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atural History Survey

BULLETIN

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VOLUME 31, ARTICLE 9
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CONTENTS

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Robert L. Metcalf is Professor of Biology and Research Professor of Entomology, University of Illinois. James R. Sanborn is an Assistant Entomologist, Illinois Natural History Survey.

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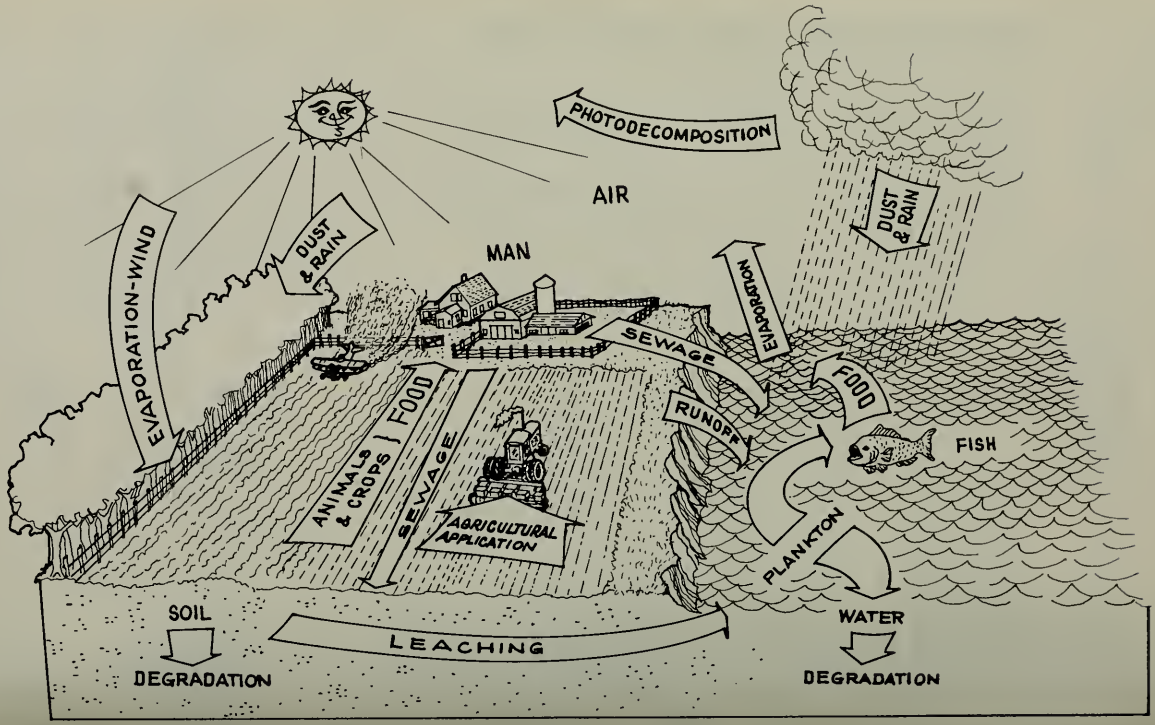

Frontispiece.—Ways in which pesticides move away from the target site to contaminate the total environment, entering into a variety of cycles in

Pesticides and Environmental Quality in Illinois

Robert L. Metcalf

James R. Sanborn

ILLINOIS has 29,039,000 acres (1.18×10^7 ha) of farmland, amounting to 84 percent of its land surface. This land is among the most fertile and productive in the world, and Illinois ranks as the second state, after California, in producing farm crops, valued at $3.167 billion in 1973. Illinois land produced 996,010,000 bushels (2.53×10^{10} kg) of corn (17.6 percent of the U.S. total), 290,745,000 bushels (7.9×10^8 kg) of soybeans (18.6 percent of the U.S. total), 37,800,000 bushels (1.03×10^9 kg) of wheat (2.2 percent of the U.S. total), 19,780,000 bushels (2.88×10^8 kg) of oats (30 percent of the U.S. total), 3,251,000 tons (2.95×10^9 kg) of hay (2.4 percent of the U.S. total), and 4,225,000 pounds (1.92×10^6 kg) of red clover seed (15 percent of the U.S. total). From these plant products Illinois produced an additional $1.906 billion worth of livestock (4.2 percent of the U.S. total) (Illinois Cooperative Crop Reporting Service 1973).

The value of Illinois farmland exceeds $30 billion by current land value, and its corn crops alone have been valued at more than $30 billion over the past 100 years. However, in terms of its capability to help to feed a world which is growing ever hungrier, the value of Illinois soil can scarcely be overestimated.

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USE OF PESTICIDES

Modern agricultural practices—involving superior plant varieties, improved cropping methods, heavy applications of nitrogenous fertilizers, and extreme reliance on agricultural chemicals, especially herbicides and insecti-

cides—have been responsible for the state's immense agricultural productivity. These innovations have seen Illinois corn yields increase from 30 bushels per acre (1,601 kg per ha) in 1920 to 105 bushels per acre (6,605 kg per ha) in 1973. The use of pesticides in corn production has been described as being "as significant as the plow." Their use has increased phenomenally, and in Illinois more total acreage, more than 14 million acres (5.67×10^6 ha), is treated with pesticides than is treated in any other state (Fowler & Mahan 1972). In 1972 herbicides were applied to 14,326,000 acres (5.79×10^6 ha) (49 percent of Illinois farmland) and insecticides to 5,946,000 acres (2.41×10^6 ha) (20 percent of Illinois farmland) (Illinois Cooperative Crop Reporting Service 1973). On an acreage basis 14.7 percent of the herbicides and 14.1 percent of the insecticides used in U.S. agriculture were applied in Illinois although the state has only about 2.5 percent of the total cultivated land. We estimate (U.S. Environmental Protection Agency 1972*a*; Illinois Cooperative Crop Reporting Service 1973) that about 34 million pounds (1.54×10^6 kg) of the active ingredients of pesticides were applied to Illinois farm soil in 1971—equivalent to 1 pound for each acre (1.1 kg per ha) in the state or 3 pounds (1.36 kg) for each of the state's 11 million inhabitants.

Much of the total amount of pesticides applied is dispersed throughout the environment (Frontispiece), entering air, water, and food through volatilization and air currents, runoff and leaching, and uptake and concentration in food chains.

NEED FOR SURVEILLANCE

The heavy use of pesticides, changing agricultural technology, and the rapid introduction of new pesticide products present a continuing demand for evaluation and surveillance of the effects of pesticides upon environmental quality. The long-term effects of widely used pesticides are not well appreciated. Thus, von Rümker and Horay (1972), after a detailed survey of the most widely used pesticides, concluded that for 20 of the 35 compounds studied there was inadequate information about the nature of the environmental degradation products and their effects on environmental quality. Considering that many of these pesticides, such as chlordane, toxaphene, dieldrin, propanil, captan, zineb, and maneb, were introduced 20 or more years ago, the magnitude of the problem is apparent. Furthermore, insect resistance to the organochlorine insecticides, together with increasingly severe effects of their use upon environmental quality, have resulted in their gradual replacement with organophosphorus and carbamate insecticides (Table 1).

New pesticides are being introduced at a rate much faster than that of our scientific appreciation of their environmental effects. During the 30 years since World War II, the number of synthetic fungicides, herbicides, insecticides, nematocides, and rodenticides has increased from less than 100 to over 900. The scene changes constantly with the development of new products and new technologies such as no-till farming. During 1974, for example, the following new pesticides were introduced under experimental permit into Illinois agriculture: cyprazine (Prefox®), metribuzin (Sencor®), bentazon (Basagran®), oryzalin (Surflan®), profluralin (Tolban®), dinitramine (Cobex®), bifenox (MODOWN®), glyphosate (Round-up®), Rowtate®, and Counter®. Pesticides introduced under such experimental permits may be used on hundreds of thousands to millions of acres of Illinois soil in a few years. Thus, carbofuran, introduced in 1968, was used to treat 706,000 acres (287,000 ha) in 1971, and trifluralin, introduced in 1964, was used to treat 1,226,000 acres (496,000 ha) in 1971 (Petty & Kuhlman 1972).

Table 1.—Use of organochlorine insecticides on Illinois farms.

Year	Insecticide Used and Acres Treated					
	aldrin	dieldrin	DDT	chlordane	heptachlor	toxaphene
1968	3,438,000[a]	...	...	82,500	822,000	...
1969	3,512,000	11,000	9,000	160,000	1,131,000	24,000
1970	2,690,000	...	...	63,800	822,000	...
1971	1,690,000 (2,240,000)	0	0	233,000 (87,000)	232,000 (654,000)	...
1972	1,268,000 (1,883,000)	0	0	375,000	181,000	(35,000)
1973	...	...	...	...	...	...
1974	1,400,000	0	0	200,000	400,000	(100,000)

[a] Data from Petty (1974) and data in parentheses from Illinois Cooperative Crop Reporting Service (1970 and 1973).

In addition, farmers are increasing their use of combinations or mixtures of pesticides, either prepackaged or in-tank mixed. This proliferation of materials and their persistence may provide unintended soil mixtures. Pesticides are, by design, highly reactive biological compounds and may interact with one another in many ways to produce unintended effects, e.g., synergism in which the combined action is far greater than that of either of the components alone. Thus, the study of pesticide interactions in relation to environmental quality is much more complicated than the study of the individual components. As an example of this complexity, 29 combinations of herbicides were registered for use on corn and soybeans in Illinois in 1974 (McGlamery et al. 1974).

BENEFIT-RISK OF PESTICIDE USE

The use of pesticides in such a prodigal way obviously poses benefit-risk questions which are very difficult to answer satisfactorily, especially in regard to the effects of pesticides on the total quality of the environment and on the long-term productivity of Illinois soil. Two examples will illustrate this point.

The use of certain preemergence herbicides allows no choice between planting corn or soybeans. The unusually wet May and June of 1974 prevented corn production in many areas on land already treated with atrazine. This herbicide is highly toxic to soybeans so that this crop was precluded as an alternative although it might have been the most profitable crop over a shortened growing season.

The soil insecticide aldrin is converted by the action of air, bacteria, and enzymes in plants and animals to the epoxide dieldrin, one of the most persistent of all pesticides. More than 60 million pounds (2.72×10^7 kg) of aldrin have been applied in Illinois since 1954, and the soil of this state has the highest average levels in the nation of aldrin (0.13 ppm) and dieldrin (0.11 ppm) (Wiersma et al. 1972). The national averages are 0.02 ppm for aldrin and 0.03 ppm for dieldrin. Soybeans grown on soil long planted in corn average about 0.01 ppm of dieldrin although they have no federal tolerance. Dieldrin residues in Illinois milk consistently exceed legal limits, and highly dieldrin-contaminated soybean sludges fed to poultry have resulted in the seizure and destruction of more than 25 million chickens in Mississippi (Anonymous 1974).

EARLY-WARNING TECHNOLOGY

The thoroughly unsatisfactory situation in Illinois, resulting from the

widespread use of highly persistent organochlorine pesticides with little or no prior understanding of their fates in the total environment, has prompted both scientific and lay concern about a screening methodology which could serve as a simple early-warning system against potentially undesirable or hazardous effects of the large-scale use of new agricultural chemicals or combinations of them. The wait-and-see system, followed in the use of aldrin, dieldrin, heptachlor, and chlordane and requiring a generation or more to distinguish serious environmental pollution, is demonstrably inadequate and has resulted in such disasters as the widespread contamination and seizure of milk supplies, the destruction of millions of contaminated chickens, and the devastation of valuable fishing industries.

A recent comprehensive study, *Pesticide Use on the Nonirrigated Croplands of the Midwest* (U.S. EPA 1972*a*) recommended that "a massive, interdisciplinary research effort be mounted to clarify the environmental behavior of major pesticides which are expected to continue in use for the forseeable future." Information needed includes the fates of pesticides in the environment after application; routes of metabolism, degradation, and disappearance; natures of the ultimate breakdown products; effects of long-term exposure of ecosystems to low-level residues; and interactions with other chemicals in the environment. It will be necessary to establish an order of priority among products to be investigated in this fashion.

The investigations reported here represent an effort by the State of Illinois, through the Illinois Natural History Survey and the University of Illinois, to assume the responsibility for the comprehensive research so urgently needed on the total environmental fates of new pesticides.

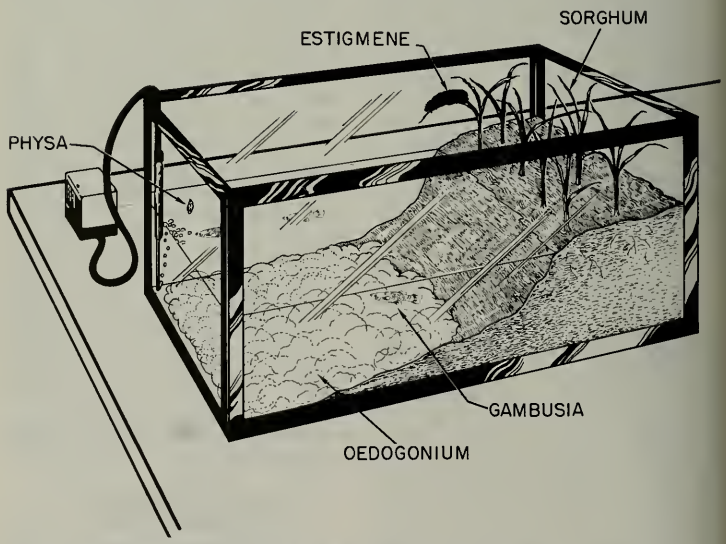

Fig. 1.—The laboratory model ecosystem used to evaluate the fates and environmental effects of radiolabeled pesticides on terrestrial and aquatic organisms, including sorghum, salt-marsh caterpillar, plankton, alga, snail, mosquito larva, and mosquito fish.

MODEL-ECOSYSTEM TECHNOLOGY

The development of model-ecosystem or microcosm technology (Metcalf et al. 1971; Metcalf 1974) has provided a quick and sensitive laboratory tool for providing answers to these questions about environmental pollution by pesticides:

1. The nature of the biological effects on non-target organisms
2. The nature of degradative pathways and the magnitudes of degradative products
3. The bioconcentration and ecological magnification (EM) of parent compounds and degradation products in living organisms
4. The quantitative estimation of persistence and biodegradability

Basically, model-ecosystem evaluation uses radiolabeled pesticides to follow qualitatively and quantitatively the movement and degradation of the compounds from a terrestrial (farm) environment into an aquatic (lake) environment and to demonstrate the passage of the parent compound and its transformation products through aquatic food webs. The experimental model is shown in Fig. 1 and consists of a 20-gallon aquarium with a sloping shelf of washed quartz sand entering a lake of 7 liters of standard reference water (Freeman 1953), which provides mineral nutrition for plankton, alga, snail, mosquito larva, and fish and for sorghum plants growing on the terrestrial farm area. The water phase of the system is aerated, and the entire system is kept in an environmental plant growth chamber at 80° F (26.5° C) with a 12-hour diurnal cycle of 5,000 foot candles of fluorescent light.

The radiolabeled pesticide to be tested is applied to sorghum plants, seeds, or to the soil of the system, using a realistic dosage of 1–5 mg per experiment, equivalent to 0.2–1.0 pound per acre (0.22–1.1 kg per ha). Ten last-instar salt-marsh caterpillars, *Estigmene acrea*, are introduced to consume the treated sorghum plants, and the caterpillars and their excretory products, leaf frass, etc., contaminate the lake portion of the model system. The radiolabeled products enter the various aquatic food chains, e.g., plankton → daphnia (*Daphnia magna*) → mosquito (*Culex pipiens*) → fish (*Gambusia affinis*) or alga (*Oedogonium cardiacum*) → snail (*Physa* spp.).

The movement of the radiolabeled products from plants to lake are measured by counting the radioactivity of duplicate 1-ml water samples by liquid scintillation at intervals of 1, 2, 4, 7, 14, 21, 28, and 33 days or whenever desired. After the system has been in operation for 26 days, 300 mosquito larvae are added, and after 4 more days 50 are removed for analysis. The food chains are completed after 30 days by adding three mosquito fish, *G. affinis*, which are left for 3 days to eat the daphnia and mosquito larvae.

The experiment is terminated after 33 days, when weighed samples of the various organisms are homogenized in small volumes of acetonitrile. Aliquots are counted for total radioactivity by liquid scintillation. One liter of water from the system is extracted three times with diethyl ether to measure total radioactivity. The residual water is hydrolyzed with 1.0 *N* hydrochloric acid for 4 hours and reextracted with diethyl ether to determine the conjugated materials, and the amount of unextractable radioactive materials is determined by counting the radioactivity of the remainder.

