Fate and Carryover Properties of Temik Aldicarb Pesticide [2-Methyl-2-(methylthio)propionaldehyde *O*-(Methylcarbamoyl)oxime] in Soil

Nathan R. Andrawes,* William P. Bagley, and Richard A. Herrett[1]

The fate of *S*-methyl-^{14}C Temik aldicarb pesticide in soil was studied under field conditions over two growing seasons. Aldicarb applied at the rate of 3.4 kg/ha in-furrow resulted in ^{14}C-residues of 13.10 ± 0.24 ppm in soil planted to potatoes and 15.36 ± 2.40 ppm in fallow ground. Total ^{14}C-aldicarb equivalents declined to 0.07 ± 0.03 ppm in the cultivated soil and 0.05 ± 0.02 ppm in the fallow ground at 90 days after application. Maximum dissipation rates were associated with heavy rainfalls at various times during the season. Aldicarb sulfoxide [2-methyl-2-(methylsulfinyl)propionaldehyde *O*-(methylcarbamoyl)oxime], aldicarb sulfone [2-methyl-2-(methylsulfonyl)propionaldehyde *O*-(methylcarbamoyl)oxime], and water-soluble metabolites were the principal transformation products of aldicarb remaining in the soil. Volunteer crabgrass growing in the treated fallow ground accumulated 1.15 ppm of total ^{14}C-aldicarb equivalents at the end of the 90-day period. Tomato plants, transplanted and grown for 7 days in the fallow ground at 90 days following treatment, contained <0.01 to 0.06 ppm of total ^{14}C-residues. Fourteen days after in-furrow application of 1.12 kg/ha the residues in the soil were 0.59 ppm of total ^{14}C-aldicarb equivalents. They were diluted to 0.02 ppm by discing.

Temik aldicarb pesticide [2-methyl-2-(methylthio)propionaldehyde *O*-(methylcarbamoyl)oxime] is a soil pesticide which acts systemically to control a number of species of plant pests. In soil, the rate of aldicarb degradation was reported to be dependent on soil type, moisture level, and temperature (Bull, 1968; Bull *et al.*, 1970; Coppedge *et al.*, 1967). Dissipation of the parent compound occurs mainly through volatilization and by its oxidation to aldicarb sulfoxide [2-methyl-2-(methylsulfinyl)propionaldehyde *O*-(methylcarbamoyl)oxime]. This product degrades slowly through further oxidation to form aldicarb sulfone [2-methyl-2-(methylsulfonyl)propionaldehyde *O*-(methylcarbamoyl)oxime] and through hydrolysis to yield 2-methyl-2-(methylsulfinyl)propionaldehyde oxime (oxime sulfoxide). Further breakdown of the latter compound in the soil results in 2-methyl-2-(methylsulfinyl)propionitrile (nitrile sulfoxide).

This investigation is concerned with the residual properties of aldicarb and its metabolites in farm soil when applied under field conditions as a systemic pesticide.

GENERAL METHODS

Radiolabeled aldicarb (*S*-methyl-^{14}C) as well as nonlabeled standards of aldicarb degradation products were prepared and authenticated according to previously described procedures (Bartley *et al.*, 1966). After purification by column chromatography (Coppedge *et al.*, 1967) to achieve 98.5% radiopurity, the material was diluted with nonlabeled technical aldicarb to obtain the desired specific activity. Radioactivity was determined with a Model 722 Nuclear Chicago or a Beckman LS-150 liquid scintillation counter with quench corrections made according to the method described by the manufacturer of each instrument. Organic extracts were counted in toluene containing 4.0 g of 2,5-diphenyloxazole (PPO) and 50 mg of 1,4-bis(5-phenyloxazol-2-yl)benzene (POPOP) per l. of solution. Aqueous extracts were counted in a solution consisting of a mixture of xylene, dioxane, and ethylene glycol monoethyl ether (1:3:3) with 1% PPO, 0.5% POPOP, and 8.0% naphthalene (Bruno and Christian, 1961). Ten milliliters of the liquid scintillation mixture were used for counting of each sample.

