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FATE OF HEPTACHLOR

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ABSTRACT

Since field ecosystems are so complex, a dynamic laboratory riverine microcosm was set up to observe the persistence and fate of heptachlor. The microcosm included aqueous, biotic, and sediment compartments capable of physical, chemical, and biological processes. Heptachlor, nutrients, and water were added to the system at a constant rate of 18.4 l/day while the dynamic processes of the system were studied.

To extend this analysis to the prototype, a model is necessary. The fate of heptachlor in the microcosm is compared to the fate in the prototype as computed by the model, EXposure Analysis Modeling System (EXAMS), developed by the Environmental Protection Agency Research Laboratory in Athens, Georgia. EXAMS is a compartmentalized model based on differential equations of the partitioning of five ionic species of heptachlor in waters, sediment, and biotic compartments, taking into account the dominant physical, chemical, and biological processes. The input parameters for EXAMS are obtained from and the literature compared with the laboratory microcosm.

The results of this study show differences between fate predictions of the theoretical and laboratory modeling systems.

1. INTRODUCTION

Development of models predicting the fate of hazardous chemicals in the aqueous environment is a field recently attaining significant importance after the surge of hazardous waste site discoveries. Many of the chemicals leaching from these sites have been found to be carcinogenic, and close attention to the fate of these chemicals is warranted. The fate of chemicals may be studied in three ways; in the field, by laboratory studies simulating field conditions, and by calculations based on theory. Study of a chemical in the field is extremely difficult because of the large number of uncontrolled variables existing in the natural environment. However, it is only by such studies that laboratory and computer model studies can be validated and verified. Are only

approximations of what actually happens in the field. These studies are usually carried out in laboratory microcosms in which a few variables are closely regulated. A chemical's fate in the environment may also be predicted by investigating its characteristics and interrelationships with the chemical, physical, and biological divisions of an aqueous system. Interrelationships between a chemical and the surrounding environment are complex and theoretical studies are often implemented with a computer model, enabling a large number of variables over a wide range of values to be used. This study compares the fate of the insecticide heptachlor in a model laboratory stream to its fate as predicted by a computer program developed by EPA scientists at the Environmental Protection Agency Research Laboratory in Athens, Georgia.

The successful development of pollutant fate prediction may be enhanced by the use of laboratory microcosms. A variety of microcosms have been used to help develop environmental theories and models. Lassiter (1979) reviewed different types of microcosms and gave examples describing the construction and theory of each. Microcosms are used for theory and modeling studies because they are easier to employ, control, and observe, both qualitatively and quantitatively, than more complex natural ecosystems. The environmental parameters and pathways used in models may be determined in laboratory microcosms with a high degree of accuracy because the variables can be tightly controlled relative to the accuracy of determinations made through field studies where the variables cannot be so easily controlled.

2. MODELING THEORY

Once a chemical is released into the environment it may be affected by chemical reactions, physical transport, and biological interactions (Cline et. al., 1981). Most mathematically based models determine the chemical's fate by looking at each process and its rate affecting the fate independent of all other processes. The rate processes are then applied independently to different compartments of the system thereby ignoring any interactions. First order differential equations are usually used in fate models, and because so little is known about their actual rates depicting the change in chemical concentration as the sum of the first order equations. Rate constants and correspondig coefficients for the equations may be found either from published data, or from experimentation and analysis. Data on movement of water and suspended material into and out of each compartment are necessary for determining the rate of chemical transport through the system. With the rate equations and transport information, the fate of the chemical in each compartment may be predicted.

The EPA program used for the heptachlor fate prediction is the EXposure Analysis Modeling System (EXAMS). The program was developed to predict the fate of chemicals in different environments eg. river, estuary, reservior, etc. The program is user interactive, and loadings, chemicals characteristics, and environmental conditions are easily changed, thereby allowing for the effects of varying conditions to be easily calculated. EXAMS uses first order or psuedo first order differential equations

along with mass fluxes across compartment boundaries to make fate predictions. The mass transport of all materials in the ecosystem is a steady state except for the mass of the organic chemical being studied. Once in the ecosystem, EXAMS allows a chemical to ionize into singly or doubly charged ionic species, and allows for each species to enter the following fate processes: vilatilization, direct photolysis, sensitized photolysis, hydrolysis, photoautotrophic degradation, microbial degradation, microbial uptake, and exchanges with sediment reservoirs. If the chemical does not enter one of the above pathways then it may either be suspended in the water column system, dissolved in the pore water of the bethic compartment, or exported out of the system while sorbed onto one of the suspended transported factions. An indepth description of EXAMS may be found in the user manual (Cline et. al., 1981).