The acetonitrile extracts of the organisms are concentrated to a few milliliters and known volumes are applied to thin-layer chromatography (TLC) plates of fluorescent silica gel (E. Merck GF-254). TLC is carried out with appropriate solvents (identified in the tables) and with the incorporation of standard known metabolites of the pesticide under study. After the chro-

matograms are developed, they are placed against X-ray film and exposed for several weeks to several months to determine the areas containing radiolabeled products. These areas are scraped into scintillation vials, and scintillation counts are made to determine the amounts of individual degradation products present. The residues from the tissue extractions are combusted to determine the amount of unextractable radioactive materials, using either the Schoeniger oxygen flask technique (Kelly et al. 1961) or a tissue solubilization method.

After the completion of these assays, the results of the experiment are assembled on balance sheets showing the amounts and natures of radiolabeled degradation products present. Wherever possible, the chemical identities of the degradation products are determined by cochromatography with known model compounds, by the use of specific microchemical reactions and by infrared and mass spectrometry. The results of such studies on 48 pesticides are shown in the tables.

HERBICIDE TEST RESULTS

The importance of examining the fates of herbicides in a terrestrial-aquatic model ecosystem cannot be overestimated, especially in view of the exponential growth in the use of herbicides over the past 20 years in the United States. Pimental et al. (1973) estimated that in 1945 the use of herbicides for controlling weeds in corn was practically nonexistent. However, in the 25-year period from 1945 to 1970 the use of herbicides increased significantly, and it was estimated that by 1970 herbicide treatment averaged 1 pound of active ingredient per acre (1.1 kg per ha). Though figures were not available for 1945, it is possible to examine figures for 1950–1970, which clearly demonstrate that herbicide use on corn increased at least twentyfold during that time.

Alachlor, or 2-chloro-2′, 6′-diethyl-*N*-(methoxymethyl)-acetanilide, is a member of a large class of chloroacetanilide herbicides used to control annual grasses in cornfields and certain broadleaf weeds in corn or soybeans. The data clearly indicate the susceptibility of this herbicide to extensive degradation, as no residues of alachlor were isolated from any of the test organisms (Table 2). The high degree of degradation is further evidenced by the large number (10) of radiolabeled products of alachlor isolated from the water section of the ecosystem. Continued use of this herbicide should not lead to its accumulation in aquatic food chains.

Atrazine, or 2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine, is one of the most extensively used herbicides for controlling weeds in corn plantings. The alga, snail, and fish of the model ecosystem contained 2.4059, 0.2386, and 0.3511 ppm, respectively, of atrazine (Table 3). The percentages of atrazine in the radioactive materials extractable from the alga, snail, and fish were 87.3, 63.1, and 59.3, respectively. The EM values for atrazine for the alga, snail, and fish were 75.6, 7.5, and 11.0, respectively. In addition, the alga, snail, and fish contained smaller amounts, 0.2100, 0.05479, and 0.07356 ppm, respectively, of *N*-dethylatrazine (compound A, Table 3). Another *N*-dealkylated product, *N*-deisopropylatrazine (compound B, Table 3), was isolated from the alga (0.04934 ppm), snail (0.02796 ppm), and fish (0.05496 ppm). The EM values of these two dealkylated metabolites were of the same order of magnitude as that observed for atrazine. Continued use of atrazine would not appear to lead to major accumulations in aquatic food chains.

Bentazon, or 3-isopropyl-1*H*-2,1,3-benzothiadiazin-4-(3*H*)-one-2,2-dioxide, is a new herbicide employed for the control of a selected number of broadleaf and sedge weeds. In the

model ecosystem (Booth et al. 1973) it was susceptible to degradation, as indicated by the lack of residues in all organisms except the clam, which contained 0.622 ppm of *N*-isopropylanthranilamide, 1.266 ppm of anthranilic acid, and 0.510 ppm of unchanged bentazon (Table 4). The percentage of bentazon in the radioactive materials extractable from the clam was 18.7, and the EM value was about 10. Continued use of this herbicide should not lead to its accumulation in aquatic food chains.

Cyanazine, or 2-chloro-4-(1-cyano-1-methylethylamino)-6-ethylamino-*s*-triazine, is used for the control of annual grasses and broadleaf weeds in cornfields. The behavior of this herbicide in the model ecosystem indicates that it is susceptible to degradation, as only the water plant, *Elodea,* contained residues of this herbicide (Table 5). Neither the fish nor the snail contained residues of cyanazine or its degradation products. The high water solubility, 171 ppm, of cyanazine and its apparent susceptibility to degradation clearly demonstrate that the continued use of cyanazine should not result in its accumulation in aquatic food chains.

Dicamba, or 3,6-dichloro-*o*-anisic acid, is an effective herbicide for the control of both annual broadleaf weeds and grasses in corn. The data indicate clearly that this herbicide is not absorbed by the organisms of the model ecosystem (Yu et al. 1975*a*) (Table 6). This fact is probably related to the pH of the aqueous portion of the model ecosystem, which is higher than the pKa (dissociation constant) of this benzoic acid derivative; therefore, the herbicide exists in the ionic form. Dicamba in the ether-extracted water constitutes about 90 percent of the extractable radioactive materials. Although the data do not indicate it, dicamba was recovered from the water only after acidification and heating for 24 hours. It is impossible to state whether the dicamba was in the ionic form and that acidification facilitated the partition of dicamba into ether, or whether the dicamba was present as a conjugate and that the acid treatment broke down the conjugate and released the free acid. In any case, very little happened to dicamba in the water of the model ecosystem other than conjugation through the carbonyl moiety.

Phenmedipham, or methyl *m*-hydroxycarbanilate *m*-methylcarbanilate, is a postemergence herbicide used in sugar beets to control a large variety of annual weeds. The fate of phenmedipham in this model ecosystem clearly indicates the susceptibility to degradation of this herbicide, as none of the organisms contained phenmedipham residues (Table 7). The radioactive material extractable from the fish remained at the origin of the TLC plate, indicating the polar nature of the radioactivity. The continued use of phenmedipham should not lead to its accumulation in aquatic food chains.

2,4-D, or 2,4-dichlorophenoxyacetic acid, is one of the oldest synthetic herbicides in use today. After more than 30 years of its continued use, problems relating to aquatic food-chain accumulation of 2,4-D are nonexistent. The data from the experiment with ^{14}C-2,4-D corroborate the "outdoor" data that have accumulated for the past three decades, as no 2,4-D residues were found in any of the organisms of the model ecosystem (Table 8). As might be expected, the alga contained the greatest number of unidentifiable ^{14}C residues even though eight standard degradation products of 2,4-D were cochromatographed. Continued use of 2,4-D does not appear to lead to environmental problems relating to its accumulation in aquatic food chains. "Real-world" data and model ecosystem results are similar and clearly demonstrate the ability of this microcosm to predict potential environmental problems.

Propachlor, or 2-chloro-*N*-isopropylacetanilide, is one of a large number of *a*-chloroacetanilide herbicides, which

include alachlor, that are used to control annual grasses and some broadleaf weeds in a number of crops including corn and soybeans. The structural similarity of propachlor to alachlor and its great susceptibility to degradation are evident, as none of the organisms contained residues of this herbicide (Table 9). There was a very minute amount of propachlor (0.0564 ppb) in the water at the end of the experiment. Clearly the α-haloacetanilides are some of the most degradable herbicides examined in this system, and continued use of these herbicides should not lead to their accumulation in aquatic food chains.

Pyrazon, or 5-amino-4-chloro-2-phenyl-3-(2H)-pyridazinone, is used for the control of annual broadleaf weeds in sugar beets and beets. The model ecosystem data clearly demonstrate that pyrazon is susceptible to degradation, as only the crab contained residues (0.476 ppm) of this herbicide, which constituted 95.4 percent of the radioactive materials extractable from the crab (Table 10). The EM value for the pyrazon in the crab was 22.5 (Yu et al. 1975*b*). Continued use of this herbicide would not appear to lead to problems related to accumulations of it in aquatic food chains.

Trifluralin, or α,α,α-trifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine, is used to control grasses and several broadleaf weeds in soybeans, cotton, and many other crops. Only the snail and fish contained 5.046 ppm and 0.261 ppm, respectively, of trifluralin as an extractable residue (Table 11). The percentages of trifluralin in the extractable radioactive materials in the snail and fish were 75.7 and 34.0, respectively. The EM values for the snail and fish were 17,872 and 926, respectively. In addition to trifluralin the snail contained lesser amounts of α,α,α-trifluoro-2,6-dinitro-*N*-propyl-*p*-toluidine (0.337 ppm), which had an EM value of 3,874. Trifluralin is the only herbicide tested that showed a propensity to accumulate in either the fish or snail. Its tendency to accumulate is undoubtedly related to its low water solubility (0.58 ppm) and high lipid solubility (Probst & Tepe 1969). Despite the accumulation in the snail and fish, trifluralin is unusual in that it is susceptible to degradation, forming at least 11 degradation products in water, yet demonstrates a tendency to be magnified to some extent through aquatic food chains. It is not, however, magnified at the level of chlorinated hydrocarbons, but at a level very similar to that of the insecticide methoxychlor, which has an EM value of about 1,500.

Metrabuzin, or 4-amino-6-*tert*-butyl-3-(methylthio) *as*-triazin-5-(4*H*)-one, is a new herbicide used for weed control in soybeans. The data in Table 12 clearly demonstrate the degradability of this herbicide in the model ecosystem, as no residues of this herbicide were isolated from the organisms. Further, the water contained numerous metabolites, which is indicative of the susceptibility of this herbicide to degradation under the conditions of this experiment. The major degradation product in the water is a mixture of DK and DADK, which were not resolvable by thin-layer chromatography. The data from this system clearly indicate that the continued use of this herbicide should not lead to its accumulation in aquatic food chains.

Bifenox, or methyl-5-(2′,4′-dichlorophenoxy)-2-nitrobenzoate, is a new preemergence herbicide somewhat related to 2,4-D. As shown in Table 13, bifenox is degraded by hydrolysis of the methyl ester to form the parent benzoic acid (compound B, Table 13), and by reduction of the nitro group to the corresponding amino compound (compound A, Table 13). There was no evidence of cleavage of the diphenyl ether moiety. Bifenox is of low water solubility (0.35 ppm) (Fig. 2) and was bioconcentrated about 200-fold by the

fish. It falls in the borderline area of moderate biodegradability and should be used with care.

ORGANOPHOSPHORUS INSECTICIDE TEST RESULTS

The decline in the use of organochlorine insecticides to control pest species (Table 1) is the result of factors such as target-pest resistance, environmental hazards, and more recently, the ban imposed by the U.S. Environmental Protection Agency (EPA) on DDT and aldrin/dieldrin as general insecticides for home and agricultural use. Further, in view of the recent action of the EPA seeking to ban the use of chlordane, heptachlor, and heptachlor epoxide, it is certain that more phosphate and carbamate insecticides will be used to fill the void left by the elimination of the organochlorine insecticides. Therefore, it is essential to examine carbamate and phosphate insecticides to insure that no problems of the environmental persistence and aquatic food-chain accumulations of these insecticides will occur.

Chlorpyrifos, or *O,O*-diethyl-*O*-(3,5,6-trichloro-2-pyridyl) phosphorothionate, had EM values in the alga, snail, mosquito, and fish of 72, 691, 45, and 320, respectively. Of the radioactive material extractable from each organism, the percentages of chlorpyrifos isolated from the alga, snail, mosquito, and fish were 30.3, 48.1, 7.9, and 49.5, respectively (Table 14). The position of the ^{14}C label in the pyridyl ring allows the investigation of the persistence of this moiety in the organisms of the system or its uptake by them or both. The ecological magnification and percentage of the extractable radioactive materials for the pyridinol in each organism were: alga, 44, 18.8 percent; snail, 443, 32.3 percent; mosquito, 191, 34.9 percent; and fish, 180, 29.1 percent. The absence of the oxon of chlorpyrifos in any of the organisms is typical, as the oxons of the phosphate insecticides were not found generally in any of the organisms.

Chlorpyrifos-methyl is an insecticide similar to chlorpyrifos except for the substitution of *O,O*-dimethyl for *O,O*-diethyl groups to yield *O,O*-dimethyl-*O*-(3,5,6-trichloropyridinyl) phosphorothionate. The chlorpyrifos-methyl ecological magnification values for the alga, snail, mosquito, and fish are 478, 544, 1,875, and 95, respectively. The values for the snail and fish are substantially lower than those found in the organisms subjected to chlorpyrifos, the result of the greater susceptibility of the *O*-methyl groups to degradation as compared to that of the *O*-ethyl moieties in chlorpyrifos. The percentages of chlorpyrifos-methyl in the radioactive materials isolated from the alga, snail, mosquito, and fish were 49.0, 49.3, 68.2, 20.7 percent, respectively (Table 15). Again, because the ^{14}C label is located in the pyridyl moiety, it is possible to investigate the fate of this group in the model ecosystem. The ecological magnification and percentage of the chlorinated pyridinol in the organisms were: snail, 41, 9.3 percent; fish, 54.5, 29.7 percent. As was observed for chlorpyrifos, none of the organisms contained the activation product, chlorpyrifosoxon-methyl.

Counter® is one of the newer phosphate insecticides under development for use as a soil insecticide, and it has the chemical name of *O,O*-diethyl S-(*tert*-butylthio)-methyl phosphorodithioate. This insecticide was therefore applied in the sand of the model ecosystem to mirror its use in the field. The similarity in structure to phorate (Thimet®) and disulfoton (Di-Syston®) is obvious, and the degradation in pathways of sulfur oxidation in the side chain of Counter® was similar to those of the other two pesticides. The percentages of Counter® in the radioactive materials extractable from the alga, snail, mosquito, and fish were 3.3, 23.5, 4.7, and 25.0, respectively (Table

16). No other metabolites were isolated from the fish or mosquito although a small amount (0.0241 ppm) of Counter® oxon was observed in the snail. The Counter® ecological magnification values from the alga, snail, mosquito, and fish were 175, 1,830, 360, and 535, respectively. These values from the fish and snail are somewhat higher than those found for most other phosphate insecticides. Undoubtedly these higher values are related both to the initial stability of the phosphorodithionate and to the application of this chemical to the sand, which does not allow for the initial metabolism and degradation by the caterpillars. The water sector of the ecosystem contained only trace amounts of Counter® and of nearly all of the possible combinations of the oxidation products of phosphorothioate and sulfide sulfur.

Temephos (Abate®), or the bis-*O,O*-dimethylphosphorothioate ester of 4,4′ dihydroxydiphenyl sulfide, is an excellent mosquito larvicide and appears to possess ideal environmental characteristics, as it is exceptionally degradable. No residues of temephos or any of its oxidative or hydrolytic metabolites occurred in the fish. Because of its high larvicidal activity, the mosquitoes were killed throughout the usual duration of the experiment, and it was extended to 53 days. The alga and snail contained small amounts (0.00195 and 0.01876 ppm, respectively) of temephos (Table 17). The EM values of temephos from the alga and snail were 1,500 and 14,431, respectively. In addition, the alga contained small amounts (0.4–2.0 ppb) of all of the cochromatographed metabolites, and the snail contained substantially fewer of the metabolites though at somewhat higher concentrations (2–27 ppb). The higher concentrations in the snail again emphasize the low titer of enzymes in this organism capable of degrading foreign compounds. The absence of data for the mosquito emphasizes the outstanding larvicidal properties of this insecticide.

Fonofos (Dyfonate®), or *O*-ethyl-S-phenyl ethylphosphonodithioate, is an effective soil insecticide which is finding increasing use as a replacement for the organochlorine insecticides. Although the organisms of the model ecosystem contained small amounts of the unchanged fonofos, none contained significant amounts of degradation products (Table 18). The percentages of fonofos in the radioactive materials extractable from the alga, snail, and fish were 32.1, 27.0, and 80.5, respectively. Further, the fonofos in the alga, snail, and fish had EM values of 108, 86, and 77, respectively. The large number of degradation products isolated from the water (14), coupled with the very low EM values, clearly indicates that fonofos does not accumulate significantly in aquatic food chains.

Fenitrothion, or *O,O*-dimethyl-*O*-(3-methyl-4-nitrophenyl) phosphorothionate, is one of the safest organophosphorus insecticides, as the LD_{50} for the rat is 500 mg per kg and for the mouse is 1,200 mg per kg. The substitution of the methyl group in the *meta* position of the nitrophenyl ring of methyl parathion is believed to be responsible for the much reduced mammalian toxicity as compared to that of methyl parathion, of which the LD_{50} for the rat is 13 mg per kg and for the mouse is 75 mg per kg. Fenitrothion EM values of 349, 2.2, and 9.8 were found for the alga, mosquito, and fish, respectively. The percentages of fenitrothion in the radioactive materials isolated from the alga, mosquito, and fish were 33.7, 6.6 and 44.4, respectively (Table 19). The only other degradation product isolated from the organisms was a small amount (5.7 ppb) of fenitroxon found in the fish. This degradation product of fenitrothion had an EM value of 6.5. The isolation of this phosphorus oxon from the fish is

unique, as none of the other oxons of the phosphate insecticides were found in the fish.