The farm plots, located at Clayton, N.C., were of Norfolk sandy loam soil having a pH of 6.0. Soil samples, 2 × 20 cm cores, were taken in triplicate and the components of each sample were thoroughly mixed. A 2-g subsample was removed for moisture determination. The remainder of the sample (90 to 140 g) was weighed to the nearest tenth of a gram and then soaked in a water–ethanol mixture (1:1 v/v) for 1 hr with occasional shaking. After filtration the insoluble residues were washed with the water–ethanol solvent. Approximately 6 ml of the solvent were used to each 1 g of soil. Total radioactivity was determined by radioassay of two 0.5- to 1-ml aliquots. After removal of ethanol under vacuum, a volume of acetonitrile equal to that of the aqueous extract was added and the mixture shaken vigorously. This mixture was partitioned with an equal volume of chloroform. After separation of the organic and aqueous layers, the aqueous fraction was further extracted three times, each with an equal volume of chloroform. Acetonitrile–chloroform extracts were combined, dried over anhydrous sodium sulfate, and filtered. The radiocarbon content in the aqueous and organic phases was determined by liquid scintillation counting of 0.5- to 1-ml aliquots.

Radiolabeled components in the organic fraction were resolved by two-dimensional thin-layer chromatography using glass plates (20 × 20 cm) coated 0.2 mm thick with silica gel G (Brinkmann Instruments, Inc., Westbury, N.Y.). The chromatograms were first developed in ether–hexane (2:1 v/v) plus 20% acetone, and then after drying were developed in the second dimension in methylene chloride–acetonitrile (3:2 v/v). Radiolabeled degradation products were located on the chromatograms by radioautography utilizing Kodak NS-54T no-screen medical X-ray film. For quantitation, the radioactive zones were scraped from the plate into scintillation vials for direct counting. Results from two chromatograms were averaged to arrive at the percentage of each component in the organic fraction. Identification of various components was accomplished by cochromatography of a radiolabeled product with the standard in several solvent

Research and Development Department, Chemicals and Plastics, Union Carbide Corp., Clayton, N.C. 27520
[1] Present address: ICI America Inc., 151 South St., Stamford, Conn. 06904

Table I. Summary of Daily Temperature and Rainfall Records Taken during the 1967 and 1968 Growing Seasons

Periods[a]	Temperature, °C High	Temperature, °C Low	Rainfall, cm
	1967 Growing Season		
April 25–May 1	19.7	6.0	4.95
May 2–May 8	22.2	8.5	1.78
May 9–May 24	22.2	10.1	6.10
May 25–June 23	27.8	15.1	12.57
June 24–July 23	29.2	18.8	7.49
	1968 Growing Season		
April 29–May 5	24.5	9.9	0.9
May 6–May 12	23.4	9.1	1.9
May 13–May 30	23.2	12.3	8.0
May 31–July 7	28.6	17.5	13.7
July 8–July 28	30.0	19.9	3.8

[a] Correspond to various sampling times.

systems previously described (Coppedge *et al.*, 1967). Extraction and determination of ^{14}C-residues in plant materials were accomplished using previously described procedures (Andrawes *et al.*, 1971).

EXPERIMENTAL, RESULTS AND DISCUSSION

Fate of Aldicarb in Cultivated Soil. During the 1967 growing season, radiolabeled aldicarb (specific activity 29.3 μCi/mmol) was applied in-furrow at the rate 3.4 kg/ha (equivalent to 3 lb per acre) at the time of planting potatoes. An area 1.5 m wide by 12.2 m long was prepared and fertilizer (10-10-10) broadcast 8 cm to the side and 5 cm below the seed furrow. A furrow, approximately 10 cm wide and 10 cm deep, was opened in the prepared area and marks were placed at 30-cm intervals. Radiolabeled aldicarb (109 mg) in 10 ml of 80% acetone in water was applied to each 30-cm section, spreading the solution over a 5-cm width. Then potato seed pieces were placed in the treated sections 30 cm apart and covered with soil. Preparation of soil and planting of potatoes were completed on April 25, 1967. A summary of weather data on the farm during the growing season is shown in Table I. In addition to the normal rainfall, the land was irrigated as needed during the months of June and July by an overhead sprinkler.

Soil samples taken immediately after application of aldicarb showed an average initial residue level of 13.1 ± 0.24 ppm of total ^{14}C-aldicarb equivalents. Although the samples were taken from the estimated center of the treated 5-cm band, a considerable variation in the total radiocarbon contents was found among the three samples at each individual sampling time. Neither moisture content nor variation in sample weights could account for the difference in the total residues recovered. Soil moisture was almost identical among the samples and ranged from 6.5 to 7.5% (w/w) at various sampling times during the 90-day test period. The data shown in Table II indicate a rapid rate of dissipation of total ^{14}C-aldicarb equivalents during the first week after application and a slower rate thereafter. Only 26.5% (or 3.47 ± 1.30 ppm) of the initial residue was found in the soil after 7 days and 0.5% (or 0.07 ± 0.03 ppm) at the end of 90 days. Therefore, an estimated half-life of the total aldicarb residues would be shorter than 1 week. This short residue life in the soil could have resulted from a number of factors. Included in these was the uptake of radioactivity from the soil by the growing potato plants which contained 3.85%, 4.06%, and 3.03% of the applied radioactivity at 30, 60, and 90 days after treatment, respectively (Andrawes *et al.*, 1971).

Aldicarb-^{14}C used in this study was labeled on the oxime moiety so that both oxidative and hydrolytic degradation products could be detected. Chromatographic analysis of soil residues at various intervals after application is shown in Table II. Although the radiochemical purity of the applied aldicarb was 98.5%, samples taken within 30 min of application contained 12.7% of the recovered radioactivity as aldicarb sulfoxide and traces of aldicarb sulfone, oxime sulfoxide, and an unidentified residue remained at the origin of the thin-layer chromatograms. Recovery of known increments of ^{14}C-aldicarb from ethanol–water solution subjected to the entire analytical procedure was essentially quantitative. Therefore the products found in the soil immediately after treatment reflected rapid transformation of aldicarb catalyzed by the soil components rather than an artifact of the workup procedure.

Since the overall loss of radioactivity from the soil was so large during the first week and between 30 and 60 days after application, it is not possible to identify the source of this loss by an examination of the relative amounts of the different components remaining at these sampling periods. However, based on the products found in the soil between 7 and 30 days, during which the ^{14}C-residue level changed only slightly, it was concluded that oxidative reactions appeared to play the primary role in the transformation of aldicarb in the soil. Seven days after treatment, approximately 48% of the recovered radioactivity was as aldicarb sulfoxide. The relative amount of this product increased progressively with time and remained as a major constituent during the first month after treatment. Thereafter the relative percentage

Table II. Relative Concentration of Radiolabeled Components Present in the Soil after In-Furrow Application of *S*-Methyl-^{14}C Aldicarb during the Summer of 1967[a]

Transformation Products	% of Recovered Radioactivity at Indicated Days After Treatment[b] 0	7	14	30	60	90
Aldicarb	82.6	34.7	6.5	1.6	ND[c]	ND
Aldicarb sulfoxide	12.7	48.6	66.9	54.6	31.1	13.1
Aldicarb sulfone	1.4	4.4	11.6	24.7	50.0	41.5
Oxime sulfoxide	1.2	1.8	0.9	0.8	2.0	2.8
Nitrile sulfoxide	ND	0.8	1.3	0.6	1.2	0.9
Nitrile sulfone	ND	1.2	0.5	1.1	3.0	4.8
Origin of tlc	0.9	3.4	2.5	8.4	3.2	13.3
Water-solubles	1.2	5.0	9.8	8.2	9.6	23.6
Total ppm ± S.D.[d]	13.1 ± 0.24	3.47 ± 1.30	2.49 ± 1.56	2.65 ± 0.91	0.17 ± 0.07	0.07 ± 0.03

[a] Aldicarb applied at the rate of 3.4 kg/ha at the time of planting potatoes. [b] Based on triplicate samples and duplicate analyses for each sample. [c] ND—none detected. [d] Total parts per million of ^{14}C-aldicarb equivalents recovered ± standard deviation.

Table III. Relative Concentration of Radiolabeled Components Present in the Soil after In-Furrow Application of *S*-Methyl-^{14}C Aldicarb during the Summer of 1968[a]

Transformation Products	% of Recovered Radioactivity at Indicated Days After Treatment[b]					
	0	7	14	30	70	90
Aldicarb	81.5	42.1	3.2	ND[c]	ND	ND
Aldicarb sulfoxide	12.9	43.7	76.4	47.2	30.8	38.0
Aldicarb sulfone	1.4	2.0	7.4	33.4	10.9	7.3
Oxime sulfoxide	1.2	ND	0.6	3.2	2.0	2.7
Nitrile sulfoxide	ND	ND	ND	ND	ND	ND
Nitrile sulfone	ND	ND	ND	6.5	4.2	4.8
Origin of tlc	1.1	ND	2.3	1.8	13.7	7.7
Water-solubles	1.9	12.2	10.1	7.9	38.4	39.5
Total ppm ± S.D.[d]	15.36 ± 2.40	11.19 ± 2.75	10.79 ± 1.00	0.66 ± 0.19	0.16 ± 0.02	0.05 ± 0.02

[a] Aldicarb applied at the rate of 3.4 kg/ha to fallow ground. [b] Based on triplicate samples and duplicate analyses for each sample. [c] ND—none detected. [d] Total parts per million of ^{14}C-aldicarb equivalents recovered ± standard deviation.

of aldicarb sulfoxide decreased slowly and represented 13.1% of the recovered radioactivity at the end of 90 days. This decline in aldicarb sulfoxide components was coincident with a relative increase in aldicarb sulfone values. The latter product increased relatively from 4.4% of the recovered residues at 7 days to 41.5% at 90 days.

Accumulation of the hydrolytic products of aldicarb sulfoxide and aldicarb sulfone in the soil was a slow process. Only small quantities of oxime sulfoxide and its dehydration product, nitrile sulfoxide, were detected in the soil throughout the 90-day test period. No oxime sulfone [2-methyl-2-(methylsulfonyl)propionaldehyde oxime] was detected in any of the soil samples. However, small quantities of nitrile sulfone [2-methyl-2-(methylsulfonyl)propionitrile] were found in the soil which may have originated from nitrile sulfoxide by oxidation.

Fate of Aldicarb in Noncultivated Soil. A seedbed was prepared for this test as described in the previous experiment. On April 29, 1968, a furrow 60 cm long, 10 cm wide, and 1.5 cm deep was prepared within the center of the bed. An acetone–water solution containing 218 mg of radiolabeled aldicarb (specific activity 80 μCi/mmol) was distributed evenly in the furrow, which was then filled with soil. The amount of aldicarb corresponded to a rate of 3.4 kg/ha in-furrow application. Immediately after application, water was sprinkled on the surface of the soil to prevent erosion. The treated area was left subject to normal weathering conditions and was neither irrigated nor fertilized during the 90-day experimental period. A summary of daily temperature and rainfall taken during the test period is shown in Table I.

The initial residue level of 15.36 ± 2.40 ppm (Table III) approximated that previously observed in the cultivated soil study. In contrast to the previous experiment, the data in Table III show that dissipation of total ^{14}C-residues proceeded at a relatively slow rate during the first 2 weeks and a faster rate thereafter. A total of 10.79 ± 1 ppm of ^{14}C-aldicarb equivalents was found in the soil at the end of 14 days after application, which represents 70.2% of the applied material. After that time total ^{14}C-residues abruptly declined with time and reached a minimum of 0.05 ± 0.02 ppm at the end of the 90-day experimental period. This level was approximately the same as that found at the end of the 1967 cultivated-soil study.

Transformation products of aldicarb isolated from the soil at various intervals after application were qualitatively similar to those previously found in cultivated soil. Again aldicarb sulfoxide was the major transformation product detected (12.9% of the recovered radioactivity) in the initial samples (Table III). In addition, aldicarb sulfone and oxime sulfoxide were also detected in trace amounts in these samples. Transformation of aldicarb continued at a rapid rate, resulting in the dissipation of more than 50% of the parent compound by the end of 7 days. Under these conditions an estimated half-life of aldicarb in the soil would be less than 1 week.

Aldicarb sulfoxide constituted 43.7% of the total residues recovered at the end of 7 days after application. The early appearance of aldicarb sulfoxide and its high concentration indicated that its formation was a key reaction in the dissipation of the applied aldicarb. Its concentration relative to the total ^{14}C-residues increased to a maximum of 76.4% or a total of 8.24 ppm at 14 days, after which it declined to 0.31 ppm at 30 days. This loss was associated with a sharp decrease in the total ^{14}C-residues between the 14- and 30-day sampling times. By calculation, approximately 80% of the ^{14}C-materials disappearing from the soil during this period were derived from aldicarb sulfoxide. Aldicarb sulfoxide concentration decreased more gradually after the 30-day sampling and reached 0.02 ppm at the end of 90 days and comprised 38% of the recovered residues at this time. Aldicarb sulfone was detected in small concentrations throughout the test period. Its concentration reached a maximum of 0.8 ppm at 14 days and continued to decrease with time. Only 0.01 ppm remained at the end of 90 days.

Carryover Properties of Aldicarb Residues. Volunteer crabgrass growing in the treated fallow ground in the 1968 test was sampled for residue determination at the end of the 90-day test period. Analysis of three samples showed an average of 1.15 ppm of total ^{14}C-aldicarb equivalents. This level is low when compared to the 4.38 ppm of total ^{14}C-residues found in potato foliage grown in the cultivated soil test discussed above. However, this would be expected on account of the late germination of crabgrass seeds and the low level of aldicarb residues in the soil at that time.

As discussed earlier in this paper, a total of 0.05 ppm of ^{14}C-aldicarb equivalents remained in the soil of the 1968 test at the end of the 90-day season. To determine if these residues would accumulate in a following crop, 3-week-old greenhouse-grown tomato plants were transplanted into the soil. After 7 days they were individually harvested, weighed, and processed for analysis. Among four replicate plants analyzed, one sample contained 0.06 ppm of total ^{14}C-aldicarb equivalents, and the other three contained <0.01 ppm. Therefore, carryover of residues to a subsequent crop was negligible.

Effect of Discing on Soil Residues. The purpose of this test was to determine the level of residues in recently treated soil

should the land be disced for planting another crop or to replace a poor stand of the original crop. This was accomplished by applying ^{14}C-aldicarb (specific activity 101 μCi/mmol) at the rate of 1.12 kg/ha in-furrow as described in the earlier tests. No crops were planted in this area and the soil remained undisturbed for a period of 14 days. Three soil samples were then removed from the approximate center of the treated band, as previously described. Immediately after sampling, the treated area was disced with a farm tractor to a depth of 15 to 20 cm and another three samples were taken from the approximate center of the treated band. Analysis of soil samples taken before discing showed a total of 0.59 ppm of ^{14}C-aldicarb equivalents. After discing, the residues declined to 0.02 ppm of ^{14}C-aldicarb equivalents. This represents approximately 30-fold dilution of residues as a result of discing. After discing, the remaining residue level was lower than that used in tomato transplant experiment; therefore, it is expected that plants grown in the disced soil would not contain sufficient aldicarb residues to contaminate a subsequent crop.

CONCLUSIONS

Aldicarb was found to be a compound of short persistence when incorporated into the soil. Three months after its application to cultivated soil and fallow ground at the rate of 3.4 kg/ha no aldicarb and only 0.05 to 0.07 ppm of transformation products remained in the soil. From the data presented in this report, it is notable that the pattern of residue dissipation is not one of a uniform rate throughout the season. The sampling error at individual sampling times does not appear to account for the sharp decline observed at certain periods after treatment. Rainfall data showed that a very rapid decline occurred only during those periods showing 3 cm or more of rain at one time. For example, in the 1967 experiment 4.2 cm of rain fell the day after aldicarb was applied, which was associated with a reduction in the total ^{14}C-residues by 73.5%. In the 1968 experiment, almost 5 cm of rain fell over a 3-day period just before the 30-day sampling date; this sample contained 93.9% less residue than the 14-day sampling. Bull *et al.* (1970) have suggested that the greater the moisture the greater the loss of aldicarb equivalents from the soil through volatilization.

It appears that the initial rapid disappearance of aldicarb from the soil is attributable to its susceptibility to oxidation to form aldicarb sulfoxide. Substantial concentrations of this product were found in the soil during the first week after treatment and remained as a major constituent during the first month of the season. The rapid increase in the relative concentration of aldicarb sulfoxide was followed by a slow decline as the season progressed. In the meantime, an increase in the relative concentration of aldicarb sulfone was noted. This product became the major component of the total residues recovered in the latter part of the 90-day test period. Tentatively, it is suggested that the major pathway of aldicarb sulfoxide transformation is its oxidation to aldicarb sulfone. Oxime sulfoxide and nitrile sulfoxide remained at low levels throughout the season. This is in agreement with data reported for the fate of aldicarb in a greenhouse cultivated soil (Coppedge *et al.*, 1967).

The formation of aldicarb sulfoxide and aldicarb sulfone partially explains the pesticidal properties of aldicarb when applied to the soil. Plants grown in the treated soil absorb these toxicants and translocate them to the various parts of the plants, especially the newly-formed tissues and, therefore, protect the plants from injurious pests (Coppedge *et al.*, 1967). Residues of aldicarb and its transformation products do not persist in the soil after a 90-day growing season; thus, the likelihood of a residual carryover to the subsequent crops which might be grown in fields previously treated with aldicarb is very remote.

ACKNOWLEDGMENT

The authors are indebted to W. J. Bartley for the synthesis of radiolabeled materials and standards used in this study and to M. H. J. Weiden and W. H. Hensley for their technical assistance.

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Received for review November 9, 1970. Accepted February 11, 1971.