MATHEMATICAL MODELING OF PESTICIDES IN THE ENVIRONMENT: CURRENT AND FUTURE DEVELOPMENTS

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ABSTRACT

Transport models, total ecosystem models with aggregated linear approximations, evaluative models, hierarchical models, and influence analysis methods are mathematical techniques that are particularly applicable to the problems encountered when characterizing pesticide chemicals in the environment. Because complete chemical, physical, and biological characterization is not available for most pesticides, research needs to be directed toward developing models for use in estimating whole system behavior based upon data representing a limited set of components and interactions.

INTRODUCTION

Pesticide chemicals present a particularly difficult problem in the environment because:

1. they are, by definition, biologically active substances;
2. many are not individual compounds but rather are poorly defined mixtures derived from varying parent substances;
3. complete chemical, physical, and biological characterization of most is is neither available nor can it be practically obtained; and
4. danger from exposure to many pesticides arises out of very minor mass flows [1].

None of the physical or chemical process studies (microscopic), the microcosm studies (macroscopic), or the toxicity effects studies presented to date gives a

complete indication of the potential effects of a pesticide on the environment. The solution to the problem of characterizing whole system effects of pesticides lies in developing an approximation technique, usually through the use of system modeling and simulation. Fortunately, several modeling and system analysis techniques are particularly applicable to the problems presented by pesticide chemicals [2].

STATE-OF-THE-ART

The response of an environmental system to a pesticide can be represented as either microscopic—component behavior resulting from specific processes—or macroscopic—system level behavior resulting from interaction of the components through the system structure [3]. Adequate microscopic models are available for delineating the chemical and biological components of environmental systems [4]. These models represent the responses of such components as nutrient chemicals and biological species to environmental variables such as temperature, hydrogen ion activity (pH), and solar radiation. An increasing number of component models representing processes specifically affecting the transport and transformation of pesticides in the environment are also becoming available [5]. These models relate volatilization, sorption, dispersion, and other similar processes to pesticide parameters such as vapor pressure, partitioning coefficients, and chemical reaction rate coefficients. Component modeling of the physical, chemical, or biological processes affecting pesticides is well developed by comparison with our ability to coordinate these components in a model of a whole environmental system.

Current whole-system or macroscopic modeling of pesticides treats the distribution of these chemicals as a transport phenomenon whereby the pesticide is associated with air, water, or soil-sediment movement. Specific process components are coupled to the transport model where they relate directly to the degradation, transformation, or transport-media exchange of the pesticide. The transport media models are typical representations of hydrologic, hydraulic, atmospheric, and porous media flows.

The Agricultural Runoff Management (ARM) Model is a good example of the representation of pesticide behavior by using a transport model framework [6]. The basic transport framework of this model is the Stanford Watershed Model [7], which is a lumped-parameter representation of the hydrologic behavior of small watersheds. As augmented to include pesticide transport, the ARM model simulates runoff, snow accumulation and melt, sediment loss, pesticide-soil interactions, and soil nutrient content of runoff from small agricultural water-sheds. Analysis of the model indicates that the component processes relating to infiltration, land surface sediment transport, pesticide-soil interactions, and pesticide degradation may be significant at the macroscopic level of an agricultural watershed.

With a realistic transport framework, suitable process components, and adequate data, these microscopic and macroscopic models can identify and characterize potential environmental problems associated with the short-term, acute effects of pesticides. However, the chronic, long-term effects and consequent ecosystem responses that are not represented in these models are now recognized to be at least as important as the short-term acute effects [8].

AREAS OF CURRENT DEVELOPMENT

The development of ecosystem level models of pesticide behavior is an attempt to estimate both the short-term or direct effects and the long-term or indirect effects of pesticide chemicals. The ecosystem model structure includes the interrelationships among the chemical nutrients and biotic components of the system and a rudimentary representation of physical and chemical transport processes. To permit representation of pesticide behavior, the environmental chemistry of a pesticide and its direct effects on target and non-target species are added to the ecosystem model structure. It should be noted, however, that quantitative understanding of terrestrial ecosystem dynamics is limited relative to similar understanding of aquatic ecosystems.

