Ecokinetics: A Study of the Fate and Distribution of Chemicals in Laboratory Ecosystems

The anticipated kinetic behavior of different amounts or forms of a chemical in the environment can be studied by introducing the chemical into a laboratory ecosystem, collecting samples of the different components of the system at various times, and obtaining a sequence of concentrations of the chemical and/or its metabolites. Conventional compartmental models can be used to characterize this concentration-time data in order to better predict the distribution and ultimate fate of a chemical introduced into the environment, to provide a quantitative measure for helping assess the environmental impact of different chemicals, and to reduce the cost of expensive laboratory testing and field work.

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SCOPE

Most progressive industrial companies are committed to exercising responsible care for all products both during manufacture and later in their use by the customer. This product stewardship concept makes it necessary to collect and interpret meaningful data to assess the environmental impact of each new or existing product so that appropriate steps can be taken to protect employee and public health as well as the environment as a whole. One method being pursued is to build laboratory ecosystems which simulate typical environmental conditions. Then the kinetic behavior of different amounts or form of chemical is examined by introducing it into the simulated ecosystem, collecting samples of the different components of the system at various times, and obtaining a sequence of concentrations or amounts of the chemical and/or its metabolites. Collection of kinetic data is a departure from the standard practice of determining the residue at one or at most two time periods remote from the exposure time. In this paper we show that a conventional compartmental analysis can be used to characterize this data. The parameters of the characterizing model make it possible to compare the potential environmental impact of different chemicals. The model itself makes it possible to predict the time distribution in the environment for different modes of exposure (for example, slow release, accidental spill, etc.) so that proper exposure levels and handling procedures can be determined even before environmental testing is initiated.

Two major problems are associated with the use of compartmental models. The first is the development of plausible models for a particular ecosystem. This requires considerable background in the field from which the problem arises. Accumulated knowledge must provide some justification for the model selected and the parameters selected must have meaning in terms of known processes and the structure of the real system. The second problem is the so-called "inverse" of the first. That is, given one or more plausible models for an ecosystem, what data should be collected to decide which model is the most suitable and to obtain meaningful estimates of the model parameters. Recently developed model discrimination and nonlinear parameter estimation techniques are combined in an iterative computer-based model building procedure to solve the problem.

CONCLUSIONS AND SIGNIFICANCE

A compartmental analysis can be used to characterize the sequential concentration-time data generated during and/or after a chemical is introduced into a laboratory ecosystem. A model building procedure based on the principle of parsimony, which can be followed by a modeling team to ensure generation of the least complex model warranted by the data, is presented. Two examples of ecokinetic modeling are presented. The first involves the modeling of a bioconcentration test for different chemicals using fish as the test organism. The parameters of this model make it possible to classify different chemicals not only by their long exposure steady state concentrations but also the rates of uptake and clearance for different exposure times and exposure levels. For those chemicals which bioconcentrate slowly, the model predicts the bioconcentration potential from relatively short exposure periods. The cost savings realized by the modeling approach were directly responsible in having this procedure adopted as a technically and economically attractive environmental screening tool.

A second example is presented to show how ecokinetics can be used to determine the distribution and ultimate fate of the active ingredient in a new insect control agent, Dursban* insecticide, introduced instantaneously into an acquatic ecosystem containing fish and soil and plants. A compartmental analysis is used to characterize the sequential chemical concentration-time data for the water, soil, and plants and fish. The modeling identifies the important stages in the distribution process. Ecokinetic studies of agricultural chemicals can serve as a very effective screening tool by identifying both environmentally attractive and unattractive features at a very early stage of development and by providing benchmark parameters for evaluating potential new products.

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In studying the distribution and ultimate fate of a chemical substance added to an ecosystem, one is particularly interested in the kinetics involved in the transformations within and between the different components of the system. In general, the more precisely or microscopically the steps in a system are represented the more complex is the overall system model. For purposes of extrapolation to conditions not encountered in an experimental investigation, the most fundamental mechanistic model possible is preferred. Unfortunately, it is usually extremely expensive to develop such a micro model because each step must be investigated separately with associated analytical, physical, and financial problems. However, there are many questions which can be answered by less precise more macroscopic models.

Rather than develop different models for the various phenomena occurring, it will suffice to use a more general analysis for the kinetics of transfer without referring to any particular mechanism of transfer, for example, diffusion, fluid flow, etc. Models satisfying these requirements are those consisting of systems of compartments. These assume that various regions of the ecosystem and its components can be represented by a series of ideal volumes in which chemical substances move from one volume to the next according to laws of kinetics analogous to the kinetics that describe diffusion phenomenon. These ideal volumes imply that all property variations are ignored and perfect mixing is assumed so that the outflow from a compartment has the same properties as the compartmental contents. Essentially, they are the macroscopic balance equations of the classic transport phenomena by Bird et al. (1960).

An extensive literature exists on the subject of ecological system modeling (for example, Patten, 1970; Keinath, 1972). The compartment analysis approach has been used in studies of academic interest but rarely to find solutions to real pollution problems. In order to characterize laboratory ecosystem data, let a compartment represent:

1. A given volume limited by boundaries such as a membrane together with that substance which occupies it, or
2. The theoretical equivalent of a given chemical compound in a given volume, that is, the formation of a metabolite may be associated with a separate compartment.

