erage recoveries for the water samples, listed in Table I, were 98 ± 7% and 92 ± 11% for the oxamyl and the oximino metabolite, respectively, while they were 92 ± 9% for both in soil as listed in Table II. Chromatography of extracts from either soil or water as shown in Figure 1 demonstrates the selectivity and sensitivity of the method. No interference is noted in the control samples and levels of 1 ppb of oxamyl and 5 ppb of the oximino metabolite give more than adequate peak height.

The soil samples used in this study were typical of those used in areas where oxamyl is normally used for nematode control. While the soil was not characterized, we feel that the method should be applicable to any soil type typical of oxamyl nematode use areas.

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A Two-Year Field Study To Determine the Fate of Oxamyl in Soil during Flood Irrigation

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A 2-year study was conducted to determine the depth of penetration and degradation of residues of oxamyl in light-textured soils where heavy use of irrigation water was necessary to maintain crop vigor. Monitoring was conducted in sandy desert soils in a southern California lemon grove where a total of 64 acre in. of irrigation water was used during the study period. Oxamyl was applied to flood irrigation basins at a normal required rate for nematode control of 1.0 lb of active ingredient $acre^{-1}$ $month^{-1}$ by metering Du Pont Vydate L Insecticide/Nematicide into the water flow. A total of 17 lb of active ingredient was applied during the 2-year test period. In addition, a single treatment using 10 lb/acre, 10 times the normal monthly use rate, was also made for comparison. Analysis of soil samples showed that under these treatment conditions, oxamyl did not penetrate the soil to depths greater than 60 in. The half-life for oxamyl was 1–4 days, consistent with results from a previous field study using [^{14}C]oxamyl. This information indicates that under these conditions, oxamyl is not likely to accumulate in soil.

DBCP (1,2-dibromo-3-chloropropane) was widely used in California until 1977 as a soil fumigant for nematode control. Agricultural use of DBCP in California was suspended in 1977 by the Department of Food and Agriculture after incidence of male sterility was discovered in workers associated with the manufacture of the product.

In 1979, the California Department of Food and Agriculture detected DBCP contamination of wells in many parts of the state where DBCP had been used, including some municipal water supplies. The Department of Health Services confirmed widespread contamination of groundwater underlying major DBCP use areas.

In a search to find replacement nematicides for DBCP, which would be useful in California agriculture but would not contribute to groundwater contamination, a study was prepared to determine the fate of oxamyl in soil during irrigation.

Members of the Department of Health Services were contacted for help in selecting a test site with a high potential for leaching. Dr. Walter J. Farmer, Associate Professor of Soil Science at the University of California, Riverside, was consulted on requirements to ensure adequate sampling and oxamyl detection. The test site selected was a lemon grove in Thermal, CA, where typical desert soils are deep sands or loamy sands, low in organic matter, and where heavy volumes of flood irrigation water must be applied frequently to maintain the crop.

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EXPERIMENTAL PROCEDURES

In April 1981, the test site was laid out consisting of $^1/_4$-acre blocks, replicated 5 times. Treatments of oxamyl (as Vydate L), at the rate of 1 lb of active ingredient/acre, were metered into flood irrigation water as it flowed from risers into the flood basin between the tree rows. "Water only" check areas were also designated.

Oxamyl treatments were repeated monthly throughout 1981 until Jan 11, 1982 (a total of 10 lb). During that same time interval, a total of 35 acre in. of irrigation water was applied to the site, with the highest volumes required during June, July, and August.

Soil samples were taken on Jan 25, 1982 (14 days after the last treatment), and again Feb 15, 1982 (35 days after the last treatment). The field was irrigated without oxamyl addition between the two soil sampling dates.

Each replicate plot was sampled by using a Giddings drilling rig. Soil samples for analysis of oxamyl residues, water content, and particle size determination were taken at depths of 0–4 in., 4–8 in., 8–12 in., 1–2 ft, 2–3 ft, 3–4

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Table I. Soil Texture Synopsis[a]

depth	no. of samples characterized as: sands	sandy loam	loamy sand	loam	silt loam	total samples
0–4 in.		7	3			10
4–8 in.		4	5	1		10
8–12 in.		2	5	1	2	10
1–2 ft		5	3	1	1	10
3–4 ft	3	2	5			10
5–6 ft		5	5			10

[a] Classification based on the U.S. Department of Agriculture system for soil texture classification: sands, 85–100% sand, 0–15% silt, and 0–10% day; sandy loam, 50–70% sand, 0–50% silt, and 15–20% day; loamy sands, 70–85% sand, 0–30% silt, and 0–15% clay; loam, 25–52% sand, 28–50% silt, and 7–27% clay; silt loam, 0–50% sand, 50–88% silt, and 0–27% clay.

ft, 5–6 ft, 7–8 ft, 9–10 ft, 13–14 ft, 15–16 ft, and 19–20 ft. An intact 3 in. diameter soil core was used to sample to a depth of 4 ft. Samples below 4 ft were taken with a 2.5 in. diameter bucket auger.

The possibility of contamination of soil samples for each increment within the bore hole by overlying soils was reduced by discarding the top portion of soil in the bucket auger, resulting in noncontinuous core samples. The remaining soil in the auger was placed on clean, heavy-dry, aluminum foil and mixed, and appropriate subsamples were taken. The subsamples for particle size distribution were placed in clean, $^1/_2$-pt cardboard containers. The subsamples for analysis of oxamyl residues and water content were wrapped in aluminum foil, placed in plastic-lined cloth samples bags, placed in field boxes containing dry ice, and transported daily to a freezer.

RESULTS AND DISCUSSION

Studies based on the statistical analysis of a number of separate soil sampling experiments (Lund et al., 1978) indicate the optimum number of cores to sample depends on the soil variability within the field under study. At times very large numbers of cores need to be obtained. However, the economics of field sampling and laboratory analysis greatly limits the ability to acquire the necessary number. The results of Lund (1982) would suggest that the procedure used in this study would give a repesentative measure of the potential for movement into soil. Lund reported that for several study areas, eight to nine sites were sufficient to give a field average that would be expected to be within at least 30% of the true mean. Since our study area was of uniform soil type and received uniform management practices, the number of repetitions sampled should provide sufficient accuracy for assessing oxamyl movement.

The soils of this field are characterized as open and porous with no restricting layers to a depth of 20 feet (Table I). The soil pH was 7.3–8.5, which is typical of the region. Surface soils range from sandy loams to loamy sands. Subsurface materials are predominantly sandy loams to loamy sands. Layers of soil ranging in texture from sands to silt loam occur randomly throughout the field. The soils are desert soils, typical of the area, with low organic matter content (<1%) as judged by their light color. Soil moisture content ranged from 4.4% to 13.6% depending on the depth (Table II).

Soils sampled after the first year's treatments were analyzed for residues of oxamyl and its oxime by the method of Holt and Pease (1976). This method determines the total concentration of both oxamyl and its oxime metabolite degradation product, which is considerably less toxic than oxamyl on an acute basis (ALD rats: 11 000 mg/kg of body weight). Soils sampled after the second year were

Table II. Soil Mositure Content by Depth

soil depth	soil moisture content, %, by weight %, σ: 14 days av	35 days av
0–4 in.	8.4 ± 3.6	11.4 ± 2.1
4–8 in.	7.0 ± 0.6	10.6 ± 3.3
8–12 in.	11.8 ± 6.4	13.6 ± 3.6
1–2 ft	12.2 ± 3.7	10.8 ± 1.7
2–3 ft	5.2 ± 4.2	7.4 ± 1.2
3–4 ft	5.6 ± 2.4	9.6 ± 2.2
5–6 ft	4.4 ± 2.0	6.0 ± 1.7
7–8 ft	6.2 ± 2.8	7.4 ± 3.0
9–10 ft	5.8 ± 3.9	8.8 ± 4.0
13–14 ft	5.4 ± 1.2	7.4 ± 5.1
15–16 ft	6.0 ± 3.7	8.0 ± 2.4
19–20 ft	6.8 ± 2.1	7.8 ± 2.1

Table III. Residues of Oxamyl in Soil Increments following Ten Consecutive Treatments with Vydate L[a]

sample	depth	residues of oxamyl plus oxime, ppm, after last application: 14 days	35 days
row 36 north	0–4 in.	0.054	0.02
	4–8 in.	0.025	0.030
	8–12 in.	0.036	0.048
	1–2 ft	0.025	0.035
	2–3 ft	<0.02	0.047
	3–4 ft	<0.02	0.024
	5–6 ft	<0.02	<0.02
	7–8 ft	<0.02	<0.02
	9–10 ft	<0.02	<0.02
	13–14 ft	<0.02	<0.02
	15–16 ft	<0.02	<0.02
	19–20 ft	<0.02	<0.02

[a] Site, Thermal, CA; of sample, 50 g of soil; treatment, Vydate L at 1 lb of a.i. acre^{-1} month^{-1}; dates treated, 4/3/81, 5/7/81, 6/4/81, 7/2/81, 8/6/81, 9/10/81, 10/1/81, 11/5/81, 12/10/81, and 1/11/82; dates sampled, 1/25/82 and 2/15/82. The data for only one of five repetitions are given: however, the other four exhibited a similar pattern.

analyzed by an HPLC method by Prince (1984), which simultaneously determines residues of oxamyl and its oxime metabolite separately. Consequently, results from the second yearαpos sampling more accurately reflect the residues of oxamyl itself in the soil.

Results of the analysis of oxamyl plus its oxime for the 1 lb acre–month–treatment for the first year are given in Table III. Fourteen days after the last applications, low levels of oxamyl plus oxime residues were found down to the 2-ft depth. After 35 days, residues of oxamyl plus oxime were found down to the 4-ft depth. No residues were detected below 6 ft.

Because oxamyl had already degraded considerably by 14 days after the first year's treatment, the test was continued using the same blocks for an additional year. Oxamyl was reapplied monthly at 1 lb/acre from April through Oct 1982 (7 lb total). Total irrigation water applied to the treated area to ensure crop growth was 29 acre in. In addition, a single 10 lb of active/ingredient acre treatment (10× the normal use rate) was applied to a previously untreated area.

Soil samples were then taken at more frequent intervals, 1, 4, 7, 14, and 21 days following the last application. In order to minimize potential contamination, and because no residues of oxamyl plus oxime were found at 6 ft or below after the first year's treatment, soil sampling was confined to the top 4 ft.

Results of analysis for oxamyl and its oxime from this second set of samples are given in Table IV. Even after 2 years of monthly treatment at the 1 lb/acre rate, very

Table IV. Residues of Oxamyl in Soil Increments following Seventeen Consecutive Treatments with Vydate L[a]

		residues, ppm, after last application									
		1 day		4 days		7 days		14 days		12 days	
sample	depth, in.	oxamyl	oxime	oxamyl	oxime	oxamyl	oxime	oxamyl	oxime	oxamyl	oxime
row 29 north	0–4	0.056	0.049	0.018	0.021	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	4–8	0.040	0.029	0.034	0.043	<0.01	<0.010	<0.01	<0.01	<0.01	<0.01
	8–12	<0.01	<0.01	0.14	0.024	0.059	0.032	<0.01	<0.01	<0.01	<0.01
	12–24	<0.01	<0.01	<0.01	<0.01	0.015	0.016	<0.01	<0.01	<0.01	<0.01
	24–36	0.022	0.023	0.017	0.015	<0.01	<0.01	<0.01	0.012	<0.01	<0.01
	36–48	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.027	<0.01	<0.01	<0.01
row 32 north	0–4	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
untreated check	4–8	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	8–12	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	12–24	<0.01	<0.01		<0.01		<0.01	<0.01	<0.01	<0.01	<0.01
	24–36	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	36–48	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

[a] Site, Thermal, CA; sample, 50 g of soil; treatment, Vydate L at 1 lb of a.i. of acre^{-1} month^{-1}; dates treated, 4/3/81, 5/7/81, 6/4/81, 7/2/81, 8/6/81, 9/10/81, 10/1/81, 11/15/81, 12/10/81, 1/11/82, 4/21/82, 5/26/82, 6/16/82, 7/22/82, 8/2/82, 9/23/82, and 10/28/82; dates sampled, 10/29/82, 11/1/82, 11/4/82, 11/11/82, 11/18/82. The results of only one of three repetitions and the check plot are given; however, the others exhibit a similar pattern.

