]←EQ13[1] ◊ R[7;16]←EQ13[2] ◊ R[8;17]←EQ13[3] ◊ R[9;18]←EQ13[4] ◊ R[10;19]←EQ13[5] ◊ R[11;20]←EQ13[6]
[22]  ⍝14 SOIL→GM
[23]   EQ14←ΔDEPTH×1.1×(10*19)×DCW×(1÷WPC)
[24]   R[15;6]←EQ14[1] ◊ R[16;7]←EQ14[2] ◊ R[17;8]←EQ14[3] ◊ R[18;9]←EQ14[4] ◊ R[19;10]←EQ14[5] ◊ R[20;11]←EQ14[6]
[25]  ⍝ELIMINATE OLD 3RD COMPARTMENT
[26]   R←(~(ι20)∊3)/(~(ι20)∊3)/R
      ∇


      ∇ Z←IDEN N
[1]   ⍝IDENTITY MATRIX OF RANK N
[2]    Z←(2ρN)ρ1,Nρ0
      ∇
```

```
      ∇ INPUT;DEFAULT;I;SAME;TR;TRI
[1]    LF,'PHYSICO-CHEMICAL DATA',LF
[2]    NAME←40↑LIP 'ENTER CHEMICAL NAME: '
[3]    NO←40↑LIP 'ENTER RUN DESCRIPTOR: '
[4]    MW← 1 0 1000 NIP 'ENTER MOLECULAR WEIGHT:'
[5]    ⍝DIFFUSIVITIES INPUTS? NO
[6]    VP← 1 0 10 NIP 'ENTER VAPOR PRESSURE (ATM.): '
[7]    SOL← 1 0 100000000 NIP 'ENTER SOLUBILITY IN WATER (KG/KG):'
[8]    WPC← 1 0 NIP 'ENTER SOIL/WATER PARTITION COEFFICIENT FOR ORGANIC FRACTION OF SOIL:'
[9]    ⍝DIFFUSIVITY INPUTS
[10]   →(~YN 'DO YOU HAVE THE DIFFUSIVITY IN AIR? ')ρDA2
[11]   TB←VC←0 ◇ DCA← 1 0 0.0001 NIP 'ENTER IT (METER*2/SECOND): ' ◇ →DW
[12]   ⍝CALCULATED DIFFUSIVITY
[13]   DA2:TB← 1 0 NIP 'ENTER NORMAL BOILING POINT (°K):'
[14]   VC← 1 0 1000 NIP 'ENTER MOLAL VOLUME AT NORMAL BOILING PT. (CM*3/G-MOL):'
[15]   DCA←CALC∆DCA MW,TB,VC
[16]   DW:→(~YN 'DO YOU HAVE THE DIFFUSIVITY IN WATER? ')ρDW2
[17]   DCW← 1 0 1E¯8 NIP 'ENTER IT (METER*2/SECOND): ' ◇ →DEND
[18]   ⍝TEST IF MOLALF MOLAL VOL HAS ALREADY BEEN INPUT PROCEED TO CALCULATION, OTHERWISE ENTER IT
[19]   DW2:→(0≠VC)/DW3 ◇ VC← 1 0 1000 NIP 'ENTER MOLAL VOL. AT NORMAL BOILING POINT (CM*3/G-MOL)' ◇ →DW4
[20]   DW3:'DIFFUSIVITY IN WATER HAS BEEN CALCULATED'
[21]   DW4:DCW←CALC∆DCW VC
[22]   DEND:
[23]   ⍝REACTION CONSTANTS
[24]   I←1 ◇ TRI←0 VIM '/AIR/WATER/SOIL' ◇ K←(1ρTRI)ρ0
[25]   LRC:TR←S∆ TRI[I;]
[26]   '' ◇ →(~YN 'DO YOU HAVE THE REACTION RATE CONSTANT IN ',TR,'? ')ρLHL ◇ K[I]← 1 0 NIP 'ENTER THE RATE (PER YEAR): '
[27]   →LRCE
[28]   ⍝CALCULATED REACTION CONSTANT
[29]   LHL:→(~YN 'DO YOU HAVE THE HALF-LIFE IN ',TR,'? ')ρLRE
[30]   K[I]←(⍟2)÷ 1 0 NIP 'ENTER HALF-LIFE (YEARS): ' ◇ →LRCE
[31]   ⍝GENERAL APPROXIMATION OF REACTIVITY
[32]   LRE:'ENTER I=INERT, P=PERSISTANT, M=MODERATE, H=HIGH, E=EXTREME'
[33]   K[I]←(⍟2)÷10*¯3+'EHMPI'⍳'IPMHE' LIP2 'ENTER THE LETTER FOR THE CHEMICAL''S GENERAL LEVEL OF REACTIVITY IN ',TR,':
       '
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[34]  LRCB:I←I+1 ◇ →(3≥I)ρLRC ◇ LF
[35]  ASECTION 2: TEMPERATURE
[36]  AASSUMED TO BE 20 DEGREES CENT.