Malathion, or *O,O*-dimethyl-S-(1,2-dicarboethoxyethyl)-phosphorodithioate, is widely used in the home and garden as an insecticide. It appears to be exceptionally degradable, as no traces were found in any of the model-ecosystem organisms (Table 20). The fish, snail, and mosquito contained several uncharacterized metabolites, which were also found in the water. It is apparent that malathion is one of the most degradable organophosphorus insecticides examined in this system. This degradability, together with malathion's low mammalian toxicity (rat oral LD_{50}, 1,300 mg per kg), makes it a safe and useful product.

Acephate (Orthene®), or *O*-methyl-*S*-methyl-*N*-acetylphosphoramidothioate, is a relatively new insecticide, which has found widespread use in the control of pests of vegetables. The parent insecticide was not isolated from any of the model-ecosystem organisms (Table 21), which is not unexpected in view of the high water solubility of acephate (650,000 ppm). However, an uncharacterized degradation product was isolated (R_f 0.93) in all of the organisms except the clam and fish. In the crab this degradation product had an EM value of 4,273 times the concentration in the water. Further research is in progress to determine the structure of this degradation product.

Leptophos (Phosvel®), or *O*-(4-bromo-2,5-dichlorophenyl)-*O*-methyl phenylphosphonothionate, is a new organophosphate insecticide now undergoing extensive development for use in controlling pests of cotton and vegetable crops. The available environmental degradation information (Holmstead et al. 1973; Aharonson & Ben-Aziz 1974) clearly indicates that this insecticide has a high degree of environmental stability. Other problems with this insecticide have been found in its use in Egypt on cotton, where it killed 1,300 water buffaloes (Shea 1974). Laboratory experiments with chickens have shown that leptophos has neurotoxic effects (Abou-Donia et al. 1974).

The behavior of leptophos in our model ecosystem indicates that it is one of the most persistent phosphorus-derived pesticides examined (Table 22). The experiment was extended to 45 days, because each time the mosquitoes were introduced, they immediately died. Even though the mosquitoes died after their introduction on the 45th day, the fish were then added to the ecosystem, and the experiment was terminated 3 days later. Every organism contained residues of leptophos, the alga having 13.221 ppm, the snail 52.27 ppm, and the fish 1.559 ppm. These residues of leptophos in the radioactive materials extracted from the alga, snail, and fish constituted 41.8, 97.3, and 83.5 percent, respectively, of the totals. The EM values for leptophos were 12,243 for the alga, 48,398 for the snail, and 1,444 for the fish, respectively. Clearly, this is the most persistent organophosphorus insecticide examined in the model ecosystem.

Parathion, or *O,O*-diethyl *O*-4-nitrophenyl phosphorothionate, and methyl parathion, its *O,O*-dimethyl analogue, were produced in the United States in 1970 in the combined amount of about 56 million pounds. The available information on the behavior of parathion and methyl parathion in the environment indicates that they have presented no problems of accumulation in aquatic food chains after more than 25 years of widespread use. The model-ecosystem data (Table 23) corroborate the outdoor data. The only organism containing a residue of parathion was the fish, and there the concentration was only 0.1006 ppm, which constituted about 52 percent of the radioactive materials isolated from the fish. The experiment was lengthened to 38 days because of the toxicity of the water to

the mosquito. The use of 2,6-^{14}C-labeled 4-nitrophenol-labeled parathion allowed the examination of the fate of this moiety, and it was determined that the water (0.000136 ppm) and fish (0.0086 ppm) contained small amounts of this moiety.

CARBAMATE INSECTICIDE TEST RESULTS

The carbamate insecticides recently have assumed a large role in Illinois agriculture with the elimination of the organochlorine insecticides because of the resistance of target pests, the environmental accumulative tendency of the organochlorine compounds, and their carcinogenic properties. The use of metalkamate, carbofuran, and carbaryl to control insect pests on corn and soybeans has proved to be effective and has eliminated the aquatic food chain accumulation problems of the formerly used chlorinated hydrocarbon insecticides.

Metalkamate is a 3:1 mixture of *m*-(1-ethylpropyl)-phenyl and *m*-(1-methylbutyl)-phenyl *N*-methylcarbamates introduced to control soil pests of corn. This insecticide does not have any tendency to accumulate in the higher members of the trophic web, though the alga (0.980 ppm); crab (0.0498 ppm), which died 7 days after the introduction of metalkamate; and *Elodea* (0.245 ppm) contained residues of the parent compound (Table 24). These residues of metalkamate in the alga, crab, and *Elodea* constituted 55.0, 17.4, and 25.9 percent, respectively, of the extractable radioactive material from these organisms. The most interesting observation here is that these three organisms were the only organisms that contained detectable amounts of ^{14}C. None of the other organisms had substantial amounts of ^{14}C residues. While this insecticide has not been as effective recently as it has been in the past in controlling pests of corn, its environmental behavior in the model ecosystem clearly indicates that should it become widely employed, no aquatic food chain accumulation problems are likely to arise.

Carbaryl, or 1-naphthyl *N*-methylcarbamate, was the first carbamate insecticide to find widespread use in the home garden and in agriculture, and it is presently the most widely used insecticide in the United States. With the banning for general use of DDT in 1972, carbaryl is being used to control the tussock moth in the Pacific Northwest; the gypsy moth, which is migrating westward from the eastern regions of the United States; and the spruce budworm. After more than 20 years of widespread use, neither problems of accumulations in food chains nor of ubiquitous food residues have been experienced. The data from the terrestrial-aquatic model ecosystem (Table 25) definitely corroborate the experience in the field, as no residues of carbaryl were found in any of the organisms. The water contained many degradation products of carbaryl, but no residues of carbaryl itself. Continued widespread use of this insecticide will definitely not lead to problems associated with accumulations in aquatic food chains.

Carbofuran, or 2,2-dimethyl-2,3-dihydrobenzofuranyl-7-*N*-methylcarbamate, is an excellent soil insecticide for the control of corn and soybean pests. The behavior of this carbamate insecticide is similar to that of the other carbamates examined in that none of the organisms in the model ecosystem contained residues of the parent insecticide (Table 26). The water contained a small amount of carbofuran (0.003889 ppm) as well as trace amounts of other metabolites and degradation products of carbofuran (Yu et al. 1974). It appears that the continued use of this insecticide will not lead to environmental problems of accumulations in aquatic food chains.

Propoxur, or 2-isopropoxyphenyl *N*-methylcarbamate, is used for household

pest control and for residual spraying for adult mosquitoes. In the model system every organism contained residues of propoxur at concentrations of 0.0360, 0.0928, 0.4441, and 0.0468 ppm for the alga, snail, mosquito, and fish, respectively (Table 27). The percentages of propoxur in the radioactive materials extracted from the alga, snail, mosquito, and fish were 7.8, 23.5, 19.4, and 39.9, respectively. The EM values for the alga, snail, mosquito, and fish are 112, 290, 1,388, and 146, respectively. In addition to the parent compound, the fish contained lesser amounts of 2-isopropoxyphenol (0.0252 ppm) and 2-isopropoxyphenyl *N*-hydroxymethyl carbamate (0.0180 ppm). Propoxur was the only carbamate examined in this model ecosystem that was accumulated by the fish. This fact may be, in part, related to the high specific activity of the radiolabeled propoxur (10.4 mCi/mM), which made it possible to determine the small residues of this insecticide in the organisms.

Aldicarb is a systemic carbamate insecticide, 2-methyl-2-methylthiopropionaldoximyl *N*-methylcarbamate. Aldicarb is readily oxidized *in vivo* to sulfoxide and sulfone metabolites, both of which are insecticidal. These metabolites and the parent compound form relatively persistent systemic toxicants in plant tissues (Metcalf et al. 1966). A single application to the roots of cotton plants kills boll weevil larvae during an entire growing season. Therefore, it was not unexpected to find these products persisting over the 33-day period of the model-ecosystem experiment (Table 28). However, the substantial water solubility of aldicarb, 0.6 percent, clearly prevented high biomagnification in the organisms, and the EM value in the fish was 42. Aldicarb was highly toxic to the snail, *Physa,* and all of these died early in the course of the experiment.

Formetanate, or 3-dimethylaminomethyleneiminophenyl *N*-methylcarbamate•hydrochloride, is a carbamate acaricide. As shown in Table 29, this compound is highly biodegradable, and no trace of the parent compound was found in the model ecosystem after 33 days. The only identifiable degradation product (compound A, Table 29) involved removal of the *N*-methylcarbamoyl group and loss of the amidino moiety. We do not expect that this compound will cause problems in environmental quality.

MISCELLANEOUS INSECTICIDE TEST RESULTS

Methoprene, or isopropyl-11-methoxy-3,7,11-trimethyldodeca-2,4-dienoate, is one of the "fourth-generation" insecticides believed to interfere with the normal metamorphic development of insects. This pesticide has shown some promise in the control of mosquitoes developing in irrigated fields in California. The degradation of methoprene has been examined in detail in several outdoor systems (Quistad et al. 1974 and 1975; Schooley et al. 1975). In the model ecosystem every organism contained residues of methoprene (Table 30), with the alga containing 2.220 ppm, the snail 1.500 ppm, and the fish 0.0176 ppm. These methoprene residues in the alga, snail, and fish constituted 48.0, 30.7, and 25.1 percent, respectively, of the radioactive materials extracted from each organism. The EM values for methoprene in the alga, snail, and fish were 25,814, 17,442, and 205, respectively. Measurable amounts of the 11-*O*-demethylated methoprene were isolated from the alga, 0.723 ppm; snail, 0.469 ppm; and fish, 0.0181 ppm though the water contained none of this degradation product. Finally, the water, snail, and fish contained small amounts of 11-hydroxy-3,7,11-trimethyldodeca-2,4-dienoic acid.

Dimilin, or 1-(2,6-difluorobenzoyl)-3-(4-chlorophenyl) urea, is a recently introduced insecticide which apparently interferes with the normal development

of the insect cuticle and leads to mortality at molting. The use of two different ^{14}C-labeled sites in dimilin enabled us to examine the fates of the two phenyl moieties. Every organism contained this insecticide (Table 31), from the high of 13.1369 ppm in the mosquito in the ^{14}C-chlorophenyl urea dimilin to the low of 0.1097 ppm in the fish in the ^{14}C-difluorobenzoyl dimilin. Despite the variation in the absolute quantity of dimilin in the fish of the two experiments, 0.1097 ppm for the ^{14}C-difluorobenzoyl and 0.3193 ppm for the ^{14}C-chlorophenyl urea, the EM values of 19.2 and 14.5 were very close. The percentage of dimilin in the extractable radioactive materials isolated from the fish was 6.7 percent for ^{14}C-difluorobenzoyl dimilin and 5.3 percent for ^{14}C-chlorophenyl dimilin, indicating again close agreement in the data for the two ^{14}C labels. While dimilin amounted to a small percentage of the extractable radioactive materials in the fish, the fractions of dimilin were considerably higher (46–98 percent) in the radioactive materials isolated from the rest of the organisms.

Chlordimeform, or *N*-(4-chloro-*o*-tolyl)-*N*,*N*-dimethylforamidine, is one of the newer insecticides and appears to be effective in controlling cotton pests. In the model ecosystem only the snail contained residues of this insecticide, with a concentration of 0.0710 ppm (Table 32). The fraction of chlordimeform in the extractable radioactive materials isolated from the snail was about 40 percent. The water contained numerous breakdown products of chlordimeform, clearly indicating the lability of this insecticide in the model ecosystem.

Banamite®, or benzoylchloride-2,4,6-trichlorophenylhydrazone, is a new pesticide that has found use on citrus for the control of mites (Table 49). Only the crab (0.0156 ppm), aquatic plant (0.041 ppm), and mosquito (0.0736 ppm) contained residues of this pesticide. The EM values for banamite in these organisms were 839 for the crab, 2,204 for the aquatic plant, and 3,957 for the mosquito. The amount of banamite in the extractable radioactive materials from these organisms ranged from 1 to 2 percent. Though neither the fish nor the snail contained residues of banamite, they contained an unidentified degradation product, designated II, that was magnified about 20,000 times in the snail and about 3,000 times in the fish. It does not appear that continued use of this pesticide will lead to problems of aquatic food-chain accumulation, but perhaps more detailed analysis of the chemical structure of some of the degradative products should be undertaken.

ORGANOCHLORINE INSECTICIDE TEST RESULTS

The organochlorines, especially the cyclodienes aldrin, heptachlor, and chlordane, have been used extensively in Illinois since they were introduced in 1954 for the control of underground insect pests of corn, particularly the corn rootworms *Diabrotica longicornis* and *D. undecimpunctata howardi* (Bigger & Blanchard 1959). Their use as soil treatments increased from about 125,000 acres (5.06×10^4 ha) treated in 1954 to a maximum of 5,601,572 acres (2.27×10^6 ha) treated in 1966 and slowly declined to about 2,100,000 acres (8.51×10^5 ha) treated in 1974 (Petty 1974). The average treatment rate is about 1.6 pounds per acre (1.76 kg per ha) of technical material for aldrin and 2.0 pounds (2.2 kg per ha) for heptachlor (U.S. EPA 1972*a*). It is estimated that over the 20-year period more than 82 million pounds (3.73×10^7 kg) of these chemicals have been applied to Illinois farm soils (Illinois Natural History Survey data). The approximate farm acreages treated with the organochlorine insecticides in Illinois are presented in Table 1 (Illinois Cooperative Crop Reporting Service 1973).

The use of cyclodiene insecticides in Illinois has been complicated by the

invasion of the western corn rootworm, *D. virgifera*, which now covers nearly all of the cornland of Illinois and is totally resistant to the toxic action of aldrin, heptachlor, and chlordane (Petty & Kuhlman 1972), and by the unpredictability of attacks by the black cutworm, *Agrotis ipsilon*.

ENVIRONMENTAL PERSISTENCE

The organochlorine insecticides in use in Illinois are generally environmentally persistent or are readily converted to environmentally persistent compounds by photochemical or microbial action or *in vivo* in the tissues of plants and animals. This is particularly true of the oxidation of aldrin to its 6,7-epoxide, dieldrin; heptachlor to its 2,3-epoxide, heptachlor epoxide; and the *cis*- and *trans*-chlordane isomers to oxychlordane. The average times required for 95-percent "breakdown" of these compounds in the soil has been estimated as: DDT, 11 years; dieldrin, 9.7 years; lindane, 6.7 years; chlordane, 4.2 years; heptachlor, 3.5 years; and aldrin, 2.5 years (Edwards 1965). Therefore, because of extremely heavy use patterns, it is no surprise to find that Illinois soils have been relatively highly contaminated by these compounds. The National Soils Monitoring Program (Carey et al. 1973) has reported these concentrations in Illinois soils: aldrin, 0.01–0.83 (average 0.07) ppm; chlordane, 0.05–1.32 (average 0.09) ppm; dieldrin, 0.01–1.08 (average 0.14) ppm; and DDT(T), 0.06–0.12 (average >0.01) ppm. These residues were among the highest found in the United States.

DDT, or 2,2-bis-(*p*-chlorophenyl)-1,1,1-trichloroethane, has the highest potential for bioaccumulation, 84,500-fold from water to fish, of any of the compounds studied (Metcalf et al. 1971). This tendency to accumulate is the result of DDT's low water solubility (0.0012 ppm) and its environmental stability. DDT also accumulates because of its partial conversion by dehydrochlorination to DDE, 2,2-bis-(*p*-chlorophenyl)-1,1-dichloroethylene (water solubility 0.0013 ppm). In the fish at the top of the food chain DDT constituted 34.3 percent, DDE 53.9 percent, and DDD 9.8 percent of the absorbed total ^{14}C-radiolabeled material (Table 33). This fact demonstrates the gravest environmental flaw in the use of DDT, i.e., the conversion to and storage in animal lipids of the highly persistent DDE. DDE constituted 52.0 percent of the total radioactive materials in the snail, 58.4 percent in the mosquito, and 54.0 percent in the fish. The percentage of unextractable radioactive materials in the various organisms, a measure of total environmental stability, was low, ranging from 0.25 percent in the mosquito to 13.5 percent in the alga, and averaging 3.9 percent for all test organisms. As shown in Table 34, DDE in the model ecosystem was degraded slowly and showed high ecological magnification.

