

presented in Table II. The essential amino acid content is compared with standards set by FAO/WHO (1973), NAS/NRC (1980), whole egg (FAO, 1970), whole maize (Bressani and Mertz, 1958), and cowpea (Evans and Bandemer, 1967).

The calculated chemical score of the essential amino acids and limiting amino acid is presented in Table III.

DISCUSSION

Table IV, Ukwa seeds appear to be low in sulfur-containing amino acids, while it is very high in aromatic amino acids when compared to provisional FAO/WHO (1973) requirements. Ukwa seed will supply just about half the requirement of sulfur-containing amino acids, methionine and cysteine, recommended by FAO/WHO (1973). However, the sulfur-containing amino acid content is higher than for most pulses (Evans and Bandemer, 1967). All the other essential amino acids and especially both phenylalanine and tyrosine exceed FAO/WHO (1973) and NAS/NRC (1980) requirements.

The calculated chemical score of the amino acids also indicate that tryptophan is the only limiting amino acid in Ukwa seed with levels being lower than that for maize (Table IV).

Fortification of Ukwa seed protein with tryptophan will greatly improve the nutritive quality. The protein content of 19% of the defatted meal compared favorably with that of most pulses (22%), suggesting that this protein can be employed favorably in mixed diets (FAO, 1970). However, toxicological studies are under way to confirm its food value and nutritional quality before use in dietary formulations.

The protein content of Ukwa seed flour coupled with the excellent amino acid profile provides another source of high-quality plant protein as a Nigerian dietary staple. Finally, findings from toxicological studies in progress will further confirm this nutritional quality of Ukwa seed flour.

LITERATURE CITED

- AOAC (Association of Official Agricultural Chemists). "Official Methods of Analysis", 10th ed.; AOAC: Washington, DC, 1970.
- Bligh, E. G.; Dyer, W. J. *Can. J. Biochem. Physiol.* 1959, 37, 911.
- Bressani, R.; Mertz, E. C. *Cereal Chem.* 1958, 35, 227.
- Ellis, S.; Simpson, M. E. *J. Biol. Chem.* 1955, 220, 939.
- Evans, R. J.; S. L. *J. Agric. Food Chem.* 1967, 15, 439.
- FAO. "Amino Acid Contents of Foods and Biological Data on Proteins"; Food Policy and Food Science Service, Nutrition Division: Rome, Italy, 1970.
- FAO/WHO. *FAO Nutr. Meet. Rep. Ser.* 1973, No. 52.
- Makinde, M. A.; Hare, L. B.; Lachance, P. A. *Nutr. Rep. Int.* 1976, 15, 95.
- Mertz, E. C.; Villegas, E. Centro Intemational de Majoramento de Maize Trigo, Mexico, 1971, Research Bulletin No. 2.
- NAS/NRC. "Pattern of amino acid requirements", 9th ed.; National Academy of Sciences, National Research Council; Washington, DC, 1980.
- Nwaokorie, V. I. M.Sc. Thesis, University of Lagos, Lagos, Nigeria, 1983.
- Osborne, J. B. "The vegetable proteins", 2nd ed.; Langmans, Green and Co.; London, 1924.
- Piez, K. A.; Morris, L. *Anal. Biochem.* 1960, 1, 187.
- Sodek, L.; Wilson, C. M. *J. Agric. Food Chem.* 1971, 19, 1144.
- Spackman, D. H.; Stein, W. H.; Moore, S. *Anal. Chem.* 1958, 30, 1190.

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Aerobic and Anaerobic Degradation of Aldicarb in Soils

Li-Tse Ou,* K. Sture V. Edvardsson, and P. Suresh C. Rao

Mineralization of aldicarb to CO₂ as well as formation of various metabolites and extractable and nonextractable ¹⁴C were measured in [¹⁴C]aldicarb-treated surface and subsurface soils. Surface soil samples were incubated under aerobic conditions, and subsurface soil samples were incubated under aerobic and anaerobic conditions. Total aldicarb, aldicarb sulfoxide, and aldicarb sulfone residue (TTR = total toxic residue) disappearance rates were also determined in soils held under aerobic conditions. These data were used to compute half-lives for aldicarb mineralization and TTR disappearance in soil. TTR disappearance in soils held under strict anaerobic conditions, despite slow mineralization, was more rapid than under aerobic conditions. Mineralization rates for surface soil samples were generally higher than for subsurface soil samples. Metabolites detected included aldicarb sulfoxide, aldicarb sulfone, aldicarb sulfoxide oxime, aldicarb sulfoxide nitrile, aldicarb sulfone oxime, TLC polar products, and two unknowns. Aldicarb sulfone and its hydrolysis products were not detected in soils incubated under strict anaerobic conditions.

Aldicarb [2-methyl-2-(methylthio)propionaldehyde *O*-(methylcarbamoyl)oxime] is widely used for the control of soil insect and nematode pests. This chemical is applied to soil in the form of granules containing 10 or 15% a.i. (trade name Temik). The insecticide is degraded in soil principally through oxidation and hydrolysis. Aldicarb is rapidly oxidized to aldicarb sulfoxide, which, in turn, is slowly oxidized to aldicarb sulfone. Aldicarb sulfoxide and aldicarb sulfone have a toxicity similar to that of their parent compound, aldicarb (Anonymous, 1983). Richey

et al. (1977) used the term "total toxic residue" (TTR) to include the three toxic compounds. Aldicarb, aldicarb sulfoxide, and aldicarb sulfone also undergo hydrolysis to corresponding oximes that are further degraded to nitriles, acids, etc., and eventually to CO₂. Microbial degradation appears to be the main factor contributing to the disappearance of aldicarb in soils. Several species of common soil fungi were capable of oxidizing aldicarb to aldicarb sulfoxide (Jones, 1976). Microorganisms capable of utilizing aldicarb as a sole source of carbon and essential energy have not been reported.

