Persistence in Soil and Losses in Runoff of Soil-Incorporated Carbaryl in a Small Watershed

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Carbaryl (1-naphthyl methylcarbamate) granules were banded into corn seed furrows in a 0.79-ha watershed at a rate of 5.03 kg/ha active ingredient. Persistence in soil was measured by sampling at ten locations in the watershed on seven occasions throughout the crop season. The potential of the treatment for contamination of nontarget areas was assessed by measuring carbaryl residues in postapplication runoff waters and sediments. The disappearance of carbaryl from soil did not conform to a first-order reaction, but 95% had disappeared in 135 days. The pesticide remained stable in the soil for 25 to more than 116 days at different points in the field, then decayed rapidly. These lag periods indicated that carbaryl degradation was primarily microbiological. Of the 4 kg of carbaryl applied to the field, only 5.77 g was lost during the season in runoff water and sediments. Over 90% of this loss occurred in a single rainfall 19 days after application. About 75% of the seasonal loss was contained in water and 25% in sediment. Carbaryl was less persistent and produced smaller losses in runoff than carbofuran applied to the same field 2 years earlier.

Although carbaryl (1-naphthyl methylcarbamate) was registered for use as a soil insecticide until 1971, studies of its persistence and fate in soil have been limited in scope and contradictory in conclusions. In one widely cited experiment, Johnson and Stansbury (1965) reported the half-life of carbaryl in soil as approximately 8 days, as determined by colorimetric analysis. The pesticide was incorporated into a single sandy loam soil and residues below application depth were not measured. Such residues could have been appreciable since carbaryl does move in soil (Helling et al., 1971). By contrast, Kazano et al. (1972), in laboratory experiments, found only 2.2–37.4% evolution of $^{14}CO_2$ after incubating carbonyl-labeled carbaryl with five moist Japanese rice paddy soils for 32 days at 25°. The data suggested that carbaryl persisted in these soils considerably longer than the previously reported 8-day half-life. Since even foliar applications of carbaryl result in soil residues (Guseinov, 1970; Ivanova and Molozhanova, 1973), firm information is needed on the persistence in soil of this widely used insecticide under field conditions.

The investigation described here was conducted on the same field and with the same management practices used 2 years previously with carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate), another important methylcarbamate insecticide (Caro et al., 1973a). The results permit a comparison of the field behavior of the two pesticides.

EXPERIMENTAL SECTION

Watershed. The treated field was a small watershed, designated as No. 118, at the U. S. Department of Agriculture North Appalachian Experimental Watershed at Coshocton, Ohio. The 0.79-ha field was fan-shaped, with an average slope of 9.6%. The Coshocton (Aquultic Hapludalf) silt loam soil, with an average pH of 5.20, contained 21% sand, 63% silt, 16% clay, and 1.7% organic matter, and had 10 mequiv/100 g of cation exchange capacity. Automatic equipment for collecting and measuring runoff was installed at the concrete discharge flume at the foot of the slope (Harrold et al., 1967).

Treatment. During the spring of 1973, the seedbed was prepared by plowing, disking, and harrowing. On May 18,

20.0 kg of 20%-active-ingredient granular carbaryl, equivalent to 5.03 kg/ha, was applied 5-cm deep across the watershed in rows 1 m apart simultaneously with corn (Zea mays L.) seeding. The granules were fed by tube from the pesticide box of a conventional two-row corn planter through the boot and into the shoe. A preemergence application of 2.2 kg/ha of atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-S-triazine) was sprayed on the soil surface for weed control.

Sampling Program. Soil samples were taken on the day of carbaryl application and 5, 12, 25, 39, 62, and 116 days after application. The soil was sampled each time at ten locations distributed across the watershed in a bowling-pin arrangement. One sample was taken from the corn row 27 m up the slope from the discharge flume, two samples from the row 50 m up the slope, three from the row 73 m up, and four from the row 96 m up.

The soil sampling technique, which was designed to minimize variability among samples, has been described by Caro et al. (1973a). Briefly, a 30 cm × 30 cm area centered over the corn row was excavated at each sampling point deep enough (20–30 cm) to ensure collection of all the pesticide within the area. The excavated soil was weighed and uniformly subdivided at the site to obtain a small analytical sample. Successive samplings at each point were made 30–60 cm further along the row than the previous excavation. The technique permitted expression of analytical results on a weight per area (milligram/square meter) basis. Since the insecticide was concentrated under a small area of soil close to the corn rows, this concentration was higher than that expected from the application rate of 5.03 kg/ha, which was calculated on a total field area basis; the application rate corresponded to an initial sample concentration of 1705 mg/m².

