Table V. Adsorption Coefficients for Niclosamide in Five Sediments

sediment	μg/mL	μg/g[a] adsorbed	% desorbed[b]	% extracted	K_d	K_{oc}
1	0.052	4.568	0.3	43	87.85	4599.5
2	0.077	4.923	n.a.[c]	25	63.94	1723.5
3	0.060	3.129	1.0	55	52.15	2307.5
4	0.045	6.230	1.7	62	138.44	4979.9
5	0.034	6.340	n.a.	29	186.47	1948.5

[a] Dry weight basis. [b] % desorbed = (μg/g adsorbed − μg/g adsorbed after desorption)/μg/g adsorbed × 100. [c] Not analyzed.

the predicted value of 1801 for niclosamide, which is based on the equations of Kenaga and Goring (1978) relating aqueous solubility to soil sorption. Only small amounts of radioactivity could be desorbed from sediment (23-h samples, Table V) by shaking for 24 h with water. Extraction of sediments with MeOH–water (4:1) following the desorption experiment released from 25 to 62% of the radioactivity sorbed to the sediment. TLC–autoradiography of these extracts, carried out on silica gel plates with MeOH–chloroform (3:1) as the solvent system, indicated that the extractable radioactivity consisted of niclosamide and aminoniclosamide. Thus, due to the rapid degradation of niclosamide in sediment–water systems, the sorption that was measured represented the sum of niclosamide and aminoniclosamide adsorption. Despite the strong adsorption of niclosamide to sediment, the percent in solution in river water containing (for example) 50 mg/L suspended solids would be greater than 99% according to the equations of Wolfe et al. (1977). Thus sorption of niclosamide (or aminoniclosamide) is unlikely to play a dominant role in the environmental fate of niclosamide under field conditions. The rapid degradation of niclosamide to aminoniclosamide could be a major factor in reducing the efficacy of niclosamide following application. Aminoniclosamide is reportedly 80-fold less toxic to snails than the parent compound (Strufe and Gonnert, 1967). In view of the much greater persistence of aminoniclosamide in sediment, further studies are needed on the environmental fate of the compound and on its availability to sediment-dwelling organisms.

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Behavior and Degradation of Chlorpyrifos-methyl in Two Aquatic Models

S. Y. Szeto[1] and K. M. S. Sundaram*

At 15 °C, (1) the movement, persistence, and degradation of 400 ppb of chlorpyrifos-methyl in the top 1.5-cm layer of flooded sandy loam soil (model I) and (2) the behavior and degradation of 200 ppb of this chemical in natural water (model II) were investigated for a period of 90 days. In model I chlorpyrifos-methyl was strongly adsorbed on the flooded soil; very little was desorbed and then dissolved in the water. The maximum concentration in the water was 1 ppb, detected after 0.7 day (16.5 h) of incubation. Chlorpyrifos-methyl degradated readily in the flooded soil. The toxic breakdown product was 3,5,6-trichloro-2-pyridinol, which reached a maximum concentration in about 27 days and declined thereafter. The pyridinol was never detected in the water. Both compounds had almost completely disappeared in 90 days. In model II chlorpyrifos-methyl moved rapidly from the water to the flooded, clean soil. After incubation for 13 days, its concentration increased from nondetectable to a maximum of 560 ppb in the top 1.5-cm layer of the soil but decreased from 200 to 40 ppb in the water. Both the parent compound and its breakdown product were degraded readily in soil and water; only 0.1 and 10 ppb remained in the water and in the flooded soil, respectively, after incubation for 83 days.

Chlorpyrifos-methyl [*O,O*-dimethyl *O*-(3,5,6-trichloro-2-pyridyl)phosphorothioate] is a broad-spectrum insecticide developed in 1966 by Dow Chemical Co. under the trade name Reldan. It has been used to control pests of stored grain, adult mosquitoes, flies, aquatic larvae, household pests, and various pests of leafy crops (Martin and Worthington, 1979). Since 1977 the Forest Pest Management Institute of the Canadian Forestry Service has conducted several studies to evaluate chlorpyrifos-methyl as a control agent against the spruce budworm, *Choristoneura fumiferana* (Clem.), a serious coniferous forest defoliator in eastern Canada and the United States.

Little is known about the presistence, distribution, and

Forest Pest Management Institute, Canadian Forestry Service, Environment Canada, Sault Ste. Marie, Ontario, Canada P6A 5M7.
[1]Present address: Agriculture Canada, Research Station, Vancouver, British Columbia, Canada V6T 1X2.

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dynamics of chlorpyrifos-methyl residues in the aquatic ecosystem. Its hydrolysis under laboratory conditions was studied by Meikle and Youngson (1978), who found that 45.1% of the chemical added to canal water (pH 8.0) remained after incubation for 29 days at 15 °C. By contrast, Szeto and Sundaram (1981) reported that chlorpyrifos-methyl dissipated very rapidly in stream water within 24 h after its aerial application. They suggested that the rapid dissipation was due primarily to the water flow but that nevertheless translocation from water to other matrices and uptake by living organisms were also important. Since chlorpyrifos-methyl is known to be relatively toxic to fish and other aquatic organisms, especially some species of crustaceans (Dow Chemical Company, 1976), it is important to understand its movement between water and sediment as well as its persistence in different components of the aquatic ecosystem. This paper describes the behavior and degradation of chlorpyrifos-methyl in two aquatic models under laboratory conditions.

MATERIALS AND METHODS

Aquatic Model Studies. Sandy loam soil (pH 5.5, organic content 1.1%) and natural water (pH 6.2) were taken respectively from a forest and from Hargraft Lake, northeast of Sault Ste. Marie, Ontario, Canada. Five kilograms (wet weight) of soil was treated with chlorpyrifos-methyl (5 mg/mL in acetone) to give a concentration of approximately 400 ppb (dry weight). The treated soil was thoroughly mixed and allowed to stand for 24 h at 4 °C. Four 20-g aliquots (wet weight) of the treated soil were extracted and analyzed for chlorpyrifos-methyl immediately before setting up the aquatic model. The mean (423 ppb dry weight) was considered as the soil residue at time zero, and the standard deviation (±17 ppb) confirmed the homogeneity of the fortification.

Model I was set up according to Isensee et al. (1973) and Isensee and Jones flooded except that only lake water and forest soil were included. Twenty-five kilograms of untreated soil was placed in a glass aquarium (74 cm × 32 cm × 46 cm), forming a layer 4.5 cm deep. Twenty-five Petri dishes (1.5 cm × 5.4 cm i.d.) with Teflon straps for easy retrieval were laid on the surface, and 5 kg of chlorpyrifos-methyl treated soil was then placed so as to form a layer 1.5 cm deep, just to cover the upper edge of each Petri dish. The aquarium was then carefully filled with 80 L of lake water. Model II was set up similarly, except that 5 kg of untreated soil was used for the upper layer. After settling for 24 h, the water of model II was fortified with chlorpyrifos-methyl (5 mg/mL in acetone) to give a concentration of 200 ppb in the water. The control model consisted of untreated water and soil, set up in similar fashion. All three aquaria were held for incubation at 15 °C in a termpature-controlled greenhouse cubicle for a period of 90 days. During incubation natural light was extended to 16 h/day by using 400 W multivapor discharge lamps. At various intervals during incubation a 50-mL sample of water and one Petri dish containing flooded soil were carefully retrieved from each aquarium for the analysis of chlorpyrifos-methyl and its breakdown product, 3,5,6-trichloro-2-pyridinol.

Extraction and Cleanup. Each water sample was acidified with 10% sulfuric acid (10 mL) and extracted twice in a 250-mL separatory funnel with benzene (50 and 25 mL). The combined extract was dried with anhydrous sodium sulfate and then concentrated to 2 mL for chemical derivatization and gas chromatographic (GC) analysis.

Each flooded soil sample was first filtered under aspiration through Whatman No. 1 filter paper in a Büchner funnel to remove excess water. The filter cake including the paper was extracted twice with 100 mL of a mixture of 20% acetone in hexane, and the extracts were filtered through anhydrous sodium sulfate in a Büchner funnel lined with Whatman No. 1 filter paper. An aliquot of the combined filtrate equivalent to 40 g of flooded soil (wet weight as determined immediately after filtration) was transferred to a 500-mL separatory funnel, 50 mL of benzene was added, the funnel was shaken for 0.5 min, and 150 mL of 1% aqueous sodium carbonate was added and shaken again for 1 min. After the two phases had separated, the aqueous phase was drained into a 1000-mL beaker. The organic phase was washed with another 150 mL of 1% aqueous sodium carbonate, and the aqueous phase was then drained into the beaker. The organic phase, which contained chlorpyrifos-methyl, was dried with anhydrous sodium sulfate and cleaned on a Florisil column as described by Szeto and Sundaram (1981). The breakdown product, 3,5,6-trichloro-2-pyridinol, was isolated from the combined aqueous phase and derivatized with BSA [*N,O*-bis(trimethylsilyl)acetamide] for GC analysis (Braun, 1974; Chapman and Harris, 1980).

Gas Chromatographic (GC) Analysis. Two gas chromatographs, a Hewlett-Packard 5730A equipped with a flame photometric detector and a Hewlett-Packard 7610 equipped with a Ni^{63} electron capture detector, were used for the analysis of chlorpyrifos-methyl and 3,5,6-tri-

Table I. GC Operating Conditions for Detection of Chlorpyrifos-methyl (FPD) and 3,5,6-Trichloro-2-pyridinol (ECD)

parameter	Hewlett-Packard 5730A flame photometric detector	Hewlett-Packard 7610 electron capture detector
detector temp, °C	200	295
detector mode	phosphorus	
inlet temp, °C	200	200
column	120 cm × 4.0 mm i.d. 3% OV-17 on Chromosorb W "HP", 80-100 mesh	120 cm × 2.0 mm i.d. 5% DC-200 on Chromosorb W "HP", 80-100 mesh
column temp, °C	210	110
carrier gas	nitrogen at 40 mL/min	5% methane and 95% argon mixture at 30 mL/min
hydrogen flow rate, mL/min	200	
oxygen flow rate, mL/min	20	
air flow rate, mL/min	60	
retention time, min	2.0 (chlorpyrifos-methyl)	2.42 (3,5,6-trichloro-2-pyridinol)

Table II. Recovery of Chlorpyrifos-methyl and 3,5,6-Trichloro-2-pyridinol from Fortified Forest Soil and Lake Water Samples

substrate	fortification, ppm	% recovery ($\bar{X}$ ± SD, $n = 4$)
Chlorpyrifos-methyl		
soil	0.5	94.0 ± 2.8
	0.05	90.5 ± 7.8
water	0.1	89.5 ± 0.7
	0.01	99.2 ± 2.8
3,5,6-Trichloro-2-pyridinol		
soil	0.5	86.3 ± 1.8
	0.05	77.0 ± 7.1
water	0.1	93.5 ± 5.0
	0.01	77.5 ± 6.4

Table III. Model I: Movement and Degradation of 423 ppb of Chlorpyrifos-methyl in Flooded Soil, Held at 15 °C in an Environmental Chamber

incubation time, days	chlorpyrifos-methyl, flooded soil, ppb (dry wt)	chlorpyrifos-methyl, flooded soil, μg	chlorpyrifos-methyl, water, ppb	chlorpyrifos-methyl, water, μg	3,5,6-trichloro-2-pyridinol, flooded soil, ppb (dry wt)	3,5,6-trichloro-2-pyridinol, flooded soil, μg	total residue[a], μg	total residue[a], %[b]
0	423	1875	ND[c]		ND		1875	100
0.7	299	1325	1.0	80	4.0	18	1434	76.5
1.0	287	1271	0.7	53	7.4	33	1377	73.4
1.7	235	1041	0.5	42	10.9	48	1161	61.9
2.0	253	1121	0.5	40	15.2	67	1270	67.7
2.7	230	1019	0.5	40	16.6	74	1178	62.8
4.0	206	913	0.5	39	17.1	76	1057	57.3
6.0	183	811	0.5	42	19.8	88	996	53.1
7.0	200	886	0.5	38	17.8	79	1052	56.1
10	180	797	0.4	35	58.2	258	1251	66.7
13	194	859	0.4	28	56.6	251	1294	69.0
15	212	939	0.3	23	63.1	280	1416	75.5
21	149	660	0.2	14	57.8	256	1090	58.1
27	64.8	287	0.1	8	65.5	290	767	40.9
37	61.2	271	ND		46.3	205	604	32.2
44	26.6	118	ND		38.4	170	394	21.0
56	31.1	138	ND		35.6	158	394	21.0
72	11.4	51	ND		17.5	78	177	9.4
90	8.0	35	ND		8.0	35	93	5.0

[a] Total residue = chlorpyrifos-methyl plus 3,5,6-trichloro-2-pyridinol (converted to its equivalence of the parent compound). [b] Percent = percent of the chlorpyrifos-methyl added in 5 kg (wet weight) of forest soil. [c] ND = not detectable at the limits of 0.05 ppb of chlorpyrifos-methyl in water and 2 ppb (dry weight) of the pyridinol in flooded soil.