Because of its persistence, degradation to the even more stable DDE, bioaccumulation, and effectiveness in inducing mircosomal oxidase enzymes (Peakall 1970), DDT has been banned as an insecticide by both the U.S. and Illinois Environmental Protection Agencies. The high degree of bioconcentration and the preponderance of storage as DDE found in the model ecosystem study are representative of the values found in nature, e.g., fatty tissues of humans in the USA contain an average of about 2.3–4.0 ppm of DDT and 4.3–8.0 ppm of DDE (Durham 1969). DDT in Lake Michigan at a concentration of 0.000006 ppm is biomagnified in lake trout to levels of 10–28 ppm (U.S. EPA 1972*b*), and in herring gulls to 99 ppm (Hickey et al. 1966). The lake trout residues averaged 53 percent DDE, 15 percent DDD, and 32 percent DDT (U.S. EPA 1972*b*). DDT applied to a marsh in New Jersey for mosquito control was found in fish at 0.17–2.07 ppm and in gulls at 75 ppm (Woodwell et al. 1967).

DDD, or 2,2-bis-(*p*-chlorophenyl)-1,1-dichloroethane, exhibited similar model-ecosystem behavior to that of

DDT (Table 35) and is, in fact, a degradative product of DDT (Table 33). DDD constituted 58.9 percent of the total extractable radioactive materials in the snail, 59.0 percent in the mosquito, and 85.4 percent in the fish (Metcalf et al. 1971). Thus, although DDD is a step on the degradative pathway of DDT and does not form the environmentally recalcitrant DDE, DDD seems to offer only slight improvement over DDT in regard to environmental hazard. Its ultimate fate in higher animals is conversion to and excretion as DDA (4,4′-dichlordiphenyl acetic acid), but this is an extremely slow process. DDD applied to Clear Lake, California, to control the Clear Lake gnat, *Chaoborus astictopus,* was found to be bioconcentrated through food chains from 0.02 ppm in the water to 903 ppm in the fat of plankton-eating fish and to 2,690 ppm in the fat of carnivorous fish (Hunt & Bischoff 1960).

Methoxychlor, or 2,2-bis-(*p*-methoxyphenyl)-1,1,1-trichloroethane, differs from DDT in two important ways. It is 500 times more soluble in water, and the aryl CH_3O groups (degradophores) are readily biodegradable to OH groups, further increasing the polarity and water solubility. Thus, as shown in Table 36, methoxychlor is much less accumulative than DDT is in most animals. Methoxychlor amounted to 84.0 percent of the total extractable radioactive materials in the snail and 51.5 percent in the fish. In contrast to the ready conversion of DDT to DDE (Table 33) and the storage of the latter in animal tissues, only very small amounts of the corresponding methoxychlor ethylene are stored by animals. The principal degradation pathway for methoxychlor is through conversion to the mono-OH and di-OH derivatives, which are readily converted to polar conjugation products in animals (Metcalf et al. 1971).

Methoxychlor is classed as a moderately persistent insecticide and does not accumulate to high levels in most animal tissues or milk.

It offers a severe toxic hazard to fish but is degraded in fish much more readily than is DDT (Reinbold et al. 1971). When used for control of the elm bark beetle, *Scolytus multistriatus,* vector of Dutch elm disease, methoxychlor has not resulted in environmental problems of transfer from earthworms to birds, as has DDT (Hunt & Sacho 1969).

Aldrin, or 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-*endo, exo*-5,8-dimethanonaphthalene, is rapidly converted in the model ecosystem and its organisms to the very persistent 6,7-epoxide, dieldrin (Table 37). In the model ecosystem treated with aldrin, dieldrin was stored as 85.7 percent of the total extractable radioactive materials in the alga, 91.6 percent in the snail, and 95.8 percent in the fish (Metcalf et al. 1973). The bioaccumulation of both aldrin and dieldrin is high, directly proportional to their water insolubility, but not as high as that of DDT and DDE. Only minor amounts of two degradation products, 9-keto dieldrin and 9-hydroxy dieldrin, were found, attesting to the stability of dieldrin, and these two products were also concentrated in the alga, snail, and fish. The ultimate degradative pathway is through *trans*-dihydroxydihydro aldrin. Aldrin, because of its rapid conversion to the highly persistent dieldrin, its bioaccumulation, and its carcinogenicity (Walker et al. 1973), has been banned as an insecticide by the U.S. Environmental Protection Agency.

Dieldrin. When the model-ecosystem evaluation of dieldrin, the 6,7-epoxide of aldrin, was begun (Table 38), little difference was found between it and the evaluation of aldrin (Table 37). Dieldrin is slightly more water soluble than aldrin and exhibited slightly lower bioconcentrations in the fish. The stability of dieldrin was shown by the storage of dieldrin as 98.7 percent of the extractable radioactive materials in

the alga, 99.0 percent in the snail, and 97.8 percent in the fish (Sanborn & Yu 1973). However, 9-OH and 9-C=O dieldrin were identified as important degradation products along with *trans*-dihydroxydihydro aldrin.

The several thousandfold accumulation of dieldrin in the fish of the model ecosystem following the application of aldrin is in agreement with observations in nature. Humans in the USA have average values of 0.29–0.31 ppm of dieldrin in fatty tissues (Durham 1969). Dieldrin in Lake Michigan at a concentration of 0.000002 ppm in water is biomagnified in lake trout to levels of 0.14–0.45 ppm (U.S. EPA 1972*b*). The average bioconcentration of dieldrin from the waters of Illinois farm ponds to the tissues of fish was 5,000- to 20,000-fold (W. F. Childers & W. N. Bruce, Illinois Natural History Survey, unpublished data).

Toxaphene has been shown to be a mixture of at least 177 components (Holmstead et al. 1974) about two-thirds of which are $C_{10}H_{11}Cl_7$, $C_{10}H_{10}Cl_8$, and $C_{10}H_9Cl_9$ compounds. The highly insecticidal components are heptachlorobornanes (Casida et al. 1974). The ^{14}C-radiolabeled toxaphene used in the model-ecosystem experiments was supplied by the manufacturer as the chlorination product of -[8-^{14}C]- camphene to 67–69 percent Cl (sample X19093-4-2K) and is presumably representative of the technical product. As shown in Table 39, the ^{14}C-radiolabeled toxaphene behaved in a surprisingly homogenous fashion in the extracts from the organisms of the model ecosystem. The major ingredients referred to as "toxaphene" (R_f 0.70) were highly persistent and accumulated to several thousandfold levels in the organisms of the system. "Toxaphene" constituted 82.6 percent of the total extractable radioactive materials in the alga, 86.6 percent in the snail, 62.7 percent in the mosquito, and 64.9 percent in the fish. The unextractable ^{14}C-labeled materials averaged 19 percent of the total radioactive materials in all of the organisms. Thus, toxaphene exhibited model-ecosystem behavior rather like that of endrin (Table 40).

The behavior of toxaphene in the environment is little known because its enormous number of constituents poses almost insurmountable analytical problems. Toxaphene in Big Bear Lake, California, at 0.2 ppm was found to be biomagnified to 200 ppm in goldfish (Hunt & Keith 1963), and in Lake Poinsett, South Dakota, from 0.001 ppm in the water to 0.176 ppm in the tissue and 1.152 ppm in the fat of the carp, *Cyprinus carpio* (Hannon et al. 1970). These instances of thousandfold biomagnification are in perfect agreement with the model ecosystem results.

Endrin is a highly water-insoluble pesticide that was also bioconcentrated in the organisms of the model ecosystem to a high degree (Table 40). Endrin, or 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo*,*endo*-5,8-dimethanonaphthalene, is the *endo*,*endo*-isomer of dieldrin and is less environmentally persistent than dieldrin. Endrin was stored as 84.9 percent of the total extractable ^{14}C-labeled materials in the alga, 83.0 percent in the snail, and 75.9 percent in the fish. Degradation appeared to be largely through an unknown compound designated II, probably 9-OH endrin in analogy with dieldrin. Unknown compound III is probably 9-C=O endrin (Metcalf et al. 1973).

Biological observations on the organisms of the system were particularly informative. Endrin was not only highly toxic to the salt-marsh caterpillar, which had difficulty consuming the treated sorghum leaves, but repeatedly killed all the daphnia, mosquito larvae, and fish in the aquatic portion of the system. The high toxicity of the water phase persisted for more than 60 days from the beginning of the experiment and occurred at endrin concentrations of 0.001–0.002 ppm. Because of this toxicity the experiment was extended

to nearly twice the usual 33-day period, and thus the data in Table 40 were measured after 63 days. Fish added to the model system had violent convulsions within 10–15 minutes after being placed in the contaminated water. These biological observations demonstrated the substantial predictive value of the model-ecosystem investigations and could have given a preview of the Mississippi River fish kills associated with the leaching of endrin wastes (Barthel et al. 1969). Endrin, because of its great bioaccumulation, persistence, and extremely high toxicity to a wide variety of organisms, is a highly dangerous insecticide.

Lindane, or gamma-1,2,3,4,5,6-hexachlorocyclohexane, has a higher water solubility than many of the other organochlorine insecticides and appears to be less readily bioconcentrated in animal tissues (Table 41). In the model ecosystem lindane was stored as 20.6 percent of the total extractable radioactive materials in the snail and 91.7 percent in the fish. None could be detected in the alga or the mosquito. The principal degradation product appeared to be gamma-pentachlorocyclohexene. Lindane is substantially more biodegradable than DDT and the cyclodiene pesticides, and it appears to be degraded environmentally to a series of trichlorophenols (Metcalf et al. 1973).

BHC residues have been found widely distributed in human fatty tissues in the USA at 0.20–0.60 ppm (Durham 1969). The *beta*-isomer (an ingredient of technical BHC insecticide) is the most persistent isomer of lindane, and the environmental persistence of the *gamma*-isomer (lindane) is not well understood.

Mirex, dodecachloro-octahydro-1,3,4-metheno-2H-cyclabuta-{c,d}-pentalene, was one of the least degradable compounds that we evaluated and was stored as 97.8 percent of the total extractable radioactive materials in the alga, 99.4 percent in the snail, 99.6 percent in the mosquito, and 98.6 percent in the fish (Table 42) (Metcalf et al. 1973). It is clearly a highly persistent pollutant and showed a substantial degree of bioaccumulation. Mirex is of environmental importance, as it is one of the most effective inducers of microsomal oxidase enzymes. Mirex, following its widespread use as a bait for the fire ant, has been found in tissues of wild birds at levels of up to 3 ppm and in rodents at nearly 20 ppm (Unpublished data). It has also been found in tissues of northern pike and longnose gar from Lake Ontario at 0.020–0.050 ppm (Kaiser 1974).

Heptachlor, or 1-*exo*-4,5,6,7,8,8-heptachloro-3a,4,7,7a,-tetrahydro-4,7-methanoindene, has a low level of water solubility and a high potentiality for bioaccumulation (Table 43). Heptachlor is rapidly converted in the model ecosystem and its organisms to the very persistent 2,3-epoxide, heptachlor epoxide. In the model ecosystem heptachlor epoxide was stored as 59.1 percent of the total extractable radioactive materials in the alga, 45.6 percent in the snail, and 60.6 percent in the fish. These values are considerably lower than the corresponding values for the storage of dieldrin after the treatment of crops with aldrin (Table 37) and reflect the existence of an alternate degradative pathway in heptachlor, the replacement of the 1-Cl atom by OH to give 1-hydroxychlordene. This degradative product is more polar and water soluble than heptachlor and is not as highly accumulative. It can also be epoxidized *in vivo* to the 2,3-epoxide, 1-hydroxychlordene epoxide, which was found stored in the snail, mosquito, and fish. This latter degradative product could also be formed by hydrolysis of heptachlor epoxide. Heptachlor epoxide in the model ecosystem (Table 44) showed a persistence comparable to that of dieldrin (Table 38).

In the heptachlor test the unextractable ^{14}C-labeled materials averaged 29 percent of the total radioactive materials in the various organisms. Hepta-

chlor epoxide is widely distributed in the environment, and the average level in the body fat of humans in the USA is 0.1–0.24 ppm (Durham 1969). Yellow perch from Lake Michigan had heptachlor epoxide body residues ranging from 0.060 to 0.097 ppm (U.S. EPA 1972*b*). Heptachlor and heptachlor epoxide are under surveillance by the U.S. EPA because of their carcinogenicity (Carter 1974).

Chlordane, or 1,2,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane, is chemically related to heptachlor except that the double bond has been chlorinated. The behavior of this insecticide in the model ecosystem clearly demonstrates its persistence and tendency to accumulate in the organisms of this system (Table 45). The water of the model ecosystem contained only 5.98 percent chlordane, but the alga, snail, mosquito, and fish contained 94.51, 91.17, 47.64, and 77.86 percent, respectively, of their radioactive materials as chlordane. The EM values for chlordane for the alga, snail, mosquito, and fish were 98,386, 132,613, 6,132, and 8,261, respectively. Clearly, the continued use of chlordane, along with its minor contaminant, heptachlor, will lead to problems of accumulation in food chains, which can lead to residues of these two pesticides in humans. Unpublished data accumulated by federal monitoring agencies have indicated that 95 percent of the adipose tissue taken from humans in the United States contains residues of heptachlor. Further, nearly 70 percent of U.S. poultry, fish, and dairy products contain residues of heptachlor. The data of this model-ecosystem experiment provide background information which explains the high incidence of heptachlor residues in humans and food.

FUNGICIDE TEST RESULTS

Captan, or *N*-trichloromethylthio-4-cyclohexene-1,2-dicarboximide, is the most versatile of the general foliar fungicides for the treatment of fruits and vegetables. In the model ecosystem it was found to be extensively degraded, producing at least 15 degradation products in the water phase (Table 46). No intact captan was identified in any of the organisms of the system, and only trace amounts of degradation products were found. Captan appears not to offer any environmental problems following normal use.

Hexachlorobenzene has had some use as a fungicide in seed treatment, replacing in part the organomercurial fungicides. In the model system it was extremely persistent and substantially bioaccumulative, the parent compound comprising 85.1 percent of the total extractable radioactive materials in the alga, 87.2 percent in the daphnia, 58.3 percent in the mosquito, and 27.7 percent in the fish (Table 47) (Metcalf et al. 1973). EM values ranged from 144 to 1,248. The degradation of hexachlorobenzene occurs through hydrolysis to pentachlorophenol and other chlorophenols of increasing water solubility.

Hexachlorobenzene used as a fungicide on wheat caused an epidemic of thousands of cases of cutaneous porphyrinuria in humans in Turkey (Schmid 1960), and the compound has been found in human tissues nearly everywhere, ranging up to 0.29 ppm in adipose tissues in Great Britain (Abbott et al. 1972). Hexachlorobenzene is clearly an undesirable environmental pollutant.

Pentachlorophenol is the fungicide in largest scale use in the United States as a timber and paper pulp preservative and mildewproofer. It is also used as a soil and timber poison against termites and as a nonselective herbicide. In the model ecosystem pentachlorophenol accumulated in the various organisms to a moderate degree (Table 48). EM values were 5–205. Pentachlorophenol constituted 15.1 percent of the total extractable radioactive materials in the alga, 12.2 percent in the snail, 33.3 percent in the mosquito,

55.5 percent in daphnia, and 51.2 percent in the fish. It is apparently degraded through a series of chlorinated phenols, and 10 degradation products were found in the water phase.

Pentachlorophenol, because of its high toxicity to nearly all forms of life as an oxidative phosphorylation uncoupler and its stability, can be a dangerous environmental pollutant. Its use as an herbicide in Japan has resulted in its presence in almost all Japanese river waters at concentrations of 0.01–0.1 ppb (Goto 1971).

DISCUSSION

The data shown in the preceding tables, illustrating the fates of a variety of pesticides in the laboratory model ecosystem, can be used for predictive purposes in a number of ways.

BIOLOGICAL EFFECTS

The dosages applied in the model ecosystem are realistic in terms of those used in the field, i.e., 0.2–1.0 pound per acre (0.22–1.1 kg per ha). Therefore, the biological results observed are meaningful as predictors of the environmental impact of the pesticide studied. The most dramatic results on nontarget species were found with the organochlorine insecticides endrin, dieldrin, and heptachlor epoxide. Endrin applied at the equivalent of 0.2 pound per acre (0.22 kg per ha) repeatedly killed all daphnia and mosquitoes in the system, and the necessity for restocking delayed the termination of the experiment to over 60 days. Fish added to the endrin system showed violent convulsions within 10–15 minutes and died within a few hours. Similar results were experienced with heptachlor epoxide, which killed daphnia and mosquitoes for 56 days after having been applied at 0.2 pound per acre (0.22 kg per ha). Dieldrin was highly toxic to daphnia and mosquitoes, which did not survive at any time during the experiment.

Temephos, the highly effective mosquito larvicide, killed mosquito larvae so persistently that the experiment was prolonged to 53 days. Chlorpyrifos and methyl chlorpyrifos even at the 1.0-mg dosage were highly toxic to daphnia, and chlorpyrifos adversely affected algae.

The carbamate insecticides carbaryl and carbofuran were extremely toxic to daphnia in the initial stages of the experiments.

