The Fate of Dieldrin in a Model Ecosystem

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The current interest in environmental quality has stimulated research into the nature and persistence of agricultural chemicals and their metabolites. The widespread occurrence of undesirable residues from the ubiquitous use of the chlorinated hydrocarbons as pest control agents, particularly DDT, has resulted in the gradual termination of these materials as environmentally unsuitable insecticides in the United States. To insure that future pest control agents or their degradation products are not persistent and therefore undesirable, an initial screening must take place before they are put into large-scale use. The development of a model ecosystem (Metcalf et al. 1971) clearly establishes a means for evaluation of the environmental suitability of currently employed pesticides as well as those in developmental stages. As a part of a continuous program to investigate the effects of pesticides on the environment, the fate of dieldrin has been examined in a model ecosystem.

METHODS

The model ecosystem described by Metcalf et al. (1971), was used and the experiment with dieldrin was replicated two times. In addition to the standard components of the Metcalf model ecosystem, one crab (Uca minax), two small fingernail clams (Corbicula manilensis) and a water plant, Elodea (species not identified), were added to the system. All organisms except the clam, the Daphnia, and the crab survived the initial application of the pesticide and lived the duration of the experiment. Periodic restocking of these organisms over the duration of the experimental period resulted in death to the organisms. However, clams placed in the systems on the 30th day and crabs and Daphnia placed on the 28th day survived until the termination of the experiment.

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Into the two model ecosystems 7.905 mg ^{14}C dieldrin (specific activity 2.41 Mci/mm >99% pure by tlc ether-n-hexane, 3:2 and radioautography) as an acetone solution (0.5 ml) were applied to the leaves of the sorghum. The two aquaria were housed in a Hotpack environmental chamber held at 27±1° and a 12-hour photoperiod. In addition, the water portion of each system was aerated with a small aquarium pump.

The procedures outlined by Metcalf et al. (1971) were followed for the 34-day program of the system and the work-up with the exception of the following: The organisms were extracted with acetone instead of acetonitrile. The acetone insoluble radioactivity, termed unextractable, was solubilized with Protosol (New England Nuclear) for liquid scintillation counting in Aquasol (New England Nuclear). For the purpose of separation, identification and quantitation of metabolites and/or degradation products, extracts of the individual components of the system were spotted on tlc plates (Silica Gel F-254, Brinkmann) and the plates were developed using ether-n-hexane, 3:2. Another solvent system, ether acetone 95:5 gave similar results as to metabolite distribution but did not give as good resolution of the polar metabolites and degradation products. Radioautograms were prepared (No-screen X-ray film, Eastman Kodak) to facilitate the location of the metabolites and degradation products. The spots were identified by co-chromatography with known compounds. The distribution of metabolites was determined by scraping the spots from the plate for liquid scintillation counting in a dioxane based scintillation fluid containing PPO 7 g, POPOP 0.05 g, and napthalene 120 g in 1 liter dioxane. An external quench correction method was employed.

RESULTS AND DISCUSSION

Data for the accumulation, metabolism and degradation of ^{14}C dieldrin in the model ecosystem by the various elements are collected in Tables I - VI.

Examination of the data in Tables I and V clearly demonstrates the great resistance of dieldrin to undergo biological and chemical transformations in this model ecosystem. The stability of dieldrin is demonstrated by examination of the data in Table VI as an average of ∿97% of the extracted radioactivity from the organisms was determined to be dieldrin. This figure is given added support when the data for the extraction efficiency are inspected in Table V as an average of only ∿9% of the total radioactivity con-

TABLE I

Concentrations (ppm) of dieldrin, metabolites and degradation products in organisms of a model ecosystem