Assume that a single parameter is sufficient to characterize either the entry or exit of a substance from a compartment. Then a system of interconnected compartments, which define a specific compartmental model characterizing an ecosystem, may be described by the notation shown in Figure 1 for the specific case of a four-compartmental model. The parameters k_{ij} represents the transfer of a substance from the ith to the jth compartment by some mechanism such as diffusion or chemical reaction which is left unspecified. The input of a substance into, say the ith compartment, from some source outside is denoted k_{oi} while the output or elimination of a substance outside the ecosystem under consideration is denoted k_{io}. If there is no exit to the outside, that is, $k_{io} = 0$ for all i, the system of compartments is called *closed*, otherwise it is called *open*.

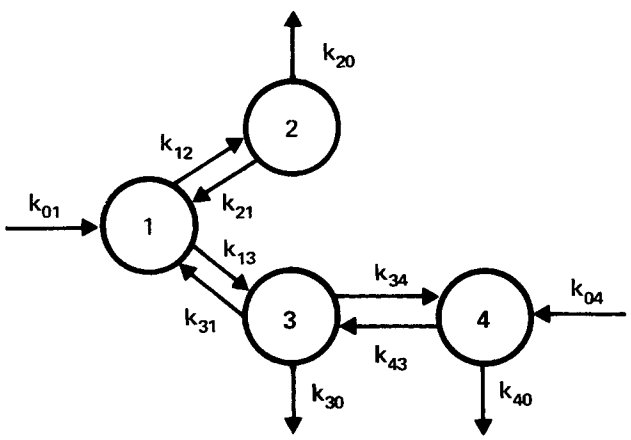

Fig. 1. A typical four-compartment open model.

There are basically two different ways a substance may be introduced into an ecosystem:

1. Bulk addition with no measurable time delay, such as the spraying of an insecticide on a pond of water,
2. Infusion over a measurable period of time, such as the release of a pollutant from industrial or municipal waste treatment plants, or
3. A combination of 1 and 2.

Suppose that an amount X_o of a substance was or, in the case of 2, is being added to an ecosystem characterized by a system of N compartments $i = 1, 2, \ldots, N$. (Note: In practice the number of compartments may be known only after data collected on the system have been analyzed statistically.) Assume that rapid mixing occurs so that the material will distribute itself throughout the various compartments which at time $t = 0$ contain the amounts $X_1, X_2, \ldots, X_N$. In addition, assume that exchanges between any two compartments occur according to first-order reactions. Then variations in the amounts of material present in the different compartments are described by the following system of linear first-order ordinary differential equations with constant coefficients corresponding to the diffusion, reaction, or transfer constants k_{ij} introduced earlier:

$$\frac{dx_i}{dt} = \sum_{j=1}^{N} k_{ji}x_j - \sum_{j=0}^{N} k_{ij}x_i + I(k_{0i}) \quad i = 1, 2, \ldots, N \tag{1}$$

where $k_{ji} = 0$ when there is no transfer from compartment j to compartment i or no addition of the material to the ith compartment from outside the system. Similarly, $k_{ij} = 0$ when there is no transfer from compartment i to compartment j or no elimination of the material from the system via the ith compartment. $I(k_{oi})$ is a function describing the process by which the material is added to the ith compartment in an open system.

Given a set of initial conditions:

$$x_i(0) = X_i \quad i = 1, 2, \ldots, N \tag{2}$$

the closed form solution to the system of differential equations is

$$x_i(t) = A_{i0} + \sum_{j=1}^{N} A_{ij}e^{-a_j t} \quad i = 1, 2, \ldots, N \tag{3}$$

where the exponent coefficients a_j associated with the jth compartment are functions of the individual rate constants

$$a_j = a_j(k_{ij}, k_{ji}) \tag{4}$$

while the coefficients A_{ij} are functions both of the rate constants and the amount and method by which the substance is introduced into the system, that is,

$$A_{ij} = A_{ij}(k_{ij}, k_{ji}, I(k_{0j}, X_{0j})) \tag{5}$$

where X_{0j} is the amount entering the jth compartment. The values of A_{ij} and a_j are developed in the literature for a variety of special cases in particular for $N \leqq 2$ (Patten, 1970; Jacquez, 1972).

Given any such system, the problem of estimating the rate constants k_{ij} or the derived coefficients a_j and A_{ij}

from measured data is a nontrivial task. Equation (3) is highly nonlinear in the parameters so that nonlinear parameter estimation techniques (Bard, 1973) must be used although methods have been developed for obtaining crude approximations to the parameters for special types of systems. These nonlinear parameter estimation techniques may be applied either to the differential equation system directly, in which case estimates of the individual rate constants are obtained, or to the closed form solution, Equation (3), in which case the derived coefficients are estimated. There is some debate over which approach to follow. Since the computation must be carried out on a high speed digital computer even if the system is only of a moderate degreee of complexity (that is, $N = 2$), a trade-off must be made between the increased computational burden associated with integrating the differential equation system numerically vs. the the problem of generating both the closed form solution and transformation formulas for calculating the individual rate constants from the derived coefficients. In either case the reliability of these estimates is an important concern. This reliability is measured by construction of confidence regions for the parameters (Draper and Smith, 1966). Since significant correlations between different parameter estimates for nonlinear functions are the rule, joint confidence regions must be constructed and used to show to what extent the estimates can be perturbed without changing some statistical performance criteria (for example, least squares, maximum likelihood) a significant amount.