[37]  MA←28.97 ATHE MOLECULAR WEIGHT OF AIR
[38]  FORG← 0.1 0.05 ,4ρ0.03
[39]  WX←(10*15)× 16.2 0.18 18.8 0.05 0.6 0.4 ,(4ρ0.2), 63.7 63.7 50 15.2 60.9 76.1 76.1 228.5 304.4
[40]  AX←ACN↑(10*11)× 0 0 1.4 0.25 7.69 0 0 0 0
[41]  →(YN 'DO YOU WISH TO USE DEFAULT VALUES FOR ALL COMPARTMENT DATA? ')ρ0
[42]  LF,'COMPARTMENT DATA' ◇ 'TO USE THE DEFAULT VALUES FOR ANY INPUT TYPE ''DEFAULT'''
[43]  ASECTION 3:  FORG INPUT
[44]  DEFAULT←FORG
[45]  FORG← 6 0 1 WIP 'ENTER FRACTION OF ORGANIC MATERIAL IN EACH OF THE 6 SOIL COMPARTMENTS:'
[46]  ASECTION 6:  MASS OF COMPARTMENTS
[47]  DEFAULT←WX
[48]  WX←(ACN,0) WIP 'ENTER THE MASS FOR EACH COMPARTMENT (KG.): '
[49]  ASECTION 7:  EFFECTIVE SURFACE AREA OF COMPARTMENTS
[50]  AONLY WATER COMPARTMENTS HAVE AREAS
[51]  DEFAULT←AX
[52]  AX←(ACN,0) WIP 'ENTER SURFACE AREA OF EACH COMPARTMENT (METER*2)'
[53]  ASECTION 8:  BULK FLOWS
[54]  ANO LONGER AN INPUT
[55]  FDOT←IIID
      ∇
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     ∇ INPUTE;BV;C;C2;DEFAULT';I;SAME;TR
[1]   LF,'EMISSION RELATED DATA',LF
[2]   ⍝SECTION 4: INITIAL CONCENTRATION CONDITIONS OR LOADINGS
[3]   DEFAULT←∆CNρ0
[4]   CX0←(∆CN,0) NIP 'ENTER ',(⍪∆CN),' INITIAL CONCENTRATIONS: '
[5]   I←LEX 'DEFAULT' ◇ LF,'FROM NOW ON, ''DEFAULT'' IS NO LONGER A VALID INPUT'
[6]   ⍝SECTION 5: EMISSION RATES
[7]   PER←0 ◇ C←0 VTM '/AIR/LAKES/STREAMS/SOIL MOISTURE' ◇ C2←¯1↑SQ(' ',RJUST C),',' ◇ BV←∆CN↑ 1 0 1 1 1 ◇ CX←(∆CN,0)ρ0
[8]   LP:'ENTER 1  FOR CONSTANT EMISSION RATES'
[9]   'ENTER 2  FOR CONSTANT PERCENT INCREASE'
[10]  'ENTER 3  FOR INCREMENTAL EMISSION RATES'
[11]  ⍝BRANCH TO THE INPUT SUBSECTION FOR THE SPECIFIED EMISSION RATE TYPE
[12]  TYPE← 1 1 3 NIP 'ENTER OPTION NUMBER:' ◇ →(L1,L2,L3)[TYPE]
[13] L1:PDOT←(1,∆CN)ρBV\((1ρρC),0) NIP 'ENTER EMISSION RATES FOR ',C2,' (KG./YEAR): '
[14]  YRS←,((-∆MAX),0) NIP 'ENTER YEARS OF INTEREST:' ◇ LEN←YRS-0,¯1↓YRS ◇ →0
[15] L2:PDOT←(1,∆CN)ρBV\((1ρρC),0) NIP 'ENTER EMISSION RATES FOR ',C2,' (KG./YEAR): '
[16]  LEN←0 ◇ PER←BV\(1ρρC) NIP 'ENTER THE ANNUAL PERCENT GROWTH FOR ',C2,':'
[17]  YRS←((-∆MAX),0) NIP 'ENTER THE YEARS OF INTEREST' ◇ YRS←YRS[⍋YRS] ◇ →0
[18] L3:LEN←(1 1 ,∆MAX) NIP 'HOW MANY INCREMENTS? '
[19]  YRS←⍳\LEN←(LEN,0) NIP 'ENTER THE ',(⍪LEN),' INCREMENTAL TIME PERIODS: '
      '
[20]  I←1 ◇ PDOT←((ρLEN),∆CN)ρ0
[21] RTI:SAME←PDOT[I;]←BV\((1ρρC),0) NIP 'ENTER EMISSION RATES',((I=1)/' FOR ',C2),' FOR TIME PERIOD ',(⍪I),' (KG./YR.):
      '
[22]  I←I+1 ◇ →(I≤ρLEN)ρRTI
      ∇