Table V. Residues of Oxamyl in Soil following a Single Vydate L Treatment[a]

		residues, ppm, after last application									
		1 day		4 days		7 days		14 days		21 days	
sample	depth, in.	oxamyl	oxime	oxamyl	oxime	oxamyl	oxime	oxamyl	oxime	oxamyl	oxime
raw 19 north	0–4	1.4	2.0	0.49	1.8	0.38	0.97	0.013	0.11	<0.01	0.036
	4–8	2.0	1.1	0.88	1.1	0.59	0.089	<0.01	0.050	0.021	0.050
	8–12	0.029	0.017	0.17	0.24	0.032	0.030	<0.01	0.020	<0.01	<0.01
	12–24	<0.01	<0.01	<0.01	<0.01	0.060	0.29	0.10	0.28	<0.01	<0.01
	24–36	0.51	0.36	0.71	0.24	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	36–48	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

[a] Site, Thermal, CA; sample, 50 g of soil; treatment, Vydate L at 10 lb of a.i./acre; date treated, 10/28/82; dates sampled, 10/29/82, 11/1/82, 11/4/82, 11/11/82, and 11/18/82. The results of only one of three repetitions is shown; however, the others showed a similar pattern.

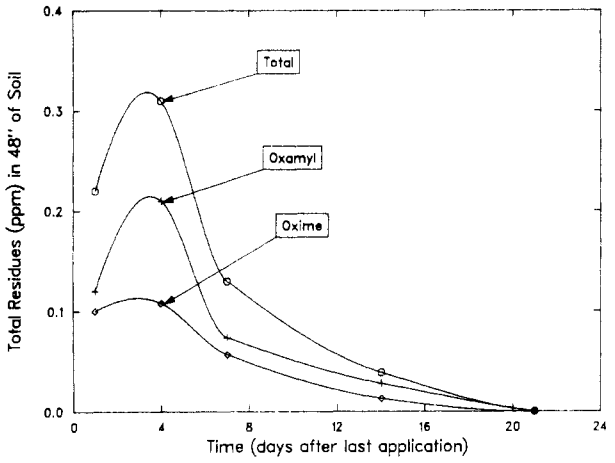

Figure 1. Total oxamyl, oxime, and oxamyl plus oxime residue in soil from 0 to 48 in. at 1 to 21 days after the last application of 17 monthly applications of 1 lb of a.i./acre Vydate L over 2 years.

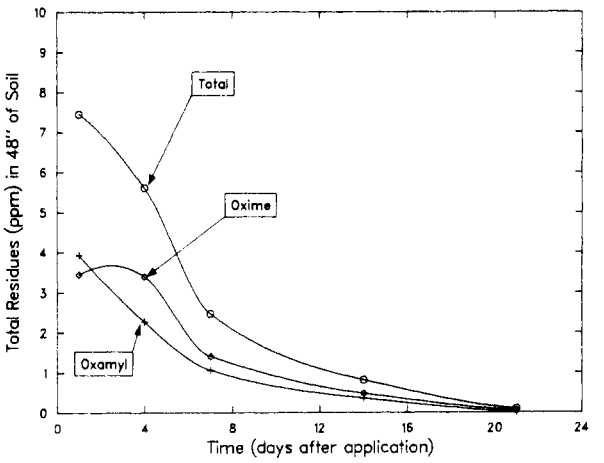

Figure 2. Total oxamyl, oxime, and oxamyl plus oxime residues in soil at 0 to 48 in. at 1 to 21 days after a single 10 lb of a.i. acre application of Vydate L.

little or no oxamyl or oxime metabolite was detected at depths below 36 in. Figure 1 shows the rapid degradation of both oxamyl and total oxamyl plus oxime metabolite to undetectable levels by 21 days. This is consistent with the results from a previous field study using [^{14}C]oxamyl done by Harvey and Han (1978).

Analysis of samples from a single treatment at the 10 lb/acre rate (Table V) showed penetration at only one test site to the 48-in. depth. At the other two test sites, an isolated layer of oxamyl and oxime was found at the 24–36-in. level. Even at this exaggerated treatment rate of 10 lb/acre, equivalent to 7 ppm of oxamyl based on application to a 6-in. depth over 1 acre, Figure 2 shows similar rapid degradation to negligible levels within 21 days.

CONCLUSION

These data illustrate that 17 treatments at monthly intervals over a period of 2 years at the normal use rate for nematode control (1 lb of active ingredient acre^{-1} month^{-1}) does not result in penetration below 60 in., even in sandy soils under heavy irrigation. It further indicates that, under these conditions, oxamyl residues dissipate rapidly and are not likely to accumulate.