The applicability of compartmental models to ecological systems is naturally limited by the basic assumptions enumerated earlier. In particular, one is limited a priori to phenomena ruled by first-order or zero-order kinetics. Fortunately, these assumptions are sufficiently valid for a number of biological phenomena occurring within the system such as simple diffusion through a membrane, excretion of a material by filtration, etc. However, nonlinear differential equations must be used for naturally occurring phenomena such as saturation for given concentrations of materials. For example, nonlinear relationships are observed in enzymatic kinetics governed by the Michaelis-Menten law. In such cases, it is frequently necessary to work with the differential equation system directly for both parameter estimation and model predictions. In reality all biological systems exhibit this saturation phenomenon to some extent and are therefore somewhat nonlinear. However, most systems behave more or less linearly, particularly in response to relatively small perturbations to the system so that linear compartmental models can be applied, although with caution and a definite end use in mind.

COMPARTMENTAL MODEL BUILDING

It is frequently possible for the ecologist to postulate several different compartmental models for characterizing the behavior of the substance added to the ecosystem. An extremely difficult problem which is receiving considerable attention at the present time is what data should be collected and how should it be used to decide which model is best. *Model discrimination* is the statistical procedure which chooses or distinguishes among the various postulated models to find the model or models most suitable for characterizing the system under consideration (Reilly et al., 1974; Blau et al., 1975). Note that this discrimination takes place only among the set of postulated models. That is, the model selected may be the best of the originally postulated models but totally inadequate for characterizing the system. Using some form of residual analysis on collected data, it is frequently possible to identify specific inadequacies in this best model. By interpreting this inadequacy in terms of some unaccounted-for biological phenomenon, it should be possible to suggest other models which include additional compartments and/or rate constants to accommodate this phenomenon. Then discrimination is carried out on these new models and the process is repeated.

Usually little difficulty is experienced in postulating a variety of models of varying degrees of sophistication. In practice, a good approach is to start with a set of simple models (that is, relatively few compartments and rate constants). Then sets of progressively more complex models are selected until no further increasing in complexity is warranted. This method of proceeding from the simple to the complex is called *Ockham's razor* or the *principle of parsimony* (Kittrell et al., 1970). In statistical terms it is analogous to the stepwise addition procedure of multilinear regression analysis (Draper and Smith, 1966). Blau et al., (1972) have demonstrated the appliability of this technique in a wide variety of model building applications.

There are really two aspects to the problem of model building. The first is the experimental design problem, that is, choosing the experimental conditions in such a way that:

1. Discrimination between rival models is possible or
2. Meaningful parameter estimates will be obtained after a suitable model is found.

This usually means multiple exposures, appropriate spacing of the collection times, and multiple sampling. The second is the analysis problem, that is, analyzing the data to assess:

1. How much discrimination has been achieved,
2. The adequacy of the best model once discrimination has been realized, and
3. The evaluation of parameter estimates including their reliability in the model selected.

The design problem is the more fundamental one. If for some reason the analysis of the data is faulty it may be repeated. However, the damage of poor design is irreparable and invalidates subsequent data analysis regardless of its level of sophistication.

A recent paper by Reilly and Blau (1974) surveys the latest methods for performing both the design phase and the analysis phase. It is beyond the scope of this report to discuss these methods in any detail. In particular, it will be assumed in the examples to follow that adequate designs have been employed so that the problem is only one of analysis.

BIOCONCENTRATION OF ORGANIC CHEMICALS IN FISH

The ability of certain chemicals to move through the food chain resulting in higher concentrations at each trophic level is called *biomagnification* or *bioconcentration* (Kenaga, 1972). The wide spread distribution of DDT (Burnett, 1971) and the polychlorinated biphenyls (Gustafsen, 1970) are classic examples of such movement. It is important to know the degree to which any chemical, if introduced into the environment, will bioconcentrate so that corrective action can be taken. Bioconcentration in aquatic organisms is one of the key criteria in establishing toxic pollutant effluent standards (Quarles, 1973) according to Section 307 of the 1972 Clean Water Law.

A laboratory test reported by Branson et al. (1975) measures the bioconcentration of chemicals in fish. Fish provide an excellent pilot plant for simulating bioconcentration because they act as a natural filter. Briefly, this method consists of exposing rainbow trout to two different, but constant, sublethal concentrations of a chemical for several days. During this uptake portion of the test proce-

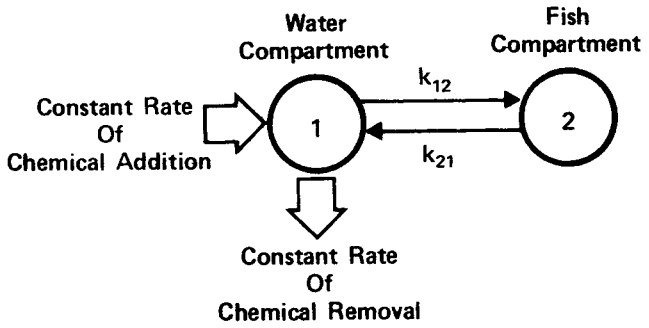

Fig. 2. Two-compartment model of bioconcentration test ecosystem.

dure, the concentration of chemical in fish muscle is determined by analyzing several fish from the aquarium at different time periods. Then the surviving fish are transferred to acquaria without addition of the chemical and concentrations are determined in an analogous fashion. This is the clearance portion of the procedure. The laboratory maintenance of fish, test equipment, and chemical analysis procedures are detailed by Branson et al. (1975).