In each runoff occurrence, samples of runoff water and suspended solids were automatically pumped into gallon jugs at the discharge flume (Harrold et al., 1967). Solids were later separated by centrifugation and analyzed separately. Water samples were acidified before storage to stabilize the dissolved carbaryl. A single representative sample of runoff (water and sediment) was also collected in a 30-gal can below the flume, from which an aliquot was taken for later analysis.

Analytical Methods. As soon as possible after collection, a 200-g sample of soil was placed into a 1-quart wide-mouth jar and shaken on a mechanical reciprocating shaker (Eberbach variable-speed box type, or equivalent) with 500 ml of acetone–95% ethanol–water (1:1:1) for 30 min at room temperature. The sealed jar also was shaken

Table I. Carbaryl Residues in Watershed No. 118 Coshocton Silt Loam Soil Samples

Days after appln	Carbaryl content, mg/m², at sampling location no.[a]										Av content, mg/m²
	1	2	3	4	5	6	7	8	9	10	
0	1812	1450	1346	1473	1085	1690	1298	1873	1681	2086	1579
5	1941	1510	1751	1462	1918	1386	2042	2173	1432	1542	1716
25	1449	1412	1214	1689	2224	1907	1685	1564*	1753	1196*	1609
39	2685*	1803	998*	2096	1481	1837	1352	325	1439	178	1419
62	261	1164*	441	1540*	943*	926*	1941	268	1280*	327	909
116	78	579	0	122	56	13	1635	0	49	6	254

[a] An asterisk designates the end of the period of carbaryl stability at the individual sampling locations.

vigorously by hand every 5 min during this period. The mixture was then filtered through a glass fiber paper on a Büchner funnel and the residue was washed with 100-150 ml of the extracting solution. The filtrate was made to 1000 ml in a volumetric flask and a 100-ml aliquot was removed for analysis. The aliquot was added to 85 ml of methylene chloride in a Wehrli continuous extractor (Caro et al., 1973b) and extracted overnight. The methylene chloride in the receiving flask was then evaporated to about 10 ml on a steam bath with a Snyder column fitted on the flask and then finally to dryness on a rotary vacuum evaporator. Ten milliliters of saturated borax solution was added to the residue followed by addition of fluorodinitrobenzene, and the 2,4-dinitrophenyl ether of carbaryl was determined by electron-capture gas chromatography (Holden, 1973).

In numerous tests of Coshocton soil fortified with carbaryl granules and allowed to equilibrate for up to 6 days, the method gave consistent recoveries of near 60%. The analytical values presented below were corrected for recovery. After the field samples had been analyzed, we discovered that the loss of carbaryl during analysis occurred entirely in the step in which the pesticide was partitioned into methylene chloride. The concentrations of ethanol and acetone in the original extractant were too high, producing a low partition coefficient. When the original extract was diluted 1:10 with water before addition to the methylene chloride, recovery of carbaryl was 98-99% in several determinations on soils fortified with granular carbaryl and equilibrated for up to 6 days.

To further verify the method, tests were run with soils fortified with the carbaryl hydrolysis product 1-naphthol, which cannot be distinguished from carbaryl in this method. The 1-naphthol could not be extracted from soil with 1:1:1 acetone-ethanol-water and, hence, would not interfere with the analysis.

Runoff sediments were analyzed in the same way as soils after removal of excess water by filtration and air drying.

Carbaryl in runoff waters was determined by a method derived from that reported by Aly (1967). A 250-ml portion of the water was acidified with HCl and shaken in a separatory funnel for 1 min each with three successive portions, 50, 25, and 25 ml, of chloroform. The chloroform extracts were combined and evaporated to dryness, and the 2,4-dinitrophenyl ether of carbaryl in the residue was determined in the same manner as with soils. The method gave 94-95% recovery in tests with carbaryl-fortified water samples.

RESULTS AND DISCUSSION

The carbaryl contents of the ten soil samples on each of the six sampling days are shown in Table I. On any given day, the variability among samples was high. Precision was best in the first three samplings, but even there the coefficients of variation of the analyses ranged from 17 to 20%. Repeating the analyses on separate portions of the soil samples did little to improve the data. The variability in these measurements is consistent with the results of

Taylor et al. (1971), who showed that coefficients of variation could not be reduced appreciably below 20% at practical sampling rates when pesticide residues were measured in field soil samples.

