MATHEMATICAL MODELING FOR PREDICTING THE FATE OF CONTAMINANTS IN FRESHWATER ECOSYSTEMS: A REVIEW

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EXECUTIVE SUMMARY

The knowledge of toxic contaminants fate in the environment is important given the large number of chemicals (about 60,000) presently in use. Mathematical models have been used to predict contaminants fate but the incomplete knowledge of the relation between the chemical structure and environmental behaviour makes predictions uncertain. Here, basic principles of fate models are reviewed with a discussion of the latest topics of interest in ecological modelling. These topics include a) expert systems to catalog information about new and existing contaminants and pesticides and to improve the registration process; and b) theory of model development to minimize the uncertainty in predictions and to identify important processes, whose detailed knowledge would improve our confidence in fate models.

ABSTRACT

Mathematical models predict the concentration of contaminants in different compartments, or state variables, according to loading rates into the system (inputs), to the rates (parameters or submodels) of degradation (photolysis, hydrolysis, oxidation, biodegradation, etc.) and to transport rates (parameters or submodels) between compartments (volatilization to the atmosphere, wet and dry deposition, adsorption on soil particles and sediments in the aquatic environment, resuspension from bottom sediments, currents). At present many factors, such as micro-climate, wind, spatial variability, uncertainty in the model structure and parameter values (for example measures of octanol water partition coefficients higher than 10^5), still preclude the usage of laboratory data and mathematical models alone to set environmental standards. Field testing is still necessary and mathematical models can help in integrating this information and possibly leading the data collection efforts. This paper reviews recent research in systems ecology: at present computer simulations are one of the tools used for predicting the fate of toxic contaminants in the aquatic environment; others, for example, are artificial intelligence and expert systems. Other research in systems ecology focuses on a) theory of model development to minimize the number of state variables and parameters, that is, to minimize the uncertainty in the model structure and parameter values, b) algorithms to compute prediction uncertainty to understand model reliability and to identify important processes, whose detailed knowledge would improve our confidence in the model and c) hierarchical and network theory to quantify the cycling rates of toxic contaminants.

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I. INTRODUCTION

In the past decade ecological modelers have shown great interest in modeling the fate and effect of toxic substances. This interest was expressed in organized form in 1983 when Jorgensen[1] organized a conference on this topic in Copenhagen. At present computer simulations are one of the tools used for predicting the fate of toxic contaminants in the aquatic environment; others, for example, are artificial intelligence and expert systems. Other research in systems ecology focuses on a) theory of model development to minimize the number of state variables and parameters, that is, to minimize the uncertainty in the model structure and parameter values, b) algorithms to compute prediction uncertainty to understand model reliability and to identify important processes, whose detailed knowledge would improve our confidence in the model and c) hierarchical and network theory to quantify the cycling rates of toxic contaminants.

The knowledge of toxic contaminants fate in the environment is important given the large number of chemicals (about 60,000) presently in use. Mathematical models have been used[2-6] to predict contaminants fate but the incomplete knowledge of the relation between the chemical structure and environmental behaviour[7] makes predictions uncertain. Here, basic principles of fate models are reviewed with a discussion of the latest topics of interest in ecological modelling.

A. Past Endeavors

The prediction of the fate of toxic contaminants in the environment was made possible in the 1970's by the realization that most environmental fate processes follow first order kinetics; therefore linear models (Eq. 1

below) are an appropriate representation of contaminant behaviour[2]. At the time, the main purpose of scientific studies was only to monitor environmental concentrations of pollutants, usually several years after the environment had been contaminated. For example, Lake Ontario was subject to contaminants as early as 1909 with the establishment of industries on the shores of the Niagara River. The highest rates of contaminant loadings took place in 1960-1963[8]; these rates were subsequently reduced in later years, while the pollution problem was only recognized in the early 1970's. The historical pollution trends are recorded in the bottom sediments of Lake Ontario.

Early investigations on the fate of toxic contaminants lead to two distinct but related lines of research: Studies on model ecosystems focused on the dynamics of contaminant fate and statistical studies focused on equilibrium conditions. This duality still exists in modeling strategies, some mathematical models include equilibrium conditions, for example the fugacity approach of Mackay and Paterson[9] and the model EXAMS[3], while others are strictly dynamic, e.g. PEST[10] and TOXFATE.[6]

Mathematical models predict the concentration of contaminants in different compartments, or state variables, according to loading rates into the system (inputs), to the rates (parameters or submodels) of degradation (photolysis, hydrolysis, oxidation, biodegradation, etc.) and to transport rates (parameters or submodels) between compartments (volatilization to the atmosphere, wet and dry deposition, adsorption on soil particles and sediments in the aquatic environment, resuspension from bottom sediments, currents). Halfon[11] has reviewed the data base necessary to develop and verify ecosystem fate models. Figure 1 shows compartments and environmental processes which

affect contaminants behaviour. Figure 2 shows compartments often used in modeling exercises and chemical properties usually associated with contaminant partition in these compartments. At present many factors, such as micro-climate, wind, spatial variability, uncertainty in the model structure and parameter values (for example measures of octanol water partition coefficients higher than 10^6), still preclude the usage of laboratory data and mathematical models alone to set environmental standards. Field testing is still necessary and mathematical models can help in integrating this information and possibly leading the data collection efforts. An example to that effect will be discussed later.

B. Physical and Chemical Properties Related To Environmental Behaviour

The transfer and degradation parameters constrain the behaviour predicted by a mathematical model; the transfer parameters are based on the physico-chemical properties of the contaminant, K_{ow}, K_{oc}, log P, solubility, and of the environment, wind speed, current velocities, etc. To reduce the impact of lack of experimental data, quantitative structure activity relationships (QSAR) have been used[7] in the formulation of the model equations. With QSAR, physical and chemical properties of the contaminants, measured in the laboratory or estimated from the molecular structure, have been used to predict the environmental behavior of the contaminant itself.

A large number of statistical models, usually linear regressions, has been published to relate properties such as the octanol water partition coefficient (K_{ow} or log P) with bioconcentration in fish, adsorption on suspended sediments, etc. The main problem, still debated, is whether this information is sufficient to make extrapolations from the laboratory to the

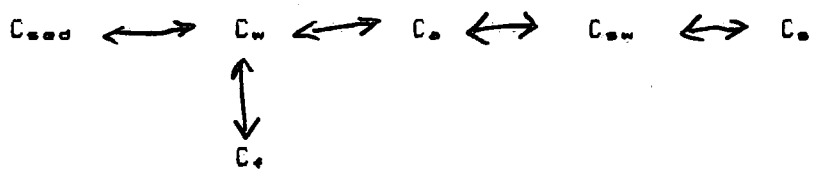
field, and whether mathematical models developed from laboratory data are valid under field conditions. Linear regression models can be used if appropriate observations are not available; errors and uncertainty must be taken into consideration when predictions are made based on these models. For example the boiling point of a chemical can be used to compute the vapor pressure of a chemical and, if the solubility is known, to predict the Henry's Law constant, or the ratio of equilibrium concentrations of a chemical in the water and in the air. This ratio is always used in models to compute the volatility of a chemical. Halfon[12] analyzed the appropriate procedure in the computation of the statistical linear regression models when both variables are subject to measurement error and natural variability as is the case in most ecotoxicological models.

Toxic contaminants in the environment might be degraded or converted into other chemicals which might also be toxic. Most fate models do not simulate the fate of these byproducts and therefore, once the chemicals are degraded they are considered lost from the system. These degradation processes can be of a variety of classes including hydrolysis, oxidation, reduction, substitution, elimination, isomerization and ion-exchange. Most of these environmental reactions are bimolecular (e.g. in hydrolysis, water is a reagent). Nevertheless, when one of the reactants is present in large excess then the process becomes a pseudo first order process and can be included in the model as a linear formulation.

II. EQUILIBRIUM AND DYNAMIC MODELS

The basic framework of fate models is usually based on linear

ordinary differential equations; nevertheless, any process formulation might be nonlinear. Within this framework, two approaches have been used: 1) In the dynamic approach the changes of concentration in time are considered important; 2) in the equilibrium approach the main assumption is that enough time has lapsed for the contaminant loadings in the environment to have reached equilibrium in the environment. This second approach has been used by Mackay and Paterson[9], Burns et al.[3] and McCall et al.[4] The last model has a structure of the following kind



where C are the concentrations of the contaminant in the water (C_w), sediment (C_{sed}), fish (C_f), air (C_a), soil water (C_{sw}) and soil (C_s).

The importance of equilibrium models lies in their ability to indicate which compartment would be the main recipient of the contaminant if conditions remain constant in time. This approach is useful for regulatory agencies to assess the possible hazard level of a new contaminant. Predictions on average agree with monitoring data but not too well at specific sites.

