

**DETERMINATION OF LEACHING IN SOIL OF NEMATICIDES  
APPLIED THROUGH DRIP IRRIGATION**

**February, 1990**



**STATE OF CALIFORNIA  
Department of Food and Agriculture  
Division of Pest Management, Environmental Protection and Worker Safety  
Environmental Monitoring and Pest Management Branch  
1220 N Street, Sacramento, California 95814**

**EH 90-2**

DETERMINATION OF LEACHING IN SOIL OF NEMATICIDES APPLIED  
THROUGH DRIP IRRIGATION

BY

D. J. WEAVER,<sup>1</sup> M. V. MCKENRY<sup>2</sup> AND S. J. MARADE<sup>1</sup>

FEBRUARY, 1990

- 1 Environmental Hazards Assessment Program, California Department of Food and Agriculture, Sacramento, CA.
- 2 University of California at Riverside, Kearney Field Experiment Station, Parlier, CA.

## ABSTRACT

The use of drip irrigation systems to deliver pesticides to crops is increasing in California. Soil coring studies were carried out at three locations in Fresno County, California to determine the leaching potential of non-fumigant nematicides applied through drip irrigation systems. A truck-mounted drill rig was used to sample to a maximum depth of 40 feet using a split barrel collection system. A Veihmeyer tube was also used to take shallow samples and study horizontal movement of the chemicals.

Two of the sampling locations supported mature grape vines growing on Tujunga sand or loamy sand soils. At the first location, multiple applications of four non-fumigant nematicides, aldoxycarb, ethoprop, fenamiphos and oxamyl had been made for 2 years prior to sampling. Deep cores collected at those locations had to be taken approximately 3-4.5 feet away from the nearest emitter because of the logistics involved with sampling with a truck-mounted drill rig. Aldoxycarb and ethoprop were detected in the upper portions of the deep cores; fenamiphos and oxamyl were not detected. Residues of all four nematicides were measured in shallow soil samples taken directly beneath the emitters but not 2 feet away. Also, pesticide residue was not found in ground water collected from the bottom of deep core holes. At the second location, fenamiphos had been applied during three growing seasons. No fenamiphos was detected in soil segments or in ground water sampled from the bottom of one deep soil core taken to a depth of 23 feet at the end of the third growing season.

The third location was an experimental plot of young walnut trees planted 3 feet apart on a Hanford sandy loam soil. Deep soil cores taken directly beneath emitters and shallow samples located 8, 16 or 24 inches away from emitters were collected in June, November and December during the second year of monthly applications of aldoxycarb, fenamiphos and oxamyl. After 9 applications, aldoxycarb concentrations near the detection limit (0.01-0.02 ppm) were found at maximum depths of 4.3-5.5 feet in the soil beneath

emitters and at a distance of 24 inches away in the top 4 feet of the soil profile. Fenamiphos and its oxidation breakdown products were more persistent in soil and leached deeply into the soil profile. After nine applications, the parent compound, the sulfoxide and sulfone were detected at soil depths of 29.3 feet, 22.2 feet and 21 feet, respectively. Oxamyl also leached deeply into the soil profile within weeks after the ninth application was made. Concentrations at the detection limit of 0.01-0.02 ppm were present 11-27.2 feet deep in soil. Again, none of the nematicides was detected in ground water samples taken from the bottom of core holes.

Drip application of nematicides provided good distribution of residues in soil to the plant root zone. However, application of fenamiphos and oxamyl under the conditions tested could result in ground water contamination in locations where shallow water tables were present. Additional work is needed to develop the methodology necessary to deliver nematicides through drip systems and at the same time prevent the deep leaching of the chemicals into the soil profile.

## **ACKNOWLEDGEMENTS**

The authors thank Roger Sava, Chris Collison, and Cindy Garretson for their assistance in collecting soil core samples.

We also acknowledge the pesticide analyses of soil and ground water samples performed by Rick Maykoski and Nirmal Saini.

## **DISCLAIMER**

The mention of commercial products, their source or use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

## TABLE OF CONTENTS

ABSTRACT.....	1
ACKNOWLEDGEMENTS.....	iii
LIST OF TABLES.....	v
LIST OF FIGURES.....	vii
INTRODUCTION.....	1
MATERIALS AND METHODS.....	2
Soil Sampling And Analytical Procedures.....	2
Deep Soil Core Sampling.....	2
Shallow Sampling With Veihmeyer Tube.....	2
Ground Water Sampling.....	3
Soil Particle Size And Organic Matter Content Analyses.....	3
Pesticide Analytical Methods.....	3
Aldoxycarb.....	4
Ethoprop.....	4
Fenamiphos.....	4
Oxamyl.....	4
Study Site Descriptions And Soil Sampling Design.....	4
Location I.....	4
Location II.....	5
Location III.....	6
RESULTS AND DISCUSSION.....	8
Location I.....	8
Location II.....	11
Location III.....	12
Aldoxycarb.....	12
Fenamiphos.....	17
Oxamyl.....	26
CONCLUSIONS.....	33
REFERENCES.....	35
APPENDICES.....	38

## LIST OF TABLES

Table 1.	Concentrations of nematicides in soil samples taken with a Vei hmeyer tube at two distances from drip emitters at Location I.....	9
Table 2.	Concentrations of nematicides in segments of soil cores taken near drip emitters at Location I.....	10
Table 3.	Concentrations of aldoxycarb in segments of shallow and deep soil cores collected on three different dates from Location III using a truck-mounted drill rig.....	13
Table 4.	Mean concentrations of aldoxycarb found in soil collected with a Vei hmeyer tube at varying distances from drip emitters at Location III on three sampling dates.....	15
Table 5.	Concentrations of fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone in segments of three soil cores collected at Location III using a truck-mounted drill rig on June 4, 1985, 6 days after the fourth fenamiphos application.....	18
Table 6.	Mean concentrations of fenamiphos residues (fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone) found in soil collected with a Vei hmeyer tube at varying distances from drip emitters at Location III on three sampling dates..	20
Table 7.	Concentrations of fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone in segments of three soil cores collected from Location III using a truck-mounted drill rig on November 5, 1985, 13 days after the ninth fenamiphos application.....	22
Table 8.	Concentrations of fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone in segments of three soil cores collected from Location III using a truck-mounted drill rig on December 17, 1985, 55 days after the ninth fenamiphos application.....	24
Table 9.	Concentrations of oxamyl and oxamino in segments of shallow and deep soil cores collected from Location III on three different dates using a truck-mounted drill rig .....	27

Table 10. Mean concentrations of oxamyl residues (oxamyl plus oxamino) found in soil collected with a Veihmeyer tube at varying distances from drip emitters at Location III on three sampling dates..... 31



## LIST OF FIGURES

- Figure 1. Locations of aldoxycarb residues in the soil profiles of three cores collected on each of three sampling dates..... 14
- Figure 2. Locations of total fenamiphos residues (fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone) in the soil profiles of three cores collected on each of three sampling dates..... 19
- Figure 3. Locations of total oxamyl residues (oxamyl plus oxamino) in the soil profiles of three cores collected on each of three sampling dates..... 29

## INTRODUCTION

The use of drip irrigation has become a common practice in commercial agriculture in recent years. Drip irrigation is desirable because water can be applied in small quantities at more frequent intervals directly to the crop root zone generally resulting in reduced water usage. Drip irrigation systems also have the advantage of being used for application of agricultural chemicals including fertilizers and pesticides. Agricultural chemicals can be placed directly to the needed site through drip emitters and applications can be timed to correlate with susceptible life stages of pests, periods of active nutrient uptake, or to coincide with root initiation periods of established perennial crops.

The acreage of California crops that is irrigated through drip systems has increased dramatically over the past several years, particularly in the higher-value commodities but also in those areas having sandier soils with poor water holding capacity. It is in those soils that nematode damage from root knot nematodes is also most prevalent. This problem has led to the use of the drip systems for application of nematicidal chemicals to the grape root zone. Commercial treatments of fenamiphos, oxamyl and carbofuran have been used successfully through dripper systems to control nematodes on grapes and tree fruits. Other nematicidal chemicals are being tested for their potential use. The persistence of the chemicals in soil and their potential for leaching into the subsoil layers where they could pose a threat to shallow ground water after drip application has not been thoroughly studied. The studies described in this report were conducted to provide information on the persistence and movement through soil of nematicides that have potential for use through application in drip irrigation systems.

## **MATERIALS AND METHODS**

### **Soil Sampling And Analytical Procedures**

#### **Deep Soil Core Sampling**

Undisturbed soil samples were collected down to a maximum depth of 40 feet using a truck-mounted Mobile Drill, model B-53 drilling rig fitted with 8-inch diameter hollow-stem augers. Soil core segments were collected with a split barrel sampler, 20 inches long and containing three 6-inch-long stainless steel cylinders stacked end to end. The interior of the cylinders was rinsed with methanol prior to the split barrel being lowered by the Moss Wireline sampler into the hollow augers. As drilling proceeded, the split barrel was pushed into the soil ahead of the the rotating auger and collected an undisturbed sample. After drilling 20 inches of soil, the sampler was withdrawn and opened. The cutting tip held a 2-inch segment of soil which was discarded leaving 18 inches of sample (three 6-inch segments) encased in steel cylinders. After removal, the ends of the cylinders were sealed with aluminum foil and tightly fitting plastic caps. They were placed on dry ice and stored frozen. After samping was completed, the bottom 3-5 feet of the hole was refilled with soil and then a 50 pound bag of bentonite was poured in to form a seal to prevent contamination of the groundwater below. The remainder of the bore hole was filled with soil and packed down until it was level with the field surface.

Prior to chemical analysis, a mechanical sample splitter was used to push each frozen segement from the steel cylinder and divide it longitudinally into three portions. One portion was used for a moisture content determination, another was to be used for soil texture analysis and the third portion was kept frozen and used for analysis of nematicide residues.

#### **Shallow Sampling With Veihmeyer Tube**

A 1-inch diameter Veihmeyer tube was used to collect soil samples down to 4 feet. Before each core was collected, the Veihmeyer tube was washed with a

brush in laboratory grade detergent mixed with water, rinsed with tap water, rinsed with distilled water and finally rinsed with methanol. The sample was collected by pounding the tip of the sampling tube into the soil to the desired depth with a sliding hammer that fit over the tube. The tube was then pulled from the ground by hand or retracted with a specialized jack. Plugs of soil were carefully dumped into a 1/2 pint wide mouth jar, sealed with a foil lined screw cap and placed on dry ice. Soil samples were kept frozen until extraction.

