Degradation of Niclosamide (2',5-Dichloro-4'-nitrosalicylanilide) in Sediment and Water Systems

D. C. G. Muir* and A. L. Yarechewski

Degradation of [^{14}C]niclosamide (2',5-dichloro-4'-nitrosalicylanilide) was studied in river and pond sediments (water to sediment ratio 10–20:1) incubated under aerobic and anaerobic conditions over a 128-day period (25 °C). Niclosamide degraded rapidly under these conditions with half-lives ranging from 1.1 to 3.9 days in sediment. The major degradation product was aminoniclosamide (2',5-dichloro-4'-aminosalicylanilide), which represented more than 50% of the radioactivity extractable from sediments. Greater amounts of aminoniclosamide were formed under anaerobic conditions (redox potential <350 mV) than in aerobic systems. 2-Chloro-4-nitroaniline, a hydrolysis product of niclosamide, was also detected but 5-chlorosalicylic acid was not detected in sediment or water extracts. From 6.8 to 37.7% of radioactivity added to respirometer flasks was trapped in a $^{14}CO_2$ trapping agent over a 93-day period. Studies on the adsorption of niclosamide to five different sediments gave an average sediment sorption coefficient (K_{oc}) of 3111 ± 1552. Only from 0.3 to 1.7% of the sorbed radioactivity could be desorbed by shaking with water for 24 h.

Niclosamide (2',5-dichloro-4'-nitrosalicylanilide) formulated as its ethanolamine salt (Bayluscide) has been used in Canada in the control of the sea lamprey (*Petromyzon marinus*) in the Great Lakes. Bayluscide is widely used as a molluscicide in tropical regions for control of freshwater snails that are vectors for schistosomiasis (Hamilton, 1974). Niclosamide is also used as an intestinal taeniacide in humans (Griffiths and Facchini, 1979). Studies on the fate of niclosamide in the aquatic environment following application as a lampricide have been limited to following the disappearance of the parent compound through bioassays or spectrophotometric measurements (Hamilton, 1974). Intense sunlight, high pH (>9.0), and the presence of sediment have been shown to reduce the efficacy of niclosamide treatments (Hamilton, 1974). Schultz and Harman (1978) found that ^{14}C-labeled niclosamide had a half-life of about 150 h in water exposed to ultraviolet light (>290 nm) but found negligible hydrolysis of the compound after 56 days in buffered aqueous solution or in pond water. These authors reported 5-chlorosalicylic acid as a minor photoproduct (3.8% of radioactivity) of niclosamide exposed to UV light on thin-layer plates.

The objective of the present work was to study the fate of niclosamide in laboratory sediment–water systems so as to provide information on the rates of degradation, degradation products, and sorption equilibria that might be expected following addition of the chemical to aquatic systems.

MATERIALS AND METHODS

Analytical Standards. Niclosamide (99.4% purity) was obtained from the Analytical Standards Laboratory, Agriculture Canada, Ottawa, and [^{14}C]niclosamide (salicylic acid, ring labeled, sp act. 10 mCi/mM) from the U.S. Fish and Wildlife Service, La Crosse, WI. [^{14}C]Niclosamide was purified by reverse-phase thin-layer chromatography (TLC) on Whatman KC18 plates using a solvent system of ethanol–water–formic acid (75:25:1) and was diluted with unlabeled niclosamide before use. Aminoniclosamide (2',5-dichloro-4'-aminosalicylanilide) was synthesized from niclosamide by reduction of the nitro group using chromous chloride (Forbes et al., 1975). The reduction product was recrystallized from benzene and purified by chromatography on a column of Florisil (methanol as the eluting solvent). The identity of the product was confirmed by mass spectrometry of the methylated derivative (Muir and Grift, 1980). Amino[^{14}C]niclosamide was synthesized by an identical procedure and purified by reverse-phase TLC. Specific activity of the purified product was 10 mCi/mM. Hydrolysis products of niclosamide, 5-chlorosalicylic acid and 2-chloro-4-nitroaniline (CNA), were obtained from Aldrich Chemicals.