Dynamic models - time dependent - can describe site specific nonequilibrium conditions and can address the question of residence time. One of the earliest models was developed by Neely and Blau[2]; this model describes the behaviour of a chemical, chlorpyrifos in a fish pond; transfer among the different compartments depends on six parameters which describe volatilization, hydrolysis, fish uptake, fish excretion, adsorption to soil

and desorption from soil. The model has a linear formulation and the equation describing concentrations in water has the following formulation.

$$V \frac{dC_w}{dt} = -k_1 A C_w - k_2 V C_w - k_3 F C_w + k_4 F C_f - k_5 S C_w + k_6 S C_s \qquad (1)$$

where V is the volume of the pond, A is its area, F is the fish biomass, S is the weight of soil and k_1 - k_6 are the parameters which quantify the different transport and removal processes. Most fate models, with more or fewer state variables and parameters, have a similar structure. Neely and Blau[2] estimated the rate constants k_3-k_6 from laboratory ecosystem studies of Smith et al.[13] following a procedure described by Blau et al.[14]. The rate constant for evaporation, k_1, was estimated by the Liss and Slater technique[15]. The hydrolyis rate k_2 was estimated from the observation that the half-life of Chlorpyritos in water at pH 7 is three days.

III. MODEL APPLICATIONS

Fate models have been used to describe the fate of toxic contaminants in small microcosms and in very large lakes, like Lake Ontario, 300 km long and 70 km wide. In this section results from two simulation studies are described. In the first the purpose of the model was to predict the residence time of Fenitrothion in ponds after aerial spraying. This purpose was accomplished by quantifying the parameter values as ranges to include the natural variability of observation in the ponds. The purpose of the second study was to predict the fate of perchloroethylene (PERC) in Lake St. Clair, or to predict the proportion of PERC that would be volatilized, the

proportion transported downstream and the resident time in the system. Note that in both these examples the loading rates of the contaminant were unknown. The modeling exercise provided means to estimate past loadings.

A. Fenitrothion in New Brunswick Ponds

Halfon and Maguire[16] developed stochastic fate models to describe the variability in the data, variability which is often observed when multiple measurements are taken of the same compartment. Their model describes the fate of fenitrothion in three compartments: the surface microlayer, the main water body and the bottom sediment of a pond. The model parameters were estimated by fitting a stochastic model to the whole range of observations (Fig. 3); thus, parameter values were quantified as ranges rather than as best fit values. When used for prediction, the model computes the time needed for fenitrothion to be removed from a pond, after an aerial spraying, with a 95% probability. The 95% removal time was estimated to be 20% higher than the time predicted by the deterministic model thus showing that pollution persisted longer than previously expected (Fig. 4).

B. Perchloroethylene in the St. Clair - Detroit River System

Perchloroethylene (PERC) was found in sediment samples collected in 1984 and 1985 at the bottom of the St. Clair River at Sarnia near the Dow Chemical plant[17,18]; PERC is a volatile chemical commonly used as a solvent; it is water soluble and it has a relatively low octanol-water partition coefficient ($\log_{10} P$ is 2.69); in the aquatic environment PERC does not have much affinity for suspended sediments once it is in the dissolved state. The spill created the black puddles because a large amount of PERC and of Carbon tetrachloride (CTC) was released into the river; since PERC and CTC are

heavier than water with a density of about 1.6, most of it stayed on the river bed.

The purpose of this modeling effort[19], using the model TOXFATE[6], was to evaluate the relative importance of water transport and volatilization in the removal of PERC from the St. Clair-Detroit River system and to perform a mass balance calculation.

1. The Mathematical Model

TOXFATE is a contaminant fate model[6] which integrates information on the properties of a chemical, such as molecular weight, solubility, vapor pressure, octanol-water partition coefficient (see Fig. 2 for the relation of the chemical properties with environmental behaviour), with information about the environment where the chemical is found, such as water circulation, wind speed, the amount of suspended solids, etc. The model can be used to predict concentrations at different locations and estimate the importance of removal processes such as volatilization. Figure 5 shows the model structure, the arrows identify the model parameters.

In the model the spatial description of the St. Clair River system follows the observation that the river is not well mixed horizontally and therefore contaminants which enter the river near the east shore stay near that shore rather than mix uniformly across the whole river. These river water masses can be easily recognized in Lake St. Clair by following the plumes of suspended sediments by remote sensing[20]. Simons[21] who has developed a hydrodynamical circulation model of the lake, provided estimates of the water flows and therefore Lake St. Clair was divided into five cells (Fig. 6). The boundaries of the five cells were chosen to integrate information on the

long term annual circulation of the lake and the observed contaminant plumes in the lake waters. The Detroit River is spatially divided into two cells to complete the description of the system and to compute the proportion of the loadings which arrive in Lake Erie dissolved in water.

2. Model Results

The water retention time in the St. Clair-Detroit River system is about ten days[21] and the simulation[19] was run for forty days for water concentrations to reach a steady state with constant loadings.

The main purpose of the study was to estimate pathways of PERC in the system, thus the model computes volatilization and transport processes. PERC is very volatile with a Henry's Law constant of 8.3 10^{-3} [(Atm-m^3) / mol]. Assuming loadings of 64 kg PERC per day in dissolved form, the model predicts that 3.4 kg per day (5% of loadings) are lost through volatilization in the St. Clair River system up to Port Lambton, another 3.3 kg per day (5%) volatilizes from the delta, 44.3 kg per day (69%) from the lake and 1.8 kg per day (3%) from the Detroit River. The TOXFATE simulations show that up to about 82% (78-87% under a range of wind speed and water temperature conditions) of loadings are lost from the system before reaching Lake Erie. In Lake St. Clair the model predicts that about 69% of PERC loading is lost to the atmosphere through volatilization. Also simulations show that in the St. Clair Detroit River system, the average residence half life of PERC lost through volatilization is 80-85 hours while the average travel time of PERC transported in the water to Lake Erie from Sarnia is about 350-400 hours.

Given the availability of concentration data of PERC in water (Fig. 7) collected by Kaiser and Comba[22] in June 1984 the simulations were also

compared with the available data. Without calibration the computed concentrations (Fig. 6) agree well with observations (Fig. 7); the predicted values (Fig. 6) are about 300 ng/L at Port Lambton near the Canadian shore and 8-9 ng/L near the US shore, 105 ng/L near the cutoff channel and 16-39 ng/L at the head of the Detroit River. The model also predicts that the main loss of PERC from the system might be due to volatilization to the atmosphere. Unfortunately at present no plans exist to repeat a similar sampling program and therefore the model can not be verified correct since one cruise does not provide sufficient data for model verification.

IV. UNCERTAINTY

A. Model Structure

Two major problems in developing fate models are the choice of state variables and the quantification of parameter values. The appropriate choice of the state variables is a common problem in systems ecology: this choice is often left to the modeler and therefore somewhat arbitrary. Halfon[23-25] has analyzed the choice process using system methods. His conclusion was that no best model structure exists but an appropriate choice may be made by using the appropriate decision making tool. Hirata and Ulanowicz[26] in a review paper recently suggested that research in systems ecology should shift from deterministic, numerical simulations of ecosystems and instead consider more basic concerns on how to represent the ecosystem structure.

From a theoretical point of view modeling the fate of toxic contaminants should be a straightforward exercise. Contaminants are found in water and from there they adsorb into suspended sediments, fish and algae;

suspended sediments might sediment to the bottom of the lake or of the ocean to be buried by other sediments or to be resuspended according to the levels of turbulence near the bottom. The choice of state variables and of their relations however is quite arbitrary. For example, some questions that need to be addressed are use one class of suspended sediments or several size fractions, one class of seston or several species of plankton and zooplankton, representation of the food chain, one class or several classes of fish, etc. The problem of the interrelations is the decision of the representation of dynamic or equilibrium processes, food chain structure, etc. Each process added implies one more parameter that need to be estimated or measured.

Choice and quantification of the parameters is even a more difficult problem. If a simple linear formulation is used in the model then the parameters are a composite of several processes. For example in Neely and Blau 's model[2] the parameter k_1 describes volatilization; k_1 can be also be computed by a submodel which describes the behaviour of a contaminant at the air-water interface - for example the two layer model of Whitman[27]. The important point is that any parameter can be expanded into a submodel and given a more accurate description. Even so, no unique formulation has been universally accepted for any particular process; field and laboratory experiments are performed under specified conditions. Generalization of a set of data to a model that is generally applicable, for example to all aquatic environments, is difficult.