Some of the herbicides, especially metrabuzin and bifenox, were highly toxic to algae in the model ecosystem. Surprisingly, the insecticide methoxychlor, or its degradation products, also affected algae adversely.

DEGRADATIVE PRODUCTS

This parameter is, of course, the direct measure of biodegradability. In general, the larger the number of degradative products in the water and in the organisms of the model ecosystem, the lower the degree of ecological magnification and the higher the amount of unextractable radioactive materials. Thus, DDE with two degradation products and DDT with four were the worst offenders in ecological magnification in contrast to temephos, carbaryl, and metrabuzin, each with 11 degradative products, and chlordimeform with 13; each of the latter four compounds showed zero ecological magnification. Clearly, the relationship is not precise, because the variety of positions of radiolabeling limits the extent to which degradative products can be identified. Moreover, the formation of secondary toxicants, such as the epoxides, e.g., dieldrin from aldrin and heptachlor epoxide from heptachlor, provides products that are substantially more environmentally stable and ecologically magnified than are the parent compounds.

Nevertheless, knowledge of the key degradative products of any pesticide is important in characterizing its environmental impact. The model ecosystem not only provides useful information about the chemical nature of degradation products and about

degradative pathways, but also indicates potential rates and locations of storage and bioconcentration of pesticides and their degradation products. As examples, in addition to those of dieldrin and heptachlor epoxide, Banamite (Table 49) produced an unidentified degradation product, designated II, which was ecologically magnified 3,013-fold in fish and 19,824-fold in snails. Metrabuzin (Table 12) produced an unidentified product, designated II, which was ecologically magnified 175-fold in fish. Even the highly degradable malathion produced an unidentified product, designated III, which showed apparent ecological magnification of about 19,500-fold (Table 20).

ECOLOGICAL MAGNIFICATION

The accumulation of lipid-soluble, water-insoluble pesticides in living organisms is one of the most disturbing features of environmental pollution by pesticides. The laboratory model ecosystem is particularly suitable for determining "ecological magnification," or the pesticide concentration in an organism divided by the pesticide concentration in the water. When ecological magnification is considered for the fish (*Gambusia*), we find that the values from the data in the tables vary from 0 to 10^5. Such ecological magnification is a function of the partition coefficient in lipid/water and the stability of the pesticide and its metabolites in the animal. As shown in Fig. 2, an effective approximation is obtained when the water solubility of the pesticide in parts per billion (ppb) is plotted as a log function against ecological magnification. There is clearly an inverse relationship, with the least water-soluble pesticides accumulating to the highest degree. This relationship is highly significant, with a correlation coefficient of $r = -0.76$, and it is sub-

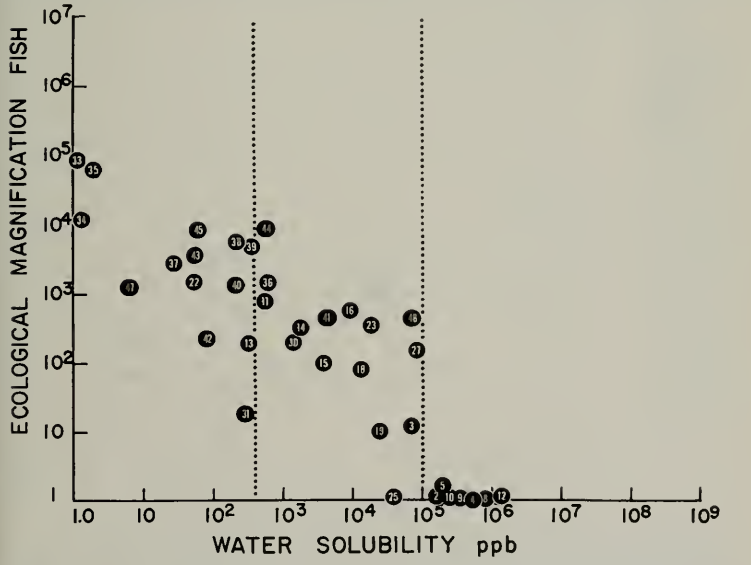

Fig. 2.—The relationship between the water solubility of pesticides, numbered as in Tables 2–49, and the ecological magnification of parent compounds in the mosquito fish in the laboratory model ecosystem. A highly significant correlation ($r = -0.76$) exists.

stantially predictable. Thus, it is of great importance to know the water solubility of even the least soluble compounds. From this information it is possible to make a reliable estimate of the potentialities of new pesticides to accumulate in the tissues of fish and other aquatic organisms. Our study suggests a classification of pesticides as:

1. water solubility<0.5 ppm, *likely to be environmentally hazardous*
2. water solubility>50 ppm, *likely to be environmentally nonhazardous*
3. water solubility from 0.5 to 50 ppm, *to be used with caution*

The lines of demarcation between the three classes obviously are not sharp, and the ultimate hazard also depends upon lipid partitioning, the rapidity of pesticide degradation in living animals, use patterns, and amounts applied. However, practical experience has already shown that most of the pesticides with water solubilities of <0.5 ppm demonstrate bioaccumulation following field use and that most of those with water solubilities of >50 ppm have not shown bioaccumulation. The large group of pesticides with water solubilities between 0.5 and 50 ppm represent those which may demonstrate bioaccumulation under some conditions of use, e.g., in lakes or oceans with very cold water. Their use patterns should be judged accordingly.

UNEXTRACTABLE RADIOACTIVE MATERIALS

This parameter measures the conversion of the pesticide under investigation and its primary degradation products into simple degradation products which enter the metabolic pool of an organism and are resynthesized into normal tissue ingredients. The percentage of unextractable radioactive materials can be determined for many of the pesticides investigated by adding the amount of

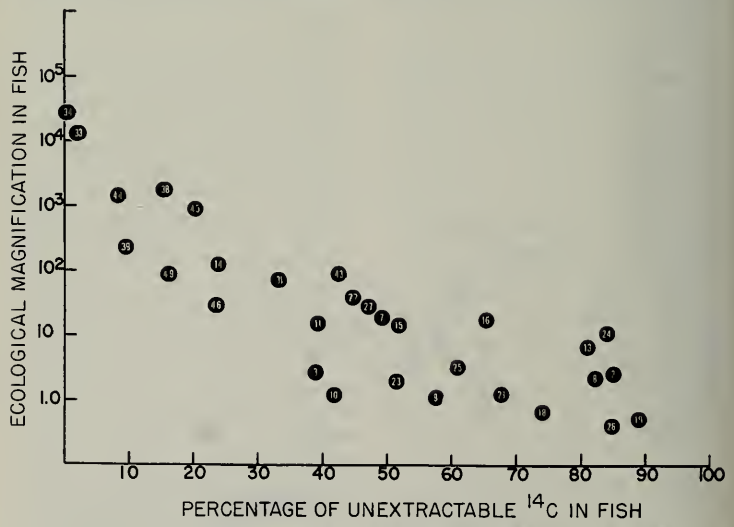

Fig. 3.—The relationship between the percentage of radioactive materials extractable from the mosquito fish of the laboratory model ecosystem and the total body accumulation of parent pesticide, numbered as in Tables 2–49, and all of its degradation products. There is a highly significant correlation ($r = -0.74$).

unextractable radioactive materials to the total extractable radioactive materials and determining the fraction. The values obtained in the fish (*Gambusia*), for example, range from 0.34 percent for DDE to about 90 percent for fenitrothion. As shown in Fig. 3, a highly significant correlation ($r = -0.74$) exists between the percentage of unextractable radioactive materials and the *in vivo* stability of the pesticide and its principal degradation products as measured by the total biomagnification of the radioactive materials from the water to the fish (or other organism).

Considering that two different methods for determining amounts of unextractable radioactive materials were used, i.e., total combustion analysis and solubilization, the results are surprisingly predictable. Clearly, pesticides and their degradation products which are highly lipid soluble in the tissues of organisms are almost quantitatively extractable and leave small amounts of unextractable radioactive materials. As a tentative guideline we suggest that pesticides which produce 40 percent or more of unextractable radioactive materials in the fish in the model ecosystem evaluation will not be likely to cause serious problems with environmental quality.

Table 2.—R_f values and amounts, in parts per million, of alachlor[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Uca* (crab)	*Daphnia* (water flea)	*Elodea* (aquatic plant)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.0457	0.0898	0.321	0.00	1.767	0.843	0.0452	0.125
I[c]	0.70	0.000948	...	...	...	...	...	...	...
Alachlor	0.61	0.00105	...	...	...	...	...	...	...
II	0.51	0.00344	...	...	...	...	...	...	...
III	0.43	0.0141	...	...	...	...	...	...	...
IV	0.33	0.00224	...	...	...	...	...	...	...
V	0.27	...	...	...	...	...	0.658	...	...
VI	0.20	0.00169	...	...	...	...	...	...	...
VII	0.13	0.00172	...	...	...	...	...	...	...
VIII	0.07	0.00369	...	...	...	...	...	...	...
Origin	0.00	0.00501	...	...	...	...	0.185	...	...
Unextractable ^{14}C		0.0118	0.569	0.524	0.422	2.961	0.544	0.244	0.106

[a]2-chloro-2',6'-diethyl-*N*, *N*-(methoxymethyl)-acetanilide, ^{14}C-ring UL.
[b]Silica Gel GF-254, methanol-benzene, 5:95 by volume.
[c]Roman numerals indicate compounds whose chemical structures are unknown.

Table 3.—R_f values and amounts, in parts per million, of atrazine[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.2281	2.7562	0.3779	0.5352	0.5916
Atrazine	0.43	0.03181	2.4059	0.2386	...	0.3511
A[c]	0.41	0.01575	0.2100	0.05479	...	0.07356
B[d]	0.38	0.005398	0.04934	0.02796	...	0.05496
I[e]	0.30	0.003681	...	...	...	...
II	0.25	0.001323	...	...	...	...
III	0.17	0.0008116	0.01792	...	...	0.03302
IV	0.11	0.001200	...	...	...	...
V	0.05	0.0004273	0.01020	0.02226	...	0.01462
Origin	0.00	0.002644	0.06284	0.03424	...	0.06436
Unextractable ^{14}C		0.1651	4.1907	0.04981	1.6726	0.2290

[a] 2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine, ^{14}C-ring UL.
[b] Silica Gel GF-254, benzene: acetic acid: water, 50:50:3.
[c] A = 2-amino-4-chloro-6-(isopropylamino)-*s*-triazine.
[d] B = 2-amino-4-chloro-6-(ethylamino)-*s*-triazine.
[e] Roman numerals indicate compounds whose chemical structures are unknown.

Table 4.—R_f values and amounts, in parts per million, of bentazon[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Uca* (crab)	*Corbicula* (clam)	*Daphnia* (water flea)	*Elodea* (aquatic plant)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.514	0.109	0.032	2.725	0.182	0.092	0.084	0.146	0.0120
A[c]	0.77	0.0207	...	...	0.622	...	...	...	...	...
B[d]	0.63	...	...	...	1.266	...	...	...	...	...
Bentazon	0.52	0.0505	...	...	0.510	...	...	...	...	...
Origin	0.00	0.00306	...	...	0.327	...	...	...	...	...
Unextractable ^{14}C		0.440	0.759	0.021	3.08	0.407	0.168	0.378	0.716	0.036

[a] 3-isopropyl-1*H*-2,1,3-benzothiadiazin-4-(3*H*)-one-2,2-dioxide, ^{14}C-ring UL.
[b] Silica Gel GF-254, benzene-ethanol, 60:40 by volume.
[c] A = *N*-isopropylanthraniamide.
[d] B = Anthranilic acid.

Table 5.—R_f values and amounts, in parts per million, of cyanazine[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Corbicula* (clam)	*Daphnia* (water flea)	*Elodea* (aquatic plant)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.0322	0.129	0.311	0.0196	0.629	0.0454	0.0277	0.0354
Cyanazine	0.55	0.00321	...	...	...	0.621	...	...	...
A[c]	0.47	0.0107	...	0.172	...	...	...	...	...
B[d]	0.37	0.000142	...	...	...	...	...	...	...
C[e]	0.26	0.0000568	...	...	...	...	...	...	...
I[f]	0.16	0.0000768	...	...	...	...	...	...	...
II	0.07	0.0000868	...	0.0579	...	...	...	...	...
Origin	0.00	0.0000534	...	0.0812	...	0.00818	...	...	...
Unextractable ^{14}C		0.00357	0.127	0.209	0.0202	0.6253	0.0624	0.0751	0.0157

[a]2-chloro-4-(1-cyano-1-methylethylamino)-6-ethylamino-*s*-triazine, ^{14}C-ring UL.
[b]Silica Gel GF-254, methanol-acetone-chloroform, 5:45:50 by volume.
[c]A=2-chloro-4-amino-6-(1-methyl-1-cyanoethylamino)-*s*-triazine.
[d]B=2-chloro-4-ethylamino-6-(1-methyl-1-carboxamidoethylamino)-*s*-triazine.
[e]C=2-chloro-4-amino-6-(1-methyl-1-carboxamidoethylamino)-*s*-triazine.
[f]Roman numerals indicate compounds whose chemical structures are unknown.

Table 6.—R_f values and amounts, in parts per million, of dicamba[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Corbicula* (clam)	*Uca* (crab)	*Daphnia* (water flea)	*Elodea* (aquatic plant)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.183	0.228	0.0128	0.743	0.000	0.325	0.0720	0.0736	0.00665
Dicamba	0.86	0.162	...	...	...	...	...	...	...	...
A[c]	0.38	0.0185	...	...	...	...	...	...	...	...
B[d]	0.04	0.000182	...	...	0.743	...	...	...	...	...
Unextractable ^{14}C		0.0022	1.390	0.0144	0.374	0.167	0.593	0.252	0.281	0.0122

[a] 3,6-dichloro-o-anisic acid, ^{14}C-ring UL.
[b] Whatman No. 1 filter paper, benzene-acetic acid, 2:1 by volume.
[c] A = 3,6-dichloro-5-hydroxy-2-methoxybenzoic acid.
[d] B = Conjugated metabolite.

Table 7.—R_f values and amounts, in parts per million, of phenmedipham[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.028	4.22	2.69	1.312	0.545
Phenmedipham		...	...	...	...	...
A[c]	0.64	0.0102	...	...	...	...
B[d]		trace[e]	...	...	...	...
I[c]	0.99	...	0.067	0.497	0.131	...
II	0.96	...	0.131	0.153	0.101	...
III	0.76	...	0.139	...	...	...
IV	0.68	...	0.372	...	...	...
V	0.35	...	0.355	...	...	...
VI	0.18	...	0.506	...	...	...
Origin	0.00	0.0178	2.65	2.04	1.080	0.545
Unextractable ^{14}C		0.018	13.08	7.00	1.978	0.535

[a] Methyl *m*-hydroxycarbanilate *m*-methylcarbanilate, ^{14}C-ring UL.
[b] Silica Gel GF-254, diethyl ether :petroleum ether :chloroform, 6:3:1 by volume.
[c] A = *N*-(3-hydroxyphenyl)-methyl urethane.
[d] B = 3-methylaniline.
[e] Roman numerals indicate compounds whose chemical structures are unknown.
[f] Determined by gas chromatography.

Table 8.—R_f values and amounts, in parts per million, of 2,4-D[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Elodea* (aquatic plant)	*Physa* (snail)	*Gambusia* (fish)
Total ^{14}C		0.2048	5.498	2.752	0.757	0.0454
I[c]	0.97	...	0.282	0.178	0.285	...
II	0.89	...	1.030	0.456	...	...
III	0.80	...	0.477	0.477	0.301	...
IV	0.65	...	0.377	...	...	...
V	0.58	0.0000641	0.295	...	...	0.0431
VI	0.63	0.00269	...	...	...	...
VII	0.56	0.00212	...	...	...	...
VIII	0.49	0.00226	...	...	...	...
IX	0.39	0.000417	...	...	...	...
X	0.10	0.000474	1.675	0.768	...	...
XI	0.067	0.000271	...	...	...	...
Origin	0.00	0.000185	1.362	0.873	0.171	0.00226
Unextractable ^{14}C		0.012	17.625	7.555	6.421	0.211

[a] 2,4-dichlorophenoxyacetic acid, ^{14}C-ring UL.
[b] Silica Gel GF-254, benzene-dioxane-acetic acid, 90:25:4 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.

