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Adsorption–Desorption, Degradation, and Distribution of Permethrin in Aqueous Systems

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Laboratory studies showed that more than 95% of applied permethrin was adsorbed on lake sediment. Less than 10% of the adsorbed insecticide was desorbed by four 10-mL water rinses. Degradation of permethrin was more rapid in lake water than in flooded sediment, indicating that adsorbed permethrin was more stable than permethrin in the aqueous phase. The cis isomer was more stable toward chemical and biological degradation than the trans isomer. The only major degradation product was *trans*- and *cis*-(dichlorovinyl)dimethylcyclopropanecarboxylic acid. Permethrin applied in aqueous solution on the surface of a sediment column did not penetrate through more than 2 cm of the sediment.

Permethrin [3-phenoxybenzyl (±)-*cis,trans*-3-(2,3-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate] and other synthetic pyrethroid insecticides have been shown to be more effective against insects and less hazardous to mammals than natural pyrethrins (Abernathy and Casida, 1973). However, they are also more stable and more toxic to fish than the natural pyrethrins (Mauck and Olson, 1976; Zitko et al., 1977). Permethrin is currently being tested against many agricultural and forest insect pests.

Information on the behavior and fate of this insecticide in soil and aquatic systems is essential in assessing its impact on the environment. Recent studies have indicated that permethrin degradation in soil is rapid, with a half-life of approximately 4 weeks or less (Kaufman et al., 1977; Kaneko et. al., 1978; Williams and Brown, 1979). This study reports on the adsorption–desorption of permethrin to a lake sediment, its degradation in water and flooded sediment, and its depth of penetration through sediment columns.

MATERIALS AND METHODS

[*carbonyl*-^{14}C]Permethrin (40:60 cis/trans) with a specific activity of 50 mCi mmol^{-1} was supplied by Chipman, Inc., Canada. The sediment was collected from the top 15 cm at a depth of 5 m of Lake St. George, King City, Ontario, Canada. The sediment contained 43% organic matter as measured by weight loss with ignition at 450 °C and 34% mineral matter after removal of organic materials and carbonates. Clay, silt, and sand represented 48, 34, and 18% of the mineral fraction, respectively. The scintillation cocktail consisted of 0.2 g of POPOP, 10 g of PPO, 666 mL of Triton X-100, and 1334 mL of toluene. Radioassays were carried out in a Nuclear Chicago Unilux II scintillation counter, and counts were converted to disintegrations per min (dpm) by the channels-ratio method. The study was conducted at a room temperature of 21 ± 1 °C.

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Adsorption–Desorption of Permethrin. Two-hundred milligrams (186.56 mg oven-dry weight) of freeze-dried sediment samples was weighed and placed in 15-mL glass tubes. Solutions of permethrin with concentrations of 6.14, 12.52, 24.50, and 41.68 μg L^{-1} were prepared by adding the appropriate amount of radiolabeled compound in 20 μL of acetone to distilled water. For each concentration, triplicate 5-mL aliquots were added to the sediments, and the tubes were covered with aluminum foil lined screw caps. Controls containing only the insecticide solution were included. The tubes were agitated on a wrist-action shaker for 4 h. Preliminary investigation indicated that equilibrium was established within 1 h. The tubes were centrifuged at 3000 rpm for 20 min. After centrifugation, 3.5 mL of the supernatant liquid was pipetted off and permethrin concentration determined. The difference in permethrin concentration between sample and control tubes was attributed to adsorption on sediment.

The same sample tubes (excluding the tubes that contained the highest permethrin concentration) were used for determining successive desorption of permethrin from sediment. After removal of 3.5 mL of the supernatant, 8.5 mL of distilled water was added to each tube to make a total aqueous volume of 10 mL. The tubes were capped and agitated for 4 h to establish a new equilibrium. The tubes were then centrifuged and 8.5 mL of the supernatant was pipetted off. Two milliliters of the pipetted supernatant was used to determine permethrin concentration. Another 8.5 mL of distilled water was then added to each tube, and the desorption process was repeated another 3 times. The amount of insecticide remaining adsorbed to the sediment after each desorption process was calculated and expressed as percent of the initial amount adsorbed to the sediment.