B. In Prediction

The topic of uncertainty can not be resolved only at the stage of model development, since the model structure and parameter values influence

the predictions made the computer model. The problem of model uncertainty was recognized as early as 1973 by O'Neill[28] but a formal theory of model uncertainty did not originate until later[29-31]. The purpose of uncertainty analysis is to quantify the amount of error present in a simulation due to different sources, the errors might be due to the model structure, uncertain parameter values, uncertain inputs and uncertain data from which the model was developed. All these factors must be taken into account. Several methods now exist to compute this uncertainty but the most used are those that rely on Monte Carlo simulations.

Halfon[5] developed a fate model of Mirex in Lake Water. Figures 8 and 9 shows the observed concentration of Mirex in 1968 in the bottom sediment of Lake Ontario (this information was used as initial condition) and the predicted concentrations in 1982. Given the large scale of the system, model simulations had to include such factors as currents and wind drive circulation. To account for uncertainty in the model Halfon[5] performed an error analysis of the model. This analysis was accomplished by running the model 200 times with different parameter values sampled from a known frequency distribution. In practical applications of error analysis the frequency distribution might be normal, triangular with minimum and maximum limits, or uniform if the parameter values are uncertain within given bounds. Correlation among parameters can also be included in the analysis. Once model simulations were performed the simulations were displayed with confidence limits[5] (Fig. 10). The two limits could be considered worst and best cases.

In error analysis parameter variability is assumed due to incorrect assumptions and poor parameter estimates in addition to the natural

variability of the parameters. The purpose of the error analysis if twofold, to produce tolerance limits associated with the simulations (Fig. 10) and to assess the effects of individual parameter errors, that is, which parameters produce the maximum error in the simulation. This analysis identified parameters whose precise knowledge would allow better prediction, i.e. smaller tolerance limits.

For the Mirex model the error analysis showed that the most important parameter for a reliable simulations were the bulk density of the sediments and the sediment-water exchange rate. The analysis also shows that percentage reduction in error rates if these two processes could have been measured exactly. Error analysis proved to be a very useful tool in the identification of weak areas of knowledge. A time analysis of parameters controlling the behaviour of Mirex showed that different parameters are in control at different times. Over the short term biological parameters are important whereas over the long term, geological properties are more relevant. Physical parameters, such turbulence and currents, are important both over the short as well over the long term. By concentrating research efforts on processes and variables identified by error analysis we can obtain results useful in reducing prediction uncertainty. Error analysis has focused our attention on the processes responsible for resuspension from the sediments. Mirex is located in the bottom sediments and only processes at the bottom of the lake are important for long term dynamics.

The relation between prediction uncertainty and error associated with model parameters has been studied by a number of investigators (O'Neill et al.[29] for a review). In general, parameters should be measured or

estimated from field and laboratory experiments. When these measurements are not available or possible, then parameters must be estimated mathematically or from laboratory experiments. All the information available on the system parameters is utilized for the analysis. Gardner et al[30] suggest that the correlation coefficient computed between a state variable and a parameter is a reasonable way to rank model parameters according to their contribution to prediction uncertainty.

In the analysis of the Mirex model Halfon[5] showed that only 15% of the 96 parameters in the model were important. One of the efforts of this study is to produce information on areas that should be the focus of research projects to reduce prediction uncertainty, i.e., if the identified parameters were measured with smaller variance we should observe a reduction in prediction error uncertainty. The correlation coefficient when squared represents the percentage of variability in the state variable due to one parameter when the variability in the other parameters is uncontrolled. For each state variable, by summing the variability reduction due to each parameter we can compute the variability that can be obtained by better measuring those state variables.

V. ARTIFICIAL INTELLIGENCE

The problem with computer simulations is that the chemical properties used to quantify model parameters are seldom available for the hundreds of new products produced each year. Hazard assessment of new contaminants is presently evaluated using experts, who by analyzing the available information can decide whether given contaminants might prove to be

a hazard or not. For example, given some information on the octanol water partition coefficient, solubility, vapour pressure, etc., experts might be able to estimate whether a compound is acceptable. This decision making process can be automated with the use of the so called artificial intelligence systems, e.g., decision trees, decision tables and expert systems. The purpose of these methods is to store expertise in the computer and have an algorithm take decisions in a reputable way according to prespecified criteria. Lemmon[32] for example developed an expert system for cotton crop management called COMAX. One of the advantages of expert systems is that if the computer if given a set of rules and some information on the process of which decision has to be made, the decision process can be reconstructed[33] Note that also experts in their decision making use mental models. Inputs usually consists of observations, or in this case the physico-chemical data of the new contaminants, and the output will be in the form of a decision, acceptance or rejection or request for more information. The advantage of using a formal algorithm is that the decision making process is transparent[33]. If we use an expert his experience is like a model which we are not allowed to see. The expert might give results, even good results, but it is difficult to argue about the way the results were obtained and the chemical company might object. The weakness with the artificial intelligence approach is that we do not know whether we have completely debriefed an expert to include all his/her knowledge in the computer program. However by combining the expertise of many scientists we can improve the knowledge of the computer and we can identify weaknesses or lack of knowledge and areas where improvements are necessary.

Artificial intelligence can be subdivided into three relatively

independent research areas: Natural Language Processing, Robotics and Expert Systems[34]. The first area is concerned primarily with developing computer programs that can read, speak or understand language as people use it in everyday conversation. The second area is concerned with developing smart robots or how to develop visual and tactile programs that allow robots to observe the ongoing changes that take place as they move around in an environment. A third area is concerned with developing programs that use symbolic knowledge to simulate the behaviour of human experts. This last area is of interest to develop program that can be used in setting regulations for the use and distribution of toxic contaminants. At present three approaches can be used to represent expert system in fate modeling.

A. Decision Trees[33]

The decision structure is similar to a dichotomous key for classifying plants. To use the tree we start at the top and we answer questions until we are led to a decision. A decision tree is easy to use once it has been built but it is very difficult to built and difficult to modify once they are built to include new knowledge. This drawback is fundamental since the problems with toxic contaminants are complex and the model should be amended in light of new experience.

B. Decision Tables[33]

The information included in the decision tree is rewritten in Table form. The decisions are written in any order and the entries of the table consists of T (true), F (false) or X for irrelevant.

Note that while there is only one row for each question there can be more than one column corresponding to each decision. Each column represents a

set of conditions that would lead to (or validate) that decision and there are often two or more ways of validating a particular decision. Decision tables are easier to built than decision trees since the order of the questions is no longer important. As more information become available the the decision table can be modified by adding a new row and if new set of circumstances that leads to a new decision become available than we add a column.

Decision tables are easily implemented on computers and the information is stored in a matrix. The computer program asks the user to reply true or false for each statement and then the program compares these replies with the stored matrix to see which decisions are valid.

The major disadvantage[33] is that rows and columns tend to proliferate, in fact each question has to be written as a question with a true or false answer and questions with two or more answers have to be broken down in single questions, adding more rows.

C. If-Then Rules and Expert Systems

A knowledge based system is easier to build than a conventional model because it has a well defined format[33]. The expert system consists of a decision list (which specifies the problem to be solved), a list of questions with answers (which tells us what information is needed to solve the problem) and a list of rules (which describes how one progresses logically from the answers to the decisions).

As is in any modeling exercise the first step is to establish the objective of a quantitative model. By first drawing up a list decisions before the rest of the knowledge base is collected we make sure that the model addresses the right issues and that we approach the right experts.

The next step is to decide what information is needed to reach the decisions and to write this information in the form of questions and answers. The expert should be asked to list all the necessary information appropriate for a well taken opinion. When complex problems are analyzed an interdisciplinary workshop provides an ideal environment for building the knowledge. In the case of decision making for toxic contaminants, several committee meeting might be followed to assess the process making in deciding whether a compound is acceptable or not.

The most difficult part in the construction of a knowledge basis is the formulation of the rules. For example we can ask ourselves " Under what circumstances would this chemical hydrolyze ?" or "what distinguishes a volatile compound from a less volatile compound", "how does the weather influences the volatilization process", water mixing ?" The rules should flow from the answers to the questions. The advantage of the if-then structure is that the rule base can be built slowly, one rule at the time: we do not need to grasp the nature of the whole decision making process. We do have to make sure that each rule is correct and appropriate. It is always advantageous to have a number of shorter rules (each with an appropriate explanation) rather than a few long and complicated rules. One of the disadvantages of the if-then structure is that it is sometimes difficult to decide whether the set of rules is adequate or complete. The only way to test this is to implement and exercise the knowledge base via an expert system. If the system frequently fails to find a decision, than the rule base is probably too slim. The process of exercising and interfacing with the knowledge base helps to identify those situations that need to be addressed by additional rules.

