to fish, wildfowl, livestock, or man.

Fonofos was found in only one tailwater pit in 1973 (Table III) and seven in 1974 (Tables IV and V) but is occurred in concentrations of up to 771 ppb in pit bottom soil. It was found only in very low concentrations in the water. Fonofos residues were more persistent throughout the year than were any of the other insecticides. Residues of this chemical should cause no damage to crops irrigated with tailwater. However, fonofos is toxic to fish (Stauffer Chemical Co., 1972), and where turbulence disturbs the bottom soil it could contaminate or kill fish in stocked pits.

Fonofos is highly toxic to mammals (Stauffer Chemical Co., 1972; Wiswesser, 1976). Tailwater pits in this study contained up to one-tenth the mammalian LD_{50} of fonofos in bottom soil and one-thousandth the mammalian LD_{50} in water.

Our findings suggest a public benefit from the farmer's use of tailwater pits. Such collection and reuse of water make a virtually closed system from which, except for leaching and evaporation, no water or associated pesticide residues escape. This minimizes potential hazard to the general public.

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Distribution of Oxadiazon and Phosalone in an Aquatic Model Ecosystem

Dominique Ambrosi,[1] Allan R. Isensee,* and John A. Macchia[2]

Four species of aquatic organisms were exposed to the herbicide oxadiazon [2-*tert*-butyl-4-(2,4-dichloro-5-isopropoxyphenyl)-Δ^2-1,3,4-oxadiazolin-5-one] and the organophosphate insecticide phosalone, [*O,O*-diethyl *S*-(6-chloro-2-oxobenzoxazolin-3-yl)methyl] phosphorodithioate, in a model ecosystem for 48 and 31 days, respectively. Oxadiazon was introduced into the ecosystem adsorbed to 400 g of soil at the rate of 1 and 10 ppm, where as soil treated with 10 ppm phosalone was aged for 84 days before introduction. The organisms accumulated oxadiazon and phosalone 30 to 300 times greater than the water content, which indicates a low bioaccumulation potential. Seven degradation products of oxadiazon were found, with snails degrading oxadiazon more extensively than did algae or fish. Phosalone was toxic to daphnids and fish in the 20 to 30 ppb range, and only two degradation products were obtained.

The extensive worldwide use of pesticides has dictated that their effect on the environment be thoroughly investigated. Possible contamination of the aquatic environment, through direct application or erosion of pesticide-treated soil into lentic or lotic waters, is a primary concern. Such contamination could adversely affect aquatic organisms and/or result in biological accumulation eventually affecting higher tropic organisms. Thus, all pesticides that enter water must be evaluated to determine their potential behavior in and effect on the aquatic environment.

Oxadiazon [2-*tert*-butyl-4-(2,4-dichloro-5-isopropoxyphenyl)-Δ^2-1,3,4-oxadiazolin-5-one] is a promising herbicide useful for weed control in annual crops, such as rice and soybeans, and perennial orchard and vineyard crops. Phosalone, [*O,O*-diethyl *S*-(6-chloro-2-oxobenzoxazolin-3-yl) methyl] phosphorodithioate, is a nonsystemic organophosphate insecticide and miticide used to control several major pests in potatoes, cotton, and orchards. Since

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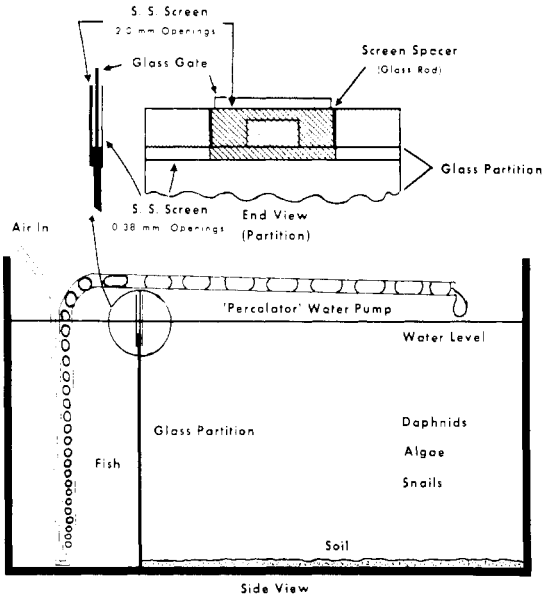

Figure 1. Recirculating static model ecosystem. Tank dimensions: 41 × 20 × 24 cm; glass partition 18 cm high. Tank volume: 16 L with a 1 cm water depth over glass partition.

their behavior and fate in the aquatic environment are not known, we examined the fate of these pesticides in an aquatic model ecosystem.