Parameters in a typical aquatic ecosystem model include temperature, dissolved oxygen, biochemical oxygen demand, acidity, alkalinity, CO_2, NH_3, NO_3, PO_4, bacteria, algae, zooplankton, detritus, sediment, benthic organisms, and fish. When the chemical and biological effects of a pesticide are superimposed on the ecosystem model structure, some of the indirect effects of the pesticide can be estimated. Also represented in these models are pesticide effects on the structure or function of the system that are mediated through the food chain or nutrient chemical cycles. The models can also reflect modified behavior of the pesticide as a result of the changing state of the biotic and chemical components.

Although ecosystem level models of pesticide behavior permit evaluation of indirect effects of the compounds, the amount of data required to support realistic simulations with models of such resolution is usually extensive. Specifically, a study of such detail can only be applied cost-effectively to widely used persistent chemicals such as DDT. Even with pesticides that have been studied in relative detail, some model parameters must be estimated. When data characterizing a pesticide are sparse, some method of approximation must be used to qualitatively estimate the indirect effects. Three typical approximation techniques are comparison relationships between homologous compounds, use of structural evaluative models, and use of process evaluative models.

The objective of the benchmark chemistry program is to classify pesticides by their functional groups (organophosphates, carbamates, etc.) and then obtain data for a detailed model of the behavior of one chemical from each class [9]. It is assumed that the behavior of other compounds in the same class will have a

qualitative similarity to the selected compound's behavior. Pesticides with more than one characteristic functional group may have behavior that is qualitatively similar to that of several selected compounds. Thus, the indirect effects of a pesticide having a sparse data base may be qualitatively estimated by comparison with the behavior of a compound in the same class that has been studied in detail.

Evaluative models, when used to qualitatively estimate the behavior of pesticides in the environment, are designed to represent a general environmental context in which a pesticide may be found. They are skeletal models, however, and do not incorporate many of the parameters necessary to simulate a specific region of the natural environment (e.g., Lake Erie or Hubbard Brook Watershed). In formulating the skeletal evaluative model, either structural detail or process detail must be sacrificed for the sake of qualitative evaluation of system responses with minimal data input.

When detailed process mechanisms for the component behavior of a pesticide are not available, a linear approximation of an ecosystem model can be used to qualitatively evaluate the behavior of the pesticide [10-12]. These models represent all processes with a first-order approximation that is valid for sufficiently small deviations of the system parameters about a point in the state space of the system. These models can be supported with considerably reduced data requirements and can provide an effective format for sensitivity analyses [13] and worst case analyses [14]. If the pesticide is relatively reactive chemically or biologically under the environmental conditions to be modeled, however, the assumption of small deviations about a point in state space may not be valid.

Relatively reactive pesticides can be modeled using an evaluative model that emphasizes process mechanisms instead of structural detail [15]. The process components relating to the reactive species are represented in these models in mechanistic detail, and the remaining environmental components are represented by the environmental variables directly affecting the key processes. The dominant processes competing for the reactive species may be determined from this type of evaluative model. Although the structure of an ecological model as it relates to the parallel and serial combinations of the key processes is represented in these models, the remainder of the structure that represents possible ecosystem effects is typically not included.

Each of these methods of approximation is directed toward estimating the indirect effects of pesticides when data for a complete ecological characterization are not available. They all rely on scientific intuition or empirical interpretation of the data and on other information available to the modeler. New developments in modeling theory, however, are directed toward establishing formal bases for the type of approximations used in the evaluative models. Thus, it may be possible to compare a confidence estimate for the model approximation with the assumed environmental risks associated with the modeled pesticide.

FUTURE PROSPECTS

The problems of identification of indirect environmental effects and evaluation of complex system interactions associated with pesticides can only be resolved through co-evolution of laboratory, field, and modeling approaches. Modeling of environmental systems is often developed on an esoteric and complex plane that does not relate to the limitations resulting from the minimal data bases available for pesticides. For example, a stream model developed for the desert biome ecosystem study of the IBP program has about thirty state variables, many of which would interact with a pesticide contaminant [16]. Many laboratory studies concentrate on measuring the distribution of a pesticide in the system and neglect the measurements necessary to estimate rates that are important to any realistic modeling. It should be inconceivable to expend the resources necessary for a field study of pesticide behavior without using a preliminary evaluative model to estimate the dominant processes in the given environmental context. At any rate, modeling and analysis techniques requiring only minimal data need to be related to laboratory studies to provide a concise and meaningful data set, and both must be extrapolated to field conditions and evaluated in a field study.