The bioconcentration test becomes too expensive both in terms of time and analytical cost if the uptake portion of the procedure is conducted until the long time or steady state concentration of chemical is achieved. It will be shown how a compartmental analysis makes it possible not only to characterize the rates of uptake and clearance of different chemicals but also to predict the steady state concentration from data collected over a relatively short time period.

Compartmental Models Describing the Bioconcentration Phenomenon

Uptake and clearance of compounds by fish appear to involve a series of complicated equilibria. These equilibria govern the movement across gill membranes. Once a compound is in the blood plasma, several equilibria also direct the distribution between plasma and tissue. Despite the complexity of the reactions involved and the numerous routes both into and out of the fish, linear compartmental models can be used to characterize the concentration data collected in the laboratory test. The simplest model which can be postulated is to treat the fish as a single homogeneous compartment and assume that:

1. Uptake of chemical by movement in through the gills by penetration through the skin and by whatever is absorbed on food can be represented by the single uptake constant k_{12}, and

2. The clearance of chemical by fecal and urinary excretion as well as movement back through the gills and skin is characterized by the single clearance rate constant k_{21}.

The ecosystem itself consisting of the aquaria and the fish is represented by a two-compartment model (Figure 2) where the first and second compartments represent the water and fish, respectively. The arrows into and out of the water compartment represent the constant chemical addition rate maintained in the system. Performing a material balance on the two compartments and assuming first-order kinetics, one obtains the differential equation system:

$$\frac{dc_1}{dt} = 0$$

$$\frac{dc_2}{dt} = \begin{cases} k_{12}c_1 - k_{21}c_2 & 0 \leq t \leq t^* \\ -k_{21}c_2 & t^* \leq t \end{cases} \qquad (6)$$

with initial conditions:

$$c_1(0) = c_w \quad \text{and} \quad c_2(0) = 0$$

where c_1 and c_2 represent the concentrations in the 1st and 2nd compartments respectively and t^* represents the elapsed time for the uptake portion of the test procedure. (Note: Concentrations will be used interchangably with amounts in this report. For the specific applications under consideration here this presents no problem. However, when this distinction must be made, it is necessary to define for each compartment a so-called "volume of distribution" which is that volume necessary to make the completely mixed assumption valid based on the observed data. Only in fortuitous situations does the volume of distribution correspond to the dimension of some physical of biological system, for example, the volume of fish, organ, etc. Hence it should be considered simply as a proportionality constant introduced to accommodate observed data.) Solving this differential equation system, the closed form solution for the concentration in the fish becomes

$$c_2 = \begin{cases} c_w \dfrac{k_{12}}{k_{21}} [1 - e^{-k_{21}t}] & 0 \leq t \leq t^* \\ c_w \dfrac{k_{12}}{k_{21}} [e^{-k_{21}(t-t^*)} - e^{-k_{21}t}] & t^* \leq t \end{cases} \qquad (7)$$

while the water concentration is $c_1 = c_w$ for $0 \leq t \leq t^*$ and $c_1 = 0$ for $t \geq t^*$. If this model is adequate, then the bioconcentration factor

$$K_B \equiv \lim_{t^* \to \infty} \left(\frac{c_2}{c_w}\right) = \frac{k_{12}}{k_{21}} \qquad (8)$$

is simply the ratio of the uptake rate constant to the clearance rate constant. That is, by obtaining estimates of the parameters of the model, it is possible to estimate the bioconcentration factor as well.

Depending on the physicochemical characteristics of the material being tested, it is probable that the fish be represented by two compartments where one of these compartments corresponds to a particular tissue in which the material may be preferentially concentrated. For example, 2,2′4,4′ tetrachlorobiphenyl, a very nonpolar chemical, is assumed to be partially concentrated in the fatty tissues and partially in muscle. It would also be necessary to use two compartments to represent the fish if the chemical is metabolized at a rate considerably different than that represented by the uptake rate constant introduced earlier.

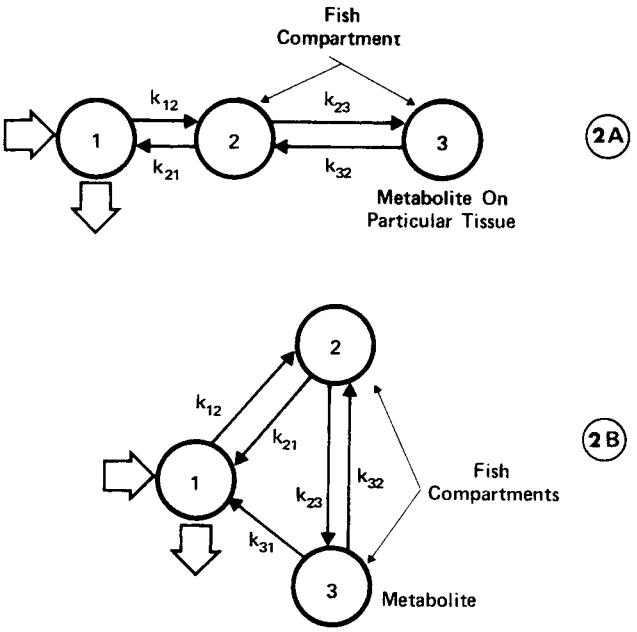

Fig. 3. Three-compartment models of bioconcentration test ecosystem.