MATERIALS AND METHODS

Model Ecosystem. The overall procedures and design of a recirculating static model ecosystem as described by Isensee et al. (1976) were slightly modified for this study (Figure 1). Compartment design allowed simultaneous exposure of different trophic level organisms representative of two food chains. The screen-gate (full-tank width) allowed water passage, yet prevented daphnids (*Daphnia magna*) from being consumed by mosquito fish (*Gambusia affinis*). The gate provided the option (not employed in this experiment) of feeding some or all of the daphnids to the fish. The percolator water pump insured uniform mixing of water between the two compartments.

Oxadiazon Experiments. We treated 400 g of Matapeake silt loam soil (pH 5.3; 1.5% O.M.; sand, silt, and clay contents of 38.4, 49.4, and 12.2%, respectively) with [^{14}C]phenyl-labeled oxadiazon (25.8 μCi/mg) at the rate of 1 and 10 ppm, placed them in the large compartments of replicate tanks, and flooded the tanks with 16 L of water. One tank received 400 g of untreated soil and served as the control. One day after flooding, four snails (*Helisoma* sp.), about 50 daphnids, and 1 g of algae (*Oedogonium cardiacum*) were added to the large compartment, and six mosquito fish were added to the small compartment. Mosquito fish were fed daily a commercial No. 2 trout chow.

Phosalone Experiment. We placed 400 g of Matapeake soil, containing "aged" phosalone, in the large compartment of replicate tanks. The Matapeake soil had originally been treated with ^{14}C-ring labeled phosalone (17.1 μCi/mg) at the rate of 10 ppm, its moisture level was adjusted to 75% field capacity, and it was stored for 84 days as described by Ambrosi et al. (1977). After 84 days, 91.8% of the original ^{14}C remained: 16.9% was extractable, 74.9% was bound, and 8.6% had been lost as $^{14}CO_2$. Approximately 8% of the extractable ^{14}C was phosalone; the amount of phosalone in the bound fraction was unknown. One control tank was prepared, as described above, and the soil flooded. Organisms were added as described for oxidiazon.

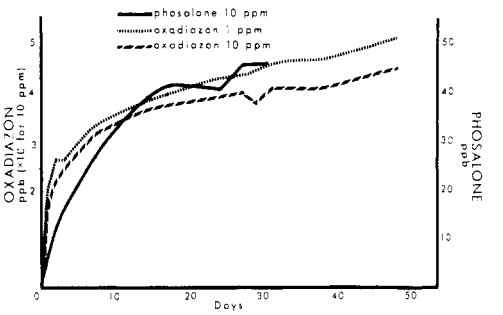

Figure 2. Concentration of oxadiazon and phosalone (based on ^{14}C measurement) in water as a function of the time after 400 g of soil treated with these pesticides was flooded in the ecosystem tanks. Phosalone treated soil had been "aged" aerobically for 3 months before flooding.

Sampling and Analysis. Water samples (duplicate 1 mL) were taken at 2-day intervals and analyzed by standard liquid scintillation methods for total ^{14}C; 50-mL samples were taken weekly and extracted with methylene chloride and subjected to qualative and quantitative analysis. After 48 days (oxadiazon) and 31 days (phosalone), the ecosystems were terminated and the daphnids, snails, and fish were harvested and analyzed as described by Isensee and Jones (1975). Algae were Soxhlet extracted for 20 h, using a hexane–acetone–methanol (8:1:1, v/v/v) solvent mixture. Extracts were analyzed by scintillation and TLC methods. Algae, fish, snail, and water extracts were spotted on silica gel TLC plates (20 × 20 cm GF-254, E. Merck, Darmstadt) and developed in hexane–acetone (6:4, v/v) for oxadiazon and ethyl acetate–chloroform–triethylamine (50:50:2.5, v/v/v) for phosalone. Each plate was autoradiographed for 2 weeks with Kodak No-Screen medical x-ray film, NS-54T.