Several studies reported that aldicarb disappeared from soils rapidly following first-order rate constants (*k*₁) of 0.078–0.80 day⁻¹ (Bromilow et al., 1980; Leistra et al., 1976;

* Soil Science Department, University of Florida, Gainesville, Florida 32611.

Table I. Selected Properties of Soils Used in This Study

soil	depth, cm	classification	soil-water content, g/100 g of soil	pH	organic C, %	mechanical analyses, %		
						sand	silt	clay
Lake Hamilton	0-30	sand	2.4	7.2	0.17	97	2	1
	152-183	sand	1.0	5.2	0.02	98	1	1
Oviedo	0-15	sand	14.2	6.7	1.04	96	2	2
	107-114	sand	20.4	6.5	0.52	93	3	4
Dougherty Plains I	0-27	loamy sand	18.7	6.0	0.66	77	19	4
	27-57	sandy loam	19.9	5.3	0.15	66	21	13
Dougherty Plains II	0-20	loamy sand	15.1	5.9	0.83	77	18	5
	20-40	Loamy sand	19.7	5.4	0.18	76	17	7

Smelt et al., 1978), which correspond to half-lives ($t_{1/2}$) of 1-9 days. Richey et al. (1977) reported that, after 63-75 days of aerobic incubation, TTR levels in soils ranged from 7.9 to 73.7% of initial concentrations. This would indicate that $t_{1/2}$ for TTR in some soils would be well below 63 days, while in other soils $t_{1/2}$ may be longer than 63 days. No information regarding the degradation rates for aldicarb and TTR in soils under anaerobic conditions has been reported. However, aldicarb sulfoxide and aldicarb sulfone were reported to degrade at faster rates under anaerobic incubation than under aerobic incubation (Smelt et al., 1983).

The degradation studies reported here were part of a larger effort to characterize the environmental fate and transport of aldicarb in Oviedo and Lake Hamilton, Florida, citrus soils and in Dougherty Plains, Georgia, soils. Results from laboratory and field studies on sorption and leaching of aldicarb in the Florida soils have been discussed by Hornsby et al. (1983) and Jones et al. (1983). In this study, results are reported for degradation and metabolism of aldicarb in surface soils held under aerobic conditions and in subsurface soils held under aerobic and anaerobic conditions. Specifically, we measured aldicarb mineralization to CO_2 as well as formation of various metabolites including the two oxidation products, hydrolysis and other products, and extractable and nonextractable ^{14}C . These data were used to determine aldicarb mineralization rates and the disappearance rates for TTR.

MATERIALS AND METHODS

Soils. Surface and subsurface soils used in this study were collected from three locations: Lake Hamilton, Florida; Oviedo, Florida; Dougherty Plains, Georgia. The two Florida sites were located in citrus groves in which aldicarb behavior was monitored during 1983 (Hornsby et al., 1983). The Dougherty Plains site was located near Albany, GA, and was covered by grass vegetation at the time of soil sampling. On this site, aldicarb persistence and leaching will be monitored during 1984. All three sites had no history of aldicarb application prior to collection of soil samples. Soils from the Florida and Georgia sites were collected in Feb 1983.

Selected properties of the soils used in this study are shown in Table I. The soils in the Oviedo grove are classified as Immokalee and Delray series, typical of the shallow "flatwoods" soils in Florida. The soils at the Georgia field site have been classified as Clarendon, Ardilla, and Tifton series. There is no published soil survey for the Lake Hamilton site. It is typical of Central Florida's "ridge" soils, which are deep, coarse-textured sandy soils.

Pesticides. Analytical-grade aldicarb, aldicarb sulfoxide, and aldicarb sulfone were provided by USEPA (Research Triangle Park, NC). S-Methyl- ^{14}C aldicarb with a specific activity of 6.06 mCi/mmol and five suspected metabolite standards (aldicarb oxime, aldicarb sulfoxide

oxime, aldicarb sulfoxide nitrile, aldicarb sulfone oxime, and aldicarb sulfone nitrile) were obtained from Union Carbide (Research Triangle Park, NC). ^{14}C aldicarb was further purified to better than 97% purity by TLC using preparative silica gel G plates.

Chemicals. Acetone, acetonitrile, methylene chloride, chloroform, hexane, ethyl acetate, and ethanol were pesticide grade. Toluene, 2-methoxyethanol, PPO, and POP were scintillation grade. All other chemicals were analytical grade.

Treatment of Soils. For measurement of $^{14}\text{CO}_2$ evolution, 100 g each of moist soils was placed in a 250-mL Erlenmeyer flask, and 1 μCi of ^{14}C aldicarb in acetone (1 $\mu\text{Ci}/\text{mL}$) was sprayed onto the soil surface. Subsequently sufficient nonlabeled aldicarb in acetone (1000 $\mu\text{g}/\text{mL}$) was applied to give a final concentration of 5 $\mu\text{g}/\text{g}$ of soil. After the solvent had evaporated in an aerated hood, the soils were thoroughly mixed. The flasks were connected to a Plexiglas manifold, and CO_2 -free moisture-saturated air (for aerobic incubation) or O_2 -free moisture-saturated N_2 (for anaerobic incubation) was passed over the soil at a rate of 10 mL min^{-1} flask $^{-1}$ as reported previously (Ou et al., 1978). The evolved ^{14}C activity was trapped by KOH solutions (0.1 N), and ^{14}C activity in KOH was determined by scintillation counting. The identity of ^{14}C activity trapped in KOH solutions in this experiment and subsequent experiments were verified to be $^{14}\text{CO}_2$ by acidifying with concentrated HCl to below pH 1 and by precipitating with 20% BaCl_2 . Less than 1% of ^{14}C activity remained in acidified KOH and in the supernatant after addition of BaCl_2 .