#### **Ground Water Sampling**

Water samples were collected when standing ground water was reached during the soil drilling process. A cylindrical Teflon<sup>®</sup> bailer, 24 inches long with a 1-1/2 inch inside diameter was lowered on the wireline sampler to the depth where water was reached. After approximately 30 seconds, the bailer was retrieved and collected water poured into 1 liter amber glass bottles that were sealed with foil-lined plastic caps. Water samples were immediately placed on wet ice and kept refrigerated until samples were extracted. The bailer was thoroughly rinsed with distilled water, followed by a methanol rinse and two rinses with double distilled water after each sample was collected.

#### **Soil Particle Size And Organic Matter Content Analyses**

A hydrometer method was used for particle size analysis of soil samples; organic matter content was determined by a dichromate reduction method. Both have been described previously (24).

#### **Pesticide Analytical Methods**

A brief description of analytical methods for each pesticide is presented here; more detailed information on each analytical procedure is presented in Appendix A.

**Aldoxycarb** - Distilled water was used to extract soil samples. Extracts were filtered through paper filters and then analyzed directly by HPLC with a fluorescence detector.

**Ethoprop** - Soil samples were extracted with acetone and the filtered extract was analyzed directly by gas chromatography with an NP detector.

**Fenamiphos** - Soil samples were extracted with a hexane-acetone (1:1) solution. The extract was evaporated to dryness, redissolved in ethyl acetate and analyzed by GLC for parent fenamiphos. When analyses were conducted for fenamiphos sulfoxide and sulfone, a portion of the extract was evaporated to dryness, redissolved in acetonitrile:water (20:80) and analyzed by HPLC with a UV detector.

**Oxamyl** - Soil samples were extracted with hexane-acetone (50:50) solution. Extracts were filtered, washed with dichloromethane, diluted with water and then analyzed by HPLC with a UV detector.

## **Study Site Descriptions And Soil Sampling Design**

### **Location I**

A treatment site had been established in a 12 acre commercial planting of 7-year-old red seedless grapes located near Reedly, California. Rows of vines were spaced 12 feet apart. The soil classification was Tujunga sand. Six nematicidal chemicals had been applied via drip irrigation to individual rows in selected areas of the vineyard in 1982 and again in 1983. Four of those nematicides, aldoxycarb, ethoprop, fenamiphos and oxamyl were selected for this study based on increases in yield and vine vigor during the two years of treatments. Aldoxycarb, ethoprop and fenamiphos had been applied once per month in April, May, June, October and November in 1982 and again in April, May, June, September and October in 1983. Applications were made

to coincide with periods of root flush. Each application consisted of 1 pound active ingredient (ai) per acre for fenamiphos, ethoprop and aldoxycarb. Oxamyl was applied twice each month at 0.5 pounds ai per acre for each application. Nematicides and water were applied through biwall tubing with drip emitters spaced 4 inches apart. The tubing was located to one side of the center of the vine row and was buried 6 inches deep in the soil.

Soil coring was conducted on November 28, 29, 30 and December 1, 1983, with one chemical sampled on each date. Veihmeyer tube samples were taken near the end vine in one treated row per chemical. Samples were collected at 6 inch intervals from the surface down to 2 feet deep directly beneath an emitter and again from a point 2 feet out from the emitter. Attempts were made to collect deep cores as close as possible to the same drip emitters. However, due to difficulty in maneuvering the truck-mounted drill rig and the relatively narrow space between vine rows, it was necessary to take deep cores 32 to 52 inches away from the emitters. One core was collected from the surface down to a depth of approximately 40 feet for each of the four nematicides. Three, 6-inch soil core segments were collected for each 20-inch depth drilled yielding a total of 72 soil samples for each nematicide. We had intended to drill until ground water was reached and it was reached at approximately 40 feet. Replicate ground water samples were collected from the bottom of each of the four drill holes after which they were refilled and sealed.

#### **Location II**

Three applications of fenamiphos had been made from January, 1981 to April, 1982 at a second commercial vineyard of 6-year-old red seedless grapes located near Reedly, California. The nematicide was applied at a rate of 3 gallons/acre (1 lb ai/gal.) as a spray to the soil surface or injected into the soil. An additional treatment was made through drip irrigation in

October, 1983 when two split applications of fenamiphos were made at a rate of 1.5 lbs/acre each. The soil classification was Tujunga loamy sand.

On December 2, 1983, one core to 23 feet (280 inches) was taken at a site 52 inches from an emitter ( 32 inches from the edge of the berm) near the second vine in from the end of the row. A total of 42 soil samples each 6-inches long were collected for analysis. Ground water was reached and a water sample was taken from the bottom of the hole. No shallow soil samples were collected at this location.

### **Location III**

An experimental plot with walnut trees was established in 1984 to study nematode control provided by treatments with the non-fumigant nematicides aldoxycarb, fenamiphos and oxamyl alone or in combination with a preplant treatment of 1,3-dichloropropene (Telone II \*), a soil fumigant. The plot was located in an area of the Kearney Field Station where the soil was a Hanford sandy loam. The site had been a walnut orchard for 20 years prior to being cleared and used for the present study. Treatments had been applied to replicated plots 50 feet long and 10 feet wide set up in a randomized block design.

Plots that were to receive soil fumigation had been treated in the fall of 1983; trees were planted 1.5 feet apart in rows 10 feet apart in winter 1983. In winter, 1984 every other tree was removed for growth evaluations leaving a 3 foot tree spacing. A drip irrigation system was established after planting; tubing with emitters spaced 8 inches apart was laid on the soil surface along the center of the row close to the trunks. Postplant treatments of nematicides were made via the drip system eight times during the period from April through October in 1984. For each application, 1.19 lbs. active ingredient (ai) of nematicide per acre was put out through the drippers. The drip system was also used for regular irrigations.

In 1985, a similar application schedule was followed. Nematicides were applied at the rate of 1.19 lbs. ai per acre at intervals of approximately 28 days from March 4 through October 23 for a total of nine applications. For each application, water containing nematicide at a concentration of 27.4 mg/l (ppm) was run through the drip system for 3 hours to attain the desired dosage. Throughout the experiment, applications of irrigation water were run for 3 hours at a frequency of two applications per week in April, May and October; three applications per week in June and September; and four applications per week in July and August.

One 50 x 10 foot plot each of aldoxycarb, fenamiphos and oxamyl was selected for sampling during 1985. The plots were selected on the outer edge of the experimental block so that the truck mounted drill rig could be used. The fenamiphos plot selected for coring had received a preplant fumigation with 15 ga./acre of Telone II but the oxamyl and aldoxycarb plots had not. Each plot was sampled in June, approximately 1 week after the fourth nematicide application; in November, approximately 2 weeks after the last (ninth) application; and in December, approximately 8 weeks after the last application. Each plot was divided lengthwise into thirds so that coring took place in only one area of the plot on each sampling date.

For each plot and sampling date two soil cores 15 feet deep and one to a maximum of 40 feet were each taken from directly beneath an emitter. The cores were located 3 to 5 feet apart in the tree row. Ground water was reached and sampled from the deep core holes in June but not in November or December. Additionally, Veihmeyer tube samples were taken at 1 foot increments down to 4 feet at distances of 8, 16 and 24 inches away from the emitter in a line perpendicular to the tree row. Before coring was started, the walnut trees in the area to be sampled were cut off near the soil line to provide room necessary for sampling. A wire surveyor flag was placed at each emitter location where a deep core was to be taken. Then, locations for Veihmeyer tube samples were measured off from those emitters and also



marked with flags. Veihmeyer tube samples were taken first, followed by deep coring with the drill rig.

## RESULTS AND DISCUSSION

### Location I

Soil cores and ground water samples were collected approximately 6 weeks after the last nematicide application. Chemical analyses were performed only for parent materials, no breakdown products were included. Nearly all results for Veihmeyer tube samples taken at the dripper line were positive (Table 1). Contrarily, all but one sample collected 2 feet away were negative; only the sample collected for aldoxycarb at the 18 to 24 inch depth was positive.

For the deep cores, residues of two of the four nematicides were detected within the upper 32 inches of the soil profile (Table 2). Aldoxycarb, at levels ranging from 0.04 to 0.09 ppm, was found in the upper 32 inches of soil and ethoprop was found at a concentration of 0.07 ppm in the top 12 inches. The low number of positive samples was probably due to the fact that cores were taken at distances ranging from 32 to 52 inches away from the dripper line, a distance beyond which most horizontal movement of nematicide probably occurred.

None of the ground water samples collected from the bottom of core holes contained nematicide. Four samples were taken for aldoxycarb with minimum detectable levels (MDL's) of 1.6, 1.8 and 2.3 ppb; two samples were taken for ethoprop with MDL's of 0.32 and 0.28 ppb; two samples were taken for oxamyl with an MDL of 2.9 ppb; three samples were taken for fenamiphos with MDL's of 0.25, 0.26 and 0.57 ppb.

Table 1. Concentrations of nematicides in soil samples taken with a Veihsmeier tube at two distances from drip emitters at Location I.

Chemical <sup>a</sup>	Depth (Inches)	<u>Concentration (ppm), dry weight soil</u>	
		At emitter	2 ft. from emitter
Aldoxycarb	0 - 6	0.07	ND <sup>b</sup>
	6 - 12	0.04	ND
	12 - 18	0.04	ND
	18 - 24	0.09	0.03
Ethoprop	0 - 6	0.27	ND
	6 - 12	1.00	ND
	12 - 18	0.92	ND
	18 - 24	0.51	ND
Fenamiphos	0 - 6	0.50	ND
	6 - 12	0.65	ND
	12 - 18	0.35	ND
	18 - 24	0.40	ND
Oxamyl	0 - 6	ND	ND
	6 - 12	ND	ND
	12 - 18	0.18	ND
	18 - 24	0.19	ND

a. Minimum detectable level (MDL) was 0.03 ppm for aldoxycarb, 0.04 ppm for ethoprop and 0.05 ppm for fenamiphos and oxamyl.

b. None detected at indicated level.

