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Aerobic and Anaerobic Degradation of Aldicarb Sulfone in Soils

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[*S-methyl*-^{14}C]Aldicarb sulfone [2-methyl-2-(methylsulfonyl)proprionaldehyde *O*-(methylcarbamonyl)oxime] was incubated under aerobic and anaerobic conditions in surface and subsurface soils from Florida and Georgia. Evolution of $^{14}CO_2$, formation of metabolites, and amounts of extractable and nonextractable ^{14}C were measured in soils incubated with [^{14}C]aldicarb sulfone. Mineralization and disappearance of the carbamate varied greatly from soil to soil. Under aerobic conditions, half-lives in the surface soils from two Florida sites (Lake Hamilton and Oviedo) were shorter than in the corresponding subsurface soils. Aldicarb sulfone nitrile and aldicarb sulfone acid were the two major metabolites. In addition, a TLC polar product, aldicarb sulfone oxime, and three unidentified products were detected.

Aldicarb sulfone [2-methyl-2-(methylsulfonyl)propionaldehyde *O*-(methylcarbamoyl)oxime] and aldicarb sulfoxide [2-methyl-2-(methylsulfinyl)propionaldehyde *O*-(methylcarbamoyl)oxime] are the primary oxidation products of the pesticide aldicarb [2-methyl-2-(methylthio)propionaldehyde *O*-(methylcarbamoyl)oxime] in soils. Aldicarb is rapidly oxidized to aldicarb sulfoxide, which is subsequently oxidized to aldicarb sulfone. Both oxidation products have a toxicity similar to that of the parent aldicarb. Since aldicarb is rapidly degraded in soils (Bromilow et al., 1980; Coppedge et al., 1967; Smelt et al., 1978; Ou et al., 1985), the two oxidation products should contribute to the pesticidal activity. Aldicarb sulfone oxime was also detected in aldicarb treated soils (Bull et al., 1970; Ou et al., 1985). This indicated that aldicarb sulfone, similar to aldicarb and to aldicarb sulfoxide, underwent hydrolysis to the oxime. This should further degrade to the nitrile and eventually to CO_2.

Limited information is available on the degradation rates and half-lives of aldicarb sulfone in soils. Smelt et al. (1978) reported that half-lives under aerobic incubation at 15 °C varied greatly from soil to soil, ranging from 18 days in a clay loam to 154 days in a peaty sand. Disappearance of aldicarb sulfone in subsoil samples was considerably slower than in soil samples from corresponding surface horizons. Half-lives for aldicarb sulfone in soils incubated under anaerobic conditions were substantially shorter (Smelt et al., 1983).

This work was initiated to supplement an earlier study on aldicarb degradation (Ou et al., 1985). Mineralization and disappearance of aldicarb sulfone, and formation of metabolites in surface and subsurface soils collected from Florida and Georgia, were determined under both aerobic and anaerobic conditions.

MATERIALS AND METHODS

Soils. Surface and subsurface soils used in this investigation were the same as those used by Ou et al. (1985). Soil samples were collected from three locations: Lake Hamilton, FL (0–30 and 152–183 cm); Oviedo, FL (0–15 and 107–114 cm); Dougherty Plains, GA (Profile I = 0–27 and 27–57 cm, Profile II = 0–20 and 20–40 cm). Detailed descriptions of the sampling sites and selected properties of these soils have been reported previously (Ou et al., 1985).