In addition to the incubation studies described above, aldicarb-treated subsurface soil samples (100 g each) were placed in 250-mL glass bottles with ground glass stoppers. A small stainless steel cup (3-mL capacity) containing 0.25 g of KOH pellets was suspended under the stopper. The bottles were purged with a stream of N_2 and were then stoppered firmly with the stoppers secured by tape. At weekly intervals the cups were removed and new cups with fresh KOH pellets were connected to the stoppers. $^{14}\text{CO}_2$ trapped in the KOH pellets was quantified by dissolving the pellets in 20 mL of distilled water and then assayed by scintillation counting. The flasks were weighed, and adequate amounts of distilled water were added to compensate for any water loss. The flasks were then purged with N_2 and resealed. At the end of the 63-day incubation period, 10 g from each soil was removed and was placed in a 50-mL glass culture tube with a Teflon-lined cap for extraction. All soils were incubated at $23 \pm 2^\circ\text{C}$.

Experiments to determine metabolites, and extractable and nonextractable ^{14}C , were conducted as follows: Five hundred grams (oven dry weight basis) each of air-dry Oviedo and Lake Hamilton soils was placed in a 2-L glass beaker, and ^{14}C aldicarb and nonlabeled aldicarb in acetone were applied to the surface of the soil to give a concentration of 4 $\mu\text{g}/\text{g}$ of soil and a radio dosage of 0.05

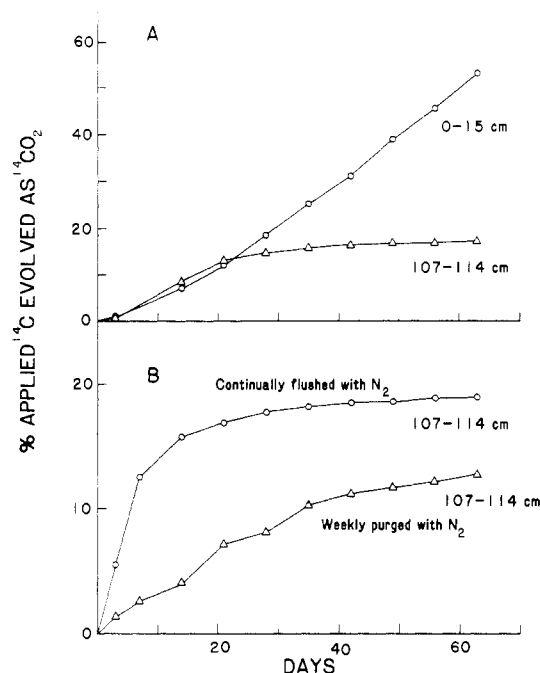


Figure 1. Percent $^{14}\text{CO}_2$ evolved from the Oviedo soils under aerobic (A) and anaerobic (B) conditions.

$\mu\text{Ci/g}$ of soil. After the solvent had evaporated, the soil was mixed thoroughly. Ten-gram samples of the aldicarb-treated soil were transferred to 50-mL glass culture tubes with Teflon-lined caps. Sufficient distilled water was added to each tube to bring the gravimetric soil-water content to 3, 6, or 12% for Lake Hamilton soils and to 3, 9, or 18% for Oviedo soils. After the samples were mixed, the tubes were incubated at $23 \pm 2^\circ\text{C}$ for 56 days. Once every 2 weeks, after the caps were removed, the weights of the tubes were checked for water loss, and distilled water was added if required. Two tubes from each treatment were removed for extraction on the 0th, 3rd, 7th, and 14th day and once every 2 weeks thereafter. All experiments were duplicated.

Extraction. Soils (10 g each) in culture tubes were extracted with an organic solvent mixture of methylene chloride-acetonitrile (3:1) with 2 drops of phosphoric acid/100 mL in a shaker for 2 h. After vacuum filtration, the soils were extracted with the same organic solvent mixture. The same extraction procedures were repeated 2 more times. The solvent extracts were combined and the ^{14}C activity in the extracts was determined by scintillation counting. The extracts were then concentrated to 2 mL. ^{14}C activity remaining in the extracted soils was combusted to $^{14}\text{CO}_2$ in a Packard Tri-Carb sample oxidizer as described previously by Ou et al. (1982).

TLC. Aldicarb and its metabolites in the concentrated organic solvent extracts were separated and analyzed by TLC-autoradiography. Aliquots (10–20 μL) of the extracts were spotted on commercial silica gel G plates. The plates were developed in chloroform-hexane-ethyl acetate-ethyl alcohol (5:1:1:1). Radioactive areas on the TLC plates were detected by placing Kodak SB-5 X-ray films on the plates. The radioactive areas on the plates were then scraped and transferred to scintillation vials, and the radioactivity was quantified by scintillation counting. ^{14}C activity remaining in the original spotted areas ($R_f = 0$) was further analyzed by reversed-phase TLC using acetonitrile- H_2O (90:10) as the eluting solvent, followed by autoradiography.