Degradation of Permethrin in Water and Flooded Sediment. Five-hundred milliliters of radiolabeled permethrin solution (15 μg L^{-1}) was made in lake water (pH 7.8). Half of this solution was treated with sodium azide (0.2% w/w). Five-milliliter aliquots of the untreated and

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azide-treated solutions were pipetted into several scintillation vials. The vials were capped and placed in the dark. Triplicate samples were removed at 0, 2, 4, 8, and 12 weeks for determination of permethrin concentration in the water.

The degradation of permethrin in flooded sediment was also conducted in scintillation vials. Eight milliliters of the untreated and azide-treated solutions was pipetted into vials containing 2 g (0.27 g oven-dry weight) of wet sediment. The vials were thoroughly shaken for 1 min and placed in the dark. Triplicate samples were removed at various time intervals for analysis.

Distribution of Permethrin in Sediment Columns. Seven grams of wet sediment (0.94 g oven-dry weight) samples was weighed and placed in 15 × 1.7 cm i.d. glass columns. The bottom of each column was plugged with a rubber stopper. Seven milliliters of lake water was then added to each tube, and the sediment was thoroughly mixed with a glass rod and then gently agitated for 1 min on a vortex shaker. The columns were left to stand for 24 h to allow the sediments to settle. Ten milliliters of radiolabeled permethrin solution (25 $\mu g\ L^{-1}$) was gently pipetted into each tube. The height of the water and sediment columns were 4 and 5 cm, respectively. At various time intervals, duplicate sample tubes were removed and frozen. The rubber stopper was removed and the frozen column pushed off from each tube. While still frozen, the water column was separated from the sediment column and divided into the top and bottom 2 cm. The sediment column was sliced into 1-cm lengths. The amount of permethrin and its metabolites in each of the slices was determined.

Analytical Procedure. The samples were acidified to a pH of 1.5 with 2 N HCl prior to extraction. The aqueous solution was shaken for 1 min with an equal volume of ethyl acetate in a separatory funnel. After separation, the aqueous phase was discarded and the solvent phase dried over anhydrous sodium sulfate. Efficiency of extraction ranged from 95 to 98%.

Each acidified sediment sample was extracted 3 times with 20 mL of ethyl acetate by shaking for 30 min in a 250-mL stoppered Erlenmeyer flask. The pooled supernatant solutions were decanted through glass wool, dried by filtering through anhydrous sodium sulfate, and evaporated to near dryness on a rotary evaporator. The residue was transferred to a test tube with three 3-mL hexane rinses and then concentrated to 1 mL by a gentle stream of air. Efficiency of extraction ranged from 86 to 90%.

An aliquot of the extract together with standards was subjected to two-dimensional thin-layer chromatography (TLC) on precoated silica gel plates (Brinkmann Instruments, Inc.). The plate was developed twice in one direction with carbon tetrachloride–benzene (4:1) [R_f values were 0.35 for *trans*-permethrin, 0.48 for *cis*-permethrin, and 0 for *cis*- and *trans*-(dichlorovinyl)dimethylcyclopropanecarboxylic acid (DCVA)] and then developed in the second dimension with benzene–ethyl acetate–methanol (15:5:1) (R_f values were 0.9 for *cis*- and *trans*-permethrin, 0.63 for *trans*-DCVA, and 0.72 for *cis*-DCVA). Detection and quantitation of permethrin and its metabolites was by UV light, autoradiography, and liquid scintillation counting of the appropriate zones of the TLC plates.

RESULTS AND DISCUSSION

Adsorption–Desorption of Permethrin. Permethrin was rapidly adsorbed to the sediment with less than 5% of the applied amount remaining in the aqueous phase after 1 min of shaking. The adsorption isotherm (Figure 1) of the insecticide on sediment follows the general linear pattern of increased adsorption with increased insecticide concentration ($r^2 = 0.99$). The high distribution coefficient (nanograms adsorbed per gram of sediment divided by nanograms per milliliter of solution) of 389 mL/g obtained from the slope of the graph clearly indicates the high adsorption of permethrin on the sediment. Once adsorbed, the insecticide was not easily desorbed from the sediment by several water rinses (Figure 2). Approximately 7–9% of the initial adsorbed insecticide was desorbed from the sediment after four successive rinses with 10 mL of water.