3. CHEMICAL INFORMATION

The compound chosen for the study is the insecticide heptachlor. Heptachlor was selected because of its chemical behaviour and potential danger to human health and the environment. The chemical is one of 129 designated by the EPA as a priority pollutant. Before being banned in 1975, two million pounds of heptachlor were produced annually (New York Times, 1975). Heptachlor is a close chemical relative of the insecticide cholodane and the two have been used interchangeably for both domestic and agricultural purposes. The wide use of these chemicals has caused them to be spread throughout the environment and residues are commonly found in dairy, meat, fish, and poultry products. Heptachlor residues have even regularly been found in the fatty tissues of humans (New York Times, 1975). Heptachlor has been shown to be quite toxic to aquatic life and because of aquatic organisms sensitivity to heptachlor, the EPA has set the freshwater quality criteria for heptachlor at 0.001 parts per billion (U.S. EPA, 1976). Heptachlor's hazardous properties and widespread use warrant the study of its behaviour in aquatic systems.

In the study, a nutrient-contaminant solution consisting of macronutrients and heptachlor was pumped into the system at a constant rate. As previously stated, once in the system the chemicals could enter either chemical, biological, or physical pathways. The major chemical pathways are degradation reactions. In aqueous systems the dominating chemical degradation reactions are oxidation, hydrolysis, and photolysis (Lassiter et. al., 1979). Biological pathways are both degrading (biotransformations) and sorptive (bioaccumultation) processes. Physical pathways involve the location of the chemical and not changes in the chemical's composition. The chemical may either become physically adsorbed onto sediment particles or carried through the system with water and suspended materials. In actuality the three basic pathways are interrelated, but for fate predictions the assumption that the pathways act independently is made.

Previous studies on chemical pathways of heptachlor suggest that hydrolysis to 1-hydroxychlordene is the major degradation

reaction of heptachlor, although photolysis and oxidation will also occur. Demayo (1972) reported the psuedo first order rate constant for hydrolysis to be 0.030/hour. Photolysis of heptachlor will only occur if a sensitizer such as benzophenone is present (McQuire, 1972). The likelihood of such a photo-sensitizer being present in the model stream is low, consequently, no photolysis rate constant was entered into the EXAMS program. Oxidation of heptachlor does take place, but only through biological mechanisms (Callahan, et. al., 1979).

The physical pathways of heptachlor include adsorption onto sediments, transportation of the chemical through the water column, and volatilization of the chemical from the epilimnion. EXAMS assumes that adsorption is linear with respect to chemical concentration. EXAMS can compute an adsorption partition coefficient, if one is not known, from the chemical's octanol-water partition coefficient and the fraction of organic carbon in the sediment. In the study performed, the octanol-water coefficient was calculated using a regression equation developed by Kenaga and Goring (1980) relating octanol-water partitioning to water solubility. EXAMS computes the transport of chemicals through the water column by summing the nondegraded fraction of the dissolved chemical concentration and the chemical fraction sorbed to suspended matter flowing through the system. Volatilization is computed in EXAMS using a theory that relates the vapor pressure of the contaminant and the mixing characteristics of the epilimnion to volatility.

Both of the biological processes (biotransformation and bioaccumulation) are known to be active in the removal of heptachlor from water. Biotransformations of heptachlor are known to exist because of the presence of heptachlor's oridation product, heptachlor epoxide, in aquatic organisms exposed to heptachlor (Lu et. al., 1975). It is difficult to determine exact uptake rates by organisms since different organisms and different body parts within organisms have different uptake rates. An estimate of the biotransformation coefficient for heptachlor of 2.34E-4/hour was calculated for use in EXAMS from data taken by Lu et. al. (1975). The bioaccumulation partition coefficient was determined from a regression equation relating bioconcentration to the contaminant's octanol-water coefficient (Southworth, et. al., 1978). Bioaccumulation of heptachlor is not thought to be a very significant process, but the bioaccumulation of its persistent metabolite, heptachlor epoxide, is reported to be an area of concern (Lu et. al., 1975).