RESULTS AND DISCUSSION

Snails were the only organisms unaffected by both oxadiazon and phosalone. Numerous egg clusters and small snails were found on the walls of both treatment and control tank by the end of the experimental period. Algae growth was severely reduced by oxadiazon but was not affected by phosalone. Daphnids and fish were unaffected by oxadiazon (daphnid population increased severalfold), but both were killed by phosalone. Details of the phosalone toxicity are given below.

Oxadiazon. The concentration of radioactivity in water, expressed as parent compound, is shown in Figure 2. The desorption rate from soil was rapid for the first 7 days, then decreased with time, but never reached equilibrium. Final water concentration (5.3 and 44.4 ppb for 1 and 10 ppm treatments, respectively) represented about 20% of the total amount of oxadiazon originally introduced into the tank with the soil. Both concentrations were far below the theoretical water solubility of oxadiazon (0.7 ppm). The shape of the curve suggested that oxadiazon is strongly adsorbed to soil and released slowly.

The accumulation of oxadiazon by the various organisms is shown in Table I. Our results are based on ^{14}C analysis, expressed as parent compound or degradation product. Total ^{14}C and oxadiazon contents of water and tissue increased about tenfold between the 1 and 10 ppm treatment rates. This suggested that the amount of oxadiazon accumulated by aquatic organisms was controlled almost entirely by the amount of oxadiazon available in water. Bioaccumulation ratios (BR = concentration in tissue/concentration in water) were, therefore, nearly the same between the two rates. The magnitude of accumulation was low and nearly the same for algae, snails, and

Table I. Concentrations of Oxadiazon and Its Degradation Products (in parts per billion) Found in Water and Organisms in a Model Ecosystem after 48 Days

		Concentration of compounds, ppb,[a] found in									
		Water		Algae		Snails		Daphnids		Fish	
Products	R_f[b]	1[c]	10[c]	1	10	1	10	1	10	1	10
Total ^{14}C		5.1	43.9	201	2487	256	2125	290	2440	1010	10 884
I[d]	0.72					16 ± 3	111 ± 16				
Oxadiazon	0.65	2.7	26.6	116 ± 20	1735 ± 271	67 ± 5	911 ± 51			487 ± 46	5647 ± 894
II	0.61		5.2								
A[e]	0.56										185 ± 130
III	0.49						47 ± 18				
B[f]	0.45	1.4	6.7		228 ± 9	106 ± 11	628 ± 107			266 ± 12	2500 ± 116
IV	0.31	0.4	2.8			11 ± 1	123 ± 26				
V	0.17					15 ± 2	126 ± 24			105 ± 10	749 ± 37
Polar	0	0.6	2.6	85 ± 2	524 ± 11	41 ± 3	179 ± 43			152 ± 14	1803 ± 205

[a] Means and standard error of means. [b] Silica gel GF-254, hexane-acetone (6:4 v/v). [c] Initial concentration (ppm) of oxadiazon in 400 g of soil placed in bottom of tank. [d] Unknowns I, II, III, IV, V. [e] 2-*tert*-Butyl-4-(2,4-dichloro-5-methoxyphenyl)-Δ^2-1,3,4-oxadiazolin-5-one. [f] 2-*tert*-Butyl-4-(2,4-dichloro-5-hydroxyphenyl)-Δ^2-1,3,4-oxadiazolin-5-one.

Table II. Concentrations of Phosalone and Its Degradation Products (in parts per billion) Found in Water and Organisms in a Model Ecosystem after 31 Days

		Concentration of compounds, ppb, found in				
					Fish[b]	
	R_f[a]	Water	Algae	Snails	15 Days	31 Days
Total ^{14}C		43.8 ± 0.6[c]	7450 ± 650	3738 ± 922	15467 ± 2726	14353 ± 1436
I[d]	0.74			600 ± 180		
Phosalone	0.68	26.1 ± 0.4	4420 ± 590	1250 ± 240	7615 ± 1590	6220 ± 351
II[d]	0.35			692 ± 203	425 ± 157	364 ± 222
Polar	0.0	17.4 ± 1.3	3030 ± 210	1196 ± 325	7426 ± 979	7768 ± 930

[a] Silica gel GF-254, ethyl acetate-chloroform-triethylamine (50:50:2.5, v/v/v). [b] 15 day fish dead, 31 day fish living, exposed for 11 days. [c] Mean and standard error of the mean. [d] Unknowns I and II.