Pesticide		Organism							
		Algae	Clam	Crab	Daphnia	Elodea	Mosquito	Fish	Snail
Total ^{14}C		16.39 (14.02, 18.74)	2.06 (0.78, 3.34)	0.715 (0.62, 0.91)	5.24 (4.75, 5.71)	2.96 (2.0, 3.91)	1.60 (1.73, 1.48	13.22 (10.20, 16.24)	234.1 (176.7, 291.6)
Unknown I	0.65*	0.0	0.0	0.0	0.0	0.23 (0.12, 0.34)	--	0.0	0.866 (0.402, 1.33)
Dieldrin	0.58	14.96 (13.18, 16.73)	2.03 (0.77, 3.30)	0.495 (3.28, 0.662)	5.07 (4.58, 5.55)	2.56 (1.74, 3.38)	--	12.29 (9.44, 15.15)	229.87 (173.2, 286.5)
Unknown II	0.43	0.0	0.0	0.0	0.0	0.0	--	0.0	0.456 (0.612, 0.300)
9-OH Dieldrin	0.38	0.20 (0.16, 0.23)	0.0	0.0	0.0	0.0	--	0.19 (0.20, 0.17)	1.11 (0.542, 1.68)
9-C=O Dieldrin	0.31	0.0	0.0	0.043	0.0	0.0	--	0.07	0.0
Polar Unknown II	0.0				0.07 (0.06, 0.07)	0.03 (0.0 0.05)	--	0.03 (0.02, 0.04)	0.044 (0.087,
Unextractable		1.23 (0.68, 1.78)	0.028 (0.01, 0.04)	0.177 (0.164, 0.191)	0.10 (0.11, 0.09)	0.14 (0.14, 0.14)	0.25 (0.38, 0.12)	0.65 (0.46, 0.83)	1.78 (1.81, 1.74)

*R.F. value; Silica Gel F-254 ether: n-hexane, 3:2

-- extract not chromatographed because < 500 cpm

0.0 not detected

( ) values for Tanks I, II, respectively

TABLE II

Concentration (ppm) of dieldrin, metabolites and degradation products in unhydrolyzed and hydrolyzed water

		Tank I			Tank II		
		U-H_2O	H-H_2O	Total	U-H_2O	H-H_2O	Total
Dieldrin	0.58*	0.00163	0.0	0.00163	0.00236	0.0	0.00236
9-OH Dieldrin	0.38	0.00051	0.0	0.00051	0.00041	0.0	0.00041
9-C=O Dieldrin	0.31	0.00043	0.0	0.00043	0.00036	0.0	0.00036
Unknown III	0.18	0.00060	0.0	0.00060	0.00008	0.00005	0.00013
Unknown IV	0.12	0.00020	0.00015	0.00035	0.00006	0.00009	0.00015
Unknown V	0.07	0.00019	0.00032	0.00051	0.00005	0.00015	0.00020
Unknown VI	0.04	0.0	0.00052	0.00052	0.00185	0.00164	0.00349
Unknown VII	0.00	0.00025	0.00170	0.00195	0.00022	0.00098	0.00120
Unextractable		0.00270	0.0	--	0.00290	0.0	--
Total ^{14}C				0.0065			0.0083

*R.F. value; Silica Gel F-254 ether: n-hexane, 3:2

U-H_2O = water extracted with diethyl ether

H-H_2O = water treated with 0.025N HC at 70° for 20 hrs. and then extracted with diethyl ether

TABLE III

Average concentration factors (C.F.)* of dieldrin in organisms of two model ecosystems

	Organism						
	Snail	Algae	Fish	Daphnia	Elodea	Crab	Clam
C.F.	114,935	7,480	6,145	2,145	1,280	247	1,015

*C.F. - dieldrin (ppm) in organism/dieldrin (ppm) in water

TABLE IV

Time dependence of ^{14}C dieldrin, degradation products and metabolites (ppm) in water of two model ecosystems

	Days							
Tank	3	6	10	14	21	25	31	34
I	0.027	0.023	0.021	0.018	0.013	0.013	0.007	0.0065
II	0.026	0.026	0.024	0.023	0.026	0.018	0.018	0.0083

TABLE V

Extraction efficiency* of radiolabeled metabolites and degradation products from organisms in the model ecosystem