Sediment–Water Studies. *Static Incubations.* Culture flasks (125 mL, Teflon-lined screw caps) were filled with 25 g of pond or river sediment (approximately 10 g dry weight) and 100 mL of dechlorinated water. The sediments were obtained 2 months before the experiment and held at −50 °C until use. Physical characteristics of the sediments are presented in Table I. The flasks were loosely capped and allowed to incubate for 21 days (25 °C). Several flasks were autoclaved for 30 min (121 °C, 1.09 atm). An acetone solution of [^{14}C]niclosamide (0.01 μCi) was added to each flask to give 1 μg/mL concentrations in water. The flasks were gently swirled, loosely capped, and held at 25 °C in a controlled environment room until sampled. Flasks were removed (duplicates for each sediment) after 4 and 14 h and 1, 2, 4, 8, 16, 32, 64, and 128 days of incubation. Autoclaved flasks were fortified under asceptic conditions, stored at 25 °C as described, and sampled after 32, 64, and 128 days.

Respirometer Flask Incubations. Pond or river sediment (25 g wet weight) and water (200 mL) were added to Erlenmeyer flasks (500 mL). The flasks were stoppered and connected to a manifold system that delivered air (CO_2-free grade) or nitrogen (zero grade, <5 ppm of O_2) via needle valves at 1–2 mL/min. Following a 14-day equilibration period an acetone solution of [^{14}C]niclosamide (0.01 μCi) was added to each flask to give 1 μg/mL concentrations in water. Each respirometer flask was equipped with a polyurethane foam plug to trap volatiles (Kearney and Kontson, 1976) and a scrubbing tube containing 35 mL of 2-methoxyethylamine (CO_2-M-met, Amersham Radiochemicals) to trap $^{14}CO_2$. The trapping solution was changed every 2–4 weeks. Samples of trapping solution (1 mL) were taken frequently over a 93-day period, diluted with PCS (Amersham Radiochemicals), and counted by liquid scintillation counting (LSC). Flasks were removed from the manifold system after 32, 64, and 93 days of incubation. Upon removal, measurements of pH and redox potential in water and sediment were made to establish the conditions prevailing under air or nitrogen flow.

Department of Fisheries and Oceans, Freshwater Institute, Winnipeg, Manitoba, Canada R3T 2N6.

0021-8561/82/1430-1028$01.25/0 © 1982 American Chemical Society

Table I. Characteristics of Sediments Used in Degradation and in Adsorption-Desorption Studies

		% [a]				E_H, mV [b]			
						water		sediment	
sediment	pH	OC	silt	sand	clay	A	AN	A	AN
1	7.8	1.9	23	0	77				
2 [c]	7.6	3.7	24	1	75	+454	+124	+434	−46
3 [c]	7.7	2.3	43	7	48	+444	+214	+444	−6
4	6.8	3.0	37	5	58				
5	7.1	9.2	36	12	52				

[a] OC = organic carbon. [b] E_H = redox potential for sediments incubated 70 days under aerobic (air) or anaerobic (N_2) conditions. Determined with a combination Pt/calomel electrode. [c] Sediments 2 and 3 are respectively the pond and river sediments used in degradation studies.

Analysis of Water and Sediment. Water and sediment phases were separated by filtration (Whatman No. 1 paper). Niclosamide and degradation products were extracted from water (adjusted to pH 3.0) by shaking with dichloromethane. Small samples of sediment (0.5-g duplicates) were combusted directly on a Packard 306 oxidizer, and the $^{14}CO_2$ released was counted by LSC in order to determine the total radioactivity in the sediment. Sediment was extracted by shaking with methanol–water (4:1), and the aqueous phase (adjusted to pH 3.0) from this extraction was partitioned into dichloromethane. Water and sediment extraction procedures are outlined in more detail by Muir and Grift (1980). Dichloromethane extracts of water and sediment were concentrated to a small volume for TLC, LC, or GC analysis. Unextractable residues in sediment were determined by combustion of extracted sediment while unextractable radioactivity in water was determined by assaying aliquots of extracted water by LSC. Some extracted sediment samples were further extracted by refluxing (2 h) with MeOH–water–concentrated NH_4OH (90:10:1) followed by a 40-h reflux in water (100 °C) to release unextractable niclosamide residues. Following the reflux steps, the extracts were partitioned with dichloromethane, which was concentrated to small volume for further analysis.