One example of environmental modeling and analysis that has developed apart from the difficulties associated with pesticide problems is ecosystem theory. The application of ecosystem theory—that is, examining all the aspects of stress, stability, energy fluxes, nutrient cycles, carbon metabolism, and trophic structure in environmental systems—is emerging as one of the modern approaches to addressing the complex problems of chemical pollutants [8, 17, 18]. For example, the fact that ecosystem mineral cycles may shift from tightly closed to open systems has important ramifications with respect to the fate and effects of pollutants in the environment [18]. Also, the structure and dynamics of carbon metabolism in an ecosystem controls the rates of biological degradation, transformation, and transport of pesticides. Although ecosystem theory and analysis allow for evaluation of complex system interactions and for quantification of indirect environmental effects, the data requirements for direct application to most pesticide problems are prohibitive.

An example of a laboratory approach to pesticide characterization that has developed apart from environmental models and the resulting ecosystem theory is the analytical use of microcosms or model ecosystems [19]. Microcosms may permit evaluation of biological transport and transformation, behavioral effects, and some indirect effects [20]. Information required for environmental models that is normally obtained from microcosm studies include rate data for inter-actions; effects on decomposers; effects on immature and juvenile forms; and whole system measures such as production/respiration ratios, trophic dynamics, and nutrient cycling. In the future, data from appropriately designed microcosm experiments [21] may be combined with emerging hierarchical system modeling

techniques and methods for the analysis of system organization to derive viable pesticide models.

The developing theory of hierarchical models with nested levels of control and interactions among subsystems has a potential application to the pesticide problem [22, 23]. Central to the theory of hierarchical models is the concept that most interactions decrease in strength with distance. This property of interactions can result in system models consisting of a multilevel organizations of weakly interacting subsystems that have strongly interacting components. Simon suggests that relationships between interaction strength and frequency response indicate that the structure of real systems may well be hierarchical [24]. Regardless of what the structure of the "real system" may be, the hierarchical-model processor developed for the coniferous forest biome study may allow approximation of indirect effects based upon an incomplete set of interaction descriptions [25].

White and Overton, in their development of the hierarchical modeling concept, present a philosophy justifying application of hierarchical modeling to ecosystems and a computer based processor for implementation of the modeling philosophy. In this approach, specific attention is paid to the holistic system properties, and the total system is represented as a coupled collection of subsystems. Each subsystem is modeled in two ways: holistically, with the subsystem viewed as an object, and mechanistically, with the subsystem viewed as a coupled collection of objects. The mechanistic representation of the subsystem is developed to simulate the behavior of the subsystem as accurately as necessary or possible; the holistic representation of the subsystem simulates the behavior of the subsystem as it relates to other subsystems through higher levels in the hierarchy. In operation of the total system model, the subsystems are constrained to behave such that their combined behavior reproduces that of higher levels in the system.

If an ecosystem is modeled hierarchically with subsystems mechanistically modeled but constrained to behave in conjunction with other subsystems to produce holistic behavior at the next higher level in the hierarchy, then indirect effects and system level responses can be estimated from model simulations. In applications of hierarchical modeling to pesticides in the environment, subsystems of a hierarchical, ecological model that are directly affected by the pesticide can mechanistically represent the effects of the pesticide. The behavior of the holistic model, consisting of coupled subsystems, may be observed as indirect responses to the pesticide in the context of higher level control and interaction. One of the problems associated with this application of hierarchical modeling theory is that environmental systems have a closed causal structure that makes it hard to determine the mechanistic resolution necessary in the hierarchy of subsystems. Thus, the lowest levels in the hierarchy may be directly

coupled to the highest, and the identification of nearly decomposable subsystems [24] is not obvious.