D. Decision Support Systems[33]

An expert system can be integrated into a decision support system via a data base and computer terminals. For example if a decision must be taken about a new chemical compound, the present option is to call a meeting of experts to decide whether the new chemical can be marketed. Alternatively the decision might be taken by running the program with the expert system and to take a decision accordingly. The advantage of using this approach is that the chemical industry can immediately understand the reasoning at the base of the decision of acceptance or rejection of the marketing application in basis on the information provided. If a decision is asked to be reconsidered some additional information might be provided in an interactive fashion until a compromise of environmental safety and industrial gain is reached. In this way decisions to be taken within ecological management can be taken routinely. In toxic contaminants management these decisions might related to production quota. A decision support system is a pretentious but apt title for an expert system shell that exercises a knowledge base containing the rationale behind any of these routine decisions[33]. Rykiel et al[38] present a clear example of a computer-aided decision support in pest management systems.

Starfield[33] clearly states the advantages of using decision support systems:

"1. at the simplest level the decision support system provides a safety for the inexperienced staff and intelligent checklist for more experienced staff.

2. it helps to ensure continuity despite changes in staff.

3. it helps to differentiate between situations that are routine and those when more careful analysis or data collection (or the opinion of an expert) are needed.

4. it could provide a stable reference when emotion runs high. Those who disagree with its recommendations would be forced to give explicit reasons for their disagreement

5. it is an effective communication device, either for explaining the reasoning behind a recommendation to those who have to authorize the decision or to present the same reasoning to the public."

VI. CONCLUSIONS

Mathematical models are usually built for two main purposes, to improve out understanding of the problems at hand and as a tool to predict the fate of toxic contaminants once they enter the environment. Simulation models are one of the methods used by systems ecologists to develop and test theories about the environment. In addition to working on simulation models a number of systems ecologists work on methods to improve the simulation methodology and to improve our understanding of the environment and how it is affected by human influence. In recent years we have made significant improvement in our ability to predict the fate of toxic contaminants and error analysis has allowed us to quantify the model reliability and to interact with field ecologists to decide which data should be collected for maximum amount of information.

Building models for ecological management is not an easy task. While there is often a pletora of data that are peripheral to our problem,

there tend to be a conspicuous lack of data we really need. For example to model[19] the fate of toxic contaminants in Lake St. Clair we need data collected in lake water during different seasons and under different hydrological conditions; one time surveys are not enough either from a modeling point of view or from an empirical point of view since they do not provide enough information to lead to as theory of contaminant behaviour. Figure 11 shows the modeling process and the continuous interaction of ecological modelers and field scientists to improve the understanding of the system and the predictive ability of the model. In the case of PERC in Lake St. Clair[19], even if concentration data to compare model simulations with were not available, the model simulations have provided insight in the behaviour of PERC in the system. For example some conclusion of this study were that about 82% of the very volatile PERC entering the St. Clair River at Sarnia would be lost to the atmosphere before reaching Lake Erie; in Lake St. Clair alone, the volatilization losses are about 69-74% of all loadings at Sarnia under a variety of temperature and wind conditions. The high water levels in the St. Clair River system do not influence the fate of PERC and prediction of PERC water concentrations strongly depends on the knowledge of the loadings. Local temperature and wind conditions might affect water concentrations locally but not drastically. The average residence half-life of PERC lost through volatilization is 80-85 hours while the average travel time of PERC transported in the water to Lake Erie from Sarnia is about 350-400 hours. During the field programs of 1984 and 1985 no field measurements of PERC losses through volatilization or sedimentation were performed, thus a verification of the model predictions through a program of field observations

or independent estimates of PERC volatilization is essential. This observation is valid for any fate model to be used in the St. Clair Detroit River System; at present the model is only prognostic and could be used to estimate contaminants pathways. We have also learnt to use mathematical models to improve our understanding of the problem or our appreciation of the management alternatives.

The recognition of model uncertainty was a significant development,[5,26,28-31] another is also the subject of how we can draw conclusions without calculations.[33-35] We know that people do it all the time and the basis on which they do is their experience. The artificial intelligence methods of decision trees, decision tables and expert systems based on if-then rules can be used to analyze the problem of licensing new contaminants when industry does not provide much chemical information on its properties. Although very large expert system have been successfully built and used in other fields[34], for example avionics in airplanes and medical diagnostic systems, the idea of using an expert system in environmental management is novel and relatively untested. It offers a mechanism that captures and organizes the type of information scientists are accustomed to using. The process of building a decision support system is always stimulating and effective.

The way in which a decision support system is implemented (first build a prototype model, consult it regularly, compare its performance with what actually happened, and update it on a regular basis) is in line with concepts of adaptive management (Fig. 11). A properly designed and implemented decision support system can capture long-term management

experience in the same way as data banks capture long term information.

Experts or people with field experience do not always agree with each other. They are seldom able to pinpoint where they disagree. Experience is not a commodity that is easy to communicate, and how and why a person reaches a decision is something that tends to be distorted with hindsight. Ultimately there can be no real progress in any subject unless those working in it have a common and unambiguous form of communication. Perhaps the more important quality of models, be they quantitative of qualitative, is that they provide a disciplined basis for discussion and argument.

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FIGURE LEGENDS

Figure 1: State variables, environmental factors, transfer and degradation processes present in fate models.

Figure 2: Physical properties used in equilibrium models and their relation with the transfer rates of toxic contaminants among compartments in the aquatic environment.

Figure 3: Stochastic simulation of Fenitrothion in pond water. The stochastic simulation, expressed as a range, includes most data points. The stochastic simulation allows the computation of prediction with specified probabilities.

Figure 4: Prediction of Fenitrothion concentrations in water at different times after aerial spraying. The deterministic solution suggest that 99% of fenitrothion will disappear from the pond waters in 57 hours. Stochastic simulations show that most likely the disappearance will take about 20% longer or 66-67 hours. The two graphs represent different assumptions about the uncertainty in the parameters.

Figure 5: TOXFATE model structure. The suspended sediments are represented as three size fractions, clay, silt and sand; the plankton compartment includes both phyto- and zooplankton.

Figure 6: Chart of Lake St. Clair. The five cells were identified after analysis of plume behaviour and long term current movements. The numbers in the cells represent the predicted concentration of PERC in the water [ng L^{-1}]. PERC loadings to the systems were estimated at 64 kg per day[17].

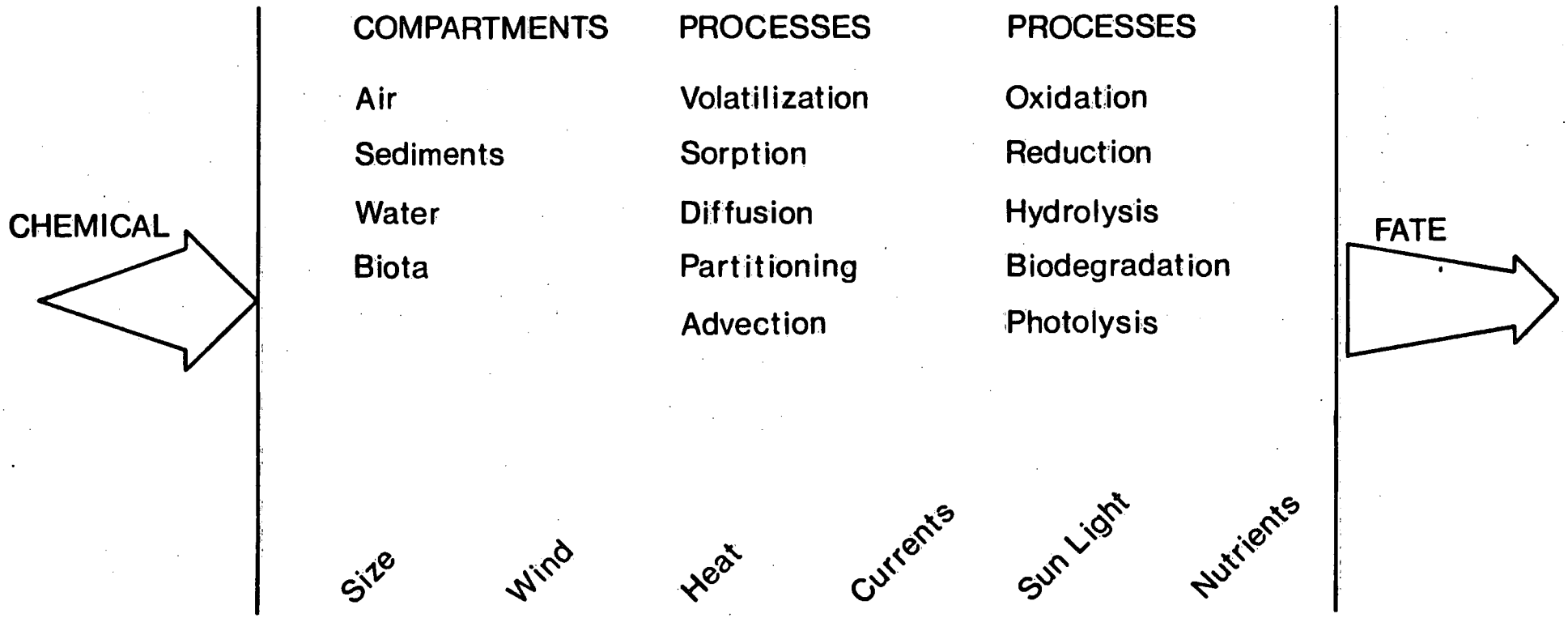
Figure 7: Chart of Lake St. Clair. Predicted concentration of Perchloroethylene in lake waters[7] [ng L^{-1}].