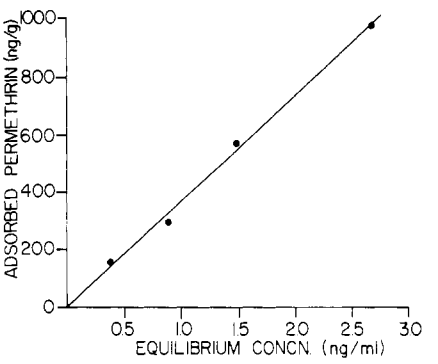

Figure 1. Adsorption of permethrin on sediment. (Each point is the mean of three replicates which generally differ by less than 10%.)

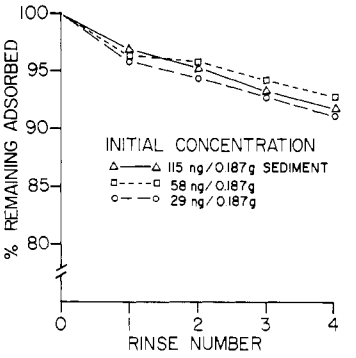

Figure 2. Desorption of permethrin from sediment. (Each point is the mean of three replicates which generally differ by less than 10%.)

Degradation of Permethrin in Water and Flooded Sediment. The chromatography system utilized in this investigation was capable of separating the cis and trans isomers of permethrin, as well as the cis and trans isomers of DCVA. However, no attempt was made to separate the isomers of DCVA, and DCVA in this text refers to both isomers. The unidentified compound(s) exhibited little movement from the origin and comprised approximately 10% of the total radioactivity on the chromatogram after 12 weeks.

The individual degradation rates of *cis*- and *trans*-permethrin and the production of DCVA are given in Figure 3. It shows that the cis isomer is more stable toward biological as well as chemical degradation. The change in the cis/trans ratios of the residues is given in Table I. The amounts of *trans*-permethrin left in solution after 12 weeks of incubation in untreated lake water, azide-treated lake water, untreated flooded sediment, and azide-treated flooded sediment were 0, 30, 32, and 55% of the initial amount applied, respectively. The loss of *trans*-permethrin in azide-treated water indicated that chemical hydrolysis played an important role in the degradation of this isomer in the slightly alkaline azide-treated water of pH 8 (Figure 3B). The cis isomer was fairly persistent in azide-treated water and in both untreated and azide-treated flooded

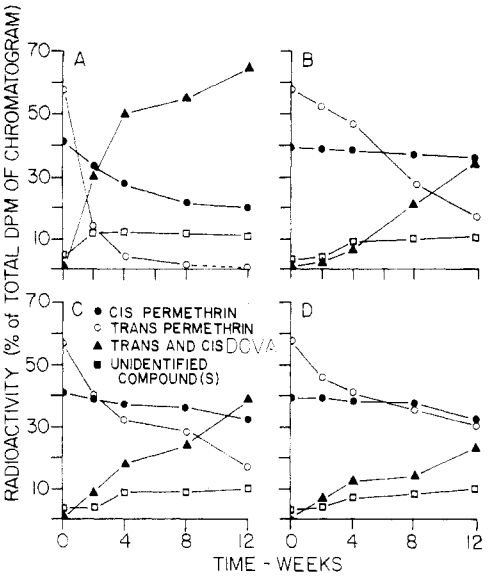

Figure 3. Degradation of permethrin in lake water and the sediment–water system. (A) Unsterilized lake water; (B) sterilized lake water; (C) unsterilized sediment–water; (D) sterilized sediment–water. (Each point is the mean of three replicates which generally differ by less than 10%.)