Another promising approach to development of holistic pesticide models for environmental systems is influence theory [26]. The influence between two components is a unique, quantitative measure of the number and nature (complexity) of the paths for interaction between the components based on a system model. The theory of influence provides quantitative measures of the organization of system model structure (e.g., levels of hierarchy or cycling) and thus, abstractly, system structure. This theory of system structure may be developed to produce models that estimate indirect effects based on a subset of the total interactions in the system. There are two approaches to this problem using influence theory: the base model concept and the expansion of key processes method [27].

In the context of the theory of finite-state machines, Zeigler [27] has defined structure-preserving homomorphisms that are a step toward a formal theory of aggregation of variables in a system model [28, 29]. Although discrete and continuous-state models are theoretically transmutable, the actual translation from one to another is operationally obscure. The theory of influence provides a complete set of mathematical invariants for the linear graph representing the patterns of interaction among components in the system. Logical manipulation of the invariants theoretically corresponds to an analogous manipulation of the system structure. This property of the graphic invariants indicates that it is possible to operate formally on the system structure as defined by the system model to produce a condensed or simplified model under the constraint of preserving some aspects of the system behavior. Thus, influence theory may permit reducing a complex ecosystem model to a minimal subset of aggregated components and a condensed pattern of interactions such that the behavior of the original, complex model is qualitatively preserved.

Conceptually, the expansion of a key process model is the inverse of the reduction of a complex base model. If a model such as the evaluative process model is developed to represent a pesticide in an environmental context, then the nature of the parallel and serial combinations of processes in the model (i.e., its structure) necessarily implies a particular structure for the underlying ecosystem model. Thus, the structure of an ecosystem model represented in a simple process model can be determined quantitatively. For example, if a pesticide showed no effect on the nitrogen cycle, it would be acceptable to use an evaluative model that included little if any of the ecosystem model structure associated with the nitrogen cycle. Both hierarchical modeling and influence theory are attempts to formalize an approach to aggregation of both model variables and model structure. It is in the structural aspects of modeling complex environmental systems where the most fruitful developments may be made for application to the problems of pesticides in the environment.

RESEARCH NEEDS

Research needs to be directed toward mathematical modeling that allows translation of laboratory measurements of pesticide effects on growth, physiology, and environmental interaction to field conditions. Thus, models need to be developed that estimate whole system behavior based upon data representing a limited set of components and interactions. Hierarchical models with constrained subsystems and behavior-preserving structures derived from influence analysis may accomplish these goals in the near future.

REFERENCES

1. I. C. T. Nesbet, Banning DDT: An Ill-Planned Biogeochemical Experiment, *Technology Review, 77*, pp. 10-11, 1974.
2. J. W. Gillett, J. Hill, IV, A. W. Jarvinen, and W. P. Schoor, *A Conceptual Model for the Movement of Pesticides Through the Environment,* EPA-600/3-74-024, Government Printing Office, 1974.
3. H. T. Odum, An Energy Circuit Language for Ecological and Social Systems: Its Physical Basis, *Systems Analysis and Simulation in Ecology,* B. C. Patten, (ed.), Academic Press, *2,* 1972.
4. R. R. Lassiter, *Modeling Dynamics of Biological and Chemical Components of Aquatic Ecosystems,* EPA-660/3-75-012, National Environmental Research Center, Corvallis, Oregon, 1975.
5. J. W. Falco and L. A. Mulkey, Modeling the Effect of Pesticide Loading on Riverine Ecosystems, *Environmental Modeling and Simulation,* W. R. Ott, (ed.), EPA-600/9-76-016, 1976.
6. A. S. Donigian, Jr. and N. H. Crawford, *Modeling Pesticides and Nutrients on Agricultural Lands,* EPA-600/2-76-043, US Environmental Protection Agency, 1976.
7. N. H. Crawford and A. S. Donigian, Jr., *Pesticide Transport and Runoff Model for Agricultural Lands,* EPA-660/2-74-013, US Environmental Protection Agency, 1974.
8. M. Waldichuk, Trends in Methodology for Evaluation of Effects of Pollutants on Marine Organisms and Ecosystems, *CRC Critical Reviews in Environmental Control,* pp. 167-210, February, 1973.
9. R. Hague, Benchwork Chemistry Program, *Substitute Chemical Program-Proceedings,* Office of Pesticide Programs, USEPA, Washington, D.C., July, 1975.
10. G. M. Woodwell, P. P. Craig, and H. A. Johnson, DDT in the Biosphere: Where Does it Go?, *Science, 174,* p. 1101, 1971.
11. H. L. Harrison, O. L. Loucks, J. W. Mitchell, D. F. Parkhurst, C. R. Tracy, D. G. Walls, and V. J. Yannacone, Jr., System Studies of DDT Transport, *Science, 170,* p. 503, 1970.