Figure 8: Observed concentrations of Mirex in the bottom sediments of Lake Ontario in 1968. The total amount of Mirex in the bottom sediments is about 950 kg.

Figure 9: Predicted concentrations of Mirex in the bottom sediments of Lake Ontario in 1982. The total amount of Mirex in the bottom sediment is about 1500 kg. A large increase since 1968.

Figure 10: Simulation of Mirex in the bottom sediment of Lake Ontario with confidence limits. The dark middle line represent the average of the 200 Monte Carlo simulations and the dotted line represent the deterministic solution.

Figure 11: Steps in the development of mathematical models. Note the close relation with experimentalists for the integration of system theory and field work.


CHEMICAL
COMPARTMENTS
Air
Sediments
Water
Biota
PROCESSES
Volatilization
Sorption
Diffusion
Partitioning
Advection
PROCESSES
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Reduction
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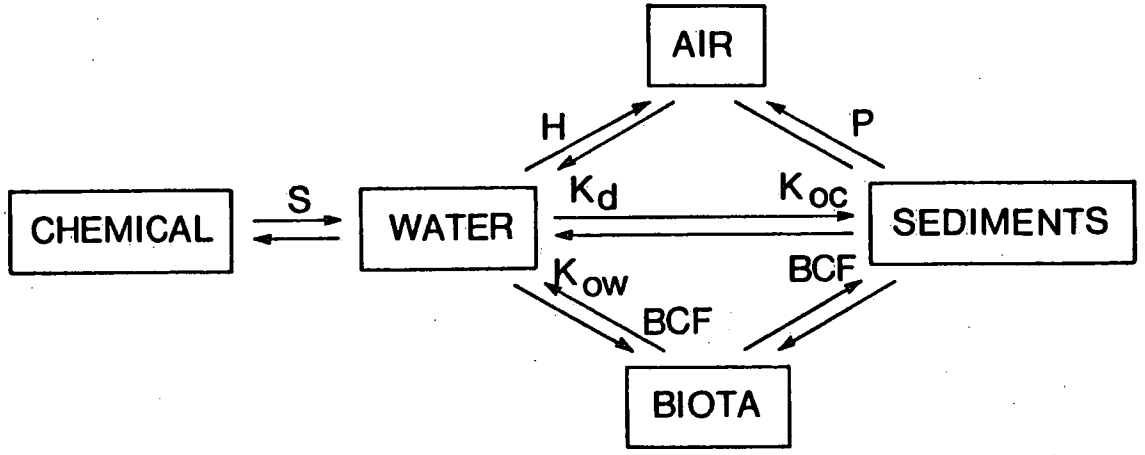
Wind
Heat
Currents
Sun Light
Nutrients



S = saturated water solubility ; P = vapor pressure ;

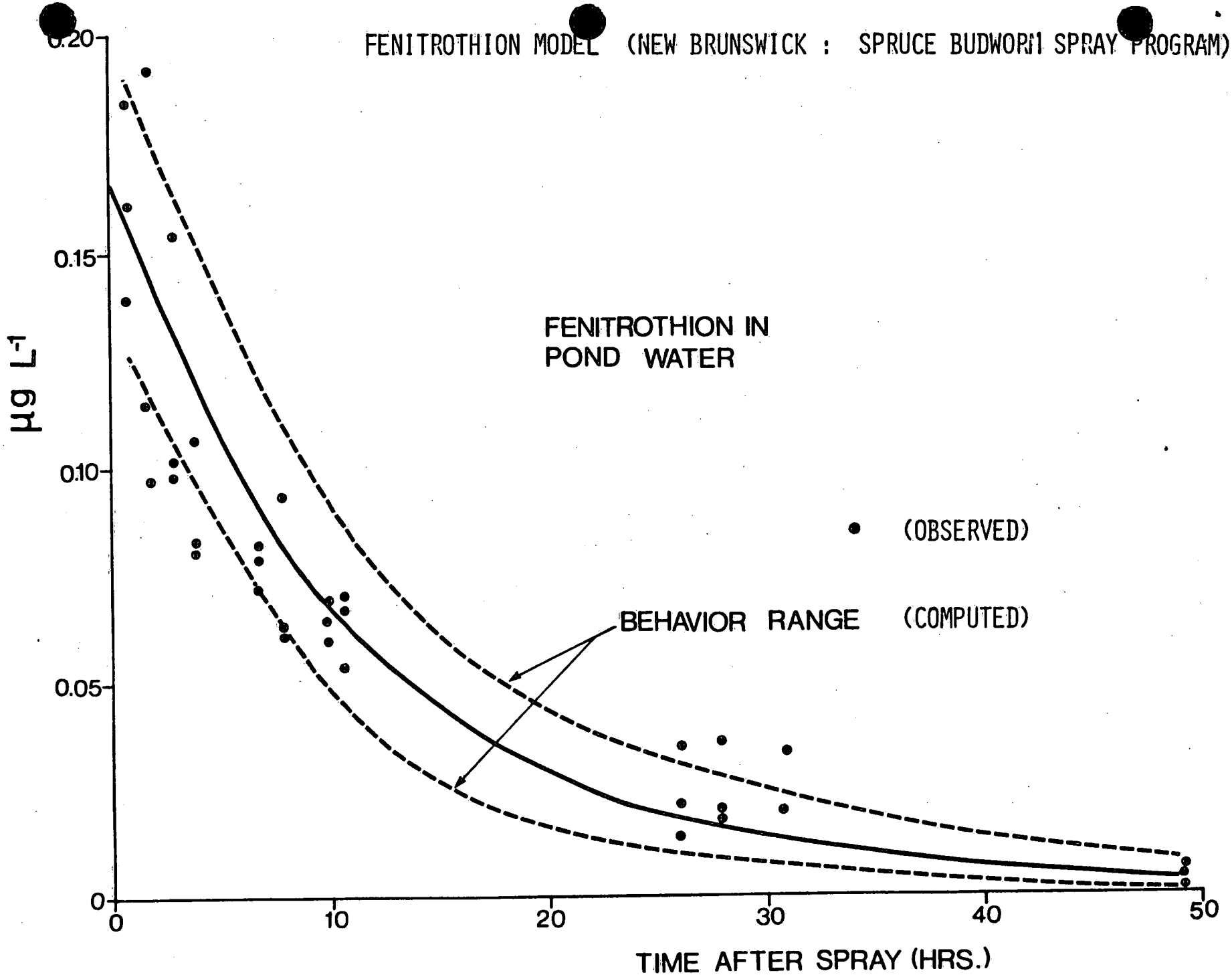
K_{ow} = octanol-water partition coefficient ($\frac{\text{conc in octanol}}{\text{conc in water}}$);

BCF = bioconcentration factor ($\frac{\text{conc in organism}}{\text{conc in medium}}$);

H = Henry's law constant ($\frac{\text{conc in air}}{\text{conc in water}}$);