RESULTS AND DISCUSSION

Table II summarizes the mineralization rate constants (k_1) and half-lives ($t_{1/2}$) for [^{14}C]aldicarb as well as the

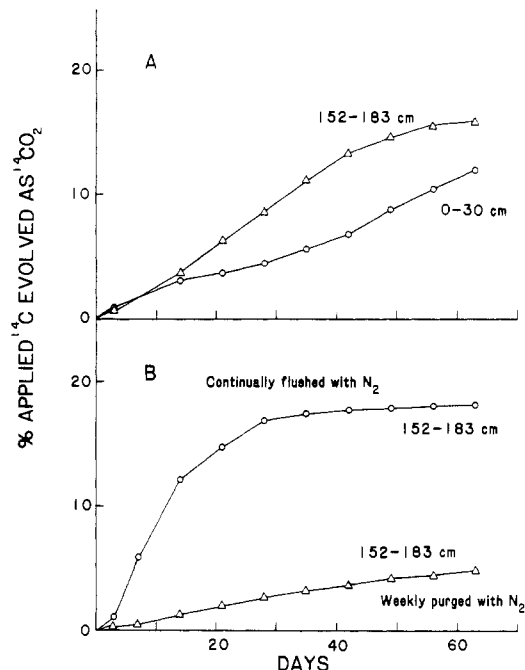


Figure 2. Percent $^{14}\text{CO}_2$ evolved from the Lake Hamilton soils under aerobic (A) and anaerobic (B) conditions.

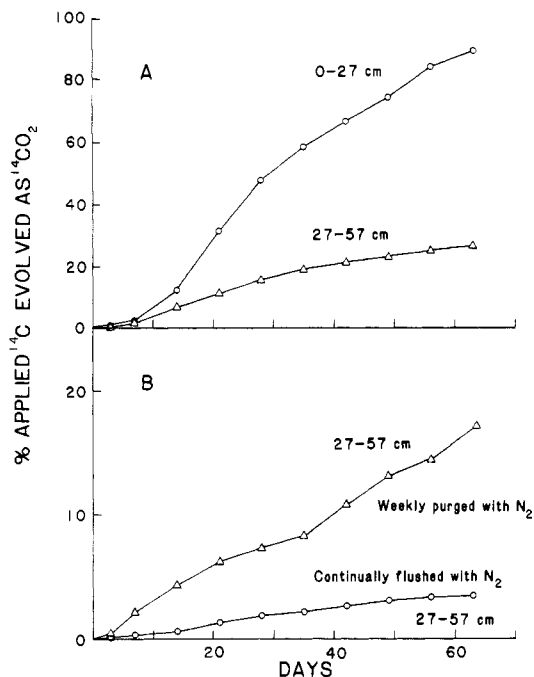


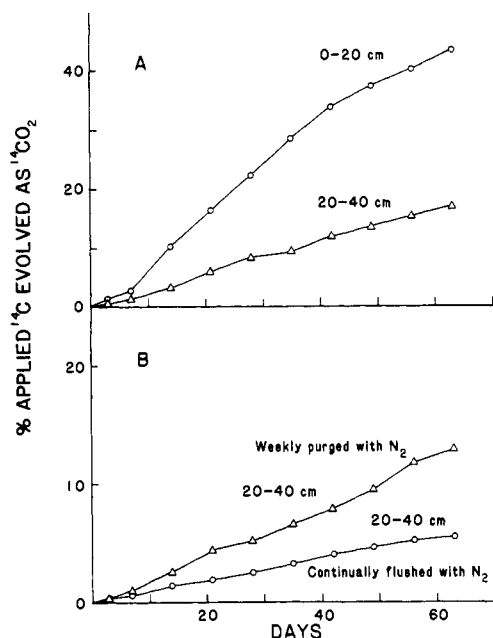
Figure 3. Percent $^{14}\text{CO}_2$ evolved from the Dougherty Plains I soils under aerobic (A) and anaerobic (B) conditions.

distribution of ^{14}C activity in soils incubated under aerobic and anaerobic conditions. Under aerobic incubation, $t_{1/2}$ values for the surface soils were substantially shorter than for the subsurface soils, with the exception of the Lake Hamilton soils in which the $t_{1/2}$ value for the surface soil was larger than that for the subsurface soil. More $^{14}\text{CO}_2$ was evolved from the surface soils than from the subsurface soils during 63 days of aerobic incubation with the exception of the Lake Hamilton soils (Figures 1–4). In Lake Hamilton soils, more $^{14}\text{CO}_2$ was evolved from the subsurface soil than from the surface soil. The amounts of applied [^{14}C]aldicarb evolved to $^{14}\text{CO}_2$ during the 63-day incubation period varied greatly, ranging from 12.0 to 89.1%. $^{14}\text{CO}_2$ evolution also varied greatly in other soil types as reported by Richey et al. (1977). Higher mineralization rates in surface soils could be due to a higher

Table II. Mineralization Rate Constants (k_1) and Half-Lives ($t_{1/2}$) of [^{14}C]Aldicarb and Recoveries of Applied ^{14}C Activity in Surface and Subsurface Soils after 63 Days of Aerobic and Anaerobic Incubation

soil	depth, cm	k_1 , day ⁻¹	$t_{1/2}$, days	r^2	% of applied ¹⁴ C			
					¹⁴ CO ₂	extractable	nonextractable	recovery
Aerobic Incubation								
Lake Hamilton	0-30	1.93×10^{-3}	361	0.978	12.0	76.7	4.1	92.8
	152-183	2.99×10^{-3}	232	0.978	15.8	76.8	2.4	95.0
Oviedo	0-15	1.17×10^{-2}	59	0.958	52.9	54.9	7.9	115.7
	107-114	2.97×10^{-3}	233	0.809	16.9	67.2	13.4	97.5
Dougherty	0-27	3.42×10^{-2}	20	0.960	89.1	5.1	15.3	109.5
Plains I	27-57	5.28×10^{-3}	131	0.983	26.7	70.7	5.1	102.5
Dougherty	0-20	9.58×10^{-3}	72	0.995	43.4	66.7	8.3	118.4
Plains II	20-40	3.04×10^{-3}	228	0.996	16.9	79.8	5.3	102.0
Anaerobic Incubation								
Lake Hamilton	152-183	3.11×10^{-3}	223	0.763	18.1	8.2	1.5	27.8 ^a
	152-183	8.09×10^{-4}	857	0.988	4.8	59.9	4.0	68.7 ^b
Oviedo	107-114	2.56×10^{-3}	271	0.639	18.9	5.6	5.0	29.5 ^a
	107-114	2.25×10^{-3}	308	0.926	12.6	48.7	7.5	68.8 ^b
Dougherty	27-57	6.13×10^{-4}	1130	0.988	3.5	41.9	15.0	60.4 ^a
Plains I	27-57	2.85×10^{-3}	243	0.990	17.2	79.3	6.4	102.9 ^b
Dougherty	20-40	9.12×10^{-4}	760	0.996	5.5	56.2	9.1	70.8 ^a
Plains II	20-40	2.20×10^{-3}	315	0.992	12.9	83.1	6.8	102.8 ^b

^a Continually flushed with O_2 -free N_2 . ^b Purged with O_2 -free N_2 at weakly intervals.