Pesticides. Analytical grade aldicarb sulfone was supplied by USEPA (Research Triangle Park, NC). [*S-methyl*-^{14}C]aldicarb sulfone with a specific activity of 7.1

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Table I. ^{14}C Distribution for [^{14}C]Aldicarb Sulfone in Soils after 63 Days of Aerobic and Anaerobic Incubation

soil	depth, cm	% of applied ^{14}C			
		$^{14}CO_2$	extractable ^{14}C	nonextractable ^{14}C	recovery
		Aerobic Incubation			
Lake Hamilton	0–30	7.4	84.2	9.0	100.6
	152–183	1.7	93.8	2.7	98.2
Oviedo	0–15	52.4	34.5	9.6	96.5
	107–114	1.2	96.8	2.2	100.2
Dougherty	0–27	34.7	49.7	11.0	95.4
Plains I	27–57	11.6	72.9	7.8	92.3
Dougherty	0–20	27.6	57.1	11.7	96.4
Plains II	20–40	15.7	84.5	3.2	103.4
		Anaerobic Incubation			
Lake Hamilton	0–30	16.4	64.3	15.0	95.7
	152–183	1.0	97.0	1.6	99.6
Oviedo	0–15	44.4	43.9	10.8	99.1
	107–114	1.2	95.8	5.4	102.4
Dougherty	0–27	19.6	57.8	10.3	87.7
Plains I	27–57	23.5	65.7	5.2	94.4
Dougherty	0–20	3.8	84.5	7.2	95.5
Plains II	20–40	24.8	60.3	5.3	90.4

Table II. Metabolites of [^{14}C]Aldicarb Sulfone in Soils after 63 Days of Aerobic and Anaerobic Incubation

soil	depth, cm	% of applied ^{14}C				
		aldicarb sulfone	TLC[a] polar product	aldicarb sulfone[a] nitrile	aldicarb sulfone[a] acid	unknown I (R_f 0.30)
		Aerobic Incubation				
Lake Hamilton	0–30	41.2	18.0	0	25.0	0
	152–183	86.3	7.5	0	0	0
Oviedo	0–15	26.7	7.8	0	0	0
	107–114	44.4	30.0	0	0	22.4
Dougherty	0–27	41.4	1.4	0	3.5	3.4
Plains I	27–57	60.6	4.9	0	0	7.4
Dougherty	0–20	39.9	2.8	0	0	14.4
Plains II	20–40	66.6	3.7	0	0	14.2
		Anaerobic Incubation				
Lake Hamilton	0–30	16.6	22.0	0	25.7	0
	152–183	45.4	51.6	0	0	0
Oviedo	0–15	29.4	14.5	0	0	0
	107–114	55.9	15.9	0	24.0	0
Dougherty	0–27	36.4	19.3	0	2.1	0
Plains I	27–57	44.7	0	0	21.0	0
Dougherty	0–20	23.7	29.6	0	31.2	29.6
Plains II	20–40	14.5	12.8	5.2	20.9	12.8

[a] R_f values for TLC polar product, aldicarb sulfone nitrile, and aldicarb sulfone acid were 0.00, 0.60, and 0.36, respectively.

mCi/mM and standards for the three metabolites, aldicarb sulfone oxime, aldicarb sulfone nitrile, and aldicarb sulfone acid, were provided by Union Carbide (Research Triangle Park, NC). [^{14}C]Aldicarb sulfone was further purified by TLC using preparative silica gel G plates to better than 97% purity.

Chemicals. Acetone, acetonitrile, chloroform, ethyl acetate, ethyl alcohol, hexane, and methylene chloride were pesticide grade. Toluene, ethylene glycol monomethyl ether, PPO, and POPOP were scintillation grade. All other chemicals were analytical grade.

Treatment of Soils. $^{14}CO_2$ production from [^{14}C]aldicarb sulfone treated soils was measured with an experimental setup similar to that employed by Ou et al. (1985). The initial ^{14}C activity in soils was 1 μCi/100 g of soil, and the initial aldicarb sulfone concentration was 5 μg/g of soil. Half of the soil samples were incubated aerobically under the same conditions as employed for the mineralization of [^{14}C]aldicarb, while the remaining samples were incubated anaerobically. For anaerobic incubation, soils were placed in 250-mL glass bottles which were then filled with O_2-free N_2. All soils were incubated at 23 ± 2 °C. At the conclusion of the 63-day incubation period, 10-g subsamples were removed and transferred to 50-mL glass culture tubes with Teflon-lined caps for extraction.