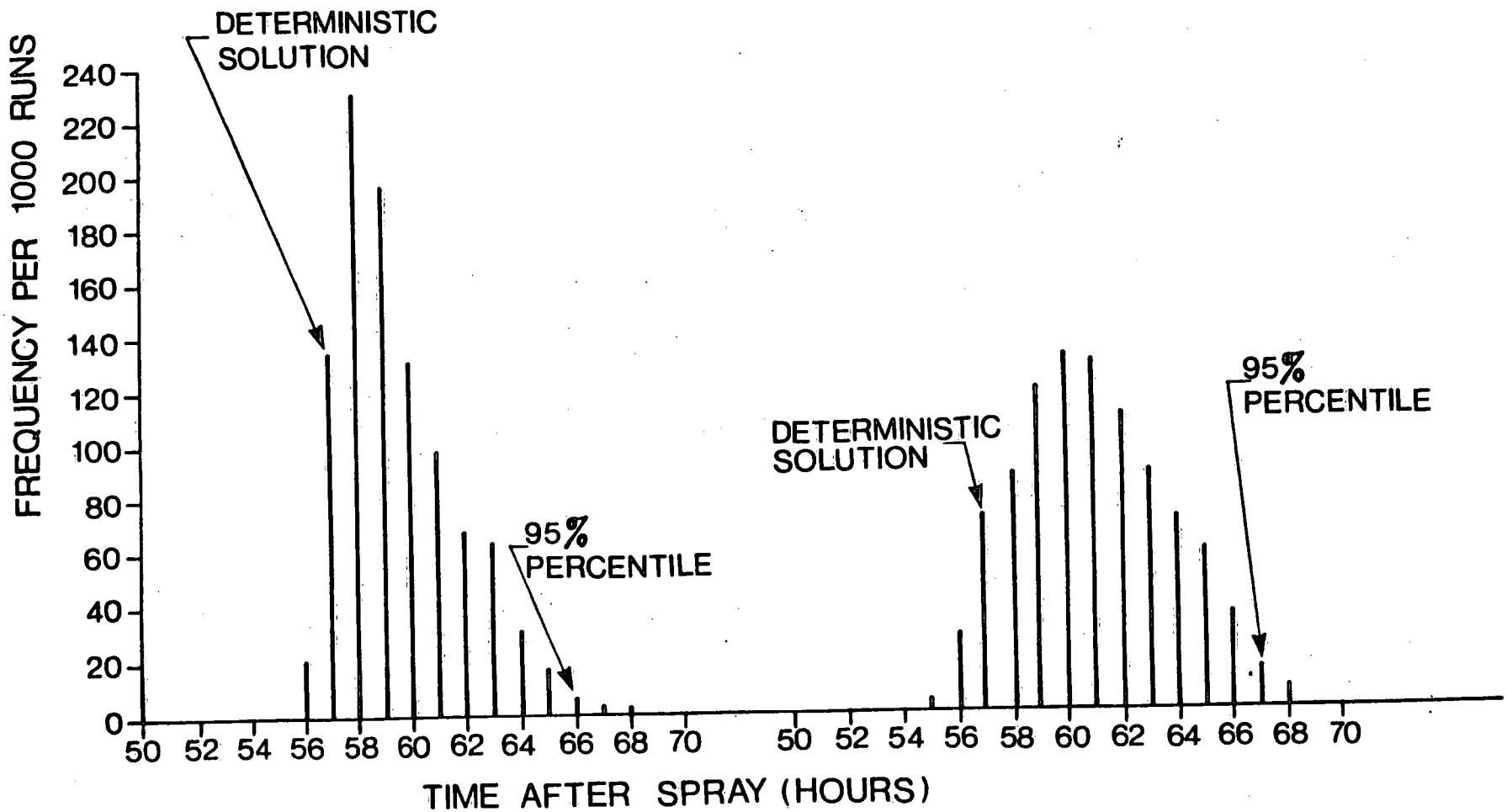
K_d = soil sorption coefficient ($\frac{\text{conc in soil}}{\text{conc in water}}$);

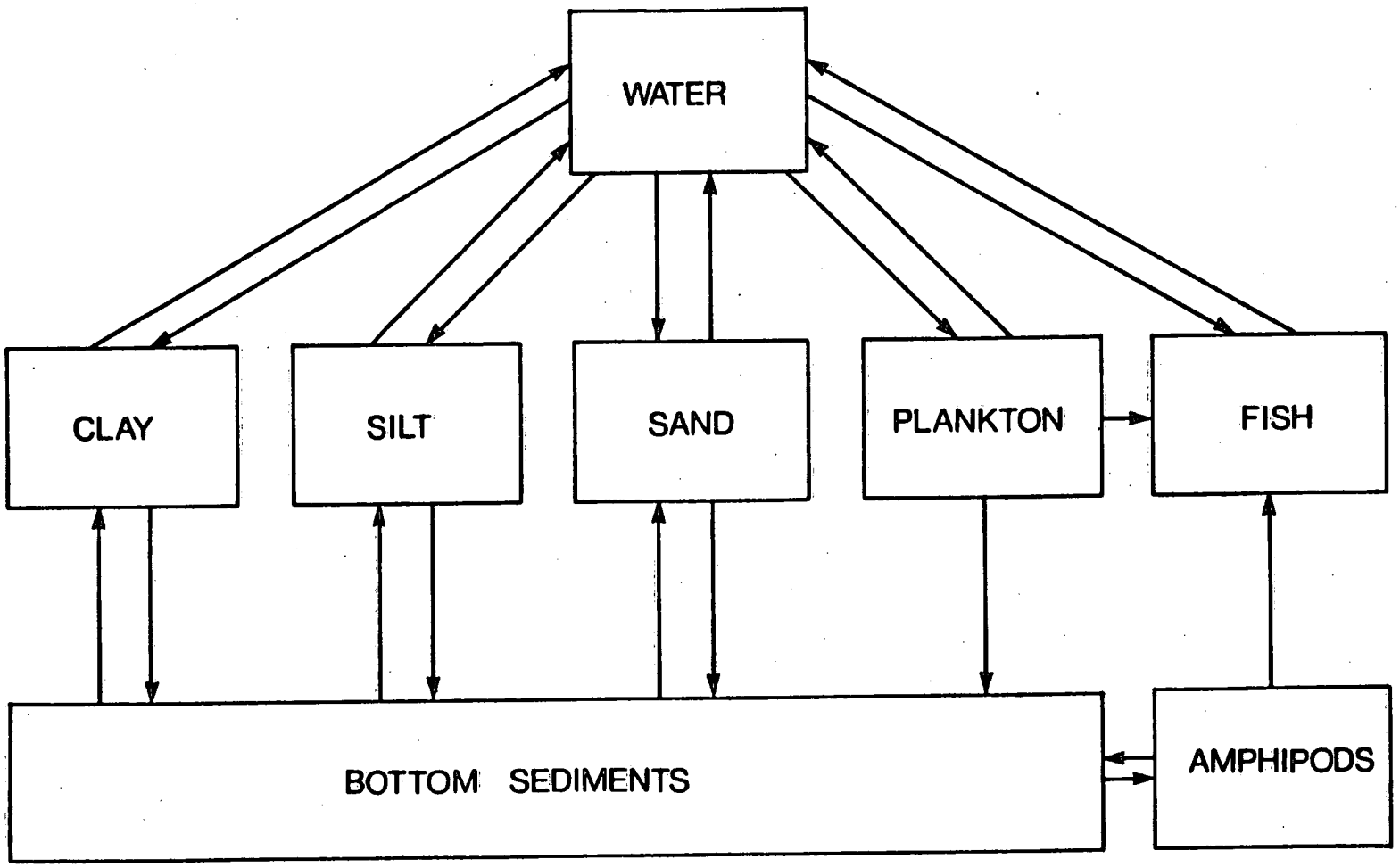
K_{oc} = soil sorption coefficient expressed on an organic carbon basis.