4. EXPERIMENTAL PROCEDURE

The laboratory microcosm was set up in a chemically resistant tray with dimensions of 631 x 52w x 6.6d (cm) and volume of 15.6 liters. Sediments were placed evenly across the bottom of the tray at a depth of 1.6 cm. The sediments were originally taken from a slow moving section near the mouth of Mill Creek in Nashville, Tennessee. Dechlorinated tap water flowed from a constant head flask into the system. The water was dechlorinated by aerating the constant head flask. This dechlorination technique was tested, with results showing the residual chlorine

before aeration to be 1.5 mg/l, and undetectable after aeration. The dechlorinated tap water was fed into the system at an average flowrate of 9.90 ml/min. A nutrient-heptachlor solution was pumped into the system at a rate of 2.85 ml/min, allowing a 4.47 to 1.0 dilution. The nutrients consisted of basic chemicals for microbial growth as described by Legner et. al., (1976). Strips of teflon were dangled into the water as a means to collect growth and prevent external contamination of the biota tested. A bank of windows situated in front of the microcosm supplied light to the system.

Heptachlor was mixed daily into the nutrient solution just prior to restocking the pump reservoir. The heptachlor solution was prepared from 99+% pure crystals, received from the EPA Triangle Research Park Laboratory located in North Carolina. Heptachlor stock solution was prepared by dissolving the crystals into isopropyl alcohol. The heptachlor concentration in the nutrient-heptachlor solution was 9.90 ppb. After dilution the microcosm was being fed a 1.0 ppb concentration of heptachlor. The system was monitored twice a day during the course of the experiment to check the flow rate and replenish the pump reservior.

Initially, sediments and creek water taken from Mill Creek were placed in the tray and allowed to remain static for ten days. Nutrients were then fed into the system for 33 days to allow for growth and acclimation to occur. The water, sediments, and biota were sampled 1,2,5,10,22, and 31 days after the heptachlor was added. Three samples of each of the three system components, water, sediments, and biota, were taken for each sampling interval. Water samples were prepared for analysis by adding one ml of pesticide-grade hexane to 100 ml of sample, and then shaking rapidly for one minute. The sediment samples were prepared by adding five ml of pesticide-grade hexane to one gram of sediments followed by shaking. Biota samples were prepared by removing growth from the teflon strips dangling in the system. The growth was then weighed and one ml of pesticide-grade hexane added prior to shaking. Gravimetric analysis was performed on each of the three components to determine the dry solid weight and volatile fractions of the components. The sediment results were adjusted to account for the high percentage of pore water contained in the freshly sampled sediments and biota using results from the gravimetric analysis. The analysis was performed as outlined in Standard Methods (1983). The prepared samples were analyzed by gas chromatography using Shimadzu gas chromatograph equipped with a 50-meter glass capillary column and a nickel-63 electron capture detector. The dector signals were sent to a Shimadzu C-R1B recorder which integrated and reported the peak times and areas through a microcomputer. A lindane internal standard was used to improve the accuracy and precision of the heptachlor analysis. All testing procedures are identical to those used by the Vanderbilt University Student Environmental Health Project (Wilson, 1983).

5. RESULTS AND DISCUSSION

The heptachlor concentration in the water, sediments, and biota all decreased with time. After the heptachlor was entered into the system there was an increase in heptachlor concentration followed by an unexpected decrease, eventually reaching zero. The results show that the physical fate pathways did not play a major role after the system became acclimated to the heptachlor. The fate pathways must therefore be dominated by chemical and biological degradation pathways. During the study the system changed and was better able to degrade the contaminant. This is likely to be the result of increased microbial growth, unrelated to the heptachlor introduction, but leading to more organisms that may either act as transformers or catalysts. Except for the first sampling interval, the biota did not contain detectable levels of heptachlor. The results of the gas chromatographic analysis showed that new peaks were present, indicating the presence of breakdown products. The peaks were not quantitatively analyzed, but from data given by Demayo (1972) the peaks are suspected to be from the presence of 1-hydroxychlordene, the major product of heptachlor hydrolysis. The data for all the model stream's sampling intervals and data for the steady state heptachlor concentration as predicted by EXAMS are shown in the following table.