When the inherent variability in the measurements is considered, the disappearance of carbaryl does not conform to a first-order reaction. A linear plot of the data from Table I showing standard deviations (Figure 1) re-
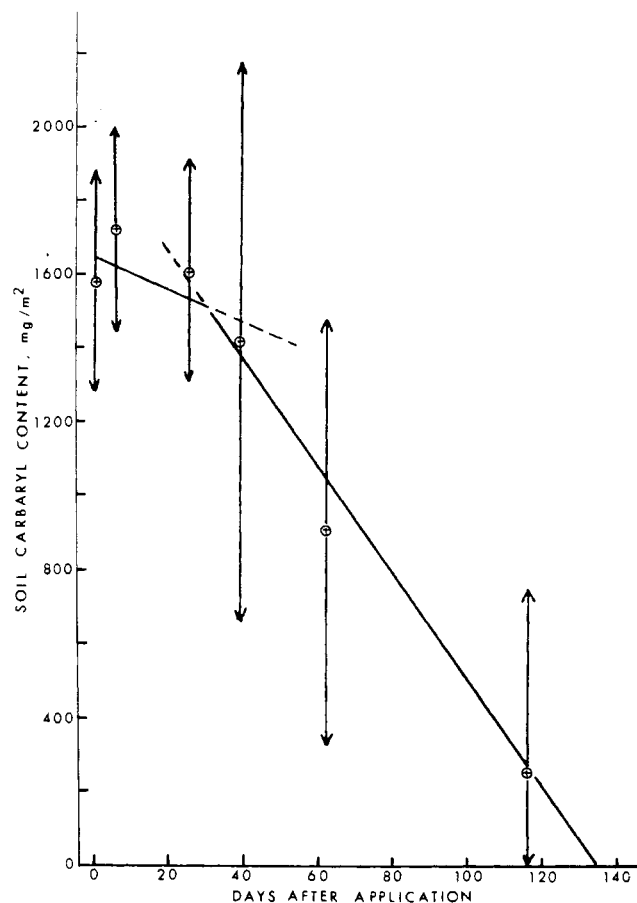

Figure 1. The disappearance curve for carbaryl in Coshocton silt loam soil. The circled crosses designate the analytical means for each sampling day. The vertical arrows on each side of the means each designate one standard deviation about the mean.

veals that no statistically significant loss of carbaryl occurred during the first 40 days after application to the soil. The two-branched linear regression line suggests that about 135 days were required for 95% of the pesticide to disappear, in contrast to the 8-day half-life (equivalent to 35 days for 95% disappearance) for carbaryl in soil reported by Johnson and Stansbury (1965).

The 135-day period is an overall value for the entire watershed, but the data for the individual sampling points in
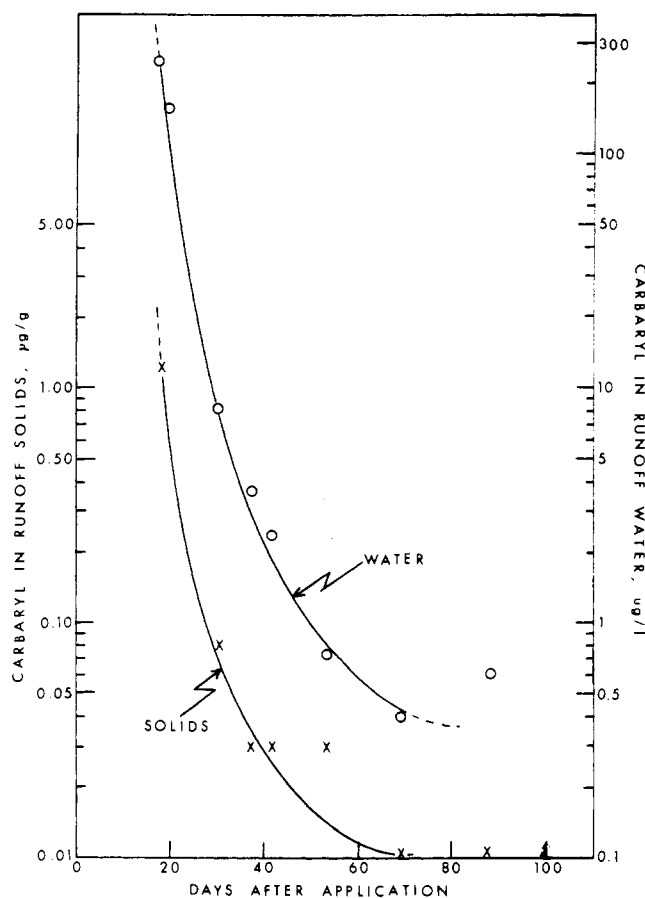
Figure 2. Carbaryl content of runoff water and associated solids, watershed No. 118.