12. L. L. Eberhardt, R. L. Meeks, and T. J. Peterle, Food Chain Model for DDT Kinetics in a Freshwater Marsh, *Nature, 230,* p. 60, 1971.

13. R. Tomovic, and M. Vakobratovic, *General Sensitivity Theory,* Elsevier, New York, 1972.

14. J. Hill, IV, H. P. Kollig, D. F. Paris, N. L. Wolfe, and R. G. Zepp, *Dynamic Behavior of Vinyl Chloride in Aquatic Ecosystems,* EPA-600/3-76-001, US Environmental Protection Agency, 1976.

15. R. R. Lassiter, J. L. Malanchuk, and G. L. Baughman, Comparison of Processes Determining the Fate of Mercury in Aquatic Systems, *Environmental Modeling and Simulation,* W. R. Ott, (ed.), EPA-600/9-76-016, April, 1976.

16. D. Porcella, and D. Koob, Plant Subroutine, *IBP Desert Biome Stream Model,* manuscript, Utah State University, Logan, 1974.

17. H. A. Reiger, and E. B. Cowell, Applications of Ecosystem Theory, Succession, Diversity, Stability, Stress and Conservation, *Biol. Conserv., 4,* p. 83, 1972.

18. D. E. Reichle, Advances in Ecosystem Analysis, *Bioscience, 25,* pp. 247-264, 1975.

19. R. L. Metcalf, G. K. Sanyha, and I. P. Kapoor, Model Ecosystem for the Evaluation of Pesticide Biodegradability and Ecological Magnification, *Environ. Sci. and Technol., 5,* p. 709, 1971.

20. J. W. Gillett, and J. D. Gile, Progress and Status Report on Terrestrial In-House System, *Substitute Chemical Program – The First Year of Progress,* US Environmental Protection Agency, Washington, D.C., pp. 5-26, 1975.

21. J. W. Gillett, and J. Haefner, Mathematical Modeling of Pesticide Fate, *Substitute Chemicals Program – The First Year of Progress,* US Environmental Protection Agency, Washington, D.C., pp. 65-71, 1975.

22. H. H. Pattee, *Hierarchy Theory: The Challenge of Complex Systems,* George Braziller, New York, 1973.

23. M. D. Mesarovic, D. Macko, and Y. Takahara, *Theory of Hierarchical Multi-Level Systems,* Academic Press, New York, 1970.

24. H. A. Simon, The Organization of Complex Systems, *Hierarchy Theory: The Challenge of Complex Systems,* H. H. Pattee, (ed.), Braziller, New York, p. 156, 1973.

25. C. White, and W. S. Overton, *Users Manual for the FLEX 2 and FLEX 3 Model Processors for the FLEX Modeling Paradigm,* School of Forestry, Oregon State University, Corvalis, p. 154, 1974.

26. J. Hill, IV, *Influence: A Measure of Structural Organization of Systems,* Ph.D. Dissertation, University of Georgia, Athens, 1979.

27. B. P. Zeigler, The Base Model Concept, *Theory and Applications of Variable Structure Systems,* R. R. Mohler, and A. Ruberti, (eds.), Academic Press, New York, pp. 69-93, 1972.

28. B. P. Zeigler, *The Aggregation Problem,* manuscript, University of Michigan, 1974.

29. _____, *Theory of Modeling and Simulation,* John Wiley and Sons, New York, 1976.

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