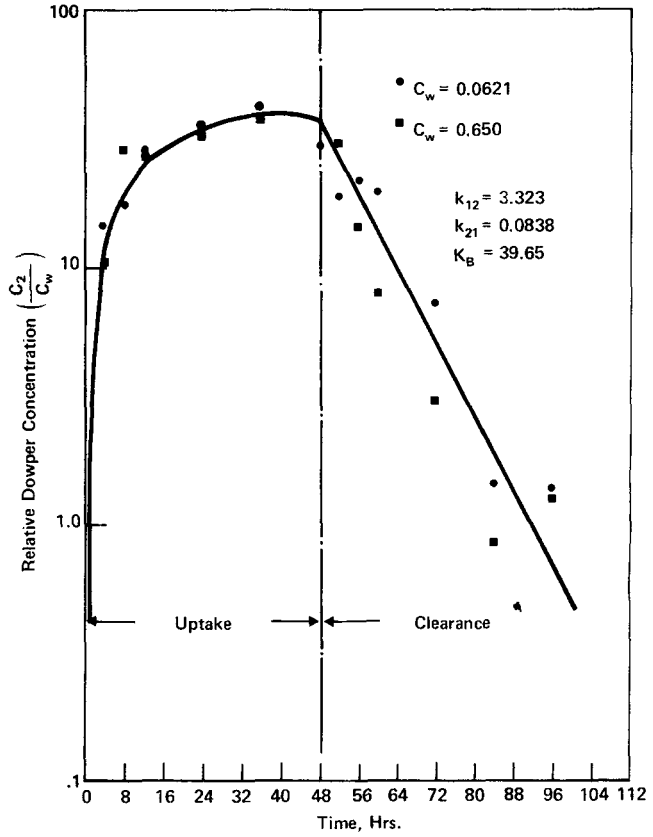

Fig. 4. Relative concentration-time data for tetrachloroethylene. Each point is the mean value for two fish.

Further, if this metabolite is preferential stored in fatty tissues of the fish, a second compartment will be needed. In either case, three compartment models, such as those shown in Figure 3, can be postulated to describe these phenomena. In terms of a compartmental model system, models 2A and 2B differ only in that 2A accommodates a rate constant for clearance from the third compartment back to the water compartment. The actual interpretation of the rate constants k_{23} and k_{32} corresponds to the different biological phenomena taking place. For example, if compartment 3 represents the organ of the fish in which the chemical is preferentially concentrated, then k_{23} and k_{32} represent diffusion or transfer constants. In the case of metabolite formation, however, they may represent reaction rate constants. The more complex the model, the less specific one must be in interpreting any rate constants. It is frequently necessary to collect additional experimental data to resolve these differences.

Bioconcentration of Tetrachloroethylene

Tetrachloroethylene is a commercial solvent used by the dry cleaning industry and known as Dowper*. Concentration-time data were generated by exposing trout to two different tetrachloroethylene concentrations according to the bioconcentration test procedure. Based on the physicochemical characteristics of tetrachloroethylene, Model 1 was postulated as the most likely candidate. A nonlinear parameter estimation routine was used to find the maximum likelihood estimates of the rate constants $k^*_{12} = 3.323$ h^{-1}, $k^*_{21} = 0.0838$ h^{-1}, so that $K_B{}^* = k^*_{12}/k^*_{21} = 39.65$. The observed and calculated concentrations using the optimal parameters are shown in Figure 4. The good agreement between the observed and calculated values is reflected in a lack of fit test which indicates that Model 1 is adequate for characterizing the data.

The parameter estimates quoted above are point estimates. The nonlinear confidence regions for the rate constants have been calculated and are shown in Figure 5. A 95% confidence region means that the probability is 0.95 that the true values of the rate constants lie somewhere within the region. The uncertainties in the parameters must be reflected in the calculation of the bioconcentration factor by Equation (8). A numerical evaluation technique suggested by Hsiang et al. (1971) was used to calculate a distribution function for the bioconcentration factor from the likelihood function and the joint probability density function for the parameters. This distribution function shown in Figure 6 reflects both uncertainty in the

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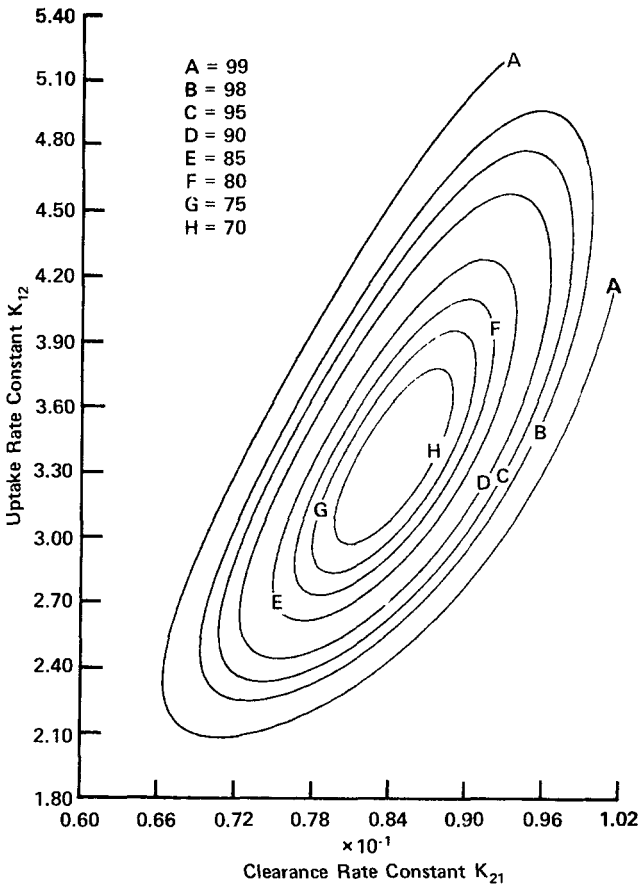

Fig. 5. Confidence regions for tetrachloroethylene parameters.