The procedures for determination of extractable and nonextractable ^{14}C and metabolites of [^{14}C]aldicarb sulfone in the Lake Hamilton and Oviedo soils under aerobic conditions were the same as for [^{14}C]aldicarb (Ou et al., 1985). Gravimetric soil–water contents for the Lake Hamilton soils were held at 3 and 6%, and for the Oviedo soils were held at 3, 9, and 18%. The soil samples (10 g) in 50-mL glass culture tubes were incubated at 23 ± 2 °C for up to 42 days. On the 0th, 7th, 14th, 28th, and 42nd days, two tubes from each treatment were removed for extraction. All experiments were duplicated.

Extraction. Extraction of the soils and subsequent concentration of the solvent extracts were performed as described previously (Ou et al., 1985).

Thin-Layer Chromatography (TLC). TLC–autoradiography was employed to separate and to identify aldicarb sulfone and its metabolites. The mobile phase was composed of chloroform–hexane–ethyl acetate–ethyl alcohol (5:1:1:1). Kodak SB-5 X-ray films were used for the autoradiographic analysis. ^{14}C activity remaining at the original spotted areas was further separated by reversed-phase TLC by using acetonitrile–water (9:1) as the mobile phase, followed by autoradiography.

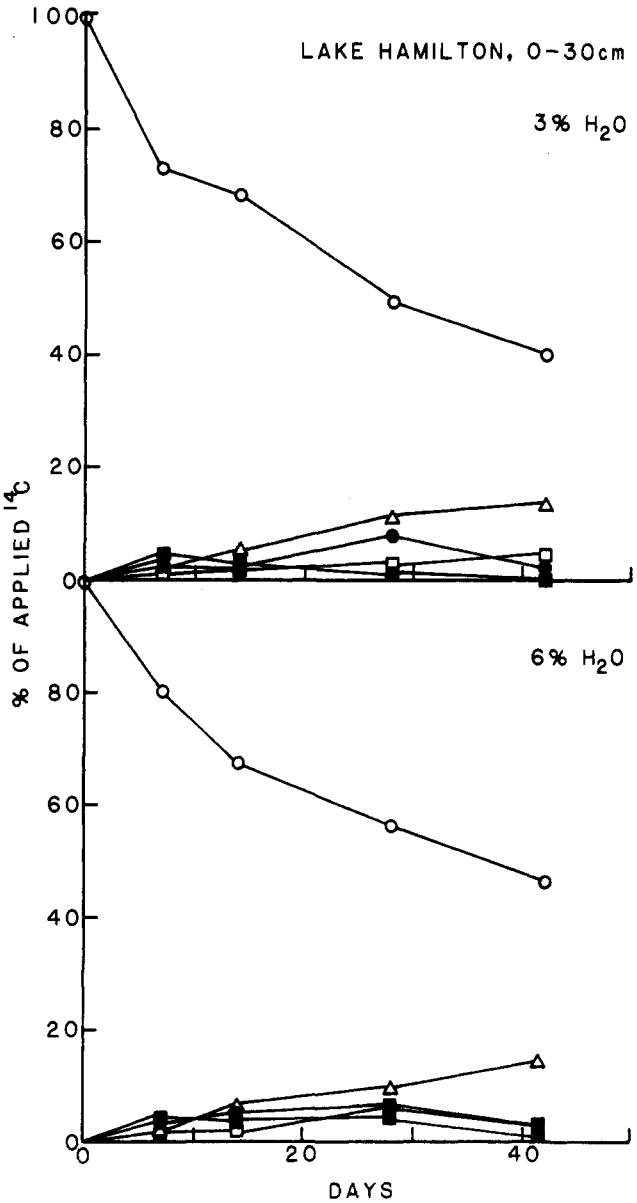

Figure 1. Distribution of aldicarb sulfone and its metabolites in Lake Hamilton surface and subsurface soils incubated for 42 days under aerobic conditions: (○), aldicarb sulfone; (●), aldicarb sulfone nitrile; (△), aldicarb sulfone acid; (□), TLC polar product; (■), others including aldicarb sulfone oxime and three unknowns.