daphnids, but about five times higher for fish. These ratios suggested that the bioaccumulation potential of oxadiazon is low, even for fish. They were similar to, or lower than, ratios obtained for several herbicides (23 to 339 for six dinitroaniline herbicides; Kearney et al., 1977) and far lower than those normally encountered for chlorinated hydrocarbon insecticides or related compounds, i.e., daphnids accumulated 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT), 1,2,3,4,10,10-hexachloro-1,4,4*a*,5,8,8a-hexahydro-1,4-*endo*,*exo*-5,8-dimethanonaphthalene (aldrin), and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) at 11.4 × 10^4, 14.1 × 10^4, and 2.6 × 10^4 times water concentration, respectively (Johnson et al., 1971; Isensee and Jones, 1975).

Of the total amount of ^{14}C recovered after 48 days, oxadiazon accounted for 35, 50, 57, and 63% for snails, fish, water, and algae, respectively. Formation of the phenol (compound B) and polar materials constituted the next highest concentration of ^{14}C, indicating that considerable metabolism was occurring (Table I). Snails were far more effective than fish or algae in degrading oxadiazon. Thus, results indicated that oxadiazon degradation in the aquatic environment is extensive.

Phosalone. Water phosalone content, based on ^{14}C analysis, increased rapidly with time for the first 17 days, then at a much slower rate until day 31 (Figure 2). The final water content of 43.8 ppb represented about 19% of the total ^{14}C initially placed in the tanks adsorbed to soil.

Phosalone was toxic to daphnids and fish. All daphnids died within 10 days and freshly supplied ones died within 17 days, where as the daphnid population in the control tank increased with time. The reaction of fish to phosalone was more complex. Fish began dying by day 6, and all were dead by day 15. Four more were added on day 17, and all were dead by day 20. Four additional fish were added on day 21 and all lived until day 31. Some mortality was also noted in the control (two were dead by day 31). Phosalone concentrations, as indicated by TLC analysis of water extracts on days 10, 21, and 31, may account for daphnid and fish mortalities. Phosalone concentrations were 31.3, 31.4, and 26.1 ppb on days 10, 21, and 31, respectively. These concentrations represented 89.3, 78.4, and 60.0%, respectively, of the total ^{14}C analyzed on these days. The lower phosalone concentration after 21 days may have accounted for the lack of mortality after 21 days. The toxic response of daphnids and fish to a 20 ppb concentration of phosalone may have been reasonable. Nikulina and Sokol'skaya (1975) reported a 10-day LC_{50} value of 58 μg/L to 10-day-old carp larvae (*Cyprinus carpio*).

The distribution of phosalone among the various components of the ecosystem is shown in Table II. Of the total ^{14}C recovered, in water and organisms, phosalone accounted for 33, 49, 43, 59, and 60% for snails, fish (15 days), fish (31 days), algae, and water, respectively. The formation of more metabolites in snails and the accompanying lower phosalone content (than algae or fish) indicated that snails were the most effective organisms in degrading phosalone. Similar phosalone and metabolite concentrations were found in fish, killed after 15 days exposure, and fish still living after 10 days exposure at the end of the experiment. These results further indicated that changing water content of phosalone may not sufficiently explain observed fish mortalities. The BR ratios were 48, 170, and 240 for snails, algae, and fish, respectively. These ratios are not particularly high, but may not accurately represent bioaccumulation potential, since water concentration was obviously toxic to daphnids and fish. Therefore, additional studies should be conducted at lower phosalone concentrations.

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Photolysis of Isopropyl 3-Chlorocarbanilate in Water

Frederick F. Guzik

Photolysis of isopropyl 3-chlorocarbanilate (CIPC) in distilled water at 25 °C using simulated noonday sunlight afforded isopropyl 3-hydroxycarbanilate (3-HOIPC) as the only major photolysis product. Half-life for the disappearance of CIPC under these conditions was 130 h. A second major photolysis product, 2-isopropoxycarbonylamino-1,4-benzoquinone, was obtained when the photolysis was performed in 2% aqueous acetone.

Isopropyl 3-chlorocarbanilate (CIPC) is a widely used herbicide for the control of annual grasses and broadleaved weeds in alfalfa, soybeans, clover, and garden vegetable crops. As part of a program to determine the fate of CIPC in the environment, a study of its photolysis in water was undertaken.