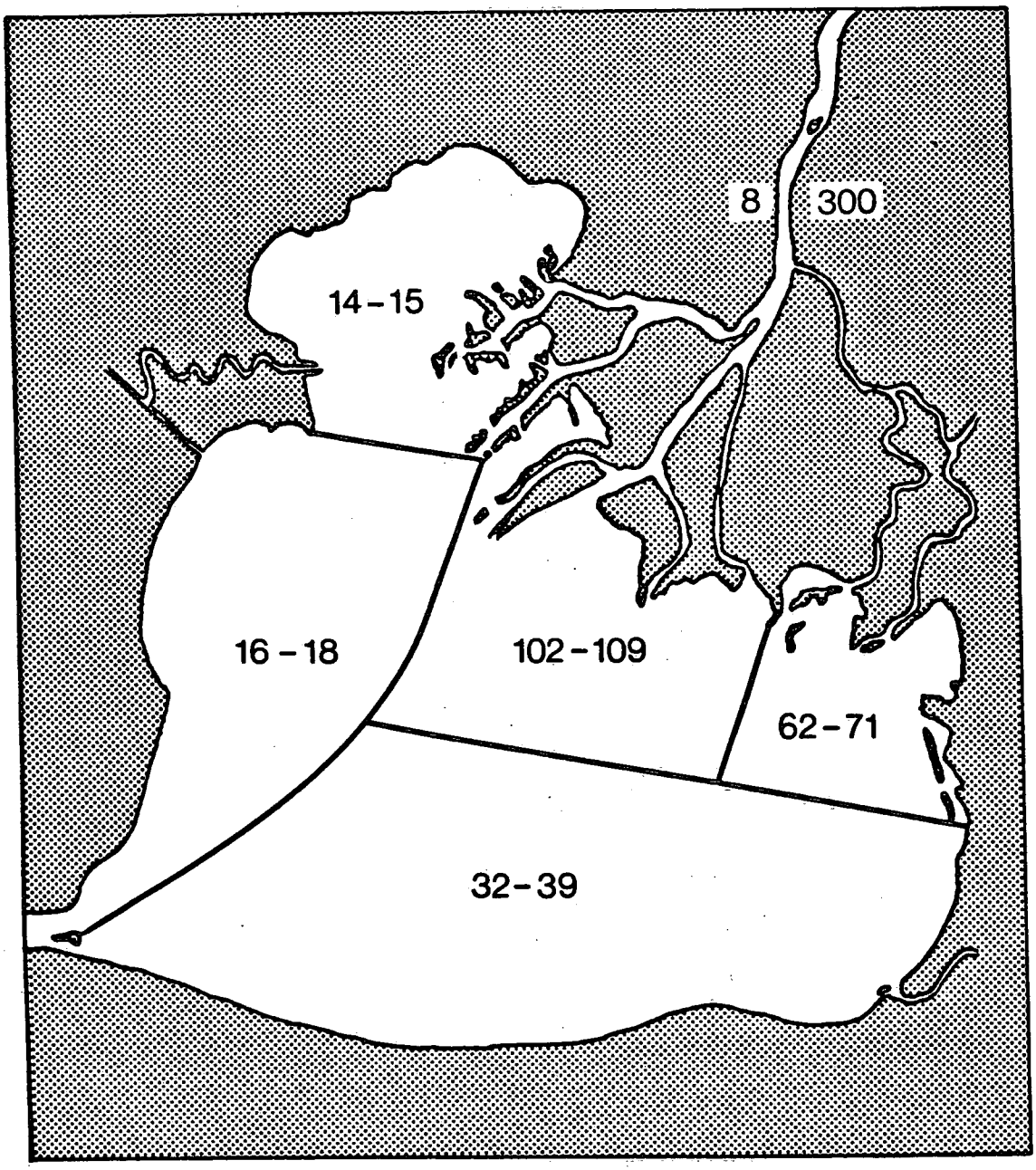

FENITROTHION MODEL (NEW BRUNSWICK : SPRUCE BUDWORM SPRAY PROGRAM)
0.20
0.15
0.10
0.05
0
µg L-1
FENITROTHION IN
POND WATER
(OBSERVED)
BEHAVIOR RANGE (COMPUTED)
0
10
20
30
40
50
TIME AFTER SPRAY (HRS.)