	Organism							
	Algae	Clam	Crab	Daphnia	Elodea	Mosquito	Fish	Snail
Percent unextractable radioactivity	7.6	12.1	24.8	1.9	4.7	4.9	15.6	0.8
				Ave = 9.05				
				S.D.= 8.07				

*Acetone extract

TABLE VI

Percent dieldrin in extracts* of organisms in the model ecosystem

	Organism							
	Algae	Clam	Crab	Daphnia	Elodea	Mosquito	Fish	Snail
Percent	98.7	99.9	92.0	98.6	90.8	--	97.4	98.9
				Ave = 96.6		S.D.= 3.7		

*Acetone extract
-- extract not chromatographed because <500 cpm

tained in the organisms was unextractable. This figure demonstrates conclusively that very little of the degradation or metabolism products are in the form of unextractable conjugates. If the figures for extraction efficiency and percentage of dieldrin isolated from the organisms are multiplied together, then a value of 88% is obtained for the percentage of dieldrin in the organisms. For comparison, DDT examined in this system constituted 20-30% (Metcalf et al. 1971). However, though DDT appears to be less stable in the model ecosystem, the major DDT metabolite, DDE, is very stable in this system and, therefore, the transformation of DDT to DDE does not contribute significantly to the breakdown of DDT to polar, non-lipid partitioning materials.

In addition to the previously discussed data which describe stability of dieldrin in the system, information regarding the concentration of dieldrin by various organisms is collected in Table III. The fish at the top of the food chain concentrated dieldrin to the extent of ∿6,000 times the concentration in the water. In comparison, DDT in the same system was concentrated in the fish ∿84,500 times that of water (Metcalf et al. 1971). However, the Physa snails which are not in the food chain of the fish, but are scavengers and can accumulate dieldrin from several sources, concentrate dieldrin ∿115,000 times the concentration in the water which is about 19 times the value found in the fish. This is the largest concentration factor for the snail in this system as DDT and DDE are concentrated ∿34,500 and ∿19,500 times, respectively (Metcalf et al. 1971).

Finally, some comments are necessary about the data in Tables II and IV, which describe the concentrations and fate of ^{14}C dieldrin, its degradation products and metabolites in the water portion of the model ecosystem. In Table IV the time dependence of ^{14}C dieldrin and its various metabolites is collected. Over the 34-day period the amount of radioactivity changes from a value of ∿0.027 ppm to about an average value of 0.0074, a decrease of about 3.5 times. The data in Table II describe the distribution of ^{14}C dieldrin and its breakdown products in the water at that end of the experimental period. In contrast to the nearly ∿97% of the radioactivity isolated as dieldrin from the organisms, dieldrin constitutes 25-28% of the radioactivity in the water. In addition, the concentration of dieldrin in the water is much less (0.00163-0.00236 ppm) than in the organisms. This smaller quantity of dieldrin in the water as compared to the organisms is probably related to the low water solubility

and high lipid-water partitioning coefficient of dieldrin. Small amounts of material which chromatographed with 9-hydroxy and 9-keto dieldrin were found in the water. This contrasts the distribution of metabolites in the organisms as these materials did not appear in amounts sufficient for their detection. Further, while 49-61% of the metabolites isolated from the water had an R.F. of <0.18, these same polar materials were not isolated from the organisms. Lastly, water in contrast to the organisms contained conjugated material as treatment with acid released 35-41% of the radioactivity.

The examination of dieldrin in this model ecosystem clearly demonstrates the stability of this insecticide towards either biological or chemical modification by the elements of this system. The demonstration that about ∿97% of the extracted radioactivity in the organisms was dieldrin emphasizes the inertness of dieldrin to metabolism or degradation to polar, nonlipid partitioning materials by the components of this model ecosystem. If information about the stability and persistence of pesticides derived from this system can be related to a real environmental situation, and it definitely seems to be in the case of DDT, then the data of this paper indicate that dieldrin like DDT, might be considered, because of its extreme stability, an undesirable pesticide for widespread generalized use in agricultural and public health entomology.

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