     ∇ Z←LIP MSG
[1]   ⍝LITERAL INPUT WITH PROMPT
[2]   ⍞←MSG←,MSG ◇ Z←(ρMSG)↓Z←⍞
      ∇


     ∇ Z←SET LIP2 MSG
[1]   ⍝LITERAL INPUT WITH PROMPT, ENTRY[1] MUST BE ELEMENT OF 'SET'
[2]  L1:⍞←MSG←,MSG ◇ →(∨/SET=Z←1↑SQ(ρMSG)↓Z←⍞)ρ0 ◇ 'TRY AGAIN' ◇ →L1
      ∇
```

```
      ∇ EC←MEXP C;B;CP;CP2;CP4;CP6;EC;I;N;NEG;POS;Q;T
[1]   A E*C   WHERE C IS A MATRIX
[2]   N←1ρρC ◇ B←1⌈⌈2⊛⌈/+/|C
[3]   ACP * 1 2 4 6
[4]   CP6←CP2+.×CP4←CP2+.×CP2←CP+.×CP←C÷2*B
[5]   Q←0.5,(7⍴60),÷ 60 624 9360 205920 7207200 518918400
[6]   POS←(IDEN N)+(CP2×Q[2])+(CP4×Q[4])+(Q[6]×CP6)+Q[8]×CP6+.×CP2
[7]   NEG←(CP×Q[1])+(Q[3]×CP2+.×CP)+(Q[5]×CP4+.×CP)+Q[7]×CP6+.×CP
[8]   T←(⌹POS-NEG)+.×POS+NEG
[9]   EC←T+.×T ◇ I←2
[10]  L1:→(B<I)ρ0
[11]  EC←EC+.×EC ◇ I←I+1 ◇ →L1
      ∇