**Figure 4.** Percent $^{14}\text{CO}_2$ evolved from the Dougherty Plains II soils under aerobic (A) and anaerobic (B) conditions.

aerobic microbial activity. Total recoveries of ^{14}C activity from soils incubated under aerobic conditions varied from 92 to 118%. Generally, smaller amounts of extractable ^{14}C remained in soils in which greater amounts of $^{14}\text{CO}_2$ were produced. Moreover, the more [^{14}C]aldicarb was mineralized, the more nonextractable ^{14}C was formed. More nonextractable ^{14}C was formed in the surface soils than in the subsurface soils, with the exception of the Oviedo soils.

In contrast to the aerobic incubation, total recoveries of ^{14}C activity in subsurface soils incubated under strict anaerobic conditions (continuous flow of O_2 -free N_2) were substantially less than 100%, especially in Oviedo and Lake Hamilton soils. Only 29.5% and 27.8% of applied ^{14}C were recovered after 63 days in Oviedo and Lake Hamilton soils, respectively. Since aldicarb is nonvolatile (vapor pressure at 25°C , 1×10^{-6} mmHg), the unaccounted ^{14}C activity appears to be associated with volatile metabolites. Continuous flushing of soils with O_2 -free N_2 over soils would create a sufficiently anaerobic environment for the activity of anaerobic microorganisms. After 63 days

of strict anaerobic incubation, redox potentials in Oviedo, Lake Hamilton, and Dougherty Plains I and II subsurface soils were 24.2, 86.3, -10.6, and -10.0 mV, respectively. The Dougherty Plains subsoil samples were collected from shallower depths than were the Florida soils. Thus, the Dougherty Plains subsoil samples could possess a smaller anaerobic microbial population than the Oviedo and Lake Hamilton subsurface soils. As a result, more volatile products could form in Oviedo and Lake Hamilton soils. Efforts are being made to trap and to identify the chemical nature of the volatile ^{14}C products. Soils in bottles that were opened and refilled with N_2 once a week may not maintain sufficient anaerobiosis for the formation of the volatile products. In fact, all applied ^{14}C was recovered for Dougherty Plains soils (Table II).

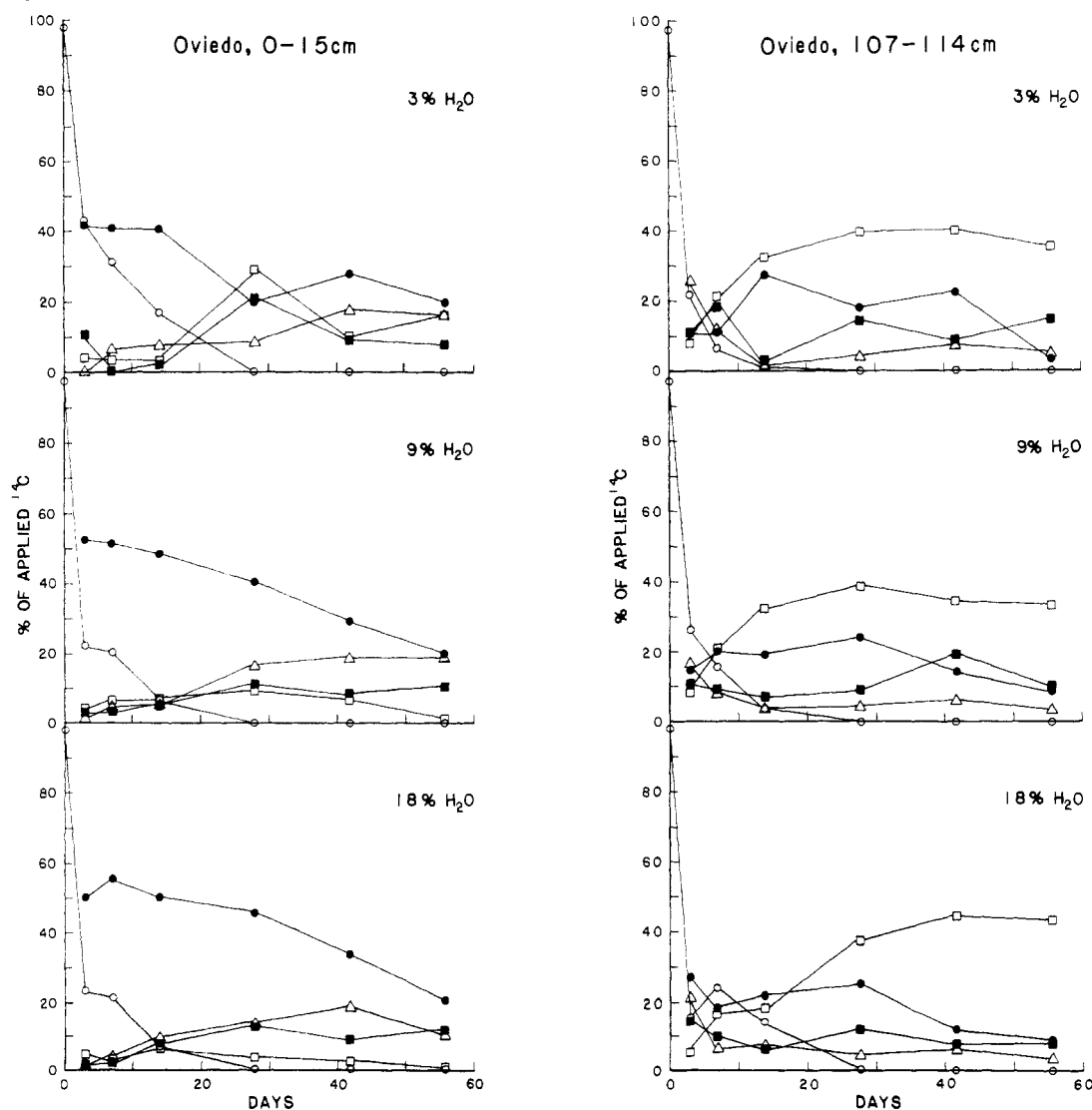
Larger amounts of $^{14}\text{CO}_2$ were evolved in Lake Hamilton and Oviedo subsurface soils under strict anaerobic conditions during 63 days of incubation than under less strict anaerobic conditions where the bottles were purged weekly with O_2 -free N_2 (Figures 1-4). In contrast, smaller amounts of $^{14}\text{CO}_2$ were produced in Dougherty Plains subsurface soils under strict anaerobic conditions. As a result, under strict anaerobic conditions the $t_{1/2}$ values for Lake Hamilton and Oviedo subsurface soils were smaller than those under less strict anaerobic conditions, whereas $t_{1/2}$ values for Dougherty Plains subsurface soils under strict anaerobic conditions were larger.