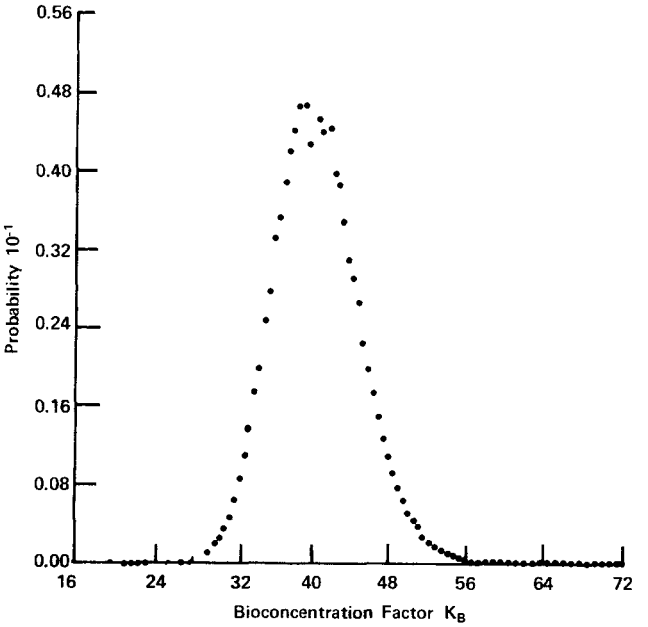

Fig. 6. Bioconcentration factor distribution for tetrachloroethylene.

data and any limitations in the model. If the model were inadequate, for example, a broad distribution would be generated reflecting little confidence in the calculated point estimates.

Bioconcentration of Other Chemicals

Although tetrachloroethylene reaches steady state during the 48-h uptake period, most compounds require longer exposure to the chemical. For example 2,2′,4,4′ tetrachlorobiphenyl requires more than 97 days exposure to reach 90% of steady state. To demonstrate the predictive capabilities of the model, the test procedure was carried out with a 5-day uptake and 20-day clearance periods for this compound. The optimal parameter estimates generated from this test were then used to predict the concentration in the fish well within experimental and biological variation during the course of a 42-day exposure (Branson et al., 1975).

A report by Neely et al. (1974) lists the bioconcentration factor and kinetic parameters for a number of different compounds. For a few of the more polar compounds, a three-compartment model was necessary to describe the data. They showed that the bioconcentration factor is directly related to their octanol:water partition coefficient, a physicochemical property of the chemical tested. This presents an ideal means of characterizing chemicals. By simply measuring the partition coefficient of a new or existing chemical, it is possible to predict the bioconcentration potential. This provides a simple screening tool but does not preclude the bioconcentration test procedure which must be carried out to determine the kinetics.

Discussion

This example has illustrated how a simple compartmental model system can be used to characterize data collected from an ecosystem despite the complexity of the biological process involved. Although the parameters of this model are interpreted as rate constants for uptake or clearance, no attempt is made to identify which of the several biological phenomena are controlling. The model has made the test procedure economically feasible by permitting one to calculate a steady state concentration from data collected under nonsteady state conditions.

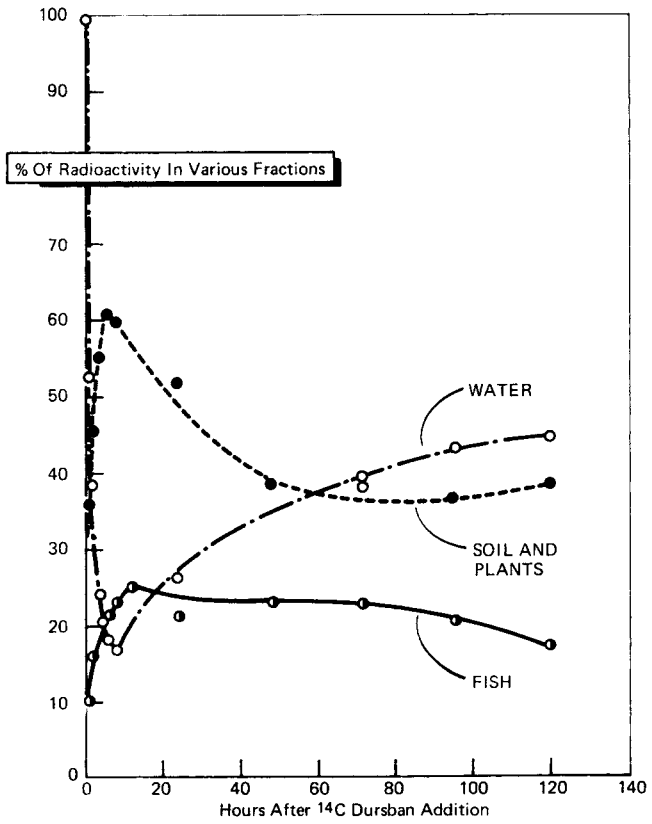

Fig. 7. Distribution of ^{14}C Dursban in the ecosystem.