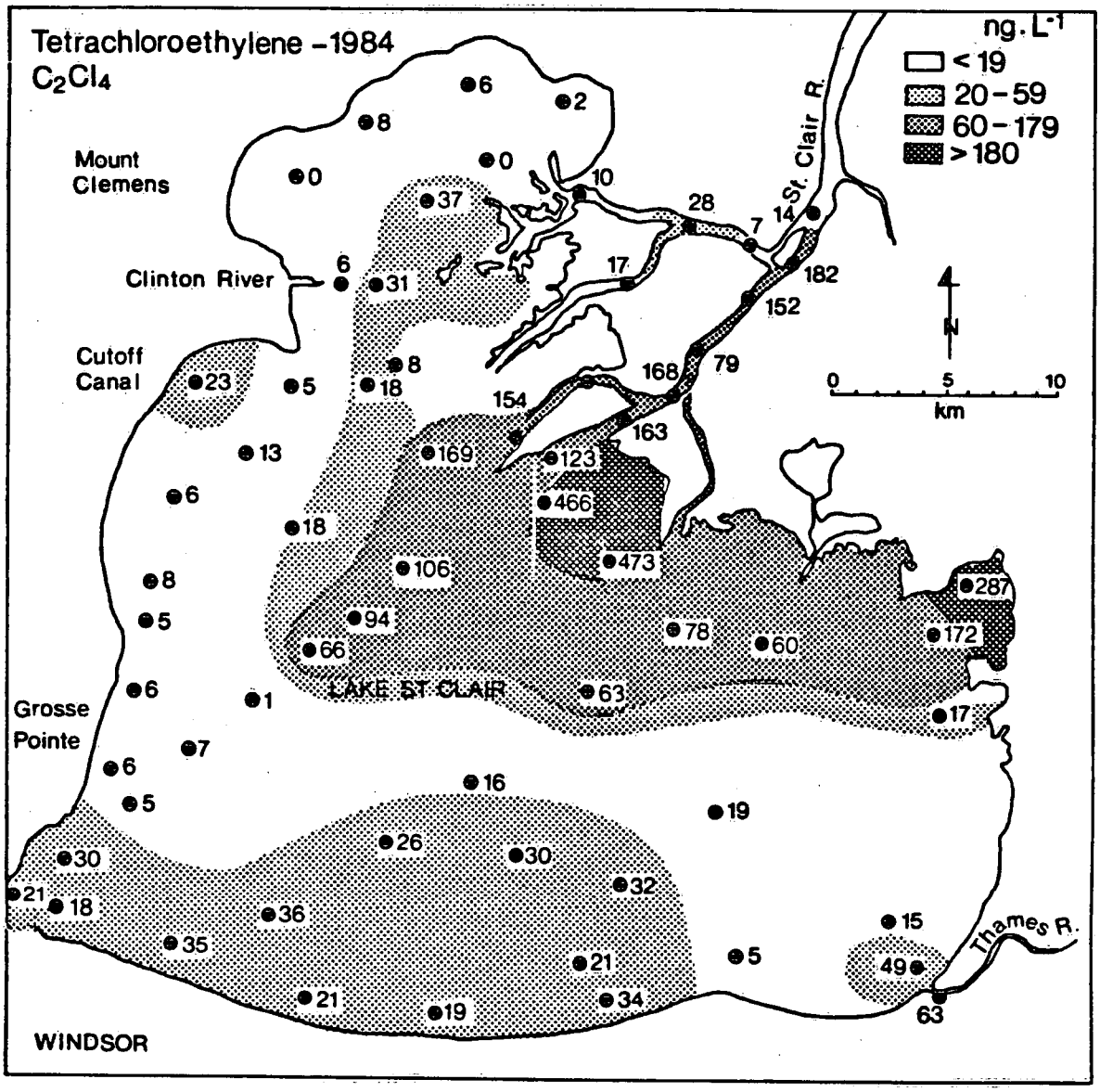
PARAMETERS WITH TRIANGULAR FREQUENCY DISTRIBUTION

PARAMETERS WITH UNIFORM FREQUENCY DISTRIBUTION




WATER
CLAY
SILT
SAND
PLANKTON
FISH
BOTTOM SEDIMENTS
AMPHIPODS


8
300
14-15
16-18
102-109
62-71
32-39


Tetrachloroethylene -1984
C_2Cl_4
ng.L^{-1}
< 19
20 - 59
60 - 179
> 180
St. Clair R.
Mount Clemens
Clinton River
Cutoff Canal
Grosse Pointe
LAKE ST CLAIR
Thames R.
WINDSOR
N
0 5 10
km
6
2
8
0
0
10
37
28
7
14
6
31
17
182
152
8
23
5
18
168
79
154
163
13
169
123
466
6
18
106
473
287
8
5
94
78
60
172
66
6
1
63
17
7
6
16
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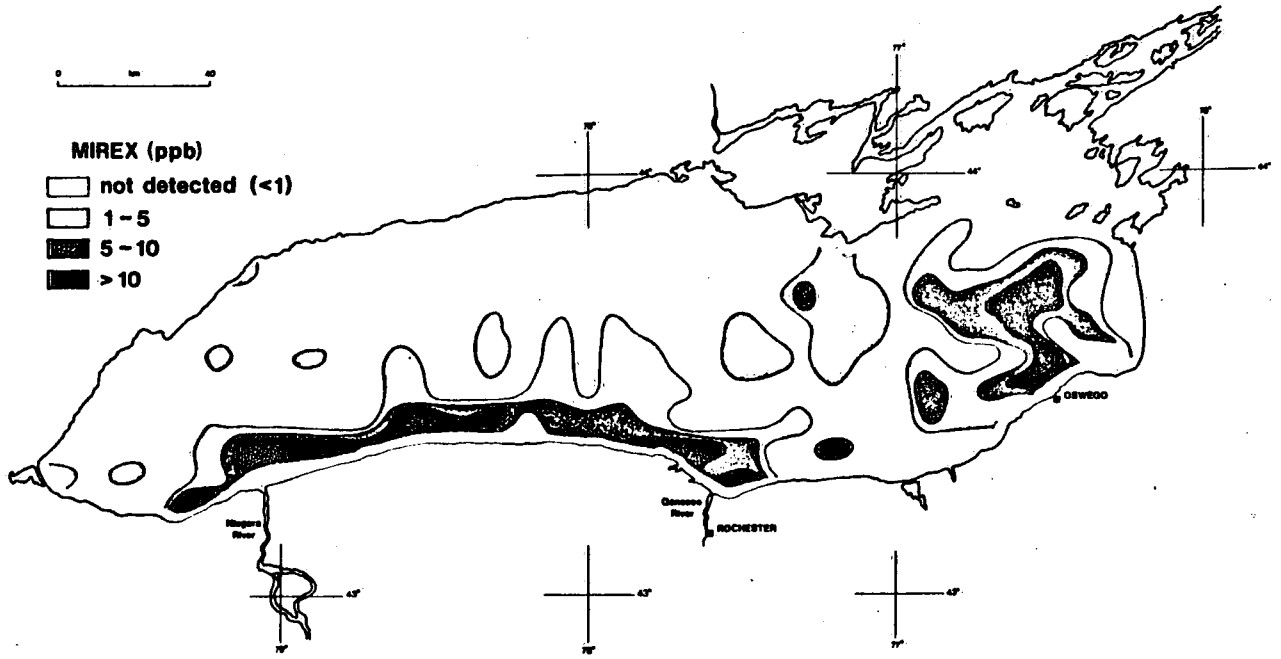
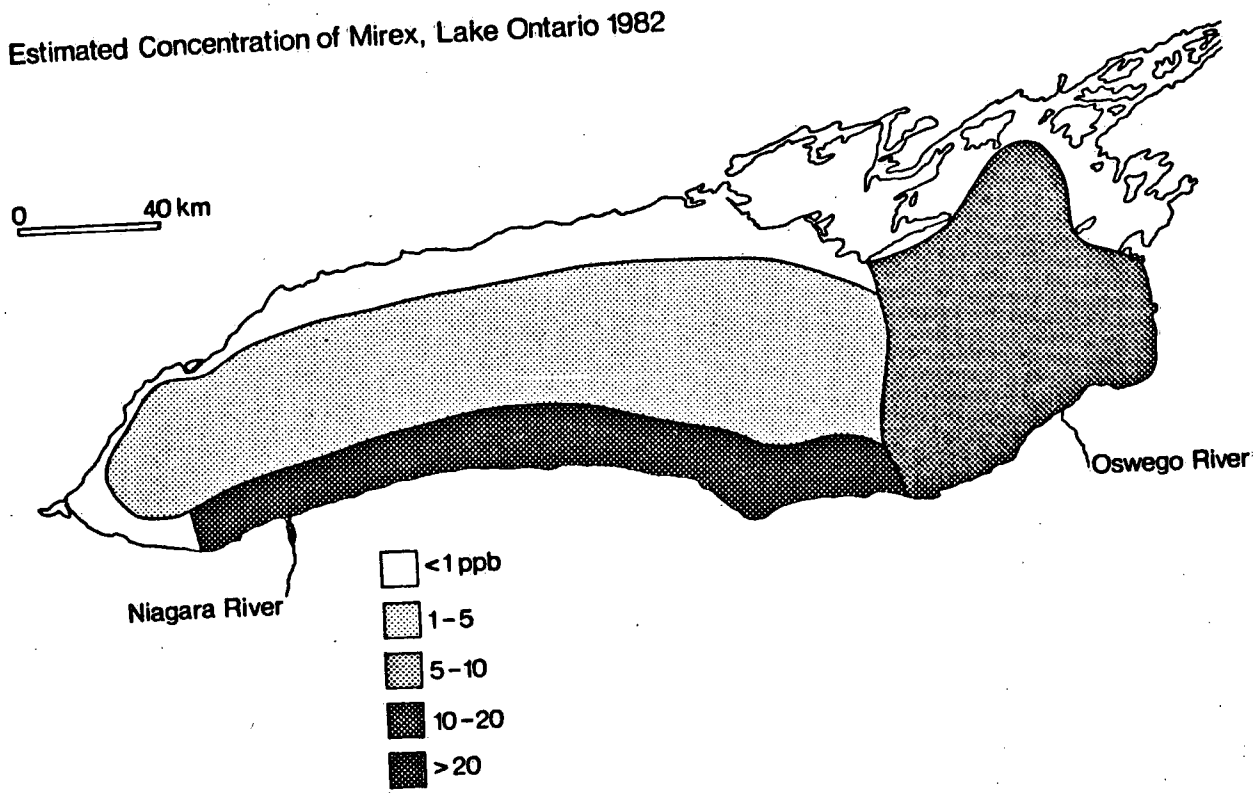
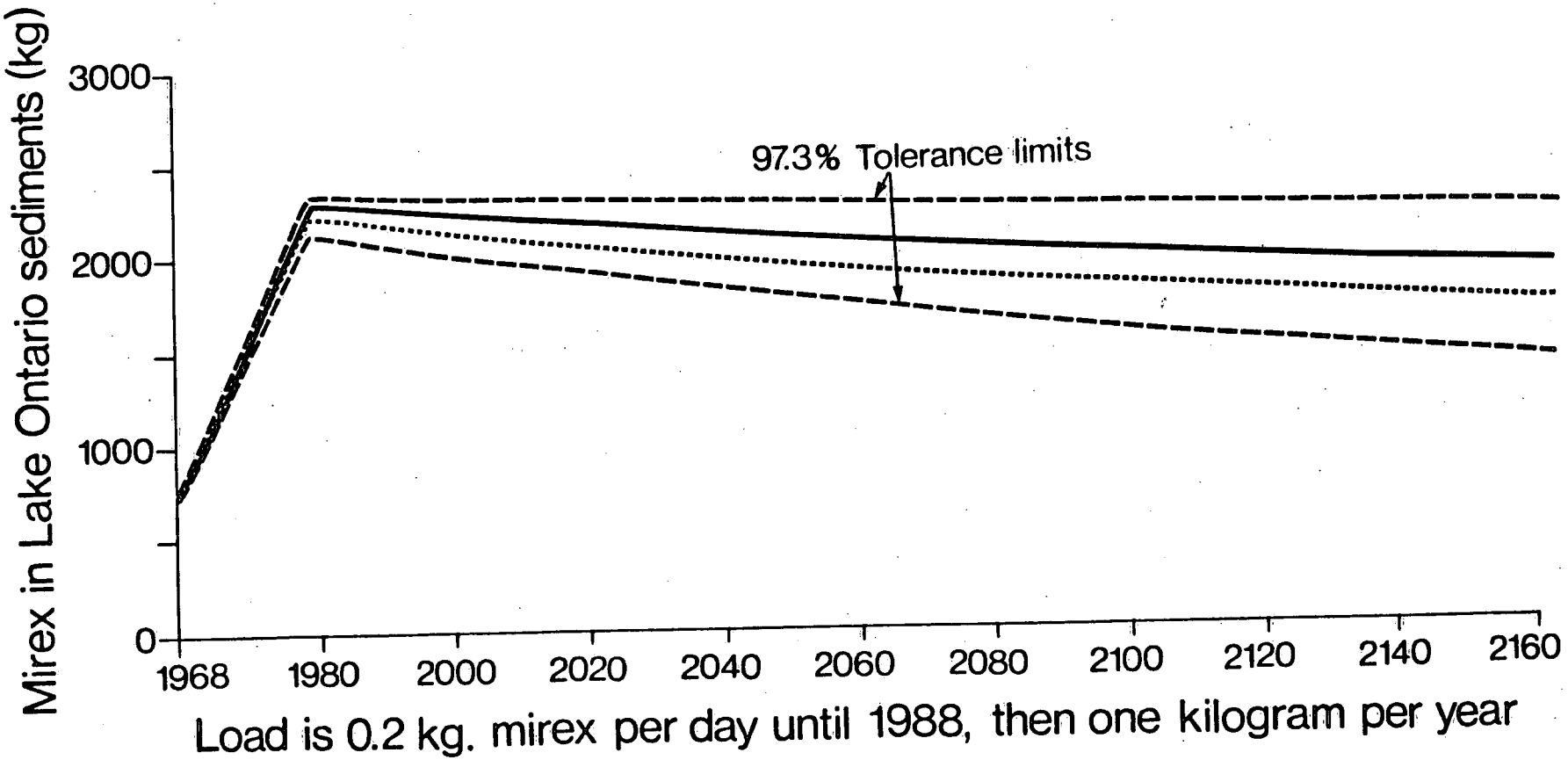
30
26
30
32
21
18
36
15
35
5
21
49
21
19
34
63


MIREX (ppb)
not detected (<1)
1 - 5
5 - 10
> 10
OSWEGO
ROCHESTER


Estimated Concentration of Mirex, Lake Ontario 1982
0
40 km
Niagara River
Oswego River
<1 ppb
1-5
5-10
10-20
>20


Mirex in Lake Ontario sediments (kg)
3000
2000
1000
0
97.3% Tolerance limits
1968
1980
2000
2020
2040
2060
2080
2100
2120
2140
2160
Load is 0.2 kg. mirex per day until 1988, then one kilogram per year

RESEARCH APPROACH