Chromatographic Techniques. Dichloromethane extracts were spotted on Whatman KC18 reverse-phase TLC plates. Development of chromatograms was accomplished with ethanol–water–formic acid (75:25:1). Radiolabeled compounds were detected by exposing the TLC plates to X-ray film (Kodak NS-2T) for 2–3 weeks. Radioactive areas were scraped, transferred quantitatively to test tubes, and extracted with methanol. Aliquots of the methanol extracts were counted by LSC to determine the radioactivity in each spot. TLC spots with identical R_f values were pooled for LC and GC analysis. R_f values and LC and GC retention times for niclosamide and possible degradation products are listed in Table II.

LC was carried out by using a Waters 4000A pump and Model 450 UV detector set at 310 nm. A reverse-phase column (Ultrasphere ODS, 25 cm × 4.6 mm i.d.; Beckman Instruments) was used with a solvent system consisting of methanol–water–formic acid (75:25:0.2) at 1.5 mL/min. A Tracor 560 GC equipped with a Model 702 N-P detector was used to determine CNA and methylated derivatives of niclosamide and aminoniclosamide. Pooled TLC samples were methylated with CH_3I by using the procedure of Muir and Grift (1980). Methylated niclosamide was chromatographed on a column of 3% OV-101 (1.8 m × 2 mm i.d.) operated at 260 °C. Detector and injector temperatures were 280 and 250 °C, respectively. CNA was determined on the same column at 185 °C. Gas chromatography–mass spectrometry was carried out on a Du Pont 321 GC–MS by using a 0.6 m × 2 mm i.d. column of 3% SP-2100 operated at 230 °C in the EI mode (70 eV).

Table II. Retention Times and R_f Values for Niclosamide and Some Potential Degradation Products

compound	TLC R_f [a]	LC, [b] min	GC, min
niclosamide	1.0	26.0	4.8 (260 °C) [c]
aminoniclosamide	2.13	8.0	6.0 (260 °C) [c]
2-chloro-4-nitroaniline	2.25	5.6	4.0 (185 °C)
5-chlorosalicylic acid	3.00	4.0	

[a] Where niclosamide = 1.0 (approximately 45 mm from the origin under the conditions used). [b] Solvent system: MeOH–water–formic acid (75:25:0.2) at 1.5 mL/min. [c] Methylated derivatives. Temperatures of the column oven are in parentheses.

Adsorption–Desorption Experiments. Partitioning of niclosamide between sediment and water was studied by using five different pond and river sediments. Some physical characteristics of these sediments are listed in Table I. Sediment (equivalent to 1.0 g dry weight) was placed in Corex glass tubes along with 9 mL of an aqueous solution of [^{14}C]niclosamide (0.003 μCi/mL, 0.5 μg/mL). Tubes were stoppered with rubber stoppers and shaken vigorously in a horizontal position (22 °C, Eberbach shaker). Controls consisting of the niclosamide solution without sediment were also included. Tubes were removed (duplicate) at 1, 4, 7.5, and 23 h and centrifuged at 30000*g* for 20 min. A portion of the supernatant was dissolved in PCS and assayed by LSC. Desorption was studied by replacing 7 mL of the supernatant with 7 mL of distilled water and reshaking for 24 h. Following completion of the desorption study the sediment was extracted with methanol–water (4:1) to identify the form of the extractable radioactivity.