      ∇ MODEL;A
[1]   ACONTROL PROGRAM
[2]   L0:LF,'OPTIONS ARE:'
[3]   '0 - EXIT FROM MODEL'
[4]   '1 - INPUT ALL DATA'
[5]   '2 - INPUT ONLY PHYSICO-CHEMICAL DATA'
[6]   '3 - INPUT ONLY EMISSION-RELATED DATA'
[7]   '4 - PRINT CURRENT DATA'
[8]   '5 - PRINT INTERMEDIATE RESULTS'
[9]   '6 - RUN MODEL BASED ON CURRENT DATA'
[10]  '7 - EXAMINE LAST OUTPUTS'
[11]  A← 1 0 6 NIP 'ENTER OPTION NUMBER' ◇ →(0,L1,L1,L3,L4,L5,FIN,L7)L1+A]
[12]  L1:INPUT ◇ →(A=2)/FIN
[13]  L3:INPUTE
[14]  FIN:FORMAR ◇ FORMAN ◇ →(A=6)/L6 ◇ LF ◇ →(~YN 'WOULD YOU LIKE TO PRINT THE INPUTS? ')ρNP1
[15]  L4:PΔINP ◇ →(A=4)/L0 ◇ LF
[16]  NP1:→(~YN 'WOULD YOU LIKE TO PRINT THE INTERMEDIATE RESULTS? ')ρNP2
[17]  L5:PΔINT ◇ →(A=5)/L0 ◇ LF
[18]  NP2:→(YN 'ARE ALL INPUTS OK? ')ρL6 ◇ →(YN 'ARE THE CHEMICAL AND COMPARTMENT DATA OK? ')↓L1,L3
[19]  L6:RUN
[20]  →(0≠ρLIP 'ALIGN PAPER AND PRESS CARRIAGE RETURN')ρ0
[21]  L7:OUTPUT
[22]  →L0
      ∇
```

```
      ∇ Z←LIM NIP MSG;LIM1
[1]   ⍝NUMERIC INPUT WITH PROMPT
[2]    LIM1←1↓LIM←,LIM
[3]   L1:MSG
[4]    →(1<⍴⍴Z←⎕)⍴ERR0 ◊ →(0=LIM1)⍴L2
[5]    →(≤'(|LIM1)','<≠'[1+0≤LIM1],'⍴,Z')⍴ERR1
[6]   L2:→(1=⍴LIM)⍴0 ◊ →(v/Z<LIM[2])⍴ERR2
[7]   L3:→(2=⍴LIM)⍴0 ◊ →ERR3×v/Z>LIM[3]
[8]   ERR0:'RANK ERROR' ◊ →L1
[9]   ERR1:'ENTER ',(▼|LIM1),' NUMBER',(1<|LIM1)/'S',(0>LIM1)/' OR LESS' ◊ →L1
[10]  ERR2:'ALL NUMBERS MUST BE ≥ ',▼LIM[2] ◊ →L1
[11]  ERR3:'ALL NUMBERS MUST BE ≤ ',▼LIM[3] ◊ →L1
      ∇


      ∇ OUTPUT;FC;FW;PW;RTW;T1
[1]   ⍝PRINT THE RESULTS OF THE MODEL
[2]   ⍝RTW= ROW TITLE WIDTH; FW= FIELD WIDTH; FC= ⎕FMT CODE; PW= PRINT WIDTH
[3]    RTW←1+⍴COMP ◊ FW←10 ◊ FC←'E',(▼FW),'.2' ◊ PW←RTW+FW×1+⍴YRS
[4]    LF,NAME,' (',(S& NO),') ',LF
[5]    LF,PW CENTER 'CONCENTRATION DISTRIBUTION' ◊ PW CENTER '(KG./KG.)'
[6]    T1←(RTW+'COMPARTMENT'),FW COLNAMES(,'/',('P⎕YEAR ⎕I',▼FW) ⎕FMT BASEYR+0,YRS),((⍴YRS)≠1+⍴CX)/'/STEADY ST'
[7]    LF,T1,LF ◊ COMP,FC ⎕FMT CX0,CX
[8]   ⍝MASS DISTRIBUTION IS THE CONCENTRATION DIST. ON A PERCENT BASIS
[9]    LF ◊ PW CENTER 'MASS DISTRIBUTION' ◊ PW CENTER '(o/o)' ◊ LF,T1,LF
[10]  COMP,('BF',(▼FW),'.1') ⎕FMT 100×(CX0,CX)÷(0 1 +⍴CX)⍴+/[1] CX0,CX
[11]  (RTW⍴' TOTAL'),(FW,1)▼(1+(⍴CX)[2])⍴100
      ∇