Table I. Trans/Cis Ratio of Residual [^{14}C]Permethrin in Water and Flooded Sediment at Various Incubation Times

	trans/cis ratio of residual [^{14}C]permethrin			
time, weeks	untreated water	azide-treated water	untreated flooded sediment	azide-treated flooded sediment
0	1.41	1.49	1.40	1.47
2	0.43	1.35	1.05	1.18
4	0.18	1.23	0.85	1.07
8	0.09	0.76	0.76	1.01
12	*a*	0.47	0.56	0.93

[a] The trans isomer was not detectable.

sediments with approximately 85% of the initial amount still remaining in solution after 12 weeks. However, more than 50% of the applied amount was degraded in untreated water during the same incubation period. DCVA was the only degradation product that was detectable by this analytical technique. The rate of permethrin degradation (microbial and chemical) in flooded sediment was slower than in water. This is attributed mainly to adsorption of the insecticide molecules to sediment which makes them less available to microorganisms.

Distribution of Permethrin in Sediment Columns. The total radioactivity present in various sections of the sediment–water columns throughout the 28-day experimental period is given in Figure 4. The experiment was terminated on the 28th day because gas produced by anaerobic microbial metabolism started to push the bottom sediment into the water column. The amount of radioactivity in the water decreased while that in the sediment increased with time. This may be due to the gradual settling of suspended sediment. When the insecticide solution was pipetted into each tube, the surface layer of the sediment column was disturbed, and consequently some of the sediment was resuspended in the water column. Adsorption studies had already indicated that permethrin was rapidly and strongly adsorbed to sediment. Thus, it could be assumed that at the initial time of the experiment, most of the insecticide molecules were associated with suspended sediment, thus giving high radioactivity in the water column. As the suspended sediment

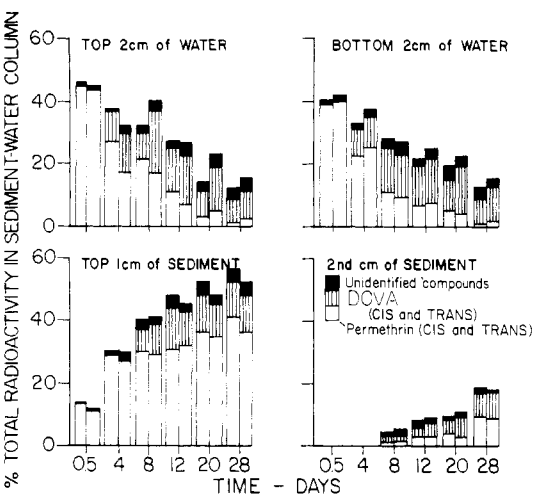

Figure 4. Distribution of permethrin in the sediment–water system.

gradually settled to the bottom with time, radioactivity in the water column decreased while that in the sediment sections, especially the top 1 cm, increased. An average of 54% of the total radioactivity was found in the top 1 cm of sediment on the 28th day of the experiment. Radioactivity was detected in the second centimeter of sediment only after 8 days, indicating that penetration through the sediment was very slow. On the 28th day, an average of 18% of the total radioactivity was detected in the 2-cm sediment section. No radioactivity was detected below 2 cm in the sediment.

The concentration of permethrin in the water column decreased with time. This may be attributed to two causes: first, permethrin associated with the suspended sediment gradually settles to the bottom and, second, rapid degradation of the insecticide occurs in water as indicated in the degradation study. It is interesting to note that after 12 days most of the radioactivity present in the water was in the form of DCVA. This could be attributed to DCVA being more water soluble than permethrin, meaning that comparatively more of it would remain in the aqueous phase rather than being associated with suspended sediment that subsequently settles out. Permethrin accumulated in the top 1-cm sediment section, and on the 28th day it represents 44% of the total radioactivity in the sediment–water column. The amount and rate of permethrin penetration into the second centimeter sediment section were slower than those of DCVA.

Permethrin may enter aquatic systems through direct application or indirectly through surface runoff of contaminated soils or spray drift. A large percentage of the insecticide that is directly applied or enters the aqueous system as spray drift will be rapidly adsorbed to suspended sediment which will gradually settle out. This assumption is in agreement with field studies which showed that a large percentage of permethrin was found in bottom sediments of limnocorrals 21 days after application (Yoo, 1980). Adsorption of the insecticide will not only reduce the effectiveness of the application against aquatic pests but may also increase the persistence of the chemical in the water, because as this investigation has shown, adsorbed permethrin was more stable than permethrin in the aqueous phase. Permethrin that enters the water as soil–insecticide complexes will be deposited on the bottom sediment with very little of it partitioning into the aqueous phase.