For Oviedo and Lake Hamilton subsurface soils that were maintained under aerobic or under strict anaerobic conditions, mineralization half-lives were not significantly different. However, $t_{1/2}$ values in anaerobic Dougherty Plains soils were significantly larger than those under aerobic conditions. Smaller $t_{1/2}$ values were observed for the subsurface soils purged with N_2 weekly.

The major identifiable constituent of TTR in Lake Hamilton and Oviedo soils after 63 days of aerobic incubation was aldicarb sulfone. Aldicarb sulfoxide and aldicarb sulfone were detected in Dougherty Plains soils, with aldicarb sulfoxide being the major metabolite (Table III). No aldicarb was detected in any soil sample at the end of the 63-day incubation. Coppedge et al. (1967) reported that 0.5, 0.8, and 6.0% of applied [^{35}S]aldicarb remained in Norwood silt clay loam, Houston clay, and Lakeland fine sand, respectively, in closed bottles after 63 days. They also reported that aldicarb sulfoxide was the major metabolite. Only TLC polar metabolites ($R_f = 0$)

Table III. Distribution of Aldicarb and Its Metabolites from Extractable ^{14}C in Surface and Subsurface Profile Soils after 63 Days of Incubation

		% of extractable ¹⁴ C					
soil	depth, cm	aldicarb sulfoxide	aldicarb sulfone	aldicarb sulfoxide oxime	aldicarb sulfoxide nitrile	TLC polar products (R _f = 0)	unknown (R _f = 0.21)
Aerobic Incubation							
Lake Hamilton	0-30	0	27	15	0	33	25
	152-183	0	0	18	0	29	53
Oviedo	0-15	0	39	0	0	27	24
	107-114	0	58	0	0	16	26
Dougherty Plains I	0-27	51	7	0	0	42	0
	27-57	51	16	16	0	17	0
Dougherty Plains II	0-20	33	39	17	0	11	0
	20-40	50	14	16	0	20	0
Strict Anaerobic Incubation							
Lake Hamilton	152-183	0	0	0	0	100	0
Oviedo	107-114	0	0	0	0	100	0
Dougherty Plains I	27-57	29	0	5	57	9	0
Dougherty Plains II	20-40	53	0	8	27	12	0

**Figure 5.** Distribution of aldicarb, its sulfoxide, its sulfone, TLC polar products ($R_f = 0$), and other products ($R_f > 0$) in surface and subsurface Oviedo soils incubated for 56 days under aerobic conditions. (○) Aldicarb; (●) aldicarb sulfoxide; (△) aldicarb sulfone; (□) TLC polar products ($R_f = 0$); (■) other products ($R_f > 0$) including aldicarb sulfoxide oxime, aldicarb sulfoxide nitrile, aldicarb sulfone oxime, and two unknowns.

were detected in Lake Hamilton and Oviedo subsurface soils incubated under strict anaerobic conditions. Aldicarb sulfoxide and aldicarb sulfoxide nitrile were the two key metabolites in the Dougherty Plains soils.

Table IV shows the distribution of TTR and hydrolysis and other products after 63 days of incubation. Sub-

stantial amounts of ^{14}C activity in Oviedo and Lake Hamilton soils were accumulated in the forms of hydrolysis and other products, while the major fraction of ^{14}C activity in Dougherty Plains soils was associated with TTR. As mentioned above, no TTRs were detected in the anaerobic Oviedo and Lake Hamilton subsurface soils. Thus,

Table IV. Distribution of TTR and Hydrolysis and Other Products in Surface and Subsurface Soils after 63 Days of Incubation

soil	depth, cm	% of applied ^{14}C					
		aerobic incubation			anaerobic incubation ^a		
		TTR ^b	hydrolysis and other products		TTR	hydrolysis and other products	
			TLC	others ^c		TLC	others
Lake Hamilton	0-30	20.3	25.6	30.8	ND ^d	ND	ND
	152-183	0	20.7	54.6	0	8.2	0
Oviedo	0-15	21.2	20.6	13.1	ND	ND	ND
	107-114	38.7	10.9	17.6	0	5.6	0
Dougherty Plains I	0-27	3.0	2.1	0	ND	ND	ND
	27-57	47.2	11.7	11.8	36.0	3.7	2.2
Dougherty Plains II	0-20	48.1	3.1	15.5	ND	ND	ND
	20-40	51.2	7.1	21.5	45.3	6.7	4.4

^a Continuous flow of O_2 -free N_2 . ^b TTR = total toxic residue defined as aldicarb, aldicarb sulfoxide, and aldicarb sulfone. ^c Others = oximes, nitriles, and unknowns. ^d Not determined.