      ∇ PRINTF;BV;FW;RTW
[1]   ⍝PRINTS OUT F-DOT
[2]    RTW←1+⍴COMP ◊ FW←8 ◊ LF,'BULK WATER FLOWS   (KG./YR.)',LF
[3]    BV←⍋CR↑0,12⍴1
[4]    (RTW+'COMPARTMENT FROM\TO'),FW COLNAMES S& '/',BV≠COMPA
[5]    ''
[6]    (BV≠COMP),(FW,⁻2)▼FDOT
      ∇
```

```
      ∇ PRINTM;FW;RTW
[1]   ⍝PRINTS OUT 'M'
[2]   RTW←1↑ρCOMP ◊ FW←10
[3]   LF,'M. MATRIX OF COEFFICIENTS (PER YEAR)',LF
[4]   ((RTW)↑'COMPARTMENT TO\FROM'),FW COLNAMES SQ '/',COMPA[ΔC+⍳10;]
[5]   ' '
[6]   ((ΔC,0)↑COMP),(FW,¯2)▼MBARL;(-ΔC)+⍳10]
[7]   LF
[8]   (RTW↑'COMPARTMENT TO\FROM'),FW COLNAMES SQ '/',(10,0)↑COMPA
[9]   ' '
[10]  ((ΔC,0)↑COMP),(FW,¯2)▼(0,10-ΔC)+MBAR
      ∇


      ∇ PRINTR;FW;RTW
[1]   ⍝PRINTS OUT 'R'
[2]   RTW←1↑ρCOMP ◊ FW←10
[3]   'CONVECTIVE FLOWS PER UNIT CONCENTRATION  (KG./YR.)',LF
[4]   ((RTW)↑'COMPARTMENT FROM\TO'),FW COLNAMES SQ '/',COMPA[⍳10;]
[5]   ' '
[6]   COMP,(FW,¯2)▼RL;⍳10]
[7]   LF
[8]   (RTW↑'COMPARTMENT FROM\TO'),FW COLNAMES SQ '/', 10 0 ↑COMPA
[9]   ' '
[10]  COMP,(FW,¯2)▼RL;10+⍳ΔCN]
      ∇
```

```
        ∇ PΔINP;A;CDF;D1;FC;FW;PF;PF2;RTW;RW2
[1]    APRINT INPUTS
[2]    FW←10 ◊ RTW←1↓ρCOMP ◊ PF←TYPE=2 ◊ PF2←PFW0=1↓ρCX ◊ D1←(PF2/ρYRS),1~PF2 ◊ RW2←22
[3]    CDF←YN 'INCLUDING COMPARTMENT DATA? '
[4]    LF,NAME,' (',(SQ NO),')',LF
[5]    A (RW2 VTM '|MOLECULAR WEIGHT:|VAPOR PRESSURE:|SOLUBILITY IN WATER:|OCTANOL/WATER COEF:'),▼ 4 1 ρMW,VP,SOL,WPC
[6]    (RW2↑'MOLECULAR WEIGHT:'),▼MW
[7]    (RW2↑'VAPOR PRESSURE:'),(▼VP),' (ATM.)'
[8]    (RW2↑'SOLUBILITY IN WATER:'),(▼SOL),' (G/G)'
[9]    (RW2↑'SOIL/WATER COEF:'),▼WPC
[10]   →(0=TB)/1+⎕LC ◊ (RW2↑'NORMAL BOILING POINT:'),(▼TB),' (°K)'
[11]   →(0=VC)/1+⎕LC ◊ (RW2↑'MOLAL VOLUME:'),(▼VC),' (CM*3/G-MOL)'
[12]   (RW2↑'DIFFUSIVITY IN AIR:'),(0 ¯5 ▼DCA),' (M*2/SEC)'
[13]   ((¯RW2)↑'WATER: '),(0 ¯5 ▼DCW),' (M*2/SEC)'
[14]   LF,'REACTION RATE CONSTANT (PER YEAR)'
[15]   (0 VTM '/AIR:/WATER:/SOIL:'), 0 5 ▼ 3 1 ρK
[16]   ACOMPARTMENT DATA DISPLAY (OPTIONAL)
[17]   →(~CDF)ρL1
[18]   LF,(RTW↑'COMPARTMENT'),1+FW COLNAMES '/F-ORGANIC/WEIGHT/AREA'
[19]   (RTWρ' '),FW COLNAMES '//(KG.)/(M*2)'
[20]   COMP,(((¯ACW),FW)↑▼ 6 1 ρFORG),('E',(▼FW),'.4') ΔFMT WX,[1.1] AX
[21]   AEMISSION-RELATED DATA DISPLAY
[22]   L1:A←(RTW↑'COMPARTMENT'),(2ΦFW COLNAMES '/CO'),PF/FW COLNAMES '/PERCENT'
[23]   LF,A,((1=D1)/(-FW)↑'EM RATE'),((1≠D1)/(FW×D1) CENTER 'EMISSION RATES')
[24]   A←'(KG/YR)'
[25]   ((RTW+FW×PF+1)ρ' '),((D1=1)/(2ρ' '),A),(D1≠1)/(FW×D1) CENTER A
[26]   ((RTW+FW×PF+1)ρ' '),,('PLYEAR ⎕',▼FW) ΔFMT BASEYR+((TYPE=2)/0),PF2/YRS
[27]   FC←'E',(▼FW),'.2,',(PF/'BF',(▼FW),'.1,'),((▼1ρρPDOT),'E',(▼FW),'.2')
[28]   '' ◊ COMP,FC ΔFMT▼'CX0.',(PF/'PER,'),((1=ρρPDOT)/'[1.1]'),'(&PDOT)'
        ∇