Table 9.—R_f values and amounts, in parts per million, of propachlor[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Corbicula* (clam)	*Daphnia* (water flea)	*Elodea* (aquatic plant)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.00901	0.0211	0.00619	0.00930	0.00243	0.0749	0.0264	0.00605
I[c]	0.69	0.0000622	...	...	...	...	...	...	...
II	0.62	0.000169	...	...	...	...	...	...	...
Propachlor	0.55	0.0000564	...	...	...	...	...	...	...
III	0.40	0.00318	...	...	...	...	...	...	...
IV	0.30	...	...	...	...	...	0.0154	...	...
V	0.27–0.15	0.000421	...	...	...	...	...	...	...
VI	0.10	0.000272	...	...	...	...	...	...	...
VII	0.03	0.000319	...	...	...	...	...	...	...
Origin	0.00	0.000394	...	...	...	...	0.0595	...	...
Unextractable ^{14}C		0.00414	0.186	0.00886	0.0476	0.0869	0.177	0.134	0.00854

[a] 2-chloro-*N*-isopropylacetanilide, ^{14}C-ring UL.
[b] Silica Gel GF-254, methanol-benzene, 5:95 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.

Table 10.—R_f values and amounts, in parts per million, of pyrazon[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Corbicula* (clam)	*Uca* (crab)	*Daphnia* (water flea)	*Elodea* (aquatic plant)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.0321	0.0758	0.0498	0.499	0.0536	0.105	0.127	0.175	0.0336
Pyrazon	0.63–0.69	0.0212	...	...	0.476	...	...	...	...	...
A[c]	0.47–0.51	0.0000714	...	...	...	...	...	...	...	...
I[d]	0.40–0.43	0.0000430	...	...	...	...	...	...	...	...
II	0.23	0.0000260	...	...	...	...	...	...	...	...
III	0.16	0.0000471	...	...	...	...	...	...	...	...
IV	0.10	0.0000764	...	...	...	...	...	...	...	...
Origin	0.00	0.000136	...	...	0.0233	...	...	...	...	...
Unextractable ^{14}C		0.0105	0.131	0.018	0.130	0.0455	0.0552	0.0592	0.148	0.0237

[a] 5-amino-4-chloro-2-phenyl-3-(2H)-pyridazinone, ^{14}C-phenyl ring.
[b] Silica Gel GF-254, benzene-ethanol, 60:40 by volume.
[c] A = 5-amino-4-chloro-3(2H)pyridazinone.
[d] Roman numerals indicate compounds whose chemical structures are unknown.

Table 11.—R_f values and amounts, in parts per million, of trifluralin[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Daphnia* (water flea)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.0489	0.445	6.663	0.238	0.767
Trifluralin	0.74	0.000282	...	5.046	...	0.261
I[c]	0.51	0.000066	...	...	...	...
A[d]	0.39	0.000087	...	0.337	...	...
B[e]	0.32	0.000374	...	...	...	...
II	0.24	0.000322	...	0.0399	...	...
III	0.20	0.000139	...	0.216	...	...
IV	0.17	0.000514	...	...	...	...
C[f]	0.13	0.000803	...	...	...	...
V	0.11	0.000686	...	...	...	...
VI	0.07	0.00141	...	0.228	...	...
VII	0.04	0.00203	...	...	...	...
Origin	0.00	0.0169	...	0.796	...	0.506
Unextractable ^{14}C		0.0253	1.017	6.648	0.520	1.011

[a] α,α,α-trifluoro-2,6-dinitro-*N*, *N*-dipropyl-*p*-toluidine, ^{14}C-ring UL.
[b] Silica Gel GF-254, hexane-acetone-methanol, 90:10:2 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.
[d] A = α,α,α-trifluoro-2,6-dinitro-*N*-propyl-*p*-toluidine.
[e] B = 2,b-dinitro-4-trifluoromethyl aniline.
[f] C = 2-ethyl-5-trifluoromethyl-7-nitrobenzimidazole.

Table 12.—R_f values and amounts, in parts per million, of metrabuzin[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.6524	1.2880	1.559	1.342
I[c]	0.87	0.2911	0.762	1.307	0.307
II	0.83	0.003118	0.3920	...	0.546
A[d]	0.57	0.008965	...	...	0.291
III	0.35	0.1292	...	...	...
IV	0.32	0.006435	...	...	...
B[e], C[f]	0.24	0.09676	...	...	0.0746
V	0.20	0.0005374	...	...	...
VI	0.17	0.001252	...	...	...
VII	0.12	0.005675	...	...	...
VIII	0.09	0.001158	...	...	...
IX	0.06	0.00005275	...	...	...
X	0.04	0.0005046	...	...	...
XI	0.01	0.002047	0.05217	0.05158	0.0140
Origin	0.00	0.005278	0.05217	0.2407	0.0769
Unextractable ^{14}C		0.1003	0.4578	3.7546	0.3498

[a] 4-amino-6-*tert*-butyl-3-(methylthio)-*as*-triazin-5(4*H*)-one 5-^{14}C.
[b] Chloroform: acetone, 9:1 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.
[d] A = Desamino metrabuzin.
[e] B = Desmercapto metrabuzin.
[f] C = Desamino desmercapto metrabuzin.

Table 13.—R_f values and amounts, in parts per million, of bifenox[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.0376	3.267	1.650	0.290	0.211
I[c]	0.82	0.000108	...	...	0.071	...
Bifenox	0.73	0.000745	3.189	1.203	0.219	0.156
A[d]	0.66	0.000125	...	0.256	...	...
II	0.60	0.000092	...	...	...	...
III	0.45	0.000125	...	...	...	...
B[e]	0.33	0.000325	...	0.088	...	0.020
Origin	0.00	0.0301	0.78	0.103	trace	0.026
Unextractable ^{14}C		0.0061				

[a] Methyl-5-(2′,4′-dichlorophenoxy)-2-nitrobenzoate, ^{14}C nitrophenyl ring UL.
[b] Silica Gel GF-254, benzene:dioxane:acetic acid, 90:30:1 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.
[d] A = Methyl-5-(2′,4′-dichlorophenoxy)-2-amino benzoate.
[e] 2,4-dichlorophenoxy-2-nitro-5-benzoic acid.

Table 14.—R_f values and amounts, in parts per million, of chlorpyrifos[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.00056	0.0261	0.158	0.063	0.0711
Chlorpyrifos	0.76	0.00011	0.0079	0.076	0.005	0.0352
A[c]	0.60	...	...	...	...	...
B[d]	0.60	0.000115	0.0051	0.051	0.022	0.0207
Origin	0.00	0.00005	0.0131	0.031	0.036	0.0152
Unextractable ^{14}C		0.00028	0.1507	0.0456	...	0.0223

[a] *O,O*-diethyl-*O*-(3,5,6-trichloro-2-pyridyl)-phosphorothionate, ^{14}C-ring UL.
[b] Silica Gel GF-254, benzene:dioxane:acetic acid, 90:15:1 by volume. Pyridinol (R_f — 0.17) and P = O ester (R_f — 0.90) separated with solvent system, acetonitrile:hexane:acetone:NH_4OH 70:10:15:5, by volume.
[c] A = Chlorpyrifosoxon.
[d] B = 3,5,6-trichloro-2-pyridol.

Table 15.—R_f values and amounts, in parts per million, of chlorpyrifos-methyl[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.00262	0.0780	0.0882	0.220	0.0367
Chlorpyrifos-methyl	0.75	0.00008	0.0382	0.0435	0.15	0.0076
A[c]	0.54	...	...	...	...	...
B[d]	0.60	0.0002	0.0087	0.0082	0.037	0.0109
Origin	0.00	0.00154	0.0051	0.0067	0.033	0.0101
Unextractable ^{14}C		0.0009	0.4703	0.2110	...	0.0398

[a] *O,O*-diethyl-*O*-(3,5,6-trichloropyridinyl) phosphorothionate, ^{14}C-ring UL.
[b] Silica Gel GF-254, benzene: dioxane:acetic acid, 90:15:1 by volume. Pyridinol (R_f — 0.17) and P = O ester (R_f — 0.83) separated by solvent system, acetonitrile:hexane:acetone:NH_4OH, 70:10:15:5, by volume.
[c] A = Chlorpyrifosoxon methyl.
[d] B = 3,5,6-trichloro-2-pyridol.

Table 16.—R_f values and amounts, in parts per million, of Counter®[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.00259	0.1063	0.1556	0.1517	0.0427
I[c]	0.83	...	...	...	0.1156	...
Counter®	0.77	0.00002	0.0035	0.0366	0.0072	0.0107
A[d]	0.66	0.00006	...	...	...	...
B[e]	0.54	0.000062	trace	0.0241	...	...
C[f]	0.40	0.000357	...	...	...	...
II	0.29	0.000046	0.0071	...	...	...
III	0.18	0.000018	...	...	...	...
D[g]	0.13	0.000017	0.0106	...	...	trace
IV	0.03	0.000007	0.0213	...	...	...
Origin	0.00	0.000283	0.0638	0.0494	0.0289	0.0320
Unextractable ^{14}C		0.00174	0.8913	0.778	0.4282	0.0813

[a] *O,O*-diethyl *S*-(*tert*-butylthio)-methyl phosphorodithioate, ^{14}C-*tert*-butyl.
[b] Silica Gel GF-254, benzene:acetone, 4:1 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.
[d] A = $(C_2H_5O)_2\overset{\overset{S}{\|}}{P}SCH_2SO_2C(CH_3)_3$.
[e] B = $(C_2H_5O)_2\overset{\overset{O}{\|}}{P}SCH_2SC(CH_3)_3$.
[f] C = $(C_2H_5O)_2\overset{\overset{O}{\|}}{P}SCH_2SO_2C(CH_3)_3$.
[g] D = $(C_2H_5O)_2\overset{\overset{O}{\|}}{P}SCH_2SOC(CH_3)_3$.

Table 17.—R_f values and amounts, in parts per million, of temephos[a] and its degradation products found in the water and organisms of a model ecosystem.

XO ⟨O⟩ Y ⟨O⟩ OZ

X	Y	Z	R_f[b]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Gambusia* (fish)
Total 3H				0.000280	0.00991	0.09161	0.00099
$(MeO)_2P=S$	S	$(MeO)_2P=S$		0.0000013	0.00195	0.01876	...
$(MeO)_2P=S$	SO	$(MeO)_2P=S$		0.000002	0.00066	0.01483	...
$(MeO)_2P=S$	SO_2	$(MeO)_2P=S$		0.0000007	0.00078	0.00396	...
$(MeO)_2P=O$	S	$(MeO)_2P=O$		0.00000014	0.00127	0.00785	...
$(MeO)_2P=O$	SO_2	$(MeO)_2P=O$		...	0.00066	...	...
$(MeO)_2P=S$	SO_2	$(MeO)_2P=O$		...	0.00040	0.00698	...
$(MeO)_2P=S$	S	$(MeO)_2P=O$		trace	0.00066	0.02705	...
$(MeO)_2P=S$	SO_2	H		0.000002	0.00036	...	...
$(MeO)_2P=S$	S	H		0.000002	0.00129	...	...
H	S	H		0.000001	0.00045	...	...
H	SO_2	H		0.0000024	0.00046	0.00175	...
$(MeO)_2P=O$	S	H		0.000008	0.00064	0.01178	...
Origin				0.00019	0.00033	0.00436	...
Unextractable ^{14}C				0.000070	...	...	...

[a] *O,O*-dimethylphosphorothioate ester of 4,4′ dihydroxydiphenyl sulfide, ^2H-ring-labeled.
[b] Silica Gel GF-254 three dimensional TLC: 1.toluene. 2.methanol:chloroform:toluene, 10:95:95 by volume. 3.nitromethane:acetonitrile, 25:65:110 by volume.

Table 18.—R_f values and amounts, in parts per million, of fonofos[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.1079	0.2977	0.2831	0.6863	0.08500
Fonofos	0.92	0.0008866	0.09556	0.07635	0.6133	0.06845
I[c]	0.76	0.0000653	0.02203	...	...	...
II	0.68	0.0002602	...	...	...	...
III	0.62	0.001504	0.07905	...	...	...
IV	0.37	0.002806	0.01887	...	...	...
V	0.29	0.0005997	...	...	...	...
VI	0.22	0.0008081	...	...	...	...
VII	0.19	0.0001472	...	...	...	...
VIII	0.13	0.0003656	...	...	...	...
IX	0.10	0.0001383	0.0401	...	...	...
X	0.09	0.0000765	...	...	...	...
XI	0.08	0.0002311	...	0.08748	...	0.01193
XII	0.04	0.0005152	0.01494	...	...	...
Origin	0.00	0.008277	0.02712	0.1193	0.07302	0.004624
Unextractable ^{14}C		0.09126	0.5247	2.2550	5.8578	0.2453

[a] *O*-ethyl, *S*-phenyl ethylphosphonodithioate, ^{14}C-*O*-ethyl.
[b] Silica Gel GF-254, chloroform:ethyl acetate, 4:1 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.

Table 19.—R_f values and amounts, in parts per million, of fenitrothion[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{32}P		0.1136	2.5579	5.270	0.0829	0.0545
I[c]	0.92	0.00238	...	...	...	...
Fenitrothion	0.81	0.00247	0.8632	...	0.0055	0.0242
II	0.73	0.00004	...	...	...	...
A[d]	0.52	0.00088	...	...	...	0.0057
III	0.22	0.00030	...	...	...	...
IV	0.13	0.00338	...	...	...	...
V	0.06	0.00030	...	...	...	...
Origin	0.00	0.02438	1.2947	5.2700	0.0774	0.0246
Unextractable ^{14}C		0.07949	10.5993	1.5802	1.0983	8.9550

[a] *O,O*-dimethyl *O*-(3-methyl-4-nitrophenyl) phosphorothionate, ^{32}P.
[b] Silica Gel GF-254, hexane (Skellysolve B):ether, 4:1 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.
[d] A = Fenitroxon or dimethyl 3-methyl-4-nitrophenyl phosphate.

Table 20.—R_f values and amounts, in parts per million, of malathion[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.01659	0.421	0.577	6.97	1.43
I[c]	0.81	...	0.319	...	1.82	...
II	0.75	0.0000447	...	0.338	...	0.119
III	0.63–0.67	0.0000335	...	...	2.34	0.655
IV	0.50	0.0000546	...	...	0.947	0.1033
V	0.36	0.0000784	...	...	0.299	...
VI	0.31	...	...	...	...	0.0254
VII	0.15	0.0000345	...	...	...	0.0737
VIII	0.05	0.0000754	...	...	0.275	0.0342
Origin	0.00	0.003868	0.102	0.139	1.283	0.420
Unextractable ^{14}C		0.0124	...	...	...	...

[a] *O,O*-dimethyl-*S*-(1,2-dicarboethoxyethyl)-phosphorodithioate, ^{14}C-*O,O*-methyl.
[b] Silica Gel GF-254, benzene:acetic acid, 4:1 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.

Table 21.—R_f values and amounts, in parts per million, of acephate[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Corbicula* (clam)	*Uca* (crab)	*Daphnia* (water flea)	*Elodea* (aquatic plant)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.0245	1.043	0.100	2.285	0.403	0.417	0.926	0.822	0.0309
I[c]	0.93	0.000477	0.936	...	2.038	0.257	0.407	0.796	0.797	...
A[d]	0.79	0.000124	...	...	...	...	...	...	...	...
Acephate	0.70	0.000282	...	...	...	...	...	...	...	...
B[e]	0.45	...	...	...	...	...	...	...	...	...
C[f]	0.33	0.0000150	...	...	...	...	...	...	...	...
II	0.25	...	0.0538	...	...	...	...	...	...	...
III	0.11	...	0.0142	...	...	0.00280	...	...	...	...
Origin	0.00	0.0000255	0.0395	...	0.247	0.143	0.0098	0.130	0.0247	...
Unextractable ^{14}C		0.0236	1.043	0.148	3.631	1.979	1.435	2.769	2.466	0.0621

[a] *O*-methyl-*S*-methyl-*N*-acetylphosphoramidothioate, ^{14}C-*S*-methyl.
[b] Silica Gel GF-254, alumina plate 15% acetic acid in benzene:propanol, 1:1 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.
[d] A = *O*,*S*-dimethyl phosphoramidothioate.
[e] B = *O*,*S*-dimethyl phosphorothioc acid-sodium salt.
[f] C = *S*-methyl *N*-acetyl phosphoramidothioate.

Table 22.—R_f values and amounts, in parts per million, of leptophos[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Gambusia* (fish)
Total ^{14}C		0.180	31.637	53.696	1.866
Leptophos	0.93	0.00108	13.221	52.270	1.559
I[c]	0.85	...	15.753	...	...
II	0.25	...	...	0.105	0.0313
III	0.24	...	...	...	0.0235
IV	0.22	...	...	0.128	...
V	0.20	...	2.357	...	...
VI	0.13	0.002712	...	...	...
VII	0.12	0.00647	...	...	...
VIII	0.10	0.000199	...	...	...
IX	0.09	0.00392	...	...	...
X	0.07	0.0000691	...	...	...
XI	0.05	0.009094	0.009	...	...
XII	0.03	0.000147	...	...	0.0235
Origin	0.00	0.02170	0.297	1.193	0.199
Unextractable ^{14}C		0.1351	57.241	11.612	1.555

[a] *O*-(4-bromo-2,5-dichlorophenyl)-*O*-methyl phenylphosphonothionate, ^{14}C-*O*-methyl.
[b] Silica Gel GF-254, benzene:chloroform, 1:1 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.