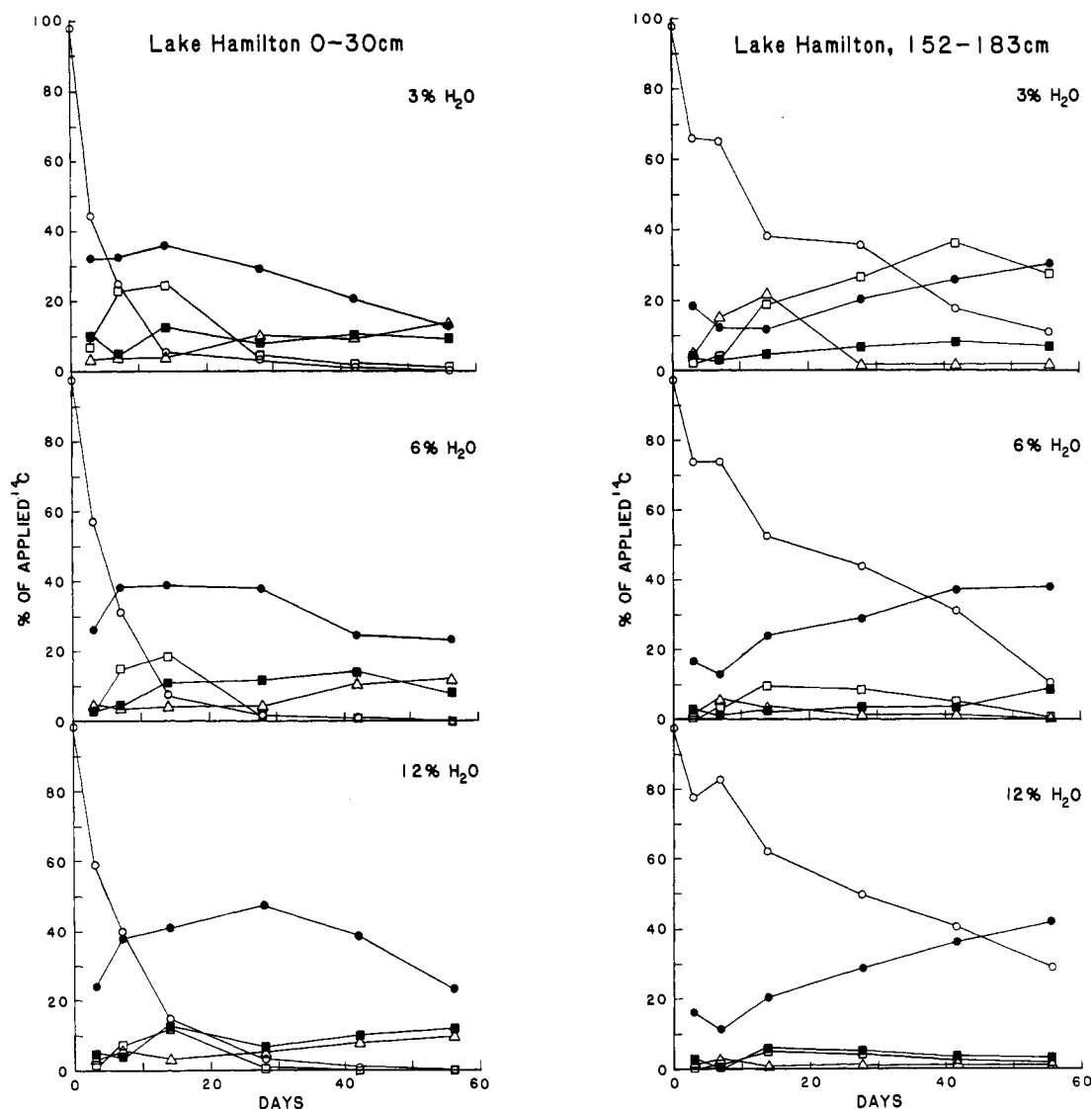


Figure 6. Distribution of aldicarb, its sulfoxide, its sulfone, TLC polar products ($R_f = 0$), and other products ($R_f > 0$) in surface and subsurface Lake Hamilton soils incubated for 56 days under aerobic conditions. (○) Aldicarb; (●) aldicarb sulfoxide; (Δ) aldicarb sulfone; (□) TLC polar products ($R_f = 0$); (■) other products ($R_f > 0$) including aldicarb sulfoxide oxime, aldicarb sulfoxide nitrile, aldicarb sulfone oxime, and two unknowns.

^{14}C aldicarb was degraded to $^{14}\text{CO}_2$, TLC polar products, and volatile metabolites.

TTR disappearance rate constants (k_1) and half-lives ($t_{1/2}$) in Lake Hamilton and Oviedo soils incubated aerobically are listed in Table V. TTR half-lives in Lake Hamilton surface soil were shorter than in the subsurface

soil, while the opposite was true for Oviedo soils. No apparent effect of soil-water content on TTR disappearance rates was observed, with the exception of Lake Hamilton subsurface soil in which $t_{1/2}$ increased as the soil-water content increased. In contrast to our findings, Bromilow et al. (1980) reported that oxidation and hy-

Table V. TTR Disappearance Rate Constants (k_1) and Half-Lives ($t_{1/2}$) in Lake Hamilton and Oviedo Soils under Aerobic Incubation^a

water content, %	k_1 , day ⁻¹	$t_{1/2}$, days	r^2
Lake Hamilton, 0-30 cm			
3	2.26×10^{-2}	31	0.895
6	1.99×10^{-2}	35	0.870
12	1.86×10^{-2}	37	0.945
Lake Hamilton, 152-183 cm			
3	1.54×10^{-2}	45	0.950
6	9.47×10^{-3}	73	0.962
12	5.40×10^{-3}	128	0.888
Oviedo, 0-15 cm			
3	1.67×10^{-2}	41	0.975
9	1.79×10^{-2}	39	0.952
18	1.71×10^{-2}	41	0.913
Oviedo, 107-114 cm			
3	3.34×10^{-2}	21	0.732
9	3.51×10^{-2}	20	0.873
18	3.44×10^{-2}	20	0.954

^aTTR = total toxic residue defined as aldicarb, aldicarb sulfoxide, and aldicarb sulfone.

hydrolysis rates of aldicarb in Woburn sandy loam soils containing 5% water were lower than in soils containing 10 and 15% water. Low oxidation and hydrolysis would indicate a slower TTR disappearance. The rapid disappearance of TTR in Oviedo subsurface soil, in spite of slow mineralization (Table II), was due to rapid formation of TLC polar products in conjunction with rapid disappearance of aldicarb and aldicarb sulfoxide (Figure 5). TTR disappearance rates were all higher than the corresponding mineralization rates. This discrepancy was principally due to the accumulation of nontoxic metabolites and the formation of nonextractable residues.

Higher aldicarb disappearance as well as more rapid oxidation to aldicarb sulfoxide in Oviedo soils in comparison to Lake Hamilton soils may be due to the higher organic matter content and thus a higher level of microbial activity (Figures 5 and 6). Aldicarb completely disappeared from Oviedo surface and subsurface soils in 28 days, while the nematicide persisted for 56 days in Lake Hamilton surface soil and longer in the subsurface soil. Higher aerobic microbial activity in surface soils appeared to account for more rapid oxidation to aldicarb sulfoxide than in subsurface soils. It was speculated that the decline of TLC polar products in Lake Hamilton surface soil after 14 days was due to further degradation to CO₂. TLC polar products in Oviedo subsurface soil persisted throughout the 56-day incubation period. Reversed-phase TLC-autoradiographic analysis revealed that three components (R_f = 0.08, 0.38, and 0.98) were detected in the TLC polar products of Oviedo soils, while two components (R_f = 0.08

and 0.38) were detected in Lake Hamilton soils.

Our results suggest certain conclusions regarding the degradation and metabolism of aldicarb in soils. Degradation patterns for aldicarb in soils under aerobic and strict anaerobic conditions appeared to be different. Under strict anaerobic conditions, a substantial fraction of applied aldicarb, in addition to the production of CO₂, could be lost due to the formation of volatile metabolites. As a result, TTR disappearance rates were higher than under aerobic conditions. Due to the limitation of available oxidants in strict anaerobic soils, aldicarb was oxidized only as far as aldicarb sulfoxide. Half-lives for TTR disappearance in Lake Hamilton surface soil and Oviedo soils ranged from 20 to 41 days. The TTR half-lives in Lake Hamilton subsurface soils were longer, especially at higher soil-water contents.

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LITERATURE CITED

- Anonymous. "Temik Aldicarb Pesticide—A Scientific Assessment"; Union Carbide: Research Triangle Park, NC, 1983; p 37.
- Bromilow, R. H.; Baker, R. J.; Freeman, M. A. H.; Gorog, K. *Pestic. Sci.* **1980**, *11*, 371.
- Coppedge, J. R.; Lindquist, D. A.; Bull, D. L.; Dorough, H. W. *J. Agric. Food Chem.* **1967**, *15*, 902.
- Hornsby, A. G.; Rao, P. S. C.; Nkedi-Kizza, P.; Wheeler, W. B.; Jones, R. L. "Proceeding of the Conference on Characterization and Monitoring of the Vadose (Unsaturated) Zone"; Nielsen, D. M., Curl, M., Eds.; National Water Well Association: Worthington, OH, 1983; p 936.
- Jones, A. S. *J. Agric. Food Chem.* **1976**, *24*, 115.
- Jones, R. L.; Rao, P. S. C.; Hornsby, A. G. "Proceeding of the Conference on Characterization and Monitoring of the Vadose (Unsaturated) Zone"; Nielsen, D. M., Curl, M., Eds.; National Water Well Association: Worthington, OH, 1983; p 959.
- Leistra, M.; Smelt, J. H.; Lexmond, T. M. *Pestic. Sci.* **1976**, *7*, 471.
- Ou, L.-T.; Gancarz, D. H.; Wheeler, W. B.; Rao, P. S. C.; Davidson, J. M. *J. Environ. Qual.* **1982**, *11*, 293.
- Ou, L.-T.; Rothwell, D. F.; Wheeler, W. B.; Davidson, J. M. *J. Environ. Qual.* **1978**, *7*, 241.
- Richey, F. A., Jr.; Bartley, W. J.; Sheets, K. P. *J. Agric. Food Chem.* **1977**, *25*, 47.
- Smelt, J. H.; Dekker, A.; Leistra, M.; Houx, N. W. H. *Pestic. Sci.* **1983**, *14*, 173.
- Smelt, J. H.; Leistra, M.; Houx, N. W. H.; Dekker, A. *Pestic. Sci.* **1978**, *9*, 293.

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