TABLE I FATE OF HEPTACHLOR IN A MODEL LABORATORY STREAM AND IN EXAMS COMPUTER SIMULATED STREAM

INTERVAL	WATER	SEDIMENTS	BIOTA
	mg/l (ave)	mg/kg (ave)	ug/g (ave)
		MICROCOSM	
1 day	8.60E-6	0.840	1.42E-3
2 day	1.66E-5	1.72E-3	U.D.
5 day	2.55E-6	3.60E-5	U.D.
10 day	U.D.	8.5E-5	U.D.
22 day	U.D.	U.D.	U.D.
31 day	U.D.	U.D.	U.D.
		EXAMS	
EXAMS (steady state)	4.68E-4	1.51E-1	2.98

NOTE: U.D. means that the heptachlor was not detected by the method used.

The results of the laboratory microcosm and those computed by EXAMS are similar in some aspects, but different in others. The sediment concentrations for EXAMS at steady state are the same for the model stream sometime between day one and day two. The heptachlor concentration in the compartment of the laboratory model is much lower than the concentration in the EXAMS water compartment. The greatest concentration difference inbetween the two models is in the biota. This reasonable though, because of the number of different microbial species and the difficulty involved in analyzing them. Although the differences are large, the EXAMS model does not take into account many unpredictable actions of the dynamic laboratory system. The changing microbial condition and the unkown complex chemical and biological reactions make predictions exceedingly difficult.

6. CONCLUSION

The primary difference between the computer model and the laboratory model is that the parameters governing chemical fate are held constant in the computer model, and vary in the laboratory model. This is not to say that a laboratory model is necessarily the better of the two though. There is no definite way to show that the changes undergone by a laboratory ecosystem parallel changes made in the natural environment. By necessity the computer model must assume that the different fate processes take place independently of one another. Even if the complex relationships were known, it would be difficult to implement them because the advanced modeling would require complex differential equations. Even if the relationships could be implemented the program would be very costly and difficult to use advantageously. The same is true when attempting to simulate a natural ecosystem. Designing and monitoring all of the variables taking place in a natural ecosystem would make any such project very complicated. Models based on relatively simple principles, such as EXAMS, can help point the scientist or engineer in the right direction when the question of chemical fate arises. Validation studies help these models become more accurate, even though a reasonably high level of uncertainty remains whenever laboratory validation models and theoretical models are compared.

REFERENCES

1. Burns, Lawrence A., David M. Cline, Ray R. Lassiter, Exposure Analysis Modeling System (EXAMS): User Manual and System Documentation, Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, Georgia, 1981.

2. Callahan, M.A., M.V. Slimak, N.W. Gobel, I.P. Mays, C.C. Fowler, J.R. Freed, P. Jennings, R.L. Durfee, F.C. Whitmore, B. Maestri, W.R. Mabey, B.R. Holt, C. Gould, Water-retated Environmental Fate of 129 Priority Pollutants, Volume 1: Introduction and Technical Background, Metals and Inorganics, Pesticides and PCB's EPA-440/4-72-029a, 1979.

3. New York Times, pp. 34, July 31, 1975.

4. Demayo, Ardrian, Bulletin of Environmental Contamination and Toxicology, Volume 8, No. 4, pp. 234-237, 1972.

5. Kenga, E.E., C.D.I. Coring, ASTM Third Aquatic Toxicology Symposium, Special Publication No. 707, 1980.

6. Lassiter, R.R., State-of-the-Art-In-Ecological-Modeling, S.E. Jorgensen, Editor, Pergamon Press, N.Y., pp. 127-161, 1979.

7. Legnor, M, P. Pundodhar, V. Strasksabora, Continuous Culture 6: Applications and New Field, A.C.R. Dean, C.G.T. Evans, J. Melling, Editors, Ellis Morwood Ltd., Chicheston, England, pp. 329, 1976.

8. W. P., R.L. MetealF, A.S. Hirwe, J.W. Williams, Journal of Agricultural and Food Chemistry, Volume 23, No. 5, pp. 967-973, 1975.

9. McQuire, R.R., Journal of Agricultural and Food Chemistry, Volume 23, No. 4, pp. 856-861, 1972.

10. Southworth, G.R., J.J. Beauchamp, P.K. Schncider, Water Research, Volume 12, pp. 973-977, 1978.

11. Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 15th edition, 1980.

12. Quality Criteria for Waters U.S. Environmental Protection Agency, Washington D.C., pp. 154-156, 1976.

13. Wilson, D.J., Personal Comnunication at Vanderbilt University, September, 1983.