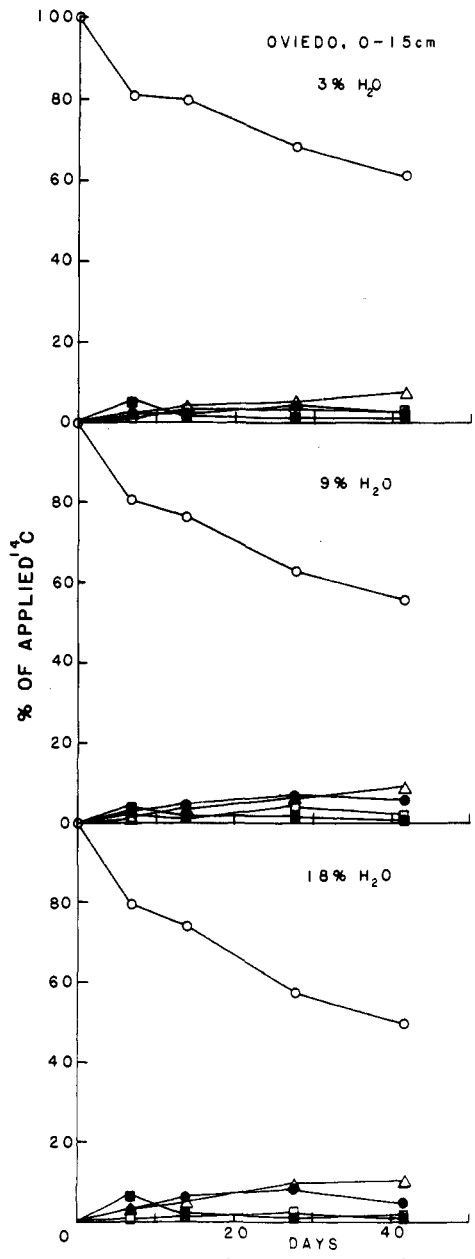

Figure 2. Distribution of aldicarb sulfone and its metabolites in Oviedo surface and subsurface Oviedo soils incubated for 42 days under aerobic conditions: (○), aldicarb sulfone; (●), aldicarb sulfone nitrile; (△), aldicarb sulfone acid; (□), TLC polar product; (■), others including aldicarb sulfone oxime and three unknowns.

RESULTS AND DISCUSSION

$^{14}CO_2$ production as well as the distribution of extractable and nonextractable ^{14}C after 63 days of aerobic and anaerobic incubation for the Lake Hamilton, Oviedo, and Dougherty Plains soils are summarized in Table I. Recoveries of ^{14}C in all samples ranged from 88 to 103%. Recovery of ^{14}C from [^{14}C]aldicarb in soils incubated under the same anaerobic conditions reported in a previous study (Ou et al., 1985) was also near 100%, although under more strictly anaerobic conditions (continuous flow of O_2-free N_2) due to higher volatilization losses less than 30% of the applied ^{14}C was recovered. This suggests that likewise for [^{14}C]aldicarb sulfone, under more strictly anaerobic conditions, a substantial fraction of the applied ^{14}C might not have been recovered due to the formation of volatile metabolite(s).

$^{14}CO_2$ production varied greatly from soil to soil. More $^{14}CO_2$ was evolved from surface soils incubated under aerobic conditions than from subsurface soils. Higher $^{14}CO_2$ evolution from the Dougherty Plains subsurface soils, which were shallower than the Lake Hamilton and Oviedo subsurface soils, could be due to higher microbial activity in these soils.

