Persistence of Aldicarb in Soil Relative to the Carry-Over of Residues into Crops

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Crops of potatoes, alfalfa, mint, mustard greens, and radishes were planted in soil treated the previous year with aldicarb. Crop samples taken from 406 to 456 days after treatment with 3.4 kg of active ingredient (a.i.)/ha were found to have combined average residues of aldicarb or its sulfoxide and sulfone metabolites of 0.15 ppm. Crop samples taken at these intervals from plots treated at the rate of 15.0 kg of a.i./ha had combined average residues of 0.77 ppm. Potato foliage was found to have the highest residues of all crops analyzed and radish roots had the lowest. Only 4 of the 18 soil samples taken from the 3.4 kg of a.i./ha treated plots had detectable carry-over residues, 406 days after treatment, but crop samples taken from these plots contained measurable residues. All soil samples taken from the 15.0 kg of a.i./ha plots, 406 days after treatment, contained residues which averaged 0.06 ppm.

Aldicarb [2-methyl-2-(methylthio)propanal, *O*-[(methylamino)carbonyl]oxime] is marketed as 10 and 15% granular formulations under the trade name Temik. This broad-spectrum soil-applied pesticide is registered for use on a variety of agricultural crops. A single application provides season-long protection against a variety of insects, mites, and nematodes.

Since the introduction of aldicarb for agricultural use, many researchers have conducted laboratory and field studies to determine the degradation pathways of this pesticide in soils. Bull (1968) and Andrawes et al. (1971) demonstrated in field tests that aldicarb in soil oxidizes in 7–10 days to aldicarb sulfoxide and then more slowly to aldicarb sulfone. Both aldicarb sulfoxide and aldicarb sulfone are more toxic to crop pests than the parent compound. They also showed that the aldicarb and its sulfoxide and sulfone metabolites underwent hydrolysis and produced aldicarb oxime, aldicarb sulfoxide oxime, and aldicarb sulfone oxime. These oximes were produced in lesser amounts than the oxidative metabolites and exhibited little or no toxic effects to insects or mammals. Metcalf et al. (1966) found that the sulfoxide metabolite is responsible for the high systemic activity and long-term persistence of insecticidal activity after the application of aldicarb. This was further substantiated by Bull (1968) and Coppedge et al. (1967) in their work with cotton plants and by Maitlen et al. (1970), who evaluated residues of aldicarb and its sulfoxide and sulfone in apples and pears. Bull et al. (1970) and Andrawes et al. (1971) found that aldicarb and its metabolites in moist soil translocated upward relative to the capillary action of water and that the movement rate and distance increased with the increase in soil moisture. It was also demonstrated that the greatest loss of aldicarb and its metabolites from soil occurred through volatization from the soil surface. More recently, Richey et al. (1977) demonstrated in laboratory tests that the aldicarb molecule in soil underwent extensive degradation to small fragments, much of which was found to be CO_2. Researchers have also studied the degradation rate of aldicarb and its metabolites in soil. These studies have demonstrated a variety of results. In potting soil experiments, Coppedge et al. (1967) determined the half-life of aldicarb and its sulfoxide and sulfone to be about 14 days. In a 2-year field experiment in which aldicarb was applied to soil in potato fields at the rate of 3.4 kg (a.i./ha), Andrawes et al. (1971) found the half-lives to be about 30 days in 1967 experiments and from 7 to 14 days in 1968 experiments. It was also shown that the degradation rate was not linear and that there were residues in soil ranging from 0.05 to 0.07 ppm 90 days after the application. Woodham et al. (1973a,b) found no detectable residues of aldicarb or its sulfoxide or sulfone in soil 42 days after a 1.68 kg of a.i./ha application of aldicarb to cotton fields. Iwata et al. (1977) applied aldicarb to soil of orange groves at rates of 2.8, 5.6, 11.2, and 22.4 kg of a.i./ha. Residues found in soil 118 days after application were 0.03, 0.16, 0.20, and 0.42 ppm for these respective treatments. In this work, the degradation rate followed the first order of kinetics. Both Andrawes et al. (1971) and Woodham et al. (1973a,b) stated that on the basis of their results, residues of aldicarb and metabolites did not persist for long periods of time and would not carry over from one growing season to another. Andrawes et al. (1971) transplanted 3-week-old tomato plants into soil that had been treated with aldicarb 90 days earlier at the rate of 3.4 kg of a.i./ha. When the tomato plants were sampled 7 days after transplant, three of the four replicate samples contained no detectable residues (<0.01 ppm), but a fourth replicate sample contained residues of 0.06 ppm. Iwata et al. (1977) found detectable residues ranging from 0.02 to 0.03 ppm in orange pulp samples taken from a 22.4 kg of a.i./ha soil treatment, 193 days after application.

Our study was initiated to determine if aldicarb and its metabolites in soil would persist sufficiently to produce residues in crops grown in this soil the following year.

EXPERIMENTAL SECTION

Soil Treatment and Crop Planting Schedules. On May 14, 1979, a 15% granular formulation of aldicarb was applied to soil at the time of potato plant emergence at rates of 3.4 and 15.0 kg of a.i./ha. The aldicarb was applied in 2.5 cm wide bands, 10 cm to each side of the crowned row at a depth of 10–20 cm (potatoes are planted in a crowned row; therefore, the aldicarb would be about 5 cm below the surface of the true level of the field). Each application rate was replicated 5 times, and the plots were irrigated by sprinklers 2 h after the application of aldicarb.

The 1979 potato crop was left in the field so that the planting row could be relocated easily in 1980. In the spring of 1980, prior to planting, a potato digger was run down each row to lift out potato tubers and loosen the soil. Potatoes, alfalfa, mint, mustard greens, and radishes were planted on the dates shown in Table I, in the same rows that the 1979 potato crop had been planted. Alfalfa was grown from seed and from transplants to determine if there

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Table I. Crop Planting and Sampling Schedules

crop	planting date	sampling date	no. of days exposed to treated soil
potatoes (1979 crop)	5-14-79[a]	7-23-79	70
potatoes (1980 crop)	4-24-80	6-26-80	64
alfalfa (transplanted)	4-21-80	8-13-80	114
alfalfa (seeded)	5-2-80	8-13-80	103
mint	4-21-80	8-13-80	114
mustard	5-2-80	6-26-80	55
radishes	5-2-80	6-26-80	55

[a] This crop was planted prior to soil treatment (April 3, 1979).

would be a difference in residues absorbed by this crop based on the planting method.

The soil was Ritzville silt loam, mesic Calciorphidic hoploxroll, with an organic content of 1.6% and a pH of 6.2. The plots were not cultivated during the growing season and were sprinkler irrigated.

Soil Sampling. On Aug 29, 1979, 98 days after treatment, soil samples were taken with a tubular soil sampler from each of the five replicated plots of each treatment rate in the area where the aldicarb was applied. Ten soil cores, 2.5 cm in diameter by 20.0 cm deep, were taken from each plot replicate, composited, and placed in a plastic bag. The samples were taken to the laboratory and sifted through a flour sifter to remove small stones and large pieces of organic matter. The samples were then repackaged and stored in a freezer until analyzed.

In 1980, four plot replicates of each treatment were subdivided to provide space for all crops to be planted, thus creating nine replicated soil plots for each treatment rate. On June 24, 1980, 406 days after treatment, each of the nine replicated plots from each treatment rate were sampled and handled in the same manner as in 1979, except that the soil cores were subdivided into two parts. The top 5.0 cm and the bottom 15.0 cm of each of the 10 cores from each replicate were composited as separate samples.

Crop Sampling. Crop samples were taken from each of the replicated plots of each treatment rate on the dates shown in Table I. Samples of potato leaves, alfalfa, and mint were taken when the plants were mature enough to provide sufficient sample for analysis without damaging the plant. Potato leaves were picked from 20 plants in each replicate and composited, and 2 complete stems were taken from 10 plants in each replicate of mint and alfalfa and composited. Mustard greens and radishes were sampled when they reached maturity. Mustard greens were sampled by taking 3 leaves from 20 plants in each replicate and then compositing them into 1 sample. Ten radishes were pulled from each replicated plot and divided into tops and roots prior to being composited. All samples, except radish roots, were placed in plastic bags and frozen. While still frozen, the samples were finely chopped in a Buffalo chopper, repackaged, and stored in a freezer until analyzed. The radish roots were washed free of soil, chopped in the chopper, packaged in plastic bags, and stored in a freezer until analyzed.

Analytical Method. Soil and crop samples were analyzed by the procedure of Maitlen et al. (1969). The residues of aldicarb and its metabolites were oxidized and determined as one compound, aldicarb sulfone. The liquid chromatographic column used to separate the toxic aldicarb sulfone from its nontoxic aldicarb sulfone oxime was modified.