RESULTS AND DISCUSSION

Sediment–Water Studies. Niclosamide degraded rapidly in both pond and river sediments incubated under static conditions (Figure 1). Disappearance of niclosamide over the first 8 days of incubation showed good agreement [R^2 from a linear regression equation of log concentration vs. time = 0.81 (pond sediment) and 0.85 (river sediments)] with a first-order kinetic rate equation. Half-lives calculated from an equation of log concentration vs. time were 3.9 days in the river sediment and 1.1 days in pond sediment. Rapid disappearance of niclosamide from water above the sediment was also observed with half-lives of 3.1 and 0.83 days in water above pond and river sediment, respectively. Since more than two-thirds of the radioactivity in the flasks was associated with the sediment fraction [Table III (A)], and degradation products isolated from water appeared to be identical with those in sediment, further discussion will be limited to sediment results.

Rapid transformation and sorption of niclosamide in the static systems were also apparent from the lower efficiency of extraction of radioactivity from sediment incubated

Table III. Proportion of Radioactivity in Each Phase and Percent Extractable from Sediment in Static Incubations and Respirometer Flasks

time, days	sediment[a]	% added ^{14}C			% extractable from sediment[b]		
		water	sediment	CO_2 trap	MeOH shaking	MeOH-H_2O reflux	H_2O reflux
			(A) Static Incubation				
0.25	R	26.7	44.6	–[c]	106.8	–	–
	P	26.8	45.6	–	87.6	–	–
2	R	20.0	47.2	–	106.1	–	–
	P	28.2	45.8	–	54.4	–	–
4	R	23.8	58.3	–	83.0	–	–
	P	32.1	53.5	–	43.0	–	–
16	R	22.4	60.1	–	66.1	–	–
	P	17.0	62.4	–	45.5	–	–
32	R	15.6	59.3	–	60.8	–	–
	P	20.1	62.3	–	28.1	–	–
64	R	14.1	62.4	–	32.2	13.3	17.0
	P	7.5	74.7	–	12.3	13.3	22.6
128	R	9.4	61.8	–	4.2	12.8	28.7
	P	4.2	75.4	–	0.7	13.4	21.9
			(B) Respirometer Flasks				
32	R-A	12.2	65.2	11.3	48.9	–	–
	R-AN	55.9	41.2	7.2	49.7	–	–
	P-A	2.5	13.6	3.5	18.1	–	–
	P-AN	37.2	48.2	6.2	36.6	–	–
64	R-A	14.8	51.5	23.7	54.5	–	–
	R-AN	51.3	29.2	8.9	47.0	–	–
	P-A	2.8	65.6	5.4	14.5	–	–
	P-AN	30.2	45.0	8.6	27.2	–	–
93	R-A	7.6	74.3	37.7	20.5	11.0	19.2
	R-AN	29.6	67.0	9.0	45.1	20.9	11.1
	P-A	1.9	77.3	6.8	10.3	11.9	20.6
	P-AN	20.7	72.5	8.7	29.6	20.1	11.9

[a] R = river sediment; P = pond sediment; A = aerobic; AN = anaerobic. [b] MeOH-water reflux carried out by using MeOH-water-concentrated NH_4OH (90:10:1). [c] Indicates not determined.