Table IV. Model II: Movement and Degradation of 200 ppb of Chlorpyrifos-methyl in 80 L of Lake Water with the Presence of Flooded, Clean Soil, Held at 15 °C in an Environmental Chamber

incubation time, days	chlorpyrifos-methyl, water, ppb	chlorpyrifos-methyl, water, μg	chlorpyrifos-methyl, flooded soil, ppb (dry wt)	chlorpyrifos-methyl, flooded soil, μg	3,5,6-trichloro-2-pyridinol, water, ppb	3,5,6-trichloro-2-pyridinol, water, μg	3,5,6-trichloro-2-pyridinol, flooded soil, ppb (dry wt)	3,5,6-trichloro-2-pyridinol, flooded soil, μg	total residue[a], μg	total residue[a], %[b]
0	200	16000	ND[c]		ND		ND		16000	100
1	180	14400	128	448	0.7	56	5.9	21	14970	93.6
2	170	13600	298	879	1.1	88	12.3	36	14682	91.8
3	137	10960	393	1158	2.1	168	33.0	97	12548	78.4
6	90	7200	447	1384	1.2	96	75.1	233	9122	57.0
7	77.7	6216	463	1478	2.5	200	72.9	233	8400	52.5
8	69.4	5552	539	1550	1.9	152	86.3	248	7753	48.5
13	40.2	3216	562	1719	1.7	136	98.1	300	5646	35.3
14	40.0	3200	471	1549	1.8	144	102	336	5527	34.5
21	20.5	1640	230	853	1.3	104	50.9	189	2968	18.6
30	6.8	544	122	429	0.3	24	40.3	142	1244	7.8
37	2.5	200	30.3	116	0.7	56	43.3	166	673	4.2
49	0.8	64	21.1	82	0.3	24	22.7	88	329	2.1
65	0.3	24	15.0	52	0.2	16	9.2	32	152	1.0
83	0.1	8	13.1	46	0.1	8	3.1	11	88	0.6

[a] Total residue = chlorpyrifos-methyl plus 3,5,6-trichloro-2-pyridinol (converted to its equivalence of the parent compound). [b] Percent = percent of chlorpyrifos-methyl added in 80 L of lake water. [c] ND = not detectable at the limits of 4 ppb (dry weight) of chlorpyrifos-methyl in the flooded soil and 0.05 and 2 ppb (dry weight) of the pyridinol in the water and in the flooded soil, respectively.

chloro-2-pyridinol, respectively. The operating conditions are given in Table I.

Chlorpyrifos-methyl and 3,5,6-trichloro-2-pyridinol were quantified by external standardization based on peak height. Pretreatment samples of lake water and forest soil were extracted and analyzed as described; no detectable GC response interfered with chlorpyrifos-methyl or 3,5,6-trichloro-2-pyridinol. Quadruplicate samples of untreated water and soil were fortified with chlorpyrifos-methyl and 3,5,6-trichloro-2-pyridinol at two levels to determine the recovery rate, and the results are given in Table II. Reported results were not corrected for recovery.

RESULTS AND DISCUSSION

Model I: Degradation of Chlorpyrifos-methyl in Flooded Soil. The concentrations of chlorpyrifos-methyl and its breakdown product, 3,5,6-trichloro-2-pyridinol, in the water and in the flooded soil of model I at different intervals during incubation are given in Table III. The pyridinol was never detected in the water during the study. Very little residue had desorbed from the flooded soil and dissolved in the water. The concentration of the parent compound in the water was at its highest (1 ppb) after 0.7 day (16.5 h) of incubation; gradually it declined to 0.1 ppb in 27 days and became nondetectable after 37 days (Table III). Since chlorpyrifos-methyl has the very low water solubility of 4 ppm at 25 °C (Martin and Worthington, 1979) and the very high octanol/water partition coefficient of 20 000, this compound would adsorb strongly onto the soil particles (Hague et al., 1977). The chlorpyrifos-methyl residue was still present in the flooded soil even after 90 days (Table III). This suggests that the minimal concen-

trations of ≤1 ppb detected in the water probably originated from treated soil that became suspended when the lake water was initially added to the aquarium rather than from desorption.