Aldicarb and its metabolites were extracted from soils by weighing 100 g of each sample into a 1-L Erlenmeyer flask. Four-hundred milliliters of a solvent mixture of 25% acetonitrile and 75% dichloromethane (DCM) and 2–4 drops of phosphoric acid were added, and the solutions were allowed to stand overnight in a refrigerator. The sample solutions were removed from the refrigerator, allowed to warm to room temperature, and then shaken on a wrist-action shaker for 1 h. Then they were filtered through a fluted filter paper into a conical beaker. A 200-mL portion of the extract solution, equivalent to 50 g of soil, was transferred to a 250-mL Erlenmeyer flask and evaporated to dryness in a 40–45 °C water bath with the aid of a gentle stream of air. The residue in the flask was then oxidized with a 1:1 mixture of hydrogen peroxide (30%) and glacial acetic acid by the procedure of Maitlen et al. (1969). After oxidation, the resultant DCM solution was evaporated to dryness and the residue dissolved in 10 mL of DCM. The aldicarb sulfone was separated from the nontoxic aldicarb degradation products by chromatography through a column of an absorbent mixture of Nuchar C-190N and silica gel (Baker's analyzed reagent grade, 60–200 mesh).

The absorbent mixture was prepared by first heating the silica gel in a 110–120 °C oven overnight, then adding 3% water (w/v), and tumbling end-over-end for 1 h to equilibrate. Next, Nuchar was added at a ratio of 2 g of Nuchar/25 g of silica gel and tumbled for 1 h. The absorbent mixture was stored in a refrigerator in a sealed glass container until needed. The chromatographic column (18-mm i.d. by 150 mm) was prepared by plugging the bottom of the column with a small amount of cotton and adding 5 g of sodium sulfate (Baker's analyzed reagent grade), 8 g of the mixed absorbent, and another small cotton plug. The column was packed with the aid of a slight vacuum from a water aspirator. The chromatography of the samples was also aided with this same vacuum.

The separation was accomplished in the following manner. The DCM solution was transferred onto the column with 25 mL of DCM, and when this solution was absorbed into the top of the column, 50 mL of DCM was added. After this solution had been absorbed into the top of the column, the collection flask was changed and the aldicarb sulfone eluted with 70 mL of a solvent mixture of 95% DCM and 5% methyl alcohol. This solution was then evaported to dryness, the residue dissolved in an appropriate amount of a 1:1 solvent mixture of hexane and acetone, and the solutions were stored in a refrigerator until analysis by gas chromatography (GC).

Crop samples were extracted by weighing 50 g of each chopped sample into a 1-L Erlenmeyer flask, and then 250 mL of the previously described solvent mixture of acetonitrile and DCM was added. These solutions were then handled in the same manner as the soil samples except that after shaking, the solutions were filtered through a funnel plugged with glass wool into a 250-mL separatory funnel. The extract solutions were slowly filtered through a funnel plugged with a small amount of cotton overlaid with sodium sulfate into a conical beaker. A 125-mL portion of the extract (equivalent to 25 g of sample) was transferred to a 250-mL flask and handled in the same manner previously described for soils.

Quantification of the aldicarb sulfone residues was accomplished with a Hewlett-Packard Model 5840A gas chromatograph equipped with a flame photometric de-

Table II. Recovery of Aldicarb and Its Sulfoxide and Sulfone Metabolites from Soil and Crops Separately Fortified with Various Amounts of the Compounds prior to Extraction[a]

sample	ppm added	% recovery found: aldicarb	aldicarb sulfoxide	aldicarb sulfone
soil	0.10	97	85	91
	0.05	101[b]	95[b]	114[b]
potato	1.00	106	104	105
leaves	0.50	92	92	111
	0.10	120	104	123
alfalfa	0.10	110[c]	89[c]	85[c]
	0.05	100[c]	87[c]	88[c]
mint	0.10	122[c]	101[c]	114[c]
foliage	0.05	105[c]	87[c]	88[c]
mustard	0.50	84	74	80
greens	0.10	113	97	104
radish	0.10	122	126	110
tops	0.05	127	118	82
radish	0.10	122	89	108
roots	0.05	108	192	119

[a] These results were determined by oxidizing the compounds and determining them as aldicarb sulfone. [b] These results are the average of three analyses. [c] These results are the averages of two analyses.

tector operated in a mode to detect sulfur compounds. The glass GC column (4.0-mm i.d. by 122 cm) was packed with Chromosorb G(HP) coated with 5% Carbowax 20M and operated at a temperature of 185 °C and a nitrogen flow rate of 60 mL/min. The detector was operated at a temperature of 190 °C, and the air, oxygen, and hydrogen flow rates were 50, 12, and 70 mL/min, respectively.

For determination of the efficiency of the analytical method, control samples of soil and crops were separately fortified with known amounts of aldicarb, aldicarb sulfoxide, and aldicarb sulfone prior to extraction and the percent recovery was determined (Table II).

RESULTS AND DISCUSSION

There were detectable residues of aldicarb and its sulfoxide and sulfone metabolites in all of the crops grown in soil treated the previous year with aldicarb (Table III). The data also show that as the application rate increased, the carry-over residues in crops increased. The average residue in all crops (1980) from the 3.4 kg of a.i./ha application was 0.15 ppm, while the average residue in crops from the 15.0 kg of a.i./ha application was 0.77 ppm. Of all the crops analyzed in 1980, potato leaves were found to have the highest residues, even though they were exposed to treated soil (Table I) for a shorter time than mint and alfalfa.

There was one exception to this. An alfalfa sample (seeded) from the 15.0 kg of a.i./ha plot (replicate 5) had a residue of 8.4 ppm—the highest of all residues found in any of the 1980 crop samples. This may be associated with the fact that the plot was located at the wet end of the field. It has been shown by Bull et al. (1970) and Andrawes et al. (1971) that aldicarb sulfoxide and sulfone move upward in soil relative to the moisture content of the soil. Residues found in crops of potato foliage, alfalfa (transplanted), and mint foliage from this same area of the field (15.0 kg of a.i./ha, replicate 5) also demonstrated this phenomenon. Soil samples from this plot also had the highest residue of any of the soil samples taken in 1980.

There were no detectable residues found in radish roots from the 3.4 kg of a.i./ha treated plots, and roots from the 15.0 kg of a.i./ha treated plots had proportionately lower residues than other crops from these plots. This is not surprising, since it has been demonstrated by George et al. (1975) in potato tubers and by Maitlen et al. (1970) in sugar beet roots and (unpublished data) in carrots that residues are low or nonexistent as compared to residues found in the leafy part of the plant. This crop had a short growing season, reducing its exposure time in treated soil.

While there were no detectable residues found in most soil samples from the 3.4 kg of a.i./ha treated plot in 1980 (Table IV), most of the crop samples grown in these plots contained residues. This suggests that plants grown in soils treated with systemic pesticides are better indicators of the presence of soil residues than a soil sample. The crop root system has the ability to draw from the total soil profile around it, whereas soil core samples examine only portions of that profile. When taking a 15.0–20.0 cm deep soil core, it is possible for the pesticide to be in only a portion of that core so that the remaining soil in the core acts as a dilutant. When pesticide residues in soil are low,

Table III. Residues (ppm) of Aldicarb and Its Sulfoxide and Sulfone Metabolites Found in Various Crops Grown in Aldicarb-Treated Soil[a]

replicate no.	crop: potato leaves[b] (70)[c]	potato leaves (408)	alfalfa (transplanted) (456)	alfalfa (seeded) (456)	mint foliage (408)	mustard greens (408)	radish tops (408)	radish roots (408)
			3.4 kg of a.i./ha Application					
1	7.65	0.52	0.14	0.16	0.02	ND[d]	0.08	ND
2	7.93	0.15	ND	0.04	0.02	0.03	0.07	ND
3	8.11	1.34	0.09	0.05	0.05	0.08	0.05	ND
4	8.74	1.27	0.24	0.14	0.10			
5	9.60	1.03	0.13	0.24	0.06			
av	8.41	0.66	0.12	0.13	0.05	0.04	0.07	ND
			15.0 kg of a.i./ha Application					
1	19.30	0.69	0.89	0.89	0.64	ND	0.27	0.04
2	14.90	1.10	0.34	1.47	0.92	0.26	0.27	0.05
3	20.80	1.12	0.43	0.26	0.37	0.40	0.18	0.03
4	19.40	0.50	0.76	0.61	0.23			
5	22.60	1.96	1.37	8.37	1.55			
av	19.40	1.07	0.76	2.32	0.74	0.22	0.24	0.04

[a] Residues in this table were determined by oxidizing the aldicarb, aldicarb sulfoxide, and aldicarb sulfone and then determining them as one combined compound, aldicarb sulfone. [b] These samples are from the crop year 1979. All others are from the crop year 1980. [c] The numbers in parentheses designate the interval in days between treatment and sampling. [d] ND (none detected) means that these residues were below the lower limit of reliable detection for these samples: <5.0 ng/aliquot analyzed or <0.02 ppm.