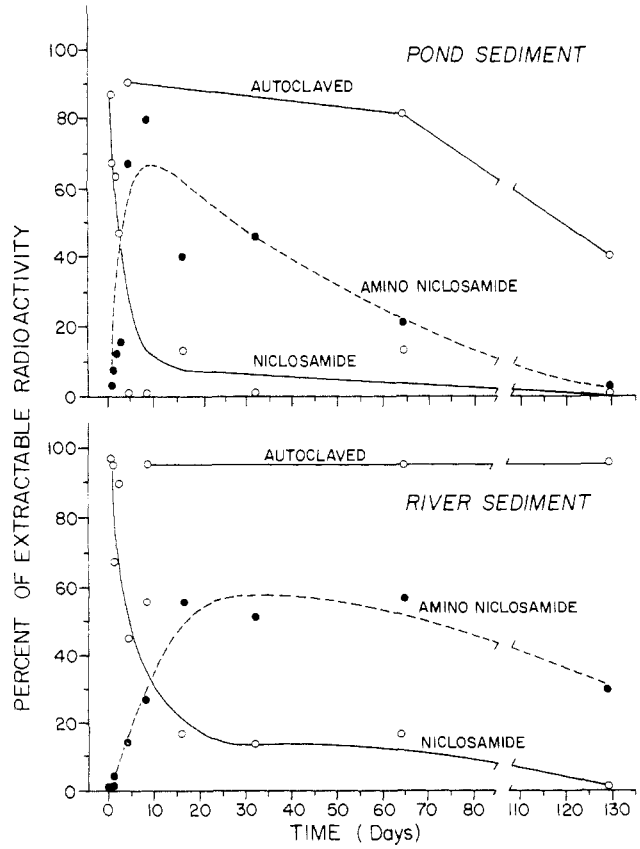

Figure 1. Degradation of [^{14}C]niclosamide in sediment incubated under static conditions.

from 16 to 128 days [Table III (A)]. Less than 100% of the radioactivity initially added to the static systems could be accounted for. These losses were likely due to loss of $^{14}CO_2$ (not monitored in these flasks) and to poor combustion of sediment in the oxidizer that was estimated to be 80–90% efficient for 0.5-g sediment samples. Degradation of niclosamide in autoclaved samples occurred at a very slow rate (Figure 1), which suggested that degradation under laboratory conditions was dependent on microbial activity. Since niclosamide absorbs ultraviolet light at wavelengths >300 nm (Daniels et al., 1965), it is likely that under field conditions photodegradation could also occur. However, the rate of degradation of niclosamide reported here for sediment is much greater than that observed in water under UV light (Schultz and Harman, 1978), suggesting that even in sunlight microbial degradation may predominate under field conditions. Confirmation of the relative importance of each degradation pathway would require field studies in which the degradation products of niclosamide were monitored.

TLC of sediment and water extracts revealed only one major degradation product. This product cochromatographed with aminoniclosamide (R_f = 2.13 relative to niclosamide). The product was methylated with CH_3I and had a similar GC retention time to that of aminoniclosamide methylated under the same conditions. Furthermore, it had a similar LC retention time to that of aminoniclosamide when chromatographed on a reverse-phase column. The mass spectrum of the methylated derivative had a parent ion at m/e 352, a prominent P + 2 peak (indicating two chlorines), and a base peak at m/e 183 corresponding to the methylated chloroaniline portion of the molecule. This spectrum was identical with that of methylated aminoniclosamide. The compound has not been previously reported as a degradation product of niclosamide in aquatic systems; however, it has been reported in rats following administration of niclosamide (Duhn et

Table IV. Proportion of Niclosamide and Aminoniclosamide as well as CNA in Sediment Extracts from Respirometer Flasks[a]

time, days	sediment[b]	niclos-amide, %	amino-niclos-amide, %	CNA,[c] μg
32	R-A	84.6	7.5	1.8
	R-AN	3.5	56.0	13.6
	P-A	51.1	30.2	10.6
	P-AN	7.2	37.4	25.6
64	R-A	85.3	2.5	n.a.[d]
	R-AN	15.4	53.1	n.a.
	P-A	65.3	12.4	n.a.
	P-AN	14.6	51.5	n.a.
93	R-A	69.5	19.6	<1.0
	R-AN	13.1	41.8	<1.0
	P-A	26.3	47.8	<1.0
	P-AN	9.1	33.2	<1.0

[a] Additional radioactivity was observed but not identified. [b] R = river sediment; P = pond sediment; A = aerobic; AN = anaerobic. [c] CNA = 2-chloro-4-nitroaniline. [d] Not analyzed.

al., 1963). Aminoniclosamide has also been shown to be formed on incubation with intestinal microflora of the rat in vitro under anaerobic conditions (Griffiths and Fucchini, 1979). Since it partitions relatively efficiently into dichloromethane and can be chromatographed by LC or GC (Table II), it should be possible to monitor for aminoniclosamide during field application of niclosamide. The rate of degradation of aminoniclosamide in static incubations appeared to be much slower than that of its parent compound (Figure 1). Half-lives of aminoniclosamide, estimated by using data from days 8 to 128, were 143 and 20 days for river and pond sediment, respectively.

The distribution of radioactivity among sediment, water, and CO_2 traps in respirometer flasks is shown in Table III (B). Radioactivity trapped by polyurethane foam plugs represented less than 1% of the quantity added to each flask and was not tabulated. Overall recovery of radioactivity averaged 89.8 ± 15.8% in aerobic flasks and 96.1 ± 9.1% in anaerobic incubations. After 93 days CO_2 traps contained 37.7% (average of three flasks) of the radioactivity added to flasks with aerobic river sediment compared to 9.0% for anerobic conditions. However, much lower levels of radioactivity were trapped from pond sediment. Approximately 5-fold less radioactivity was present in the water phase of aerobic pond sediment incubations than in water in aerobic river sediment [Table III (B)], possibly due to greater sorption of niclosamide to pond sediment. The lower CO_2 evolution from pond sediment may reflect slower mineralization of the ^{14}C-labeled chlorosalicylic acid ring due to strong adsorption.

Measurements of redox potential (E_H) of water and sediment in respirometer flasks (Table I) indicated that aerobic and anaerobic conditions were maintained during the study. However, E_H in water in anaerobic systems ranged from +124 to +214 mV, indicating that some O_2 was present. The relatively large proportion of radioactivity trapped as $^{14}CO_2$ from anaerobic incubations may therefore have been due to activity of aerobic as well as anaerobic microorganisms. Aminoniclosamide was the major degradation product detected in water and sediment extracts from respirometer flasks (Table IV). More aminoniclosamide was formed under anaerobic than aerobic conditions, especially during the first 64 days of incubation. Formation of aminoniclosamide appeared to be related to low redox potential since the greatest amounts were formed at −46 to −6 mV and in static incubation systems that had

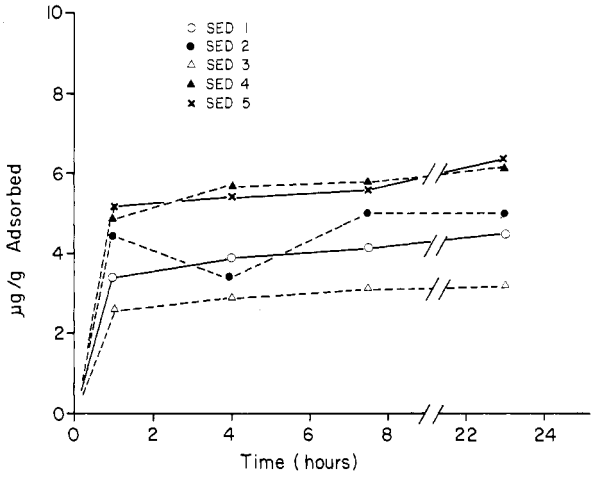

Figure 2. Sorption of [^{14}C]niclosamide (expressed as micrograms of niclosamide equivalents per gram of sediment) by five different sediments over a 23-h period.

an E_H of +354 to +384 mV but lesser amounts at an E_H of +450 mV (aerobic incubations).

CNA was also monitored in water and sediment extracts from respirometer flasks. The results (Table IV) are reported in micrograms of CNA rather than as a percentage of extractable radioactivity since this portion of the niclosamide molecule was not radiolabeled. CNA was detected in large quantity in 32-day incubations with somewhat greater amounts observed in anaerobic systems. The radiolabeled portion of the niclosamide molecule, 5-chlorosalicylic acid, was not observed in sediment or water extracts (<1% of extracted radioactivity). Since CNA was detected, hydrolysis of niclosamide must have taken place; however, the salicylic acid moiety appears to have been rapidly transformed or sorbed under the conditions of the experiment. Alternatively, transformation of the salicylic acid portion of the molecule may be required before hydrolysis occurs. The results of Schultz and Harman (1978) suggest that hydrolysis is not a major pathway of degradation of niclosamide in natural waters (without sediment) or in artificial sunlight.