Kaufman et al. (1977) showed that in flooded soil permethrin was degraded to DCVA and several other products with little production of $^{14}CO_2$. In contrast, substantial

amount (>50%) of [^{14}C]permethrin was evolved as $^{14}CO_2$ in unflooded soil. They and other workers (Gaughan et al., 1977; Shono et al., 1978; Glickman et al., 1979) showed that the trans isomer was less stable than the cis. The possibility that permethrin will be degraded to DCVA and CO_2 in the upper aerobic layer of natural aquatic systems should be investigated. Most of the applied permethrin will be associated with the bottom sediment and will be degraded to DCVA and other metabolites in the anaerobic environment of bottom sediment. The more insecticidal *cis*-permethrin will remain longer than the trans isomer, and its effect on aqueous systems should be further investigated.

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Isolation and Identification of a New Conjugated Carbofuran Metabolite in Carrots: Angelic Acid Ester of 3-Hydroxycarbofuran

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A new conjugated carbofuran metabolite was isolated from carrots that had been treated with [^{14}C]-carbofuran. The chemical structure was determined to be 2,3-dihydro-2,2-dimethyl-7-[[(methylamino)carbonyl]oxy]-3-benzofuranyl (*Z*)-2-methyl-2-butenoate. Biosynthesis of this compound apparently involves conjugation of 3-hydroxycarbofuran with (*Z*)-2-methyl-2-butenoic acid (angelic acid). This compound is the major carbofuran residue in carrots. Conjugation of xenobiotics with angelic acid has not been previously reported as a metabolic pathway for pesticides in plants.

Carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate) is a broad-spectrum insecticide–nematocide. When the efficiency of acetonitrile and methanol for the extraction of [^{14}C]carbofuran residues in root crops (potatoes, carrots, and radishes) was evaluated, the separation and characterization of carbofuran residues were performed by high-performance liquid chromatography (HPLC) using a C_{18} column (Sonobe et al., 1981). During the determination of carbofuran residues in the extracts of carrots with this HPLC system, a significant quantity of an unidentified carbofuran metabolite was found. This paper reports the isolation and identification of a new conjugated carbofuran metabolite.

EXPERIMENTAL SECTION

Reagents and Apparatus. ^{14}C Aromatic ring labeled carbofuran with a specific activity of 8.2 mCi/mmol was purchased from New England Nuclear, Boston, MA. The radiochemical purity was 99%. 3-Hydroxycarbofuran and Furadan-4 Flowable were obtained from FMC Corp., Middleport, NY. Aliquots of radioactive extracts were mixed with 10 mL of Insta-gel cocktail (Packard, Downers Grove, IL) and counted by using a Mark III liquid scintillation spectrometer (Searle, Des Plains, IL). Analyses of the unidentified compound by thin-layer chromatography (TLC) were performed on either silica gel TLC plates or KC_{18} reversed-phase TLC plates (Kontes, Vineland, NJ) developed in ethyl ether–*n*-hexane (3:1) and methanol–water (4:1), respectively. Dried TLC plates were exposed to No-Screen X-ray film (Eastman Kodak, Rochester, NY), and the film was developed as usual after 1 week of exposure. HPLC-quality *n*-hexane and 2-propanol were purchased from Fisher Scientific Co., Fair Lawn, NJ. Other reagents were analytical grade.

Treatment and Collection of Crop Samples. Carrots (Nantes half long) were grown in pots (21.6 cm diameter × 22.9 cm deep) with silt loam. When roots were ca. 1.5 cm in diameter, ^{14}C aromatic ring labeled carbofuran mixed with the commercial formulation Furadan-4 Flowable (2.56 mCi/mmol) was applied to the roots and the nearby soil at a rate of 3 lb (6.6 kg) of active ingredient/acre. The carrots were harvested at 5, 10, and 15 days postapplication. Tops were removed and discarded, the adhering soil was removed with a water rinse, and the roots were chopped in a Hobart food chopper (Model 84141, Hobart

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