        ∇ PΔINT
[1]    APRINTS INTERMEDIATE RESULTS
[2]    PRINTK
[3]    PRINTF
[4]    PRINTM
        ∇


        ∇ Z←ADJUST M
[1]    Z←(1-(' '=M)⍳1)ΦM
        ∇
```

```
      ∇ RUN
[1]    →(L1,L2,L3)[TYPE]
[2]    L1:LEN RUN1 PDOT ◊ →END
[3]    L2:YRS RUN2 PDOT ◊ →END
[4]    L3:LEN RUN3 PDOT ◊ →END
[5]    END:→(~ΔC)/0
[6]    CX←CX[1;],[1](CX[1;]×CR),[1] 1 0 +CX
      ∇


      ∇ LEN RUN1 PDOT;BV;CO;I;IMAX;M;PX
[1]    ⍝RUN FOR CONSTANT EMISSION RATE  CASE
[2]    CX←((ΔCN-ΔC),0)ρ0 ◊ CO←(BV←~ΔCN↑0,ΔC)/CX0 ◊ I←1 ◊ IMAX←ρLEN
[3]    PX←PDOT[1;]÷WX ◊ →(~ΔC)ρL1 ◊ PX←((+/PX[⍳2])÷1+CR),2↓PX
[4]    L1:M←MEXP LEN[I]×(MBAR,PX),[1] 0
[5]    CX←CX,CO←((¯1 ¯1 ↑M)+.×CO)+¯1↑M[;ΔCN←~ΔC]
[6]    →(IMAX≥I←I+1)ρL1
[7]    ⍝CALCULATE STEADY STATE IF POSSIBLE
[8]    →(∧/K=0)ρ0 ◊ CX←CX,-(⌹MBAR)+.×PX
      ∇


      ∇ YRS RUN2 PD;BV;CO;F;INT;M;NBAR;PX;PX;T;TMAX
[1]    ⍝DOES THE LOOPING FOR THE CONSTANT PERCENT GROWTH CASE
[2]    CX←((ΔCN-ΔC),0)ρ0 ◊ CO←(BV←~ΔCN↑0,ΔC)/CX0
[3]    PDOT←PD[,1;] ◊ PX←(,PDOT)÷WX ◊ →(~ΔC)ρL0 ◊ PX←((+/PX[⍳2])÷1+CR),2↓PX
[4]    L0:NBAR←(MBAR,PX),[1] 0
[5]    M←MEXP NBAR
[6]    ⍝INT= THE INTEGRAL
[7]    INT←¯1↑M[;ΔCN←~ΔC]
[8]    M←¯1 ¯1 ↑M
[9]    ⍝LOOP THROUGH THE YEARS FORM T=1 TO THE LAST YEAR SPECIFIED
[10]   T←1 ◊ TMAX←¯1↑YRS
[11]   L1:CO←(M+.×CO)+INT×(1+0.01×BV/PER)*T-1
[12]   →(~T∈YRS)ρEND
[13]   CX←CX,CO ◊ PDOT←PDOT,[1] PDOT[1;]×(1+0.01×PER)*T-1
[14]   END:→(TMAX≥T←T+1)ρL1
      ∇