After 63 days of aerobic incubation the major ^{14}C component in the organic solvent extracts was associated with the parent chemical (Table II). In addition to aldicarb sulfone, a TLC polar product (R_f 0), aldicarb sulfone acid, and an unknown (R_f 0.30) were detected. Two initial degradation products, aldicarb sulfone oxime and aldicarb sulfone nitrile, were not detected in the aerobic soils. The TLC polar product and aldicarb sulfone acid were the two major metabolites in the anaerobic soils after 63 days of incubation. Reversed-phase TLC and autoradiographic analyses revealed that the TLC polar product was composed of only a single component. It was interesting to note that two and three components of TLC polar products were found in the aldicarb-treated Lake Hamilton and Oviedo soils, respectively (Ou et al., 1985).

Figures 1 and 2 show the distribution of [^{14}C]aldicarb sulfone and its metabolites in the Lake Hamilton and

Table III. First-Order Aldicarb Sulfone Disappearance Rate Constants (k_1) and Half-Lives ($t_{1/2}$) in Lake Hamilton and Oviedo Soils Incubated under Aerobic Conditions

gravimetric soil–water content, %	k_1, day^{-1}	$t_{1/2}$, days	r^2
	Lake Hamilton, 0–30 cm		
3	2.03×10^{-2}	34	0.962
6	1.74×10^{-2}	40	0.962
	Lake Hamilton, 152–183 cm		
3	3.89×10^{-3}	178	0.722
6	5.08×10^{-3}	136	0.829
	Oviedo, 0–15 cm		
3	1.06×10^{-2}	65	0.924
9	1.31×10^{-2}	53	0.951
18	1.61×10^{-2}	43	0.965
	Oviedo, 107–114 cm		
3	7.49×10^{-3}	93	0.899
9	5.64×10^{-3}	123	0.677
18	5.43×10^{-3}	128	0.873

Oviedo soils during 42 days of aerobic incubation. Aldicarb sulfone nitrile and aldicarb sulfone acid were the major metabolites. The hydrolysis product, aldicarb sulfone oxime, was detected only during the first 7 days of incubation. This suggests that aldicarb sulfone oxime was rapidly degraded to aldicarb sulfone nitrile, which was subsequently degraded to aldicarb sulfone acid. The TLC polar product was detected generally in trace amounts. In addition, three unknowns (R_f 0.11, 0.20, and 0.80) were detected in small amounts.

Aldicarb sulfone disappearance rate constants (k_1) and half-lives ($t_{1/2}$) for the two Florida soils incubated under aerobic conditions were estimated based on first-order kinetics (Table III). Half-lives for surface soils were shorter than for the corresponding subsurface soils. In a previous study (Ou et al., 1985), we reported that no aldicarb, aldicarb sulfoxide and aldicarb sulfone were detected in aldicarb-treated Lake Hamilton and Oviedo subsurface soils after 63 days of strict anaerobic incubation. It is conceivable that aldicarb sulfone in the same soils incubated under the same anaerobic conditions would have disappeared more rapidly than for samples incubated under aerobic conditions. Aldicarb sulfone and aldicarb sulfoxide disappeared much faster from soils incubated anaerobically than from soils incubated aerobically (Smelt et al., 1983).

Results of this study and a previous study (Ou et al., 1985) revealed that $t_{1/2}$ values for total toxic residue (TTR) in the aldicarb-treated subsurface soils from Lake Hamilton and Oviedo were considerably smaller than $t_{1/2}$ values for aldicarb sulfone in the same soils. The $t_{1/2}$ values for TTR and aldicarb sulfone disappearance from the surface soils showed either no difference or only slight differences. Our findings suggest that the main route of detoxification of TTR in aldicarb-treated subsurface soils under aerobic conditions is through the hydrolysis of aldicarb and its oxidation product aldicarb sulfoxide. The main route for the disappearance of TTR from surface soils is via hydrolysis of aldicarb sulfoxide and aldicarb sulfone.

Registry No. Aldicarb sulfone, 1646-88-4; aldicarb sulfone nitrile, 14668-29-2; aldicarb sulfone acid, 25841-43-4; aldicarb sulfone oxime, 14357-44-9.

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