EXPERIMENTAL SECTION

Materials. CIPC was PPG Industries' technical material recrystallized from heptane, mp 38–40 °C. ^{14}C ring-labeled CIPC was obtained from New England Nuclear, 4.3 mC/mmol. Water was distilled from potassium permanganate. Isopropyl 3-hydroxycarbanilate was prepared from 3-aminophenol and isopropyl chloroformate (Schering, 1966), mp 80–82 °C. All solvents were analytical or reagent grade.

Apparatus. The photochemical cell had a capacity of 1050 mL. It was equipped with a standard water-cooled photochemical quartz immersion well and magnetic stirring bar. Light source was a Hanovia 654A high-pressure mercury vapor lamp filtered with a Hanovia 7740 Pyrex sleeve. The assembled unit was contained in a constant temperature water bath. The reactor was open to the atmosphere during photolysis.

Analysis. High-pressure liquid chromatography (HPLC) was performed with a du Pont Model 830 liquid chromatograph using a Zorbax ODS column (mobile phase, 60% methanol in water; column temperature, 55 °C; pressure, 1500 psig; flow rate, 0.2 mL/min). Liquid scintillation counting (LSC) utilized a Packard Model 3003 Tri-carb liquid scintillation spectrophotometer. Thin-layer chromatography (TLC) was carried out using 20 × 20 cm silica gel 60 F-254 plates of 0.25 mm thickness with fluorescent indicator (EM Laboratories). The plates were developed two-dimensionally using 60:40 hexane–acetone and 90:9:1 chloroform–acetone–acetic acid (v/v). Autoradiographs were obtained by exposing the TLC plates to Kodak SB54 single-coated, blue-sensitive, medical x-ray film. NMR spectra were run on Varian DA60IL or Varian CFT20 spectrometers. Infrared spectra were determined on Perkin-Elmer 521 or Perkin-Elmer Infracord spectrophotometers. Mass spectra were recorded on a Finnigan 1015D spectrometer.

Procedure. Two microcuries of ^{14}C ring-labeled CIPC dissolved in 40 μL of benzene was purified by TLC. The TLC scrapings containing purified [^{14}C]CIPC were placed in 1100 mL of water together with sufficient nonradioactive CIPC to obtain a 4 ppm solution. The solution was stirred for 64 h and filtered. The bulk of solution (1050 mL) was placed into the photochemical reactor, and the remaining 50 mL was set aside as a dark control. The photolysis solution was photoirradiated at 25 °C for 104 h. During this period, samples were periodically withdrawn and analyzed by HPLC, LSC, and extraction with methylene chloride (CH_2Cl_2), followed by TLC/autoradiography (AR) of the CH_2Cl_2 extracts. Half-life for the disappearance of CIPC was calculated from LSC data of appropriate HPLC fractions.

A solution containing 124 ppm CIPC was prepared by saturating 1 L of 2% aqueous acetone with nonradioactive CIPC for the photolysis of CIPC in aqueous acetone. This solution was filtered and then photoirradiated for 7 h. Samples of the solution were periodically withdrawn during the photolysis, extracted with CH_2Cl_2, and analyzed by TLC. After 3 h ca. 50% of the CIPC had disappeared and two major extractable photolysis products were observed.

Product Isolation and Identification. Isopropyl 3-hydroxycarbanilate (3-HOIPC) was isolated by CH_2Cl_2 extraction of several 50 ppm nonradioactive CIPC photolysis solutions followed by prep-scale TLC. Infrared, NMR, and mass spectra were identical with those of authentic 3-HOIPC.

2-Isopropoxycarbonylamino-1,4-benzoquinone (IBQ) was isolated from a photolysis solution of 2000 ppm CIPC in 20% aqueous acetone. Recovery involved extraction with CH_2Cl_2, elution chromatography, and prep-scale TLC. Ten milligrams of bright-yellow crystalline IBQ, mp 66–68 °C, was obtained in this manner: IR (mull), 1720 (carbamate C=O), 3290 (NH), 1665 (quinone C=O), 1635 cm^{-1} (C=C conjugated with C=O); NMR (Fourier transform, CCl_4/$CDCl_3$) δ 1.3 (d, 6, isopropyl methyls), 5.0 (sept, 1, isopropyl

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