Reextraction of sediments by refluxing with MeOH–water–concentrated NH_4OH (90:10:1) recovered additional radioactivity (Table III). TLC–autoradiography of dichloromethane extracts from this reflux step indicated only aminoniclosamide was present. Further extraction by refluxing with water (40 h) yielded additional radioactivity, most of which partitioned into dichloromethane and was chromatographed on reverse-phase TLC plates. These extracts also contained aminoniclosamide as well as another spot that cochromatographed with 5-chlorosalicylic acid. We concluded that the presence of the salicylic acid moiety in these extracts was likely to be due to hydrolysis of aminoniclosamide in hot water rather than extraction of 5-chlorosalicylic acid. The results also indicated that a reflux procedure with aqueous methanol may be superior to shaking for extraction of niclosamide from sediment.

Adsorption–Desorption Studies. Adsorption of niclosamide by sediment reached an equilibrium after 4–7.5 h of shaking (Figure 2). Soil–water partition coefficients [K_d and K_{oc} (K_d/organic carbon content)] were calculated from the ratio of micrograms per gram (dry weight) adsorbed to micrograms per milliliter in the supernatant for results from 7.5 h of shaking (Table V). Losses of niclosamide to test tube stoppers, to glass, or by centrifugation of undissolved material were less than 5% for 1–7.5-h samples, and no corrections to K_d values were made. The average K_{oc} value of 3111 ± 1552 was relatively close to

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.

ACKNOWLEDGMENT

We thank F. L. Meyer, U.S. Fish and Wildlife Service, La Crosse, WI, for his aid in providing [^{14}C]niclosamide and L. Sarna, Pesticide Research Laboratory, University of Manitoba, for GC–MS work.

LITERATURE CITED

Daniels, S. L.; Kempe, L. L.; Billy, T. J.; Beeton, A. M. *Tech. Rep.—Great Lakes Fish. Comm.* **1965**, *No. 9*, 1–18.
Duhn, B.; Maul, W.; Medenwald, H.; Patzsche, K.; Wegner, L. A. *Pfanzenschultz-Nachr.* **1963**, *16*, 1.
Forbes, M. A.; Wilson, B. P.; Greenhalgh, R.; Cochrane, W. P. *Bull. Environm. Contam. Toxicol.* **1975**, *13*, 141.
Griffiths, L. A.; Facchini, V. *Recent Dev. Mass Spectrom. Biochem. Med.* **1979**, *2*, 121.
Hamilton, S. E. *U.S., Fish Wildl. Serv., Rep.* **1974**, *FWS-LR-74-92.*
Kearney, P. C.; Konston, A. *J. Agric. Food Chem.* **1976**, *24*, 424.
Kenaga, E. E.; Goring, C. A. I. In "Aquatic Toxicology"; Eaton, J. G.; Parrish, P. R.; Hendricks, A. C., Eds.; American Society for Testing and Materials: Philadelphia, **1978**, *No. 707*, p 78.
Muir, D. C. G.; Grift, N. P. *Int. J. Environ. Anal. Chem.* **1980**, *8*, 1.
Schultz, D. P.; Harman, P. D. *Invest. Fish Control* **1978**, *No. 85*, 1–5.
Strufe, R.; Gonnert, R. *Z. Tropenmed. Parasitol.* **1967**, *18*, 193.
Wolfe, N. L.; Zepp, R. G.; Paris, D. F.; Baughman, G. L.; Hollis, R. C. *Environ. Sci. Technol.* **1977**, *11*, 1077.

Received for review February 1, 1982. Accepted July 27, 1982.

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.

0021-8561/82/1430-1032$01.25/0 © 1982 American Chemical Society