      ∇ LEN RUN3 PDOT;BV;CO;I;IMAX;M;PX
[1]    ⍝RUN FOR STEPPING CASE
[2]    CX←((ΔCN-ΔC),0)ρ0 ◊ CO←(BV←~ΔCN↑0,ΔC)/CX0 ◊ I←1 ◊ IMAX←ρLEN
[3]    L1:PX←PDOT[I;]÷WX ◊ →(~ΔC)ρL1 ◊ PX←((+/PX[⍳2])÷1+CR),2↓PX
[4]    M←MEXP LEN[I]×(MBAR,PX),[1] 0
[5]    CX←CX,CO←((¯1 ¯1 ↑M)+.×CO)+¯1↑M[;ΔCN←~ΔC]
[6]    →(IMAX≥I←I+1)ρL1
      ∇
```

```
      ∇ Z←SQ X
[1]   Z←1↓(ZV1⌽Z←' 'z×)/X←' ',,X
      ∇


      ∇ TABS X
[1]   ⎕Pw←157
[2]   ⎕H←∧×⍳32
      ∇


      ∇ Z←COL VTM V;BV;LOC;LEN;MAX
[1]   MAX←⌈/LEN←(1↓LOC,1+ρV)-1+LOC←(BV←V=1↑V)/⍳ρV←,V
[2]   Z←((ρLEN),MAX)ρ(,LEN∘.≥⍳MAX)\(~BV)/V ◇ →(0=COL)ρ0
[3]   Z←((1ρρZ),COL)↑Z
      ∇


      ∇ WSDOC;A;B
[1]   ⍝⎕←'        ⎕TS'
[2]   ⍝⎕←'        )WSID' ◇ ⍝⎕←'        ⎕WA' ◇ ⍝⎕←'        ⎕LX'
[3]   ⍝⎕←'        )FNS'
[4]   ⍝⎕←'        )VARS'
[5]   '' ◇ A←ALP ⎕NL 3
[6]   L1:→(0=1ρρA)ρ0 ◇ '' ◇ ⍎'∇',A[1;],'[⎕]∇' ◇ A← 1 0 ↓A ◇ →L1
      ∇


      ∇ Z←YN MSG;A
[1]   L1:⎕←MSG←MSG ◇ A←⎕ ◇ →(∨/A←'YN'=1↑SQ(ρMSG)↓A)ρL2 ◇ 'ENTER YES OR NO' ◇ →L1
[2]   L2:Z←A[1]
      ∇


      ∇ RES←LEFT ∆FMT RIGHT
[1]   RES←LEFT ⎕FMT RIGHT ⍝    PASS ALL REFERENCES TO STSC ∆FMT TO DING ⎕FMT
      ∇
```

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15 SUPPLEMENTARY NOTES

16 ABSTRACT

An objective system is described for ranking chemicals which may be released into the environment in order of their hazard potential. Although the major focus is on preliminary screening of new chemicals prior to full commercial manufacture ("premanufacturing"), the recommended scheme may also be applied to chemicals in production. An important design criterion is that the system make minimal demands for data, in recognition of the general paucity of available test data. Ranking is based on the ratio of estimated future environmental concentration at a specified point in time to the concentration level-of-concern causing deleterious effects.

The interactive computer model represents the air-land-water environment of the United States as a system of 19 uniformly-mixed, interconnected reactors, each containing the specified chemical at some compartment-average concentration. The temporal distribution of the chemical among the various compartments is determined by the initial concentrations, extent of direct emissions over time, and transformation and transport processes that occur. The exact dynamic solution to the governing vector-matrix differential equation is obtained. The resulting computer program calculates the concentration of chemical in each environmental compartment over time and at steady-state.

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