Table 23.—R_f values and amounts, in parts per million, of parathion[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Daphnia* (water flea)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.003	0.3969	0.2987	0.2701	0.2031	0.1935
I[c]	0.97	0.000200	0.0356	...	...	...	...
Parathion	0.90	0.00030	...	...	...	...	0.1006
II	0.73	0.000060	...	...	...	...	...
A[d]	0.55	0.000136	...	...	...	...	0.0086
III	0.33	0.00025	...	...	...	...	0.0222
B[e]	0.25	0.0047	...	...	...	...	...
IV	0.13	0.00049	...	...	...	...	...
V	0.09	0.00274	...	...	...	...	...
Origin	0.00	0.00599	0.3613	0.2987	0.2701	0.2031	0.0621
Unextractable ^{14}C		0.0854	2.6284	0.3126	0.5818	0.4685	0.2055

[a] *O,O*-diethyl *O*-4-nitrophenyl phosphorothionate, ^{14}C-ring-2,6.
[b] Silica Gel GF-254, ether-hexane, 7:3 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.
[d] A = *p*-nitrophenol.
[e] B = Paraoxon.

Table 24.—R_f values and amounts, in parts per million, of metalkamate[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Corbicula*[c] (clam)	*Uca* (crab)	*Daphnia* (water flea)	*Elodea* (aquatic plant)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.003966	1.781	0.0206	0.287	0.128	0.945	0.119	0.178	0.0449
Metalkamate	0.98	0.00009539	0.980	...	0.0498	...	0.245	...	...	...
I[d]	0.95–0.62	0.000814	0.474	...	0.168	...	0.107	...	...	...
II	0.62–0.28	0.0000151	0.252	...	0.056	...	0.206	...	...	...
III	0.28–0.02	0.0000589	0.074	...	0.0079	...	0.119	...	...	...
Origin	0.00	0.0001031	0.00111	...	0.00508	...	0.268	...	...	...
Unextractable ^{14}C		0.00288	7.825	0.0826	1.590	1.420	1.510	0.662	0.602	0.230

[a] 3:1 mixture of *m*-(1-ethylpropyl)-phenyl and *m*-(1-methylbutyl)-phenyl *N*-methylcarbamates, ^{14}C-carbonyl labeled.
[b] Microfiber absorbent sheets impregnated with silica gel, acetone-n-hexane, 15:85 by volume.
[c] Clam died 7 days after the application of metalkamate to the system.
[d] Roman numerals indicate compounds whose chemical structures are unknown.

Table 25.—R_f values and amounts, in parts per million, of carbaryl[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Corbicula* (clam)	*Uca* (crab)	*Daphnia* (water flea)	*Elodea* (aquatic plant)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.374	0.789	0.286	0.384	0.295	1.051	1.31	0.360	0.121
I[c]	0.95	...	0.175	...	0.118	...	0.057	...	...	0.03
II	0.87	0.000161	...	...	...	...	...	...	...	...
III	0.83	0.000155	...	...	...	...	...	...	...	...
A[d]	0.79	...	...	...	...	...	...	...	...	...
IV	0.67	0.000221	...	...	...	...	...	...	...	...
V	0.53	0.00006	...	...	...	...	...	...	...	...
VI	0.47	0.000133	...	...	...	...	...	...	...	...
B[e]	0.35	0.000081	...	...	...	...	...	...	...	...
C[f]	0.30	...	...	...	...	...	...	...	...	...
D[g]	0.26	...	...	...	...	...	...	...	...	...
VII	0.22	0.000018	...	...	...	...	...	...	...	...
E[h]	0.18	0.000099	...	...	...	...	...	...	...	...
VIII	0.12	0.000765	...	...	0.0098	...	0.085	0.86	...	...
IX	0.08	0.00151	...	...	...	...	...	...	...	...
Origin	0.00	0.00748	0.614	...	0.257	...	0.909	0.45	...	0.091
Unextractable ^{14}C		0.0267	3.964	1.341	0.738	2.385	3.511	3.79	2.657	0.337

[a] 1-naphthyl *N*-methylcarbamate, ^{14}C-ring UL.
[b] Silica Gel GF-254 chloroform:methanol, 49:1 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.
[d] A = 1-napthol.
[e] B = 1-napthyl-*N*-hydroxymethylcarbamate.
[f] C = 5-hydroxy-1-napthyl-*N*-methylcarbamate.
[g] D = 4-hydroxy-1-napthyl-*N*-methylcarbamate.
[h] E = 7-hydroxy-1-napthyl-*N*-methylcarbamate.

Table 26.—R_f values and amounts, in parts per million, of carbofuran[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Corbicula* (clam)	*Daphnia* (water flea)	*Elodea* (water plant)	(frog)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.115	0.815	1.087	1.089	2.697	0.502	1.645	1.071	0.0725
I[c]	0.98	0.001048	...	...	...	...	0.197	0.567	0.418	0.0462
A[d]	0.83	0.02978	...	0.0130	...	...	...	0.377	...	0.000304
B[e] and carbofuran	0.76	0.003889	...	...	...	...	...	...	...	...
C[f]	0.70	0.0005148	...	...	...	...	...	...	...	...
D[g]	0.60	0.0003728	...	...	...	...	...	...	...	...
E[h]	0.53	0.0003665	...	...	...	...	...	...	...	...
F[i]	0.46	0.0006071	...	...	...	...	...	...	...	0.00526
II	0.36	0.0007283	...	...	...	...	...	...	...	0.000828
III	0.28	0.001737	...	0.191	...	...	...	...	...	...
IV	0.13	0.003218	...	...	...	...	...	...	...	...
V	0.06	0.003328	...	...	...	...	...	...	...	...
Origin	0.00	0.017213	...	0.883	...	...	0.305	0.890	0.552	0.0216
Unextractable ^{14}C		0.0666	4.648	0.368	4.690	2.993	1.034	6.270	4.835	0.413

[a] 2,2-dimethyl-2,3-dihydrobenzofuranyl-7-*N*-methylcarbamate, ^{14}C-ring UL.
[b] Microfiber absorbent sheets impregnated with Silica Gel, acetone: *n*-hexane, 15:85 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.
[d] A = 7-hydroxy-2,2-dimethyldihydrobenzofuran.
[e] B = 3-keto-7-hydroxy-2,2-dimethyldihydrobenzofuran.
[f] C = 2,2-dimethyl-3-oxo-7-*N*-methycarbamoyloxydihydrobenzofuran.
[g] D = 3,7-dihydroxy 2,2-dimethyldihydrobenzofuran.
[h] E = 2,2-dimethy-7-*N*-hydroxymethylcarbamoyloxydihydrobenzofuran.
[i] F = 2,2-dimethyl-3-hydroxy-7-*N*-methylcarbamoyloxydihydrobenzofuran.

Table 27.—R_f values and amounts, in parts per million, of propoxur[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.00408	0.4617	0.3946	2.2913	0.1173
I[c]	0.92	...	0.2150	0.1330	0.4312	...
A[d]	0.74	0.000083	...	0.0406	...	0.0252
Propoxur	0.64	0.00032	0.0360	0.0928	0.4441	0.0468
B[e]	0.50	0.000032	...	0.0236	...	...
II	0.38	0.00001	...	...	...	...
C[f]	0.22	0.000006	0.0249	...	1.1520	0.0180
III	0.10	0.00001	...	0.0300	...	...
IV	0.08	0.000012	0.0598	...	...	...
Origin	0.00	0.00106	0.1260	0.0746	0.2640	0.0273
Unextractable ^{14}C		0.00255	3.9357	6.1600	21.900	0.1053

[a] 2-isopropoxyphenyl *N*-methylcarbamate, ^{14}C-2-isopropoxy.
[b] Silica Gel GF-254, chloroform:acetonitrile, 4:1 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.
[d] A = 2-isopropoxyphenol.
[e] B = 2-isopropoxyphenyl carbamate.
[f] C = 2-isopropoxyphenyl *N*-hydroxymethyl carbamate.

Table 28.—R_f values and amounts, in parts per million, of aldicarb[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.16	17.0	2.32
Aldicarb[c]	0.54	0.031	16.7	1.31
A[d]	0.42	trace	...	1.01
B[e]	0.28	0.04	...	...
C[f]	0.14	0.056	...	...
Origin	0.00	0.025	0.3	...

[a] 2-methyl-2-methylthiopropionaldoximyl *N*-methylcarbamate, ^{14}C-*tert*-carbon.
[b] Silica Gel GF-254, hexane: benzene: ethanol, 2:2:1 by volume.
[c] $CH_3SC(CH_3)_2CH = NOC(O)NHCH_3$.
[d] A = $CH_3SO_2C(CH_3)_2CH = NOH$.
[e] B = $CH_3SO_2C(CH_3)_2CH = NOC(O)NHCH_3$.
[f] C = $CH_3SOC(CH_3)_2CH = NOC(O)NHCH_3$.

Table 29.—R_f values and amounts, in parts per million, of formetanate[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.11	44.98	2.10	1.61	1.17
I[c]	0.81	...	...	1.53	1.07	...
II	0.75	...	2.25	...	...	...
III	0.62	...	...	0.32	...	...
A[d]	0.35	0.0666	...	...	...	...
IV	0.27	...	2.70	...	...	...
V	0.14	...	4.05	...	...	...
Origin	0.00	0.0118	35.98	0.25	0.54	1.17
Unextractable ^{14}C		0.0316	22.10	9.02	5.59	1.71

[a] 3-dimethylaminomethyleneiminophenyl *N*-methylcarbamate•hydrochloride, ^{14}C-ring labeled.
[b] Silica Gel GF-254, ethyl acetate.
[c] Roman numerals indicate compounds whose chemical structures are unknown.
[d] A = *N*-formyl-3-aminophenol.

Table 30.—R_f values and amounts, in parts per million, of methoprene[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Gambusia* (fish)
Total ^{14}C		0.00556	4.626	4.885	0.070
I[c]	0.83	...	0.0990	0.1924	...
Methoprene[d]	0.76	0.000086	2.220	1.500	0.0176
II	0.66	...	0.963	0.376	0.0305
A[e]	0.60	...	...	1.5490	...
B[f]	0.53	...	0.723	0.469	0.0181
C[g]	0.47	0.000075	...	0.0845	0.0017
Other		0.00024	0.332	0.500	
Origin	0.00	0.000576	0.289	0.45	0.0021
Unextractable ^{14}C		0.00458	...	...	...

[a] Isopropyl-11-methoxy-3,7,11-trimethyldodeca-2,4-dienoate.
[b] Silica Gel GF-254, benzene:ethyl acetate:acetic acid, 100:50:5 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.
[d] Isopropyl-11-methoxy-3,7,11-trimethyldodeca-2,4-dienoate (5-^{14}C).
[e] A = 11-methoxy-3,7,11-trimethyldodeca-2,4-dienoic acid.
[f] B = Isopropyl 11-hydroxy-3,7,11-trimethyldodeca-2,4-dienoate.
[g] C = 11-hydroxy-3,7,11-trimethyldodeca-2,4-dienoic acid.

Table 31.—R_f values and amounts, in parts per million, of dimilin[a] and its degradation products found in the water and organisms of a model ecosystem.

		Difluorobenzoyl[b] Equivalents					Chlorophenyl Urea Equivalents[c]				
	R_f[d]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)	Water	*Oedogonium* (alga)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.02356	1.0311	0.6670	5.2455	1.644	0.06909	0.6548	2.2306	13.3614	6.0701
I[e]	0.90	...	0.4028	...	0.7201	...	...	...	...	...	...
A[f]	0.83	...	...	...	...	...	0.0034	0.0778	...	...	...
II	0.77	0.00025	...	...	...	...	...	...	...	...	...
Dimilin	0.70	0.0057	0.4748	0.4891	4.4225	0.1097	0.0220	0.4019	2.0979	13.1369	0.3193
III	0.60	...	...	...	...	...	trace	...	...	...	...
B[g]	0.52	0.0018	...	...	...	0.1644	...	...	...	...	...
C[h]	0.50	...	...	...	...	...	0.0078	0.0389	...	...	0.3193
D[i]	0.45	0.00031	...	...	...	...	...	...	...	...	...
V	0.43	...	...	...	...	...	0.00055	...	...	...	...
VI	0.38	0.00020	...	...	...	...	...	...	...	...	...
VII	0.36	...	...	...	...	...	0.00061	...	...	...	...
E[j]	0.33	...	...	...	...	...	0.00056	...	...	...	0.0297
VIII	0.26	...	...	...	...	...	0.00022	...	...	...	...
IX	0.20	...	...	...	...	...	0.00015	...	...	...	...
F[k]	0.12	...	...	...	...	...	0.0072	0.0227	...	0.2071	0.1263
Origin	0.00	0.0060	0.1535	0.1779	0.1028	1.3703	0.0078	0.1135	0.1327	0.0174	5.2755
Unextractable ^{14}C		0.0093	4.9559	1.6210	1.9340	0.8227	0.0188	0.5726	0.2713	0.3436	0.8469

[a]1-(2,6-difluorobenzoyl)-3-(4-chlorophenyl) urea.
[b]^{14}C-label in 2,6-benzoyl moiety.
[c]^{14}C-label in 4-chloroaniline moiety.
[d]Silica Gel GF-254 benzene:dioxane:acetic acid, 90:30:1 by volume.
[e]Roman numerals indicate compounds whose chemical structures are unknown.
[f]A=*N*,*N*-methyl-4-chloroaniline.
[g]B=2,6-difluorobenzoic acid.
[h]C=4-chloroaniline.
[i]D=2,6-difluorobenzamide.
[j]E=4-chloroacetanilide.
[k]F=4-chlorophenyl urea.

Table 32.—R_f values and amounts, in parts per million, of chlordimeform[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C	1 2	0.0427	0.9253	1.7682	0.3626	0.5259
Chlordimeform	0.00, 0.65	...	...	0.0710	...	...
A[c]	0.33, 0.09	0.00075	...	...	...	...
B[d]	0.43, 0.00	0.00179	...	...	...	...
C[e]	0.53, 0.35	0.00016	...	...	...	...
D[f]	0.10, 0.00	0.00085	0.109	...	...	...
E[g]	0.77, 0.71	0.00041	0.0933	0.255	...	0.0553
I[h]	0.83, 0.00	0.00052	0.181[i]	...	...	...
II	0.83, 0.66	0.00031	...	...	...	...
III	0.73, 0.70	0.00026	...	...	...	...
IV	0.57, 0.90	...	...	...	...	0.0246
V	0.53, 0.03	0.00070	...	...	...	...
VI	0.52, 0.27	0.000077	...	...	...	...
VII	0.50, 0.23	0.00017	...	...	...	...
VIII	0.33, 0.23	0.00025	...	...	...	...
IX	0.23, 0.00	0.00077	...	...	...	...
Origin	0.00, 0.00	0.0125	0.542	1.442	...	0.446
Unextractable ^{14}C		0.0233	...	...	...	...

[a] *N'*-(4-chloro-*o*-tolyl)-*N*,*N*-dimethylforamidine, ^{14}C-tolyl.
[b] Silica Gel GF-254 two dimensional tlc: 1. benzene:dioxane:acetic acid, 90:30:1 by volume. 2. benzene:diethylamine, 95:5 by volume.
[c] A = 2-methyl-4-chloroformanilide.
[d] B = 5-chloroanthranilic acid.
[e] C = 2-methyl-4-chloroaniline.
[f] D = 2-carboxy-4-chloroformanilide.
[g] E = 2,2'-dimethyl-4,4'-dichloroazobenzene.
[h] Roman numerals indicate compounds whose chemical structures are unknown.
[i] Alga contained traces of unknowns totaling 0.181 ppm.

Table 33.—R_f values and amounts, in parts per million, of DDT[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Physa* (snail)	*Culex*[c] (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.004	22.9	8.9	54.2
DDE	0.53	0.00026	12.0	5.2	29.2
DDT	0.34	0.00022	7.6	1.8	18.6
DDD	0.17	0.00012	1.6	0.4	5.3
Origin	0.00	0.0032	0.98	1.5	0.85

[a] 2,2-bis-(*p*-chlorophenyl)-1,1,1-trichloroethane, ^{14}C-ring UL.
[b] Silica Gel GF-254, petroleum ether solvent, b.p. 60–80°C.
[c] Dry weight.

Table 34.—R_f values and amounts, in parts per million, of DDE[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Physa* (snail)	*Culex*[c] (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.008	121.6	168.9	149.8
DDE	0.53	0.0053	103.5	159.5	145.0
Origin	0.0	0.0027	18.1	9.4	4.8

[a] 2,2-bis-(*p*-chlorophenyl)-1,1-dichloroethylene, ^{14}C-ring UL.
[b] Silica Gel GF-254, petroleum ether solvent, b.p. 60–80°C.