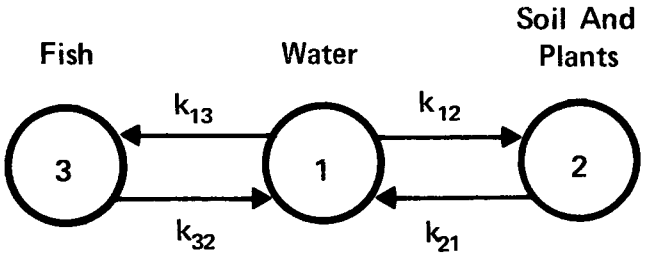

Fig. 8. Three-compartment closed model 1.

DISTRIBUTION OF AN INSECTICIDE ADDED TO AN ECOSYSTEM

Smith et al. (1966a) published some studies on the distribution and fate of a new agent for the control of insects, Dursban® insecticide. The active ingredient of Dursban insecticide 0,0-diethyl-0-(3,5,6-trichloro-2-pyridyl) phosphorothioate was labeled with radioactive ^{14}C in the pyridyl ring. Figure 7 shows the percent radioactivity observed in the water, soil and plants, and fish at various times after adding radioactive labeled Dursban insecticide to a 10-gal. aquarium. This aquarium contained two in. of soil (13.3% organic matter), plants, and initially, 45 goldfish. By characterizing this data with a compartmental model, it is possible to identify the important steps in the distribution of Dursban insecticide so that it can be applied in the most effective manner to maximize its efficacy and minimize its environmental consequences.

Building the Model

The simplest model which can be postulated to characterize the data consists of three distinct compartments corresponding to the water, compartment 1; the soil and plants, compartment 2; and the fish, compartment 3. Symbolically the model is represented by the closed system shown in Figure 8 where the rate constants correspond to the transfer of chemical between compartments as described earlier. By performing a material balance on the individual compartments and assuming first-order kinetics, we obtain the following system of differential equations:

$$\frac{dx_1}{dt} = -(k_{12} + k_{13})x_1 + k_{21}x_2 + k_{31}x_3$$

$$\frac{dx_2}{dt} = k_{12}x_1 - k_{21}x_2$$

$$\frac{dx_3}{dt} = k_{13}x_1 - k_{31}x_3 \qquad (9)$$

where x_i is the percent C^{14} activity in the ith compartment. The initial conditions reflect the fact that the system is closed with $x_1(0) = 100$, $x_2(0) = 0$, $x_3(0) = 0$. Using LaPlace transforms, an algebraically complex closed form solution can be generated. However, it is more convenient to estimate the model parameters directly from the differential equations.

Blau et al. (1975) have shown how the principle of parsimony and appropriate statistical tools can guide the decision-maker to generate a sequence of more complex models shown in Figures 9 and 10 until the most suitable model shown in Figure 11 is realized. Three additional compartments were postulated to accommodate the data. The formation of a metabolite of Dursban insecticide by the fish was postulated. Once cleared, this metabolite be-

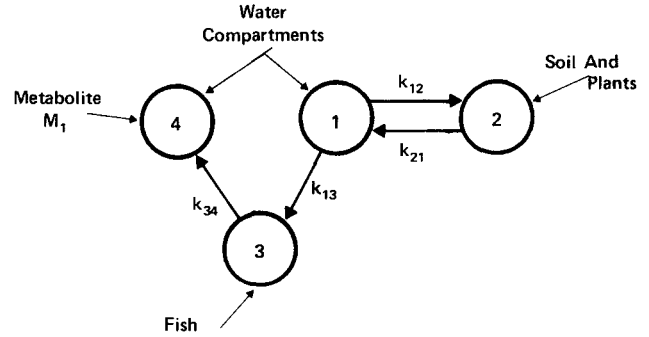

Fig. 9. Four-compartment closed model 2.

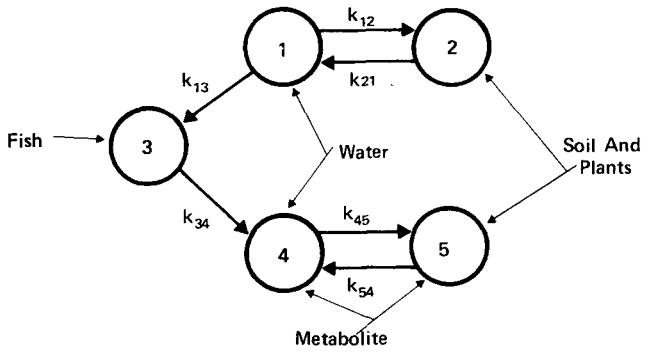

Fig. 10. Five-compartment closed model 2.