Table IV. Residues (ppm) of Aldicarb and Its Sulfoxide and Sulfone Metabolites Found in Soil[a]

treatment rate, kg of a.i./ha	replicate no.	sampling year: 1979, 0-20-cm depth (98)[b]	1980, 0-5-cm depth (406)	1980, 5-20-cm depth (406)
3.4	1	0.06	0.04	ND[c]
	2	0.04	ND	ND
	3	0.04	ND	ND
	4	0.04	ND	ND
	5	0.14	0.03	ND
	6		ND	ND
	7		ND	ND
	8		ND	ND
	9		0.03	0.03
	av	0.06	0.01	0.003
15.0	1	0.14	0.04	0.06
	2	0.14	0.03	0.07
	3	0.13	0.05	0.07
	4	0.13	0.02	0.10
	5	0.21	0.02	0.05
	6		0.03	0.06
	7		0.04	0.03
	8		0.02	0.04
	9		0.05	0.21
	av	0.15	0.03	0.08

[a] Residues in this table were determined by oxidizing the aldicarb, aldicarb sulfoxide, and aldicarb sulfone and then determining them as one combined compound, aldicarb sulfone. [b] The numbers in parentheses designate the interval in days between treatment and sampling. [c] ND (none detected) means that these residues were below the lower limit of reliable detection for these samples: <5.0 ng/aliquot analyzed or <0.01 ppm.

this diluting effect could produce a soil sample in which residues are below the lower limit of detection by the analytical method used for analysis.

In 1980, the samples were taken at two depths to determine if aldicarb or sulfoxide and sulfone residues were greater in the top 5.0 cm of the soil or at lower depths. The results of this experiment (Table IV) were inconclusive. Soil samples from the 15.0 kg of a.i./ha plots had greater residues in the lower 15.0-cm portion of the core sample, but in the 3.4 kg of a.i./ha plots, three of the nine samples from the top 5.0 cm had detectable residues. In the lower 15.0 cm of the core, only one of the nine samples was found to have residues.

Soil samples probably should have been taken from greater depths, as researchers do not entirely agree on the degree of movement of aldicarb and its metabolites in soil. Bull et al. (1970) in laboratory tests demonstrated that residues moved upward by capillary action proportional to the increase of soil moisture, but in field tests, he found that residues moved up and down (leaching) with more of the residue being found below the area of application. Woodham et al. (1973a,b) found that there was little lateral movement of residues in soil in irrigated and nonirrigated cotton fields and stated that water would not be a factor to any appreciable movement of aldicarb or its metabolites to adjacent untreated areas. Woodham et al. (1973a,b) did find residues in weeds and grasses taken from untreated areas 0.9–4.0 m from irrigated and nonirrigated fields treated with aldicarb.

For confirmation that the residues found in crops and soil were aldicarb sulfone, the extraction p-value technique of Beroza and Bowman (1965) was used. The aldicarb sulfone was partitioned between 20 mL of water and 20 mL of a solvent mixture of 70% DCM and 30% hexane, producing a p value of 0.74. The p values showed that residues in soil and crops were aldicarb sulfone. Also, in the method of Maitlen et al. (1968), it was demonstrated that aldicarb sulfone could be separated from the other degradation products of aldicarb as identified by Metcalf et al. (1966) with a liquid chromatography column. This technique was used in this work. The chromatography column used in this work was different than the one described in the procedure of Maitlen et al. (1968), but it was determined that this new column would provide the same separations and was more reliable. The variation in different batches of Florisil did not always provide the same separation and constantly had to be calibrated. This was not the case with the silica gel–Nuchar column used in this work. Furthermore, the analysis of control samples of soil and crops taken from check plots within the field from which the residue samples were taken showed that these samples contained no interfering compounds with the same GC retention time as aldicarb sulfone.

This work has demonstrated that aldicarb did persist sufficiently to produce carry-over residues in these crops grown in this soil the following year. Insect populations of Colorado potato beetle, *Leptinotarsa decemlineata* (Say), and green peach aphid, *Myzus persicae* (Sulz), were monitored during the 1980 crop year. This efficacy study (unpublished experiments) showed that there was no economic control of these insects from residues found in any of these crops.

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