Chlorpyrifos-methyl was degraded rapidly in the flooded soil. The toxic breakdown product was 3,5,6-trichloro-2-pyridinol. While the concentration of the parent compound was declining from 423 to 64.8 ppb in 27 days, that of the pyridinol increased gradually from nondetectable to a maximum of 65.5 ppb and declined thereafter. Both chlorpyrifos-methyl and the pyridinol had almost completely disappeared from the flooded soil in 90 days (Table III). The half-life of the total residue, i.e., chlorpyrifos-methyl plus the pyridinol (converted to its equivalence of the parent compound), in the flooded soil was about 21 days, but the half-life of the parent compound alone was only about 4 days.

Szeto and Sundaram (1981) studied the distribution and persistence of chlorpyrifos-methyl residues in the water and sediment of a stream after two applications of Reldan at 70 g of a.i./ha. They reported that residues were detected in both stream water and sediment 5 min after aerial application. The concentration in sediment increased steadily to a maximum in 2 days and then declined rapidly. Their findings in the field were in general agreement with our observations here, indicating that chlorpyrifos-methyl is probably nonpersistent in either flooded soil or sediment.

Model II: Behavior and Degradation of Chlorpyrifos-methyl in Natural Water. The concentrations of chlorpyrifos-methyl and its breakdown product in lake water in the presence of flooded, clean soil in model II are given in Table IV. During the first 2 days, the concentration of chlorpyrifos-methyl decreased from 200 to 170 ppb in the water but increased from nondetectable to 298 ppb in the flooded soil; only low concentrations of the pyridinol were detected in both the water and the flooded soil. More than 90% of the chemical added to the water of model II was still present after 2 days of incubation, indicating that very little of this chemical had escaped from the water into the atmosphere by volatilization or codistillation, and its disappearance was relatively slow at first (Table IV). It appeared that chlorpyrifos-methyl adsorbed rather strongly onto the waterborne particulates, which then settled out on the underlying flooded soil. A similar observation in artificial ponds was reported by Hughes et al. (1980).

This behavior correlates very well with the strong adsorption of chlorpyrifos-methyl on the flooded soil, demonstrated in model I, as well as with the field observation on the rapid movement of this chemical from stream water to sediment (Szeto and Sundaram, 1981) and is probably due to its low water solubility and high octanol/water partition coefficient (Hague et al., 1977). Similar behavior had also been demonstrated in aquatic systems for other lipophilic compounds (Oloffs et al., 1972, 1973).

After 2 days of incubation, chlorpyrifos-methyl degraded rapidly in both the water and the flooded soil. The toxic breakdown product was detected after 1 day of incubation. The concentration of pyridinol remained relatively low in the water (<3 ppb) during the study while that in the flooded soil increased steadily and reached a maximum of 102 ppb in 14 days and then decreased rapidly. Only 0.1 and 13.1 ppb were found in the water and in the flooded soil, respectively, after 83 days (Table IV). The half-life of the total residue, i.e., parent compound plus the pyridinol (converted to its equivalence of the parent compound), in model II, including both the water and the flooded soil, was about 8 days.

Our findings are considerably different from those reported by Meikle and Youngson (1978), who found that 45.1% of the chlorpyrifos-methyl added to canal water (pH 8.0) remained after incubation at 15 °C for 29 days. In spite of the fact that the pHs of our lake water (6.2) and forest soil (5.5) were much lower, less than 10% of the added compound remained after incubation at 15 °C for 30 days. This disparity was probably due to the presence of the flooded soil in model II. The soil microorganisms therein may have contributed significantly to the degradation of chlorpyrifos-methyl and its toxic breakdown product. This suggestion is supported by the evidence that significant degradation occurred in model II only after 2 days of incubation.

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