Table 35.—R_f values and amounts, in parts per million, of DDD[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.006	5.65	5.85	39.12
A[c]	0.53	...	0.24	...	2.08
I[d]	0.47	...	0.14	...	1.54
DDD	0.17	0.0004	3.3	3.43	33.4
II	0.05	...	0.87	...	...
Origin	0.00	0.0056	1.1	...	2.0

[a] 2,2-bis-(*p*-chlorophenyl)-1,1-dichloroethane, ^{14}C-ring UL.
[b] Silica Gel GF-254, hexane (Skellysolve B).
[c] A = $ClC_6H_4C = CCl_2C_6H_4Cl$.
[d] Roman numerals indicate compounds whose chemical structures are unknown.

Table 36.—R_f values and amounts, in parts per million, of methoxychlor[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Physa* (snail)	*Culex*[c] (mosquito)	*Gambusia* (fish)
Total ^{3}H		0.0016	15.7	0.48	0.33
A[d]	0.32	...	0.7	...	...
Methoxychlor	0.25	0.00011	13.2	...	0.17
B[e]	0.07	0.00013	1.0	...	trace
C[f]	0.00	0.00003	trace	...	trace
D[g]	0.00	0.00003	...	...	...
Unknowns	trace	0.00009	trace	...	trace
Origiu	0.00	0.00125	0.8	...	0.16

[a] 2,2-bis-(*p*-methoxyphenyl)-1,1,1-trichloroethane, ^{3}H-ring labeled.
[b] Silica Gel GF-254, petroleum ether solvent, b.p. 60–80°C.
[c] Dry weight.
[d] A = $CH_3OC_6HC = CCl_2C_6H_3OCH_3$.
[e] B = $CH_3OC_6H_4HCCl_2C_6H_3OH$.
[f] C = $HOC_6H_4HCCl_2C_6H_3OH$.
[g] D = $HOC_6H_4C = CCl_2C_6H_3OH$.

Table 37.—R_f values and amounts, in parts per million, of aldrin[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.0117	19.70	57.20	1.13	29.21
Aldrin	0.81	0.00005	1.95	2.23	...	0.157
Dieldrin	0.71	0.0047	16.88	52.40	1.10	28.00
I[c]	0.63	...	0.57	2.05	...	0.612
A[d]	0.45	0.00052	0.12	0.17	...	0.322
B[e]	0.34	0.0004	0.079	0.217	...	0.088
C[f]	0.08	0.00039	0.015	...	...	...
Origin	0.00	0.0040	0.015	0.097	...	0.004
Unextractable ^{14}C		0.00155	...	...	...	...

[a] 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-*endo, exo*-5,8-dimethanonaphthalene, ^{14}C-ring.
[b] Silica Gel GF-254, *n*-hexane:diethyl ether, 1:1 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.
[d] A = 9-hydroxy dieldrin.
[e] B = 9-keto dieldrin.

Table 38.—R_f values and amounts, in parts per million, of dieldrin[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Corbicula* (clam)	*Uca* (crab)	*Daphnia* (water flea)	*Elodea* (aquatic plant)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.0074	15.16	2.03	0.536	5.14	2.82	232.3	1.35	12.57
I[c]	0.65	...	...	...	...	...	0.23	0.866	...	...
Dieldrin	0.58	0.0020	14.96	2.03	0.495	5.07	2.56	229.87	...	12.29
II	0.43	...	...	...	...	...	...	0.456	...	...
A[d]	0.38	0.20	...	...	...	...	...	1.11	...	0.19
B[e]	0.31	...	...	...	0.043	...	...	...	...	0.07
III	0.18	0.00034	...	...	...	...	...	...	...	...
IV	0.12	0.00025	...	...	...	...	...	...	...	...
V	0.07	0.00035	...	...	...	...	...	...	...	...
VI	0.04	0.00101	...	...	...	...	...	...	...	...
Origin	0.00	0.00157	...	...	...	...	...	...	...	...
Unextractable ^{14}C		...	1.23	0.028	0.177	0.10	0.14	1.78	0.25	0.65

[a] 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*exo*, *endo*-5,8-dimethanonaphthalene, ^{14}C-ring.
[b] Silica Gel GF-254, ether-*n*-hexane, 3:2 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.
[d] A = 9-hydroxy dieldrin.
[e] B = 9-keto dieldrin.

Table 39.—R_f values and amounts, in parts per million, of toxaphene[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.04441	13.2941	17.6198	2.2570	10.3977
Toxaphene	0.70	0.00159	10.9743	15.2637	1.4147	6.7523
I[c]	0.57	0.00106	1.7535	1.8360	0.2359	2.4923
II	0.51	0.00076	...	0.2961	...	0.5022
III	0.45	0.00099	0.3589	0.0863	...	0.3161
IV	0.34	0.00164	0.1130	0.0585	trace	0.1487
V (strip)		0.00429	...	...	0.4042	...
VI	0.03	0.00078	...	...	...	0.0187
Origin	0.00	0.02002	0.0944	0.0211	0.2022	0.1674
Unextractable ^{14}C		0.01328	2.2156	1.1153	1.1245	4.2264

[a] $C_{10}H_{10}Cl_8$ (67–69% chlorinated camphene), 8-^{14}C.
[b] Silica Gel GF-254, Skellysolve B (b.p. 68°C) : diethyl ether :acetone, 80:20:10 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.

Table 40.—R_f values and amounts, in parts per million, of endrin[a] and its degradation products found in the water and organisms of a model ecosystem[b].

	R_f[c]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Culex*[d] (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.0135	13.62	150.58	...	4.48
I[e]	0.81	...	0.48	5.07	...	...
Endrin	0.73	0.00254	11.56	125.00	...	3.40
II	0.53	0.00385	1.58	6.55	...	1.04
III	0.42	trace	trace	5.87	...	...
IV	0.31	trace	trace	2.69	...	...
Origin	0.00	0.00436	...	1.85	...	0.04
Unextractable ^{14}C		0.0027	...	...	...	...

[a] 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo*, *endo*-5,8-dimethanonaphthalene, ^{14}C-ring.
[b] Experiment terminated after 63 days.
[c] Silica Gel GF-254, *n*-hexane :diethyl ether, 1:1 by volume.
[d] Mosquito larvae killed throughout experiment.
[e] Roman numerals indicate compounds whose chemical structures are unknown.

Table 41.—R_f values and amounts, in parts per million, of lindane[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.0232	0.375	3.70	0.75	1.02
A[c]	0.55	...	...	2.50	...	...
Lindane	0.47	0.00167	...	0.762	...	0.935
I[d]	0.27	0.000084	...	...	...	...
II	0.19	0.00304	...	...	...	...
III	0.14	0.00276	...	...	...	...
IV	0.09	0.00636	...	0.248	...	...
Origin	0.00	0.00877	0.375	0.185	...	0.085

[a] *gamma*-1,2,3,4,5,6-hexachlorocyclohexane, ^{14}C-ring.
[b] Silica Gel GF-254, *n*-hexane-acetone, 9:1 by volume.
[c] A = *gamma*-pentachlorocyclohexene.
[d] Roman numerals indicate compounds whose chemical structures are unknown.

Table 42.—R_f values and amounts, in parts per million, of mirex[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.018	9.70	18.40	13.60	3.50
Mirex	0.95	0.0157	9.49	18.29	13.54	3.45
Origin	0.00	0.0023	0.21	0.11	0.06	0.05

[a] Dodecachloro-octahydro-1,3,4-metheno-2-H-cyclabuta-[c,d]-pentalene, ^{14}C-ring.
[b] Silica Gel GF-254, chloroform.

Table 43.—R_f values and amounts, in parts per million, of heptachlor[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.02225	0.8448	2.7515	3.1258	2.0603
Heptachlor	0.64	0.00003	0.6219	1.1146	0.9421	0.1146
Heptachlor epoxide	0.56	0.00021	0.1877	1.0659	1.5332	1.6293
I[c]	0.43	0.00002	...	0.0217	0.0434	...
II	0.37	0.00001	...	0.1142	0.0328	...
III	0.32	0.00005	...	0.0490	0.0244	...
1-hydroxychlordene	0.21	0.00040	...	0.0597	0.0791	0.0471
1-hydroxychlordene epoxide	0.14	0.00659	...	0.2066	0.2694	0.1211
IV	0.07	0.00036	...	0.0272	0.0763	0.1010
V	0.03	0.00026	...	0.0055	0.0244	...
Origin	0.00	0.00677	0.0352	0.0871	0.1007	0.0472
Unextractable ^{14}C		0.00755	0.4079	0.1646	0.2363	1.5479

[a] 1-*exo*-4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene, ^{14}C-ring.
[b] Silica Gel GF-254, cyclohexane:diethyl ether, 80:20 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.

Table 44.—R_f values and amounts, in parts per million, of heptachlor epoxide[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Culex*[c] (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.00638	2.2620	101.9105	...	8.8807
Heptachlor epoxide	0.63	0.00125	2.0618	83.0774	...	6.1100
A[d]	0.18	0.00036	0.0800	8.8663	...	1.7114
Origin	0.0	0.00200	0.1202	9.9668	...	1.0595
Unextractable ^{14}C		0.00277	1.1602	0.1110	...	0.8554

[a] 1-*exo*-4,5,6,7,8,8-heptachloro-*exo*-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindane, ^{14}C-ring.
[b] Silica Gel GF-254, cyclohexane, diethylether, 80:20 by volume.
[c] All killed during the experiment.
[d] A = 1-hydroxychlordene epoxide.

Table 45.—R_f values and amounts, in parts per million, of chlordane[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.017718	110.3415	154.189	13.645	11.243
I[c]	0.92	...	0.974	2.199	...	0.451
II	0.90	...	0.664	...	...	...
III	0.84	0.000059	1.905	5.751	3.602	1.405
IV	0.78	...	1.708	...	5.502	...
V	0.73	...	...	...	...	0.658
Chlordane+	0.70	0.00106	104.289	140.570	6.500	8.754
VI	0.64	...	...	1.541	...	...
VII	0.55	0.0000135	...	0.244	...	...
VIII	0.47	0.0000027	...	...	...	...
IX	0.28	0.00127	0.474	2.088	0.509	0.217
X	0.23	0.000176	...	...	...	...
XI	0.19	0.0000939	...	...	...	0.0260
XII	0.17	0.000264	...	...	...	...
XIII	0.15	0.000415	0.358	0.478	0.339	0.0223
XIV	0.12	0.000438	0.180	0.398	...	...
XV	0.10	...	...	0.884	...	0.0744
XVI	0.06	0.000689	...	...	...	...
XVII	0.04	0.000501	...	...	...	...
XVIII	0.03	0.009305	...	...	...	...
XIX	0.02	...	0.325	...	...	...
XX	0.01	...	0.238	...	...	...
Origin	0.00	0.0123	0.324	1.516	2.169	0.205
Unextractable ^{14}C		0.00752	100.0847	1.752	6.920	2.450
cis: trans		4.02	3.08	5.39	...	6.98

[a] 1,2,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane (cis:trans, 3:1), ^{14}C-ring.
[b] Silica Gel GF-254, n-hexane:ethyl acetate, 9:1 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.

Table 46.—R_f values and amounts, in parts per million, of captan[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Daphnia* (water flea)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.001789	0.865	0.393	0.301	0.0462	0.0522
I[c]	0.93	...	0.0278	...	0.0592	...	...
II	0.85	...	0.0077	...	0.0795	...	...
III	0.81	...	...	...	0.0679	...	0.0492
IV	0.79	...	0.0166	...	...	...	...
V	0.68	...	...	...	...	...	...
VI	0.39	...	0.0105	...	...	...	...
VII	0.35	0.00000426	...	...	...	...	...
VIII	0.33	...	0.0142	...	...	...	...
IX	0.26	0.0000096	...	...	...	...	...
X	0.25	0.00000893	0.0608	...	...	...	...
XI	0.18	0.00000456	...	...	...	...	...
XII	0.14	0.0000109	...	...	...	...	...
XIII	0.10	0.00000365	0.590	...	...	...	...
XIV	0.053	0.0000891	0.0159	...	...	...	0.00215
Origin	0.00	0.0000353	0.122	...	0.0940	...	0.000861
Unextractable ^{14}C		0.001623	0.967	0.338	0.0998	0.0584	0.0158

[a] *N*-trichloromethylthio-4-cyclohexene-1,2-dicarboximide, ^{14}C-trichloromethyl.
[b] Silica Gel GF-254, petroleum ether-acetone, 4:1 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.

Table 47.—R_f values and amounts, in parts per million, of hexachlorobenzene[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Daphnia* (water flea)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.00695	1.827	0.696	4.098	0.737	3.155
Hexachlorobenzene	0.80	0.00298	1.556	0.598	3.72	0.429	0.857
A[c]	0.50	0.00034	...	...	...	...	...
I[d]	0.10	0.00023	...	...	...	...	0.446
II	0.05	...	...	...	...	0.0385	0.857
Origin	0.00	0.000143	0.271	0.098	0.378	0.269	0.995
Unextractable ^{14}C		0.00197	...	...	...	...	...

[a] 1,2,3,4,5,6-hexachlorobenzene, ^{14}C-ring UL.
[b] Silica Gel GF-254, benzene:acetone, 1:1 by volume.
[c] A = Pentachlorophenol.
[d] Roman numerals indicate compounds whose chemical structures are unknown.

Table 48.—R_f values and amounts, in parts per million, of pentachlorophenol[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	Sand	*Oedogonium* (alga)	*Daphnia* (water flea)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.05235	0.0186	0.8061	6.2441	2.9576	1.3355	4.3765
I[c]	0.86	0.00028	0.0005	0.0673	...	0.0438	...	0.0197
Pentachlorophenol	0.64	0.01693	0.0048	0.0893	3.4692	0.3619	0.4451	2.2408
II	0.56	0.00109	0.0010	0.0771	...	...	...	...
III	0.49	...	...	0.0575	...	...	...	...
IV	0.42	...	...	0.0477	...	0.8122	...	...
V	0.33	0.00009	0.0023	0.0440	...	...	...	...
VI	0.22	0.00010	0.0011	0.1700	...	0.3129	...	...
VII	0.15	0.00008	0.0013	...	...	0.2798	...	...
VIII	0.10	...	0.0020	...	...	...	...	...
IX	0.05	0.00012	...	0.0808	...	...	...	...
Origin	0.00	0.02220	0.0056	0.1724	2.7749	1.1470	0.8904	2.1160
Unextractable ^{14}C		0.01146	...	...	...	...	...	...

[a] 2,3,4,5,6-pentachlorophenol, ^{14}C-ring UL.
[b] Silica Gel GF-254, *n*-hexane:acetone:acetic acid, 80:20:2 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.

Table 49.—R_f values and amounts, in parts per million, of banamite[a] and its degradation products found in the water and organisms of a model ecosystem.

	R_f[b]	Water	*Oedogonium* (alga)	*Corbicula* (clam)	*Uca* (crab)	*Daphnia* (water flea)	*Elodea* (aquatic plant)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C		0.0271	3.194	2.341	1.365	0.941	1.872	17.553	4.153	2.322
Banamite	0.75	0.0000186	...	...	0.0156	...	0.0410	...	0.0736	...
I[c]	0.61	0.0000930	...	...	...	...	0.0928	0.565	0.266	...
II	0.53	0.000539	0.963	2.044	0.0670	0.686	1.048	10.685	0.453	1.624
III	0.35	0.00115	0.181	...	0.0568	...	0.0662	1.160	0.265	0.378
A[d]	0.27	0.000294	0.142	...	0.0364	...	0.0515	0.306	0.300	...
IV	0.21	0.000294	0.202	...	...	...	...	...	...	...
V	0.14	0.000850	0.269	0.227	0.0406	...	0.185	2.5493	0.324	0.0943
VI	0.07	0.00248	...	...	...	...	...	0.938	0.286	0.0452
VII	0.03	0.00428	0.514	...	0.140	...	0.059	0.478	0.533	...
Origin	0.00	0.0111	0.923	0.0703	1.009	0.255	0.328	0.872	1.652	0.180
Unextractable ^{14}C		0.00599	6.602	0.136	1.088	0.877	1.445	1.777	2.137	0.451

[a] Benzoylchloride-2,4,6-trichlorophenylhydrazone, ^{14}C benzoyl ring.
[b] Silica Gel GF-254, n-hexane-ethyl acetate, 80 :20 by volume.
[c] Roman numerals indicate compounds whose chemical structures are unknown.
[d] A = Benzoic acid-2,4,6-trichlorophenyl hydrazide.

LITERATURE CITED

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