Table II. Carbaryl Losses in Runoff Water, Watershed No. 118

Date, 1973	Days after appln	Runoff vol, kl	Av carbaryl concn, $\mu g/l$.	Total carbaryl lost, mg
June 4	17	0.26	248.0	60
June 6	19	25.01	160.0	4000
June 16	29	17.37	8.4	150
June 24	37	1.13	3.7	10
June 28	41	4.59	2.4	10
July 10	53	93.92	0.75	70
July 26	69	17.05	0.4	10
Aug 14	88	39.66	0.6	30
		198.99		4340

Table III. Carbaryl Losses in Runoff Solids,[a] Watershed No. 118

Date, 1973	Days after appln	Wt of solids, kg	Av carbaryl concn, $\mu g/g$	Total carbaryl lost, mg[b]
June 6	19	838	1.22	1334
June 16	29	481	0.08	48
June 24	37	99	0.03	4
June 28	41	35	0.03	1
July 10	53	1494	0.03	45
July 26	69	14	0	0
Aug 14	88	6	0	0
		2967		1432

[a] Includes both solids suspended in the water and sediments deposited on the floor of the discharge flume. [b] Weighted for different carbaryl concentrations in the suspended solids and the flume floor deposits.

Table I reveal localized differences that are informative with respect to the kinetics of degradation of carbaryl in field soil. Within the 0.79-ha plot, the pesticide disappeared from small areas in a consistent but time-variable pattern. At each location, carbaryl did not degrade measurably for some time after application. This lag period, the conclusion of which is noted by asterisks in the table, ranged from 25 days (locations 8 and 10) to more than 116 days (location 7). Once the degradation began in any one place, it proceeded quite rapidly. The result is a two-branched dissipation curve for carbaryl (Figure 1) and the data suggest that the duration of the branches varied from place to place in the field.

The lag period indicates that carbaryl degradation in soil is primarily microbiological. Lag periods have been reported by numerous investigators working with other pesticides in both field and laboratory studies (Hamaker, 1972) and are commonly thought to represent the time needed for active soil microorganisms to grow and adapt to the introduction of a foreign chemical. Several common types of soil fungi and bacteria are known to degrade carbaryl (Bollag and Liu, 1972; Zuberi and Zubairi, 1971). The lag periods may also be affected by the concentration of the pesticide. In earlier work with carbofuran (Caro et al., 1973a), placement of the pesticide in a concentrated band produced a brief lag period, whereas broadcast application did not.

The results obtained point up the necessity to sample adequately in any field study of the persistence of a pesticide in soil. Information may be lost or misleading if only a few composites representing a larger number of small samples are analyzed.

Although some rain fell on 9 of the first 15 days after application of the pesticide, no runoff resulted until day

17, when a substantial rainfall occurred. Runoff took place on seven other occasions: 19, 29, 37, 41, 53, 69, and 88 days after application. Measurable sediments were lost from the field during each of these seven events, but not in the rainfall of day 17.

The concentrations of carbaryl in both water and solids decreased by approximately two orders of magnitude in the 3-week period between days 17 and 40 (Figure 2). The pesticide had completely disappeared from the sediments by day 70, but the water contained low concentrations (<0.1 $\mu g/l$.) through the last measurements. At no time in this study were metabolites such as 4-hydroxy- or 5-hydroxycarbaryl found in the water, sediments, or soil.

Table II shows that, of the 4 kg of active carbaryl applied to the field, only 4.34 g was lost in the runoff water over the entire season. Over 90% of the total loss occurred in runoff from the single rainfall on June 6, 19 days after application. Even smaller amounts of the pesticide were carried off the field in the runoff solids (Table III); the seasonal loss totaled 1.43 g. The June 6 rainfall again accounted for over 90% of the loss. The entire loss in runoff water and solids for the year, 5.77 g, corresponded to only 0.14% of the application. Losses of carbaryl in runoff are apparently minor even when the pesticide is applied on the surface and not incorporated (Felley, 1971), but the June 6 event shows that a high-volume rainfall occurring shortly after carbaryl application in the field can generate a low-level transport of the pesticide to nontarget areas.

CONTRASTING BEHAVIOR OF CARBARYL AND CARBOFURAN

Our 1971 experiment with carbofuran (Caro et al., 1973a) provides the basis for an illuminating comparison of the behavior of the two methylcarbamate insecticides because the study with carbaryl was conducted on the

same field, using the same application technique, crop, and management.

Carbaryl, as expected, was less persistent in the soil than carbofuran: the times for 95% disappearance were 135 and 400 days, respectively. Although carbofuran exhibited a short lag period after band application, its disappearance conformed in general to a first-order reaction. This was not true for carbaryl, as shown above. Most interestingly, both pesticides degraded much faster in certain small areas of the watershed than in the remainder of the field, but the areas were not the same for the two pesticides. With carbofuran, the rapid degradation was associated with moisture content and pH of the ambient soil; no such relationship was observed with carbaryl.

The different loss of the two pesticides in runoff water reflects differences in their physicochemical properties: carbaryl is less water soluble than carbofuran (99 and 250 ppm, respectively) and is adsorbed to soil surfaces to a greater extent. The difference in adsorption was established in laboratory measurements of adsorption isotherms, in which we found Freundlich k values of 2.20 for carbaryl and 0.51 for carbofuran in two experiments run under identical conditions. Although runoff from the watershed was roughly four times as much in 1973 as in 1971, the water contained only one-third as much pesticide. The observed pesticide distribution coefficients between sediments and water (K_d) were 0.06 and 0.33 in the carbofuran and carbaryl experiments, respectively. The concentration of pesticide on sediments was below 1 mg/kg of sediment in both cases and the gross transport of both pesticides on eroded soil was consequently very low.

Because carbofuran is readily taken up through plant roots and translocated into aerial portions of the plants, it is an effective systemic insecticide. Carbaryl, on the other hand, has only slight systemic action. As evidence of this,

no residues of carbaryl or related compounds were found in harvested corn samples in these experiments, whereas carbofuran and its metabolites were readily detected in the 1971 corn plants.

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Determination of Diquat and Paraquat Residues in Soil by Gas Chromatography

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An analytical method is described for the gas chromatographic determination of diquat and paraquat residues in soil. The method involves extraction of the soil with 18 N H_2SO_4, followed by catalytic hydrogenation of the acid extract, and determination by gas chromatography. Recoveries of these two herbicides added to soils at 0.1- and 0.05-ppm levels were between 84 and 95%. The lower limit of sensitivity for this method is approximately 0.01 ppm. The method has been used for the determination of field applied diquat

and paraquat in three different types of soil. Hydrogenation of acid extracts from organic soil required more catalyst per gram of soil than from mineral soil. The pH of the soil extract from 1 to 9 had no effect on the recovery of field applied herbicide residues. The capabilities of various columns, an alkali flame ionization detector (AFID), and a flame ionization detector (FID) have also been compared for the analyses of diquat and paraquat.

The herbicides diquat (1,1'-ethylene-2,2'-bipyridylium dibromide) and paraquat (1,1'-dimethyl-4,4'-bipyridylium dichloride) are very effective contact dessicants and are widely used in the preharvest dessication of various crops, for aquatic weed control, and for postemergent nonselective weed control. They are rapidly adsorbed by soils. An ion-exchange procedure for residue determination of diquat and paraquat in soil is available (Tucker *et al.*, 1967;

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Hance and McKone, 1970). Using a 25-g soil sample, a limit of detectability of about 0.1 ppm and recoveries of the order of 70–95% are possible (Hance and McKone, 1970). However, this method involves a time consuming ion exchange step and is likely subject to interferences from certain soil extractive in the colorimetric determination. Furthermore, Corwin *et al.* (1968) pointed out that certain reduced bipyridylium compounds may not follow Beer's law in aqueous solution.

Recently Soderquist and Crosby (1972) determined paraquat in water by a gas chromatographic technique using a flame ionization detector. Although the procedure has a limit of detectability in the order of 0.1 ppm, the recov-