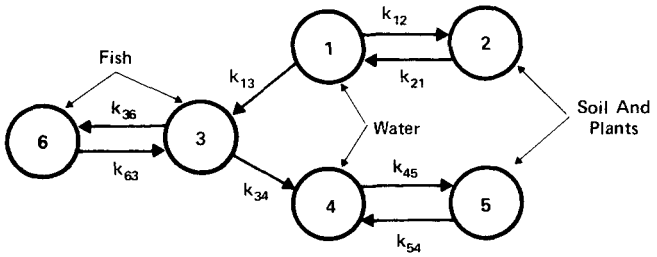

Fig. 11. Six-compartment closed model 4.

comes a separate compartment in the water, compartment 4, from where it was taken up by the soil and plants, compartment 5. It was necessary to postulate another compartment, compartment 6, for the fish in order to provide agreement between the water and fish data. This is analogous to the model shown in Figure 3 of the previous example and corresponds either to the transformation of parent compound into metabolite or to the preferential distribution of Dursban insecticide in certain tissues of the fish. The optimal parameter estimates are $k_{12}^* = 0.388\ h^{-1}$, $k^*_{21} = 0.0515\ h^{-1}$, $k^*_{13} = 0.136\ h^{-1}$, $k_{36} = 0.0670\ h^{-1}$, $k_{63} = 0.0254\ h^{-1}$, $k^*_{34} = 0.0788\ h^{-1}$, $k_{45} = 0.0068\ h^{-1}$, and $k_{34} = 0.0010\ h^{-1}$. Also, important is the fact that k_{31} and k_{43} the rate constant for transfer between the fish and water for the parent compound and metabolite cannot be distinguished from zero.

The final model that emerges from this analysis is the following:

1. There is a rapid equilibration between the applied Dursban insecticide and the soil and plant system followed by a slower uptake of the insecticide by the fish.
2. Once in the fish, the material is metabolized and excreted. The metabolite is probably the pyridinol which was identified in the water at the termination of the 120-h exposure.
3. The liberated pyridinol in the water is again taken up by the soil and plants.
4. The material is partitioned between two compartments in the fish. This tends to substantiate the data obtained by Smith et al. (1966); who demonstrated a partitioning between the viscera and the meat.
5. The final sink for the added Dursban insecticide is the soil and plants. This last item is very important since Smith (1966) has shown that the active ingredient of Dursban insecticide is metabolized readily by plants and will ultimately be degraded to CO_2, NH_3, and H_2O. Such a situation would imply that there is no persistence of Dursban insecticide in this particular ecosystem.

The fast initial absorption of the insecticide to the soil and plants has an added advantage in that this particular sink acts as a reservoir for the slow release of Dursban insecticide. This feature gives added long-term protection for the control of mosquito larvae in polluted waters. Schaeffer et al. (1970) demonstrated that a similar series of events occurred in a field trial.

Discussion

A compartmented model has generated a picture of the distribution pattern of Dursban insecticide when added to a pond of water. The existence of the various phenomena predicted by the model can be verified by existing experimental data. In this case the laboratory ecosystem was designed to simulate the type of environment which the insecticide might encounter in the field. However, the same system can readily be adopted as an important screening tool for reducing the resources required to determine the environmental input of any products on similar aquatic systems.

NOTATION

A_{ij} = function relating all inputs and outputs from the ith compartments
a_j = function relating transfer coefficients for jth compartment
c_1, c_2 = concentration in water and fish respectively
$I(k_{0i})$ = function describing the introduction of material to the ith compartment
K_B = bioconcentration factor
k_{ij} = transfer coefficient from the ith to jth compartment
N = number of compartments
t = time
X_i = amount of material in compartment i at time $t = 0$
x_i = amount of material in the ith compartment

Subscripts and Superscript

i, j = compartment index
0 = material added at time $t = 0$
w = water compartment
$*$ = optimal parameter estimates

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Pseudoplastic Falling Films with Concurrent Gas Streams

An experimental and theoretical study on gas and pseudoplastic liquid films in vertical downward flow is reported. Good agreement was obtained between predicted and measured values of the film thickness as a function of liquid shear properties and interfacial shear except in the case of the most dilute solution. Measured pressure drops in the gas in two-phase flow depend strongly on liquid shear properties and are up to five times higher than when gas flows alone.

Aqueous Carbopol solutions were used as pseudoplastic liquids.

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SCOPE

The industrial significance of gas-liquid film flow has inspired many experimental and theoretical studies. Most published work deals with Newtonian films, and no such investigation has appeared on non-Newtonian liquids as far as we know. Non-Newtonian liquids, however, are increasingly involved in food engineering, polymer processing, suspension and emulsion processing, and bioengineering. This work has been conducted to provide experimental evidence on the behavior of a pseudoplastic thin film flowing in parallel with an adjacent gas stream. When high shear is imposed at the gas-liquid interface, the film velocity profile depends strongly not only on liquid flow rate and shear properties but also on the interfacial shear. This makes an analytical solution of the momentum equations highly complex when dealing with non-Newtonian liquids. A semi-empirical method developed by Dukler (1959) for gas-Newtonian film flow is here extended to a gas-pseudoplastic film flow. Pseudoplastic liquids were selected because they are encountered more in practice than most other types of non-Newtonian liquids.

CONCLUSIONS AND SIGNIFICANCE

The experimentally determined dependence of film thickness on liquid shear properties, liquid flow rate, and gas velocity agrees satisfactorily with the theoretical predictions. Only in the case of the lowest concentration of Carbopol in water are the predicted values significantly higher. It is thought that a drag reduction effect might have been present and that it disappeared for higher concentrations, as is known to occur for turbulent flow in tubes.

The wavy gas-liquid interface greatly enhances momentum transfer, and measured values of the gas-phase pressure drop were several times higher than when gas alone was used.

It is of practical importance that a semi-empirical analysis successfully predicted the film thickness and its dependence on interfacial shear in gas-liquid flow.

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