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Characterization of Bound (Nonextractable) Residues of Dieldrin, Permethrin, and Carbofuran in Radishes

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[^{14}C]Dieldren (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-*exo*-1,4-*endo*-5,8-dimethanonaphthalene), [^{14}C]permethrin [3-phenoxybenzyl (±)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate], and [^{14}C]carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate) were applied in commercial formulations to radishes (*Raphanus sativus*) at 11.1 kg/ha and maintained in environmental growth chambers. Edible portions of the radishes were sampled 21 days postapplication, chopped, and exhaustively extracted with solvents. The amounts of nonextractable (bound) ^{14}C residues formed in the dieldrin-, permethrin-, and carbofuran-treated radishes were 23.5%, 28.6%, and 92.6%, respectively, of the total plant ^{14}C. The compounds that were present in the form of bound ^{14}C residues in radishes were identified as the parent pesticide (dieldrin, permethrin, or carbofuran) or metabolites of similar chemical structure [3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid, 3-ketocarbofuran, or 3-hydroxycarbofuran].

Tracer studies have shown that a considerable portion of pesticide residues may become bound (nonextractable) in plants. These residues are difficult to extract without chemical modification, are not detected in routine residue analysis, and are difficult to identify. Huber and Otto (1982) have reviewed bound residues of a number of pesticides in various crops.

During the course of a study on the fats of dieldrin (Stratton and Wheeler, 1983), permethrin (Stratton et al., 1981), and carbofuran (Forbes et al., 1980) in radishes (*Raphanus sativus*), it was observed that as much as 24%, 30%, and 70%, respectively, remained bound after exhaustive solvent extraction. The present study was undertaken to investigate the nature of these bound residues in radishes.

MATERIALS AND METHODS

Chemicals. Uniformly ring labeled [^{14}C]dieldrin was used to fortify a Shell Chemical Co. emulsifiable concentrate containing 18% technical dieldrin. Labeled [^{14}C]-*cis*-permethrin and [^{14}C]*trans*-permethrin was used to fortify an ICI emulsifiable concentrate containing 25% technical permethrin (a mixture containing 34% cis and 66% trans isomers). [^{14}C]Carbofuran, uniformly labeled in the benzene ring, was used to fortify an FMC commercial formulation (Furadan-4-Flowable) containing 40% technical carbofuran. The fortified formulations of dieledrin, permethrin, and carbofuran had specific activities of 0.19, 0.095, and 0.15 mCi/mmol, respectively. Dieldrin (99.7%), permethrin (99.8%), carbofuran (99.7%), 3-hydroxycarbofuran (manufacturer's standard), and 3-ketocarbofuran (manufacturer's standard) standards were obtained from the Environmental Protection Agency (Research Triangle Park, NC).

Treatment and Extraction of Plants. Red Globe radish seeds were germinated in flats containing soil and then transplanted at 1.5–2 weeks of age to 14.6-cm pots (four per pot) containing Hoagland nutrient solution and sand. The flats and pots were maintained in an environmental growth chamber (Scherer-Gillet Model CEL 512-37), with 10-h light periods and 14 h of dark. Light and dark temperatures were 27 and 16 °C, respectively; light and dark relative humidities were 80% and 60%, respectively. The radishes were treated at 5–6 weeks after germination by pipetting a known volume of the ^{14}C fortified formulated pesticide onto the roots and surrounding sand of each radish at rates of 11.1 kg/ha. An untreated control was maintained in the same growth chamber. The sand was covered with paraffin shavings immediately after the pesticide application to reduce volatilization of the insecticide.

The radishes were harvested 21 days postapplication by pulling them from the sand, rinsing them with water to remove adhering sand, and removing the tops. They were chopped with a hand-operated food chopper to particles of 0.5–1.0 mm in size prior to extraction in a Soxhlet extractor for 24 h with the solvents listed in Table II. The solvent-extracted radish tissues were dried and subjected to the Association of Official Analytical Chemists indirect lignin analysis (AOAC, 1970). Both the solvent-extracted radish tissues and resulting lignin were analyzed for bound residues.

Analysis of Bound ^{14}C Residues. The dried radish samples were subjected to the high-temperature distillation (HTD) technique (Khan and Hamilton, 1980). Six solvent

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