Table 2. Concentrations of nematicides in segments of soil cores taken near drip emitters at Location I.

Depth (inches)	Concentration (ppm), dry weight soil			
	Aldoxycarb	Ethoprop	Fenamiphos	Oxamyl
0 - 6	0.04 <sup>a</sup>	-- <sup>b</sup>	ND <sup>c</sup>	ND
6 - 12	0.04	0.07	ND	ND
12 - 18	--	ND	ND	ND
20 - 26	0.05	ND	ND	ND
26 - 32	0.09	ND	ND	ND
32 - 38	ND	ND	ND	ND
40 - 478	ND	ND	ND	ND

a. Minimum detectable limit (MDL) was 0.03 or 0.05 ppm for aldoxycarb, 0.04 or 0.05 ppm for ethoprop, and 0.05 ppm for fenamiphos and oxamyl.

b. Sample lost due to soil compaction.

c. None detected at indicated MDL.

Results of analyses of organic carbon content and particle size distribution of soil samples were similar for the four cores. Organic carbon content in the top 6 inch layer of each core ranged from 1.5 to 2.5 % but was below the 0.1 % level of detection in all but a few of the subsurface samples. Data for the particle size analysis of one of the cores is presented in Appendix B and is representative of data for all four cores. The soil profile consisted mostly of sand from the surface down to approximately 200 inches (16.6 feet) where a layer of silt and clay was present. High percentages of silt and clay were again observed from approximately 272 to 338 inches (28.2 feet) and from 420 inches (35 feet) down to the bottom of the core where ground water was reached.

#### Location II

A single soil core was taken from this site approximately 2 months after the last fenamiphos application. Soil samples were analyzed for fenamiphos but not for the sulfoxide or sulfone breakdown products. None of the samples contained fenamiphos at MDL's of 0.03 or 0.05 ppm. The ground water sample also contained no fenamiphos at an MDL of 0.26 ppb.

The failure to detect fenamiphos in soil samples from this location was not surprising since the soil core was taken 52 inches from the dripper line, probably beyond the range of horizontal movement of fenamiphos with the irrigation water. Also, fenamiphos may not have been present soon after it was applied to the soil because its oxidation to the sulfoxide breakdown product occurs rapidly followed by a slower degradation to the sulfone (12, 14, 15). Our chemical analysis did not include the two oxidation products. Analyses of soil organic carbon content and texture were not performed for samples from this site.

### Location III

A mobile drill rig was used to collect soil cores directly beneath emitters approximately 1 week after the fourth nematicide application, 2 weeks after the last (ninth) application, and approximately 6 weeks later. Veihmeyer tube samples were also taken 8, 16 and 24 inches from the emitters to study horizontal movement of the chemicals. Results for Veihmeyer tube samples are presented in this section as mean values for three replicate cores; individual results are presented in Appendix C.

Data for organic carbon content and particle size analyses were not generated because soil samples were lost.

**Aldoxycarb** - Soil samples were analyzed only for aldoxycarb, no breakdown products were included. The first set of soil cores collected in June represented residues resulting from four aldoxycarb applications over a 4 month period. Residues were detected in the upper 26 - 32 inches of soil in the three cores with concentrations ranging from 0.03 to 0.40 ppm (Table 3 and Figure 1). Results for Veihmeyer tube samples (Table 4) indicated that aldoxycarb residues were also present at similar concentrations as far as 2 feet from the emitters and 4 feet deep in the soil. Neither of the water samples collected at the bottom of the deep core hole contained aldoxycarb at an MDL of 0.7 ppb.

Five additional aldoxycarb applications had been made by the time the second set of soil core samples were taken approximately 5 months later in November. Cores were collected 15 days after the final application. Fewer positive samples were detected and the concentrations were lower, in the range of 0.01 to 0.10 ppm (Table 3 and Figure 1). However, aldoxycarb was detected at maximum depths of 38 inches in two cores and in one sample at a depth of 66 inches. Concentrations in the range of 0.01 to 0.11 ppm were found up to 2 feet from the emitter and 4 feet deep in samples collected with a Veihmeyer tube (Table 4).

Table 3. Concentrations of aldoxycarb in segments of shallow and deep soil cores collected on three different dates from Location III using a truck-mounted drill rig.

Depth (inches)	Aldoxycarb concentration (ppm), dry weight soil								
	6/6/85 (8 days after 4th appl.)			11/7/85 (15 days after 9th appl.)			12/19/85 (57 days after 9th appl.)		
	Shallow 1	Shallow 2	Deep	Shallow 1	Shallow 2	Deep	Shallow 1	Shallow 2	Deep
0 - 6	-- <sup>a</sup>	0.03	0.10	0.01	0.05	0.04	--	ND <sup>c</sup>	--
6 - 12	0.07	0.40	0.12	0.01	ND	ND	ND	ND	ND
12 - 18	0.13	0.27	L.S.	ND	ND	ND	ND	ND	ND
20 - 26	0.03	0.09	0.04	ND	ND	ND	ND	0.01	ND
26 - 32	ND	0.04	0.06	0.04	ND	ND	ND	ND	ND
32 - 38	ND	ND	ND	0.10	ND	0.03	0.01	ND	ND
40 - 46	ND	ND	ND	ND	ND	ND	--	--	0.02
46 - 52	ND	ND	ND	ND	ND	ND	0.01	ND	0.05
52 - 58	ND	ND	ND	ND	ND	ND	0.01	ND	ND
60 - 66	ND	ND	ND	ND	--	0.01	ND	ND	ND
66 - 72	ND	ND	ND	ND	ND	ND	ND	ND	ND
72 - 178	ND	ND	ND	ND	ND	ND	ND	ND	ND
180 - 478			ND			ND			ND

a Sample lost due to compaction of soil.

b None detected, minimum detectable level was 0.02 ppm for samples collected on 6/6/85 and 0.01 ppm for those collected on 11/7/85 and 12/19/85.

13

Figure 1. Locations of aldoxycarb residues in the soil profiles of three cores collected on each of three sampling dates.

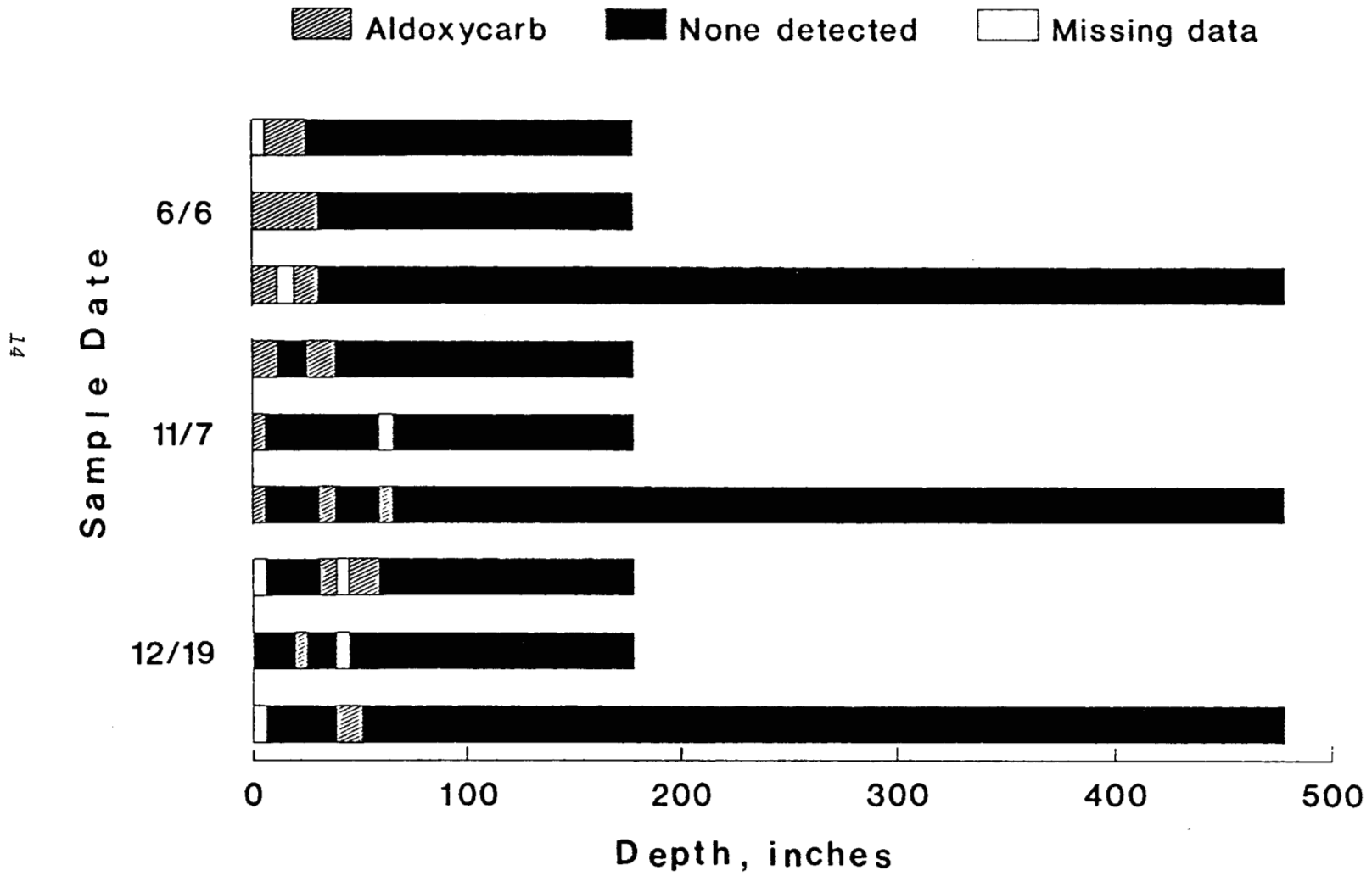


Table 4. Mean concentrations of aldoxycarb found in soil collected with a Veihmeyer tube at varying distances from drip emitters at Location III on three sampling dates.

Sample date	Depth (Inches)	Concentration (ppm, dry wt) <sup>a</sup> in soil segments taken at indicated distance from emitter		
		8 inches	16 inches	24 inches
6/6/85	0 - 12	ND <sup>b</sup>	0.08	0.01
	12 - 24	ND	0.02	ND
	24 - 36	0.13	0.05	0.02
	36 - 48	0.10	0.05	0.03
11/7/85	0 - 12	0.01	0.01	0.02
	12 - 24	0.02	0.03	0.03
	24 - 36	0.04	0.03	0.01
	36 - 48	0.08	ND	0.01
12/19/85	0 - 12	ND	ND	0.02
	12 - 24	ND	0.01	0.02
	24 - 36	0.01	0.03	0.02
	36 - 48	0.02	0.03	0.03

a. Each value is the mean concentration for three replicate cores.

b. None detected, MDL = 0.01 ppm.



Results for the final set of cores collected 42 days later showed that residues were still present but at lower concentrations. Aldoxycarb residues in the range of 0.01 to 0.05 ppm were present at maximum depths of 46 to 58 inches in two of the cores and at 26 inches in the third core (Table 3 and Figure 1). No aldoxycarb was detected in the upper 18 inches of soil although samples for the top 6 inches were missing for two of the cores. Results for Veihmeyer tube samples (Table 4) showed that generally, the occurrence and concentrations of aldoxycarb increased with distance from the emitter and soil depth. Aldoxycarb concentrations ranged from 0.01 to 0.07 ppm, similar to the range found in the deep cores. It appeared that residues had moved outward and downward over time.

The moisture content of soil segments in deep cores collected in June, November and December has been presented graphically in Appendix D for comparison. The amounts of soil moisture appear to be consistently in the 8 to 10% range in the upper 110 inches, increasing to 15 to 12% at 150 to 275 inches deep. Soil moisture content then dropped off dramatically to only 3 to 6% at the 280 to 380 inch depth and then increased to well over 20% in the lower part of the core.

Residues of aldicarb oxidation breakdown products, including aldoxycarb have been found in the ground water of 15 states (4). In California, aldoxycarb has been found in ground water in Del Norte and Humboldt counties where aldicarb was previously used in lily bulb production under conditions of cool soil temperatures and very high rainfall (22, 23). Yet, to date, no additional residues of aldicarb or its oxidation metabolites have been detected in ground water even though aldicarb has been applied to large acreages of crops grown in other parts of California (2).

Two factors which enhance the probability of aldoxycarb leaching through soil are its high solubility in water of approximately 10,000 ppm (7, 19) and its low affinity for adsorption to soil organic carbon in the range of  $K_{oc} = 1.7$  to 2.2 (25). The Hanford soil that made up the test plot is

considered to be a coarse well-drained soil with a neutral to basic pH and low organic matter content (20). The repeated use of sulfur and ammonium sulfate fertilizers tends to result in an acidic soil reaction with a pH of 4.5 in the upper confines of the soil profile. In a soil where the organic carbon content is very low, the opportunity for leaching would appear even greater because of less reaction with pesticide residues. On the other hand, high moisture content and soil temperature tend to increase degradation of aldoxycarb (9) and probably played a role in our drip irrigation plot. The moisture content of soil in the upper 100 inches was approximately 10% on all three dates and would be considered high for the relatively high sand content of the soil.

Studies conducted by Jones (10) during summer months in the San Joaquin Valley in sandy loam soils under furrow irrigation showed that aldicarb residues degraded in the upper 3 meters of the soil profile with a half-life of 1.5 to 2.0 months. More recently, Jones (11) demonstrated that aldicarb residues had longer half-lives (approximately 3.5 months) when the pesticide was applied in winter when cooler soil temperatures existed. Soil and environmental conditions for those studies were similar to conditions in the present study.

**Fenamiphos** - Soil samples collected from this plot were analyzed for fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone. Results for the first set of cores collected after four fenamiphos applications (6/4/85) showed that residues of fenamiphos sulfoxide and sulfone, but not the parent compound, were present in the upper 18 to 38 inches of soil (Table 5 and Figure 2). Concentrations of sulfoxide ranged from 0.05 to 1.21 ppm and those of the sulfone ranged from 0.03 to 0.25 ppm; greatest concentrations of both occurred at the 6-18 inch depth. Results for Veihmeyer tube samples (Table 6) showed that residues consisting of fenamiphos sulfoxide (0.02 to 1.00 ppm) and sulfone (0.02 to 0.30 ppm) were present at 2 feet away from the emitters and 1 to 4 feet deep depending on the distance from emitters. Again, no parent fenamiphos was detected. Ground water samples collected

Table 5. Concentrations of fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone in segments of three soil cores collected at Location III using a truck-mounted drill rig on June 4, 1985, 6 days after the fourth fenamiphos application.

Depth a (inches)	Fenamiphos (ppm) as total residue and fenamiphos (F), sulfoxide (SO), and sulfone (SO2)											
	Shallow Core 1				Shallow Core 2				Deep Core			
	Total	F	SO	SO2	Total	F	SO	SO2	Total	F	SO	SO2
0 - 6	0.20	ND <sup>b</sup>	0.15	0.05	0.36	ND	0.30	0.06	L.S. <sup>c</sup>	-- <sup>d</sup>	--	--
6 - 12	1.46	ND	1.21	0.25	0.70	ND	0.60	0.10	0.41	ND	0.35	0.06
12 - 18	0.33	ND	0.30	0.03	0.76	ND	0.70	0.06	1.19	ND	1.03	0.16
20 - 26	ND	ND	ND	ND	0.09	ND	0.09	ND	L.S.	--	--	--
26 - 32	ND	ND	ND	ND	ND	ND	ND	ND	L.S.	--	--	--
32 - 38	ND	ND	ND	ND	ND	ND	ND	ND	0.05	ND	0.05	ND
40 - 178	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
178 - 458									ND	ND	ND	ND

a Soil core samples were collected in 6-inch segments, three segments per 20-inch sample cylinder.

b None detected, minimum detectable level was 0.01 ppm.

c Sample was lost due to compaction of soil.

d No data.

Figure 2. Locations of total fenamiphos residues (fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone) in the soil profiles of three cores collected on each of three sampling dates.

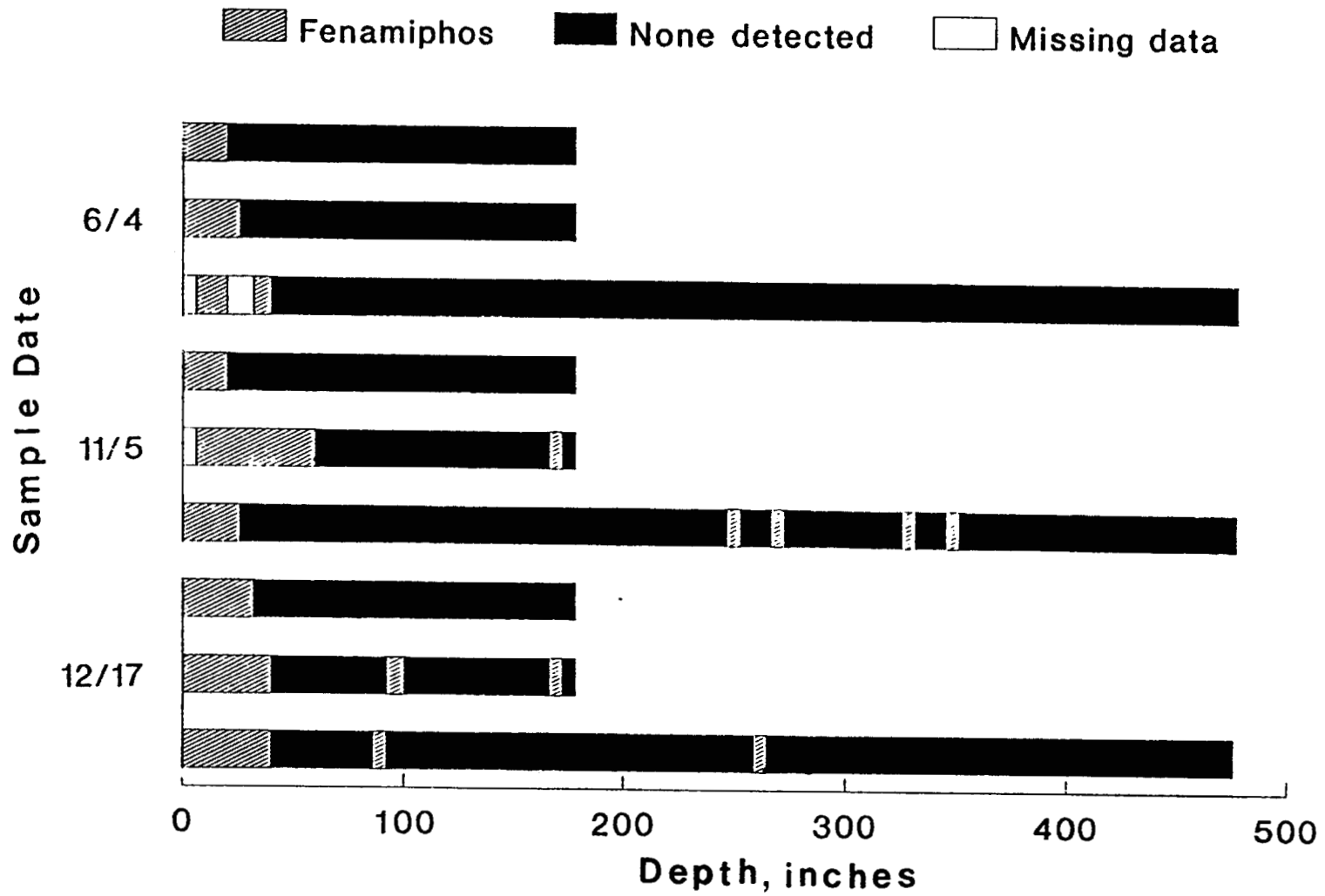


Table 6. Mean concentrations of fenamiphos residues (fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone) found in soil collected with a Veihmeyer tube at varying distances from drip emitters at Location III on three sampling dates.

Sample date	Depth (Inches)	Concentration (ppm, dry wt) <sup>a</sup> in soil segments taken at indicated distance from emitter		
		8 inches	16 inches	24 inches
6/4/85	0 - 12	1.06	0.92	0.32
	12 - 24	0.21	0.03	ND <sup>b</sup>
	24 - 36	0.02	0.02	0.01
	36 - 48	0.01	0.03	ND
11/5/85	0 - 12	1.01	0.56	0.62
	12 - 24	0.27	-- <sup>c</sup>	0.02
	24 - 36	0.18	0.12	0.01
	36 - 48	--	0.15	ND
12/17/85	0 - 12	0.48	0.52	0.30
	12 - 24	0.27	0.45	0.15
	24 - 36	0.33	0.11	0.07
	36 - 48	0.02	0.04	ND

a. Each value is the mean concentration for three replicate cores.

b. None detected, MDL = 0.01 ppm.

c. Samples were lost during sampling process.

from the bottom of the deep core hole contained no fenamiphos residue at MDL's of 0.2 ppb.

The second set of core samples was taken 11/5/85, 13 days after the ninth and final application of fenamiphos had been made. For the upper 178 inches, the results for one shallow core and the deep core were quite similar (Table 7, Figure 2). Residues of all three compounds at concentrations ranging from 0.01 to 0.73 ppm were present in the 0-26 inch depths. However, for the portion of the deep core below 178 inches, fenamiphos sulfone at 0.01 ppm was found at 246 - 252 inches and parent fenamiphos at 0.02 ppm was found at depths of 272 inches, 332 inches and 352 inches. In the second shallow core, residues of fenamiphos or one or both of the oxidation products at concentrations ranging from 0.01 to 0.26 ppm were found throughout the upper 58 inches of the soil profile. Then, fenamiphos parent at 0.03 ppm was detected again at the 166-172 inch depth. Results for Veihmeyer tube samples showed that residues of all three fenamiphos compounds were present up to 2 feet away from emitters and penetrated to a depth of 4 feet, especially in samples taken closer to the emitters (Table 6).

Results for the final set of cores collected 42 days later showed that fenamiphos compounds had leached deeper into the upper soil profile and some residues were still present in the deeper strata (Table 8, Figure 2). For all three cores, residues of parent fenamiphos, sulfoxide and sulfone were present in most soil segments throughout the upper 26-38 inches. Concentrations detected ranged from 0.03-0.58 ppm for fenamiphos, 0.02-0.58 ppm for sulfoxide and 0.01-0.12 ppm for sulfone. Fenamiphos sulfoxide at 0.03 ppm was again detected at depths of 98 inches and 172 inches in one of the shallow cores. The sulfoxide at 0.05-0.06 ppm was also found at depths of 92 inches and 266 inches in the deep core. Results for Veihmeyer tube samples showed that fenamiphos residues were present in all samples taken 2 feet away from the emitters, throughout the upper 3 feet and in one third of

Table 7. Concentrations of fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone in segments of three soil cores collected from Location III using a truck-mounted drill rig on November 5, 1985, 13 days after the ninth fenamiphos application.

Depth <sup>a</sup> (inches)	Shallow Core 1				Shallow Core 2				Deep Core			
	Total	F	S0	S02	Total	F	S0	S02	Total	F	S0	S02
0 - 6	0.36	0.16	0.16	0.04	L.S. <sup>b</sup>	-- <sup>c</sup>	--	--	0.73	0.43	0.20	0.10
6 - 12	0.13	0.04	0.08	0.01	0.01	ND <sup>d</sup>	ND	0.01	0.24	0.10	0.11	0.03
12 - 18	0.26	0.13	0.08	0.05	0.08	0.05	0.02	0.01	0.07	0.02	0.04	0.01
20 - 26	ND	ND	ND	ND	0.29	0.01	0.25	0.03	0.10	0.05	0.05	ND
26 - 32	ND	ND	ND	ND	0.18	0.06	0.11	0.01	ND	ND	ND	ND
32 - 38	ND	ND	ND	ND	0.36	0.17	0.17	0.02	ND	ND	ND	ND
40 - 46	ND	ND	ND	ND	0.18	0.01	0.17	ND	ND	ND	ND	ND
46 - 52	ND	ND	ND	ND	0.44	0.16	0.26	0.02	ND	ND	ND	ND
52 - 58	ND	ND	ND	ND	0.01	0.01	ND	ND	ND	ND	ND	ND
60 - 166	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
166 - 172	ND	ND	ND	ND	0.03	0.03	ND	ND	ND	ND	ND	ND

Table 7. Continued.

---

172 - 178	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
180 - 246									ND	ND	ND	ND
246 - 252									0.01	ND	ND	0.01
252 - 266									ND	ND	ND	ND
266 - 272									0.02	0.02	ND	ND
272 - 326									ND	ND	ND	ND
326 - 332									0.02	0.02	ND	ND
332 - 346									ND	ND	ND	ND
346 - 352									0.02	0.02	ND	ND
352 - 478									ND	ND	ND	ND

---

- a Soil core samples were collected in 6-inch segments, three segments per 20-inch sample cylinder.
- b Sample was lost due to compaction of soil.
- c No data.
- d None detected, minimum detectable level was 0.01 ppm.



Table 8. Concentrations of fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone in segments of three soil cores collected from Location III using a truck-mounted drill rig on December 17, 1985, 55 days after the ninth fenamiphos application.

Depth (inches) a	Fenamiphos (ppm) as total residue and fenamiphos (F), sulfoxide (SO), and sulfone (SO2)											
	Shallow Core 1				Shallow Core 2				Deep Core			
	Total	F	SO	SO2	Total	F	SO	SO2	Total	F	SO	SO2
0 - 6	0.38	0.17	0.14	0.07	0.30	0.12	0.14	0.04	0.55	0.24	0.21	0.10
6 - 12	0.66	0.11	0.49	0.06	0.95	0.25	0.58	0.12	0.21	0.08	0.11	0.02
12 - 18	0.09	0.03	0.03	0.03	0.38	0.18	0.18	0.02	0.11	0.04	0.06	0.01
20 - 26	0.06	0.03	0.03	ND <sup>a</sup>	0.24	0.08	0.15	0.01	0.46	0.41	0.03	0.02
26 - 32	0.07	0.05	0.02	ND	0.30	0.30	ND	ND	0.71	0.58	0.12	0.01
32 - 38	ND	ND	ND	ND	0.39	0.11	0.28	ND	0.27	0.12	0.15	ND
40 - 86	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
86 - 92	ND	ND	ND	ND	ND	ND	ND	ND	0.05	ND	0.05	ND
92 - 98	ND	ND	ND	ND	0.03	ND	0.03	ND	ND	ND	ND	ND
100 - 166	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
166 - 172	ND	ND	ND	ND	0.03	ND	0.03	ND	ND	ND	ND	ND
172 - 178	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
180 - 258									ND	ND	ND	ND
260 - 266									0.06	ND	0.06	ND
266 - 460									ND	ND	ND	ND

a Soil core samples were collected in 6-inch segments, three segments per 20-inch sample cylinder.

b None detected, minimum detectable level was 0.01 ppm.

the 4 foot deep samples (Table 6). Concentrations for the three compounds were similar to those found in the drilled cores.

Soil moisture content was similar for the deep cores collected in June, November and December (Appendix D). Soil moisture remained at or below 10% in most of the upper half of the soil profile and showed occasional increases above 20% in the lower half of the profile.

Fenamiphos has been applied to a wide range of crops in California with the largest quantity used on grapes and much smaller amounts on citrus, cotton, and more recently on peaches and prunes (2). It was also used in lily bulb production in Del Norte and Humboldt Counties from 1983 until 1987 when its use was banned based on evidence of deep leaching in soil (24). To date, fenamiphos has not been found in ground water in California although monitoring has been conducted in Del Norte County (21), portions of the San Joaquin Valley (17), and other areas (3).

Although fenamiphos or its two oxidation breakdown compounds have not been detected in ground water, the magnitude of leaching of these compounds observed in this study suggests a potential for contamination under conditions of drip irrigation. Parent fenamiphos was detected at a maximum depth of 29.7 feet, fenamiphos sulfoxide at 22.2 feet and fenamiphos sulfone at 21 feet. However, concentrations found at those depths were extremely low making the possibility of further persistence and leaching unlikely. Green and Khan (6) concluded that the presence of macropores in soil can result in the deep movement of small amounts of certain pesticides while most of the applied pesticide is prevented from leaching out of the area of application. The deep leaching of small quantities of fenamiphos observed in the present study may have been the result of flow through macropores. Troiano et al (17) concluded that the lack of positive detections of fenamiphos compounds in well water sampled in the San Joaquin Valley was caused either by degradation of the compounds before encountering ground water or by the level of fenamiphos use which may still be too low to

produce detectable levels in ground water. In a majority of the study area fenamiphos had been applied to grapes through drip irrigation systems.

Once fenamiphos has been added to soil, oxidation to fenamiphos sulfoxide is reported to occur rapidly followed by a slower degradation to fenamiphos sulfone (11, 14, 15). Fenamiphos sulfoxide has also been reported to be the most persistent and mobile form in soil (12, 16). Thus, it was surprising to find the parent compound moving deep into the soil profile. The occurrence of the sulfoxide and sulfone forms at depths of over 20 feet was less surprising. An additional factor in the fenamiphos plot was that the plot area was preplant fumigated; fumigation may have reduced or eliminated microorganisms that degrade fenamiphos making it available for leaching (18).

**Oxamyl** - Samples collected from this plot were analyzed for oxamyl and the oxamino breakdown product. Results for the first set of cores collected on 6/4/85, 6 days after the fourth application, showed residues present in the upper 12 - 18 inches of the soil profile (Table 9, Figure 3). Concentration ranges were 0.03 to 0.74 ppm for oxamyl and 0.02 to 0.36 ppm for oxamino. Results for Veihmeyer tube samples (Table 10) showed that oxamyl was present in the upper 12 to 24 inches of soil and up to 2 feet from the emitter. Oxamino was present only in the shallowest samples taken 8 inches from the emitter. Ground water samples collected from the bottom of the deep core hole contained no detectable oxamyl or oxamino residues at an MDL of 2.0 ppb for each compound.

The second set of core samples was taken approximately 5 months later on 11/6/85, 14 days after the ninth and final application of oxamyl had been made. For the two shallow cores, one core contained no oxamyl residues and the other contained oxamyl (0.01 or 0.42 ppm) but not oxamino, in the upper 32 inches of the soil profile. For the deep core, oxamino at 0.02 and 0.19 ppm was found in the top 18 inches and oxamyl at 0.06 ppm was found in the upper 6 inches of soil. However, oxamyl was again detected at 0.01 ppm in

Table 9. Concentrations of oxamyl and oxamino in segments of shallow and deep soil cores collected from Location III on three different dates using a truck-mounted drill rig.

Depth (inches)	Oxamyl or (oxamino) concentration (ppm), dry weight soil								
	6/5/85 (6 days after 4th appl.)			11/6/85 (14 days after 9th appl.)			12/18/85 (56 days after 9th appl.)		
	Shallow 1	Shallow 2	Deep	Shallow 1	Shallow 2	Deep	Shallow 1	Shallow 2	Deep
0 - 6	-- <sup>a</sup>	0.21	0.06 (0.02)	0.42	ND <sup>b</sup>	0.06 (0.19)	0.01	ND	ND
6 - 12	0.17 (0.05)	0.03	ND	ND	ND	ND	ND	ND	ND
12 - 18	0.74 (0.36)	ND	0.12	0.01	ND	ND (0.02)	ND	ND	ND
20 - 26	--	ND	ND	ND	ND	ND	0.01	ND	ND
26 - 32	--	ND	ND	0.01	ND	ND	ND	ND	ND
32 - 38	ND	ND	ND	ND	ND	ND	0.01	ND	ND
40 - 46	--	ND	ND	ND	ND	ND	ND	--	ND
46 - 52	ND	ND	ND	ND	ND	ND	0.01	ND	ND
52 - 58	ND	ND	ND	ND	ND	ND	0.02	ND	ND
60 - 66	ND	ND	ND	ND	ND	ND	--	ND	ND
66 - 72	ND	ND	ND	ND	ND	ND	0.01	ND	ND
72 - 78	ND	ND	ND	ND	ND	ND	0.02	ND	ND
80 - 86	--	ND	ND	ND	ND	ND	0.02	--	ND
86 - 92	ND	ND	ND	ND	ND	ND	0.02	ND	0.01
92 - 98	ND	ND	ND	ND	ND	ND	0.01	ND	ND
100 - 126	ND	ND	ND	ND	ND	ND	ND	ND	ND

27

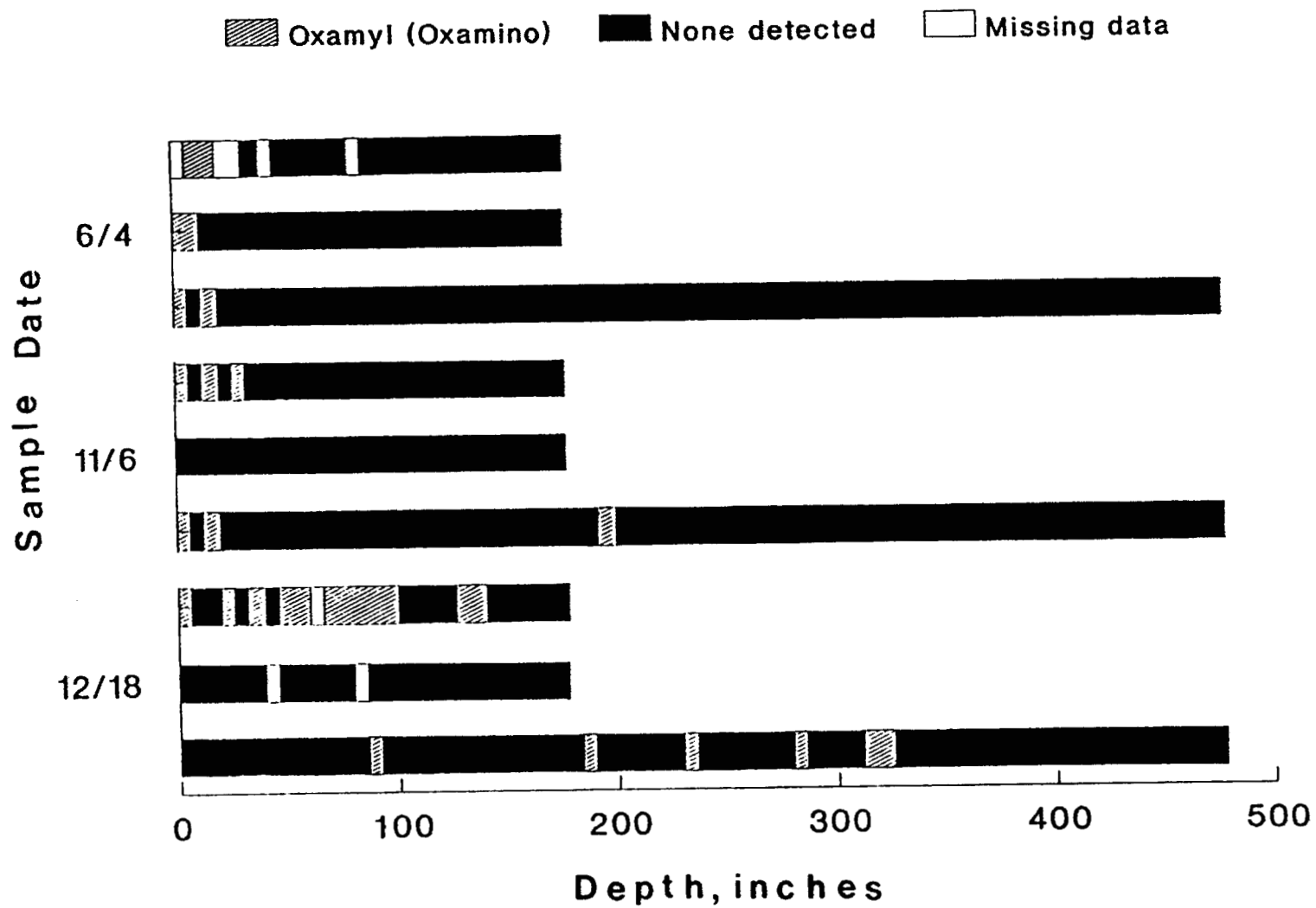
Table 9. Continued.

126 - 132	ND	ND	ND	ND	ND	ND	0.01	ND	ND
132 - 138	ND	ND	ND	ND	ND	ND	0.01	ND	ND
140 - 178	ND	ND	ND	ND	ND	ND	ND	ND	ND
186 - 192			ND			ND			0.01
192 - 198			ND			0.01			ND
200 - 232			ND			ND			ND
232 - 238			ND			ND			0.01
240 - 280			ND			ND			ND
280 - 286			ND			ND			0.01
286 - 312			ND			ND			ND
312 - 318			ND			ND			0.01
320 - 326			ND			ND			0.01
326 - 478			ND			ND			ND

a Sample was lost due to compaction of soil.

b None detected, minimum detectable level was 0.01 or 0.02 ppm.

Figure 3. Locations of total oxamyl residues (oxamyl plus oxamino) in the soil profiles of three cores collected on each of three sampling dates.



the soil segment collected at the 192-198 inch depth (Table 9, Figure 3). Results for Veihmeyer tube samples (Table 10) showed oxamyl or oxamino residues present 18 to 24 inches from the emitter at depths ranging from 12 to 36 inches.

Results for the final set of cores collected 12/18/85, 42 days later, showed that no oxamino residues were detected but that oxamyl was present in numerous samples and had moved deeper into the soil profile. No residues were present in one shallow core but in the other, low levels of oxamyl at 0.01-0.02 ppm were present in most segments from the surface down to 138 inches deep. In the deep core, oxamyl at the minimum detectable level of 0.01 ppm was found at depths of 86-92 inches, 186-192 inches, 232-238 inches, 280-286 inches, 312-318 inches and 320-326 inches. Results for Veihmeyer tube samples showed oxamyl and oxamino residues present in scattered samples in the upper 24 inches of soil and up to 24 inches away from the emitter.

Oxamyl has been found in the ground water of two northeastern states (4) but not in California where over 200 wells have been tested (3). The pesticide is used on a number of food and ornamental crops in California with the greatest quantities applied to celery, melons and tomatoes (2).

Oxamyl has a high water solubility of 280 g/liter (7) and does not adsorb strongly to soil (1, 5), factors which suggest a strong potential for leaching through soil. However, the results of studies conducted under field conditions showed that oxamyl degraded rapidly in soil (1, 5, 15) and was thus not available for leaching for a very long period after application (8, 13). Leaching of oxamyl occurred to a maximum depth of only 60 inches in a plot with sandy soil where high rates of oxamyl and irrigation water were applied during a 2 year study (13). However, the deep leaching of oxamyl that was observed in the present study suggests a potential for contamination under conditions of drip irrigation. Oxamyl at the minimum detectable level of 0.01 ppm was found at a maximum depth of 27.1 feet and

Table 10. Mean concentrations of oxamyl residues (oxamyl plus oxamino) found in soil collected with a Veihmeyer tube at varying distances from drip emitters at Location III on three sampling dates.

Sample date	Depth (Inches)	Concentration (ppm, dry wt) <sup>a</sup> in soil segments taken at indicated distance from emitter		
		8 inches	16 inches	24 inches
6/5/85	0 - 12	0.46	0.09	0.03
	12 - 24	0.03	0.04	0.01
	24 - 36	ND <sup>b</sup>	ND	ND
	36 - 48	ND	ND	ND
11/6/85	0 - 12	ND	0.11	0.01
	12 - 24	ND	0.06	0.02
	24 - 36	ND	ND	0.01
	36 - 48	ND	ND	ND
12/18/85	0 - 12	0.02	0.02	0.01
	12 - 24	0.03	0.01	0.01
	24 - 36	ND	ND	ND
	36 - 48	ND	ND	ND

a. Each value is the mean concentration for three replicate cores.

b. None detected, MDL = 0.02 ppm.



it is possible that lower concentrations moved even deeper into the soil. Movement of oxamyl residues with water by flow through macropores (6) may have been at least partially responsible for the observed low levels of pesticide found deep in the soil profile.

## CONCLUSIONS

1. Drip application of certain nematicides resulted in horizontal distribution of the nematicides into much of the crop root zone. Movement of the chemicals was measured up to 2 feet away from the emitters at depths ranging from the surface down to 2-4 feet deep.
2. Fenamiphos and oxamyl, but not aldoxycarb, leached deeply into the soil profile as a result of application through a drip irrigation system. However, very small concentrations were found at the deepest detection depths in soil. Fenamiphos, sulfoxide and/or sulfone were found at maximum depths of 29.3, 22.2 and 21 feet, respectively. Oxamyl was detected in soil collected 27.2 feet deep. Differences in chemical characteristics of the nematicides were probably responsible for the observed differences in soil persistence and leaching. Further, preplant fumigation of the fenamiphos plot, but not the oxamyl or aldoxycarb plots at the Kearney test location may have influenced the persistence of fenamiphos by reducing the microbial populations and subsequently permitted the leaching of fenamiphos compounds in soil.
3. Applications of fenamiphos or oxamyl through drip irrigation systems may result in deep leaching and potential ground water contamination in areas where porous soils and shallow ground water tables exist.
4. Multiple applications of nematicides through drip irrigation systems did not result in detectable levels of any of the nematicides in ground water collected approximately 23-40 feet beneath the soil surface after 1 or 2 years of nematicide treatments. However, at the two Reedley sites, ground water samples were collected from core holes drilled near the ends of vine rows, 32-52 inches away from the nearest emitter. Without information on the direction of ground water movement we can only say that contamination was not seen at the sampled sites. At the Kearney site, ground water samples were collected in June near the start of the

nematicide treatment period, but not in November or December after all treatments were applied.

5. Much variability existed in the detectability of nematicides at adjacent core sites. This variability demonstrates the value of field sampling and the need for replicated sampling designs.

## REFERENCES

1. BROMILOW, R. H., R. J. BAKER, M. A. H. FREEMAN and K. GOROG. 1980. The degradation of aldicarb and oxamyl in soil. *Pesticide Science* 11:371-378.
2. CALIFORNIA DEPARTMENT OF FOOD AND AGRICULTURE. Pesticide Use Report, Annual 1987. 108 pp.
3. CARDOZO, C., M. PEPPLER, J. TROIANO, D. WEAVER, B. FABRE, S. ALI and S. BROWN. 1988. Sampling for pesticide residues in California well water, 1988 update. California Department of Food and Agriculture. 151 pp.
4. COHEN, S. Z., C. EIDEN and M. N. LORBER. Monitoring ground water for pesticides. In *Evaluation of Pesticides in Ground Water*. W. Y. Garner, R. C. Honeycutt and H. N. Nigg Eds. 1986. American Chemical Society, Washington, D. C.
5. GERSTL, Z. 1984. Adsorption, decomposition and movement of oxamyl in soil. *Pesticide Science* 15:9-17.3.
6. GREEN, R. E. and M. A. KHAN. Pesticide movement in soil: mass flow and molecular diffusion. In *Fate of Pesticides in the Environment*. J. W. Biggar and J. N. Seiber Eds. 1987. Agricultural Experiment Station, University of California, Div. of Agriculture and Natural Resources, Pub. No. 3320.
7. HARTLEY, D. and H. KIDD Eds. 1988. *The Agrochemicals Handbook*, Second Edition. The Royal Society of Chemistry.
8. HARVEY, J. and J. C.-Y. HAN. 1978. Decomposition of oxamyl in soil and water. *Agricultural and Food Chemistry* 26:536-541.
9. JONES, R. L. Field, laboratory, and modeling studies on the degradation and transport of aldicarb residues in soil and ground water. In *Evaluation of Pesticides in Ground Water*. W. Y. Garner, R. C. Honeycutt and H. N. Nigg Eds. 1986. American Chemical Society, Washington, D. C.

10. JONES, R. L. 1987. Central California studies on the degradation and movement of aldicarb residues. *Journal of Contaminant Hydrology*, 1:287-298.
11. JONES, R. L. 1989. Measurement of aldicarb degradation and movement for winter application to grapes. Progress Report, Rhone-Poulenc Ag. Company., March 27, 1989.
12. LEE, C.-C., R. E. GREEN, and W. J. APT. 1986. Transformation and adsorption of fenamiphos, f. sulfoxide and f. sulfone in Molokai soil and simulated movement with irrigation. *J. Contaminant Hydrology* 1:211-225.
13. MCINTOSH, C. L., J. P. JENKINS, D. L. BURGOYNE and D. T. FERGUSON. 1984. A two-year field study to determine the fate of oxamyl in soil during flood irrigation.
14. MOBAY CHEMICAL CORP. Nema-cur technical handbook. Product profile, December, 1984. pp. 4-8.
15. OU, L.-T. and P. S. C. RAO. 1986. Degradation and metabolism of oxamyl and phenamiphos in soils. *J. Environmental Science and Health*, B21(1). pp. 25-40.
16. PETERSON, D., W. WINTERLIN and L. R. COSTELLO. 1986. Nema-cur residues in turfgrass. *California Agriculture*, March-April. pp. 26-27.
17. TROIANO, J., B. TURNER and N. MILLER. 1987. Sampling for residues of fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone in well water. California Department of Food and Agriculture. 31 pp.
18. TUDOR, M. E., S. KEADTISURE, and M. V. MCKENRY. 1988. The decline of phenamiphos in soils under different management strategies. (Abstract) *Amer. Chem. Soc.*
19. UNION CARBIDE AGRICULTURAL PRODUCTS COMPANY, INC. 1983. Product Bulletin, Standak Aldoxycarb Experimental Pesticide (UC 21865).
20. U. S. DEPARTMENT OF AGRICULTURE, SOIL CONSERVATION SERVICE. Soil Survey of Eastern Fresno Area, California. 1971.
21. WARNER, S. A. Personal communication. 1988.
22. WARNER, S. A., H. LUNDBORG, D. WHYTE, M. HEASSLER, and S. GERGUS. 1989. Groundwater pollution by pesticides on the Smith River Plains,

- Del Norte County. Volume I. California Regional Water Quality Control Board. 108 pp.
23. WEAVER, D. J. 1988. Memorandum, California Department of Food and Agriculture.
  24. WEAVER, D. J., V. QUAN, C. N. COLLISON, N. SAINI, AND S. J. MARADE. 1988. Monitoring the persistence and movement of fenamiphos in soils of lily bulb fields in Del Norte County, 1986. California Department of Food and Agriculture. 42 pp.
  25. ZHONG, W. Z., A. T. LEMLEY and R. J. WAGENET. Quantifying pesticide adsorption and degradation during transport through soil to ground water. In Evaluation of Pesticides in Ground Water. W. Y. Garner, R. C. Honeycutt and H. N. Nigg Eds. 1986. American Chemical Society, Washington, D. C.

APPENDIX A

PESTICIDE ANALYTICAL METHODS

## DEPARTMENT OF FOOD AND AGRICULTURE



CALIFORNIA DEPT. OF FOOD & AGRIC.  
ENVIRONMENTAL MONITORING SECTION  
CHEMISTRY LABORATORY SERVICES  
3292 Meadowview Road  
Sacramento, CA 95832  
(916)+427-4998/4999

Original Date: November 7, 1985  
Supercedes: NEW  
Current Date: November 7, 1985  
Method #:

## Nemacur Residues in Soil

## SCOPE:

This method has been developed and used for the analysis of Nemacur, Nemacur Sulfoxide, and Nemacur Sulfone in soil.

## PRINCIPLE:

Nemacur and its metabolites are extracted from the soil with a hexane-acetone (1:1) solution. The solution is evaporated to dryness and redissolved in ethyl acetate. A portion of the extract is prepared for the GLC analysis of Nemacur. The remaining extract was evaporated to dryness and redissolved in acetonitrile:water (20:80). This portion was then analyzed by HPLC for the metabolites.

## REAGENTS AND EQUIPMENT:

1. Acetonitrile, HPLC grade
2. Ethyl Acetate, Pesticide grade
3. Water, HPLC quality, filtered
4. Balance - Mettler PL 1200 - Mettler Instrument Corp.  
Hightstown, N.J.
5. Micro-Mate Syringes 10cc - Popper and Sons Inc.  
New Hyde Park, N.Y.
6. 500ml flat-bottom boiling flasks
7. Funnels, 60 degree short stem, 3-4 inch diameter.
8. Graduated conical centrifuge tube - 15ml
9. Bottles, 500ml amber wide-mouth with teflon lined lid - Qorpak.
10. Whatman #4 filter paper or Sharkskin - 12.5cm
11. Rannin HPLC Prefilters - 0.2 micron
12. Assorted glassware for measuring and dispensing reagents as required.
13. Reverse phase HPLC with UV detector.
14. Meyers N-EVAP - Organomation Associates Incorporated  
Northborough, Ma.
15. G-10 Gyrotory (R) Shaker - New Brunswick Scientific Co., Inc.  
(with CE-250S clamps) Edison, N.J.
16. Thermolyne Vortex Maxi Mixer II - Sybron Corporation  
Dubuque, Iowa.
17. 57mm aluminum weighing dish - Fisher Scientific  
San Francisco, Ca.



**ANALYSIS:****Extraction:**

1. Soil core samples were thawed at room temperature or in the refrigerator overnight and mixed well.
2. Weigh 15-20 gram of sample in an aluminum dish and place in an oven at 110°C for at least six hours for determining soil moisture.
3. Weigh 50 grams of soil into a 500ml wide-mouth amber bottle. Add ~ 100 gram anhydrous sodium sulfate to sample and mix well. Add 60mls of hexane-acetone (1:1), cover with foil, cap and shake vigorously for ten seconds.
4. Place on Gyrotory shaker for twenty minutes at 230 rpm.
5. Let sample set for fifteen minutes after removal from the shaker.
6. Decant solvent from sample through funnel, lined with filter paper and filled with ~ 100 gram anhydrous sodium sulfate, into a 500 ml boiling flask. Rinse sodium sulfate with 20 ml hexane-acetone.
7. Add another 60 ml of hexane-acetone (1:1) to each sample, recap and repeat steps 4, 5, and 6 two more times.
8. On the last extraction decant the organic layer and finally the soil into the funnel. Rinse the sample bottle with 20 ml of hexane-acetone and pour through funnel.
9. Rotoevaporate at 40°C under 15 inches vacuum until almost dry.
10. Using ethyl acetate, quantitatively transfer residues to a 15 ml graduated centrifuge tube and bring to final volume of 5 ml under nitrogen (50°C) on the N-EVAP.

**GLC Preparation:**

1. Place samples on the Maxi Mixer for 20 seconds.
2. Remove 2 ml of sample and place in auto sampler vial for GLC analysis.

## HPLC Preparation:

1. Return the remaining 3 ml of sample to the N-EVAP (@50°C) and evaporate the ethyl acetate to dryness.
2. Add 2 ml (with volumetric pipette) of 20% acetonitrile-water to redissolve the residues.
3. Place samples on Maxi Mixer for 20 seconds then sonicate for 2 minutes.
4. Place on Maxi Mixer for 30 seconds then transfer to a 5 cc syringe. Filter through a 0.2 micron HPLC prefilter into an autosampler vial ready for HPLC analysis.

## HPLC CONDITIONS:

Perkin Elmer Series 4 HPLC with ISS automatic sampler and column oven, or equivalent. An ultraviolet detector, Kratos SF 769Z at a wavelength of 220 nanometers.

## Column:

Sepralyte cyclohexal (CH), 5 micron, 4.6mm i.d. x 25cm  
(Analytichem International)

## Flow conditions:

Equilibrium - 1.5ml/minute for seven minutes of  
15% acetonitrile / 85% water

## Gradient - Flow 1.5ml/minute

2 minutes @ 15% acetonitrile / 85% water  
6 minute @ 25% acetonitrile / 75% water  
11 minutes @ 40% acetonitrile / 60% water  
8 minutes @ 60% acetonitrile / 40% water  
3 minutes @ 75% acetonitrile / 25% water

Oven Temperature - Ambient

Injection Volume - 100 microliters

## GLC CONDITIONS:

Varian 3700 equipped with a Thermionic Specific Detector  
and a Hewlett-Packard 7672A auto sampler.

Injector: Splitless; 210°C

Detector: 260°C  
Bead; 470  
Hydrogen; 25 psi

Temperature Program: Initial temperature; 130°C for 1 minute.  
Program Rate; 20°C per minute.  
Final temperature; 230°C for 3 minutes.

Column: Hewlett-Packard HP-1(crosslinked)  
100% Dimethyl polysiloxane (Gum)  
10m x 0.53 x 2.65 micron  
Carrier: Helium 12 ml/ minute

## CALCULATIONS:

Report data in ppm.

$$\% \text{ Moisture} = 100 - \frac{(\text{dry weight soil}) (100\%)}{(\text{wet weight soil})}$$

$$\text{PPM} = \frac{(\text{peak ht sample})(\text{ng std injected})(\text{sample final volume ml})(100)}{(\text{peak ht standard})(\text{ul injected})(\text{g of sample})(100 - \% \text{moisture})}$$

## DISCUSSION:

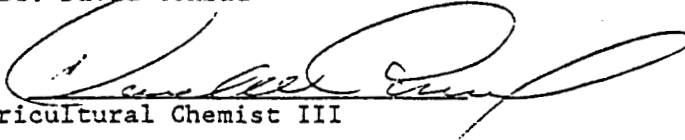
## REFERENCES:

WRITTEN BY: Jim Echelberry



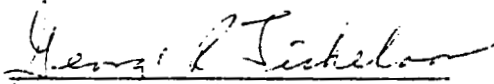
TITLE: Laboratory Technician (Chemical Analysis)

APPROVED BY: David Conrad



TITLE: Agricultural Chemist III

APPROVED BY: George R. Tichelaar



TITLE: Principal Research Chemist

\*\*\*\*\*

CALIFORNIA DEPT. OF FOOD & AGRIC.  
CHEMISTRY LABORATORY SERVICES  
ENVIRONMENTAL MONITORING SECTION  
3292 Meadowview Road  
Sacramento, CA 95832  
(916)+427-4999 or 421-4353

Original Date: 11/2/87  
Supercedes: 2/22/88  
Current Date: 7/22/88  
Method #:

Ethoprop (Mocap), Phorate (Thimet), Phorate Sulfoxide,  
and Phorate Sulfone in Soil

SCOPE:

This method is for the determination of residues of Ethoprop, Phorate, Phorate Sulfoxide and Phorate Sulfone in soil.

PRINCIPLE:

Soil samples are blended for uniformity and a representative sample (50 grams) is extracted twice with 100 ml of acetone. The extract is filtered and analyzed directly by gas chromatography with an NP detector.

REAGENTS AND EQUIPMENT:

1. Acetone- purity 99.9+%
2. Wide mouth amber pint jars.
3. Aluminum foil
4. Glass vials - seven milliliter volume with foil lined caps.
5. G10 Gyrotory<sup>R</sup> Shaker or equivalent with bracket sizes to hold round amber pint jars.
6. Filter paper and glass filter funnels 90mm/100mm
7. Na<sub>2</sub>SO<sub>4</sub> Anhydrous Granular Analytical Grade
8. Analytical standards of Ethoprop, Phorate, Phorate Sulfoxide, Phorate Sulfone.
  - a) Stock standards - 1mg/ml parent compounds; 100ug/ml-metabolites
  - b) Working standards - Dilute stock standards to several working standards to cover the linear ranges of the gas chromatograph and detector used (eg. 0.005ng to 5ng/ul).
9. Gas chromatograph equipped with NPD.
10. Column - Megabore- Carbowax 20M- 10 meters in length.
11. Top loading balance - 1000 gm or greater capacity.
12. Disposable aluminum dishes - 57mm Fisherbrand or equiv.
13. Analytical balance - four place capability.

ANALYSIS:

1. Weigh 50 grams + or - 0.1gm of the well mixed soil sample into a one pint amber glass jar on a top loading balance.
2. Add 100 ml acetone and close with screw cap lined with aluminum foil.
3. Place in bracket on the rotary table shaker and set speed to ~200 RPM. Let mix 15 to 20 minutes.
4. Remove from shaker and let settle until liquid is mostly clear. Decant through filter paper and funnel containing ~1 inch  $\text{Na}_2\text{SO}_4$  into any suitable container (fleaker, jar or flask) that will hold > 200 ml volume and allow adequate mixing.
5. Repeat steps 2 through 4 for a total of 2 extractions. Mix well.
6. A representative portion may be transferred to 7 ml screw cap vials for storage in freezer for later analysis. Direct sampling from container may be done if conditions permit immediate GC analysis.
7. Inject 2 ul portions of sample and standards into Megabore column coated with Carbowax 20M.
8. Measure and plot peak heights of standards at each attenuation used.
9. Determine % moisture in soil by weighing ~20gms into tared aluminum dish; drying in 105 C oven for > 12 hrs until constant weight; recording dry wt at room temp. Use % dry wt to correct ppm found in "as received" soil to ppm dry soil.

EQUIPMENT CONDITIONS:

Gas Chromatograph - Perkin-Elmer Sigma 2

- |    |                       |   |                 |
|----|-----------------------|---|-----------------|
| a) | Column temperature:   | Ethoprop  | 95°C isothermal |
|    |                       | Phorate   | 100°C "         |
|    |                       | Phorate Sulfoxide                                     | 150°C "         |
|    |                       | Phorate Sulfone                                       | 150°C "         |
| b) | Injector temperature: | 240°C   |                 |
| c) | Detector temperature: | 300°C   |                 |
| d) | H <sub>2</sub>        | ~25 psi   |                 |
| e) | Air                   | ~35 psi   |                 |
| f) | He                    | ~7 psi  |                 |
| g) | NP Bead               | mv adjusted to 50% chart response, atten. 8, A/Z off. |                 |

CALCULATIONS:

This GC had no integrator attachment, therefore off-scale peak responses had to be run at higher attenuations and appropriate standards run along side to allow graphs to be drawn and samples quantitated in nanograms. Direct proportional calculations of sample against stds were also done.

Peak heights of standards are linear at different levels.

Low level - 40 ppb - atten. 4  
Medium level - 600 ppb - atten. 32  
High level - 6000 ppb - atten. 256

200 ml solvent volume/50 gms soil sample - 0.5mg soil/2 ul injection.  
Final volume for calculations same as original 200 ml; actual volume is less.

ppm = ng/mg soil = ng pest. found in 2ul injection (by comparison of peak heights to Std. curves) x 2

% Moisture =  $100 \times \frac{(\text{wt of undried sample} + \text{dish}) - (\text{wt of dried sample} + \text{dish})}{(\text{wt of undried sample} + \text{dish}) - (\text{wt of dish})}$

100 - % Moisture = % dry wt soil

ppm (dry wt) =  $\frac{\text{ppm (moist soil sample)} \times 100}{\% \text{ dry wt soil sample}}$

Samples are reported in ppm (dry wt soil) of Ethoprop, Phorate, Phorate Sulfoxide, & Phorate Sulphone.

DISCUSSION:

Important to keep injection volumes approximately the same. Standards should be made to allow this consistency.

Parent compounds of Mocap and Thimet may be run quite well on several different columns 3% OV-1, OV-17, 5% Phenyl Methyl, etc. However, it is critical to use Carbowax 20M or its equivalent, if any, to achieve the kind of separation of the Phorate metabolites witnessed under these conditions.

WRITTEN BY: Michael J. Monier

Michael J. Monier  
TITLE: Agricultural Chemist I

APPROVED BY: Catherine Cooper

Catherine Cooper  
TITLE: Agricultural Chemist III

APPROVED BY: George Tichelaar

George Tichelaar  
TITLE: Principal Agric. Chemist

METHOD 8140; ORGANOPHOSPHATE PESTICIDES in soil/sediment

---

1. EXTRACTION;

Label the cal id with the suffix '8140'.

Weigh 15 grams of sample into an 8-oz bottle with a teflon-lined cap.

Add 100 ml of 1:1 methylene chloride-acetone (v/v), and shake well to disperse.

Add 30 g of washed sodium sulfate, and shake to mix well.

Add the spiking solution if applicable. No surrogates are added.

Place the sonicator probe into the extract above the sediments, sonicate for 3 minutes at 50% power setting and pulse at 5.

Be sure the sonication mixes the soil/sediment with the solvent well during the three minutes. Do not allow the probe to touch the glassware; it could break and shatter the glass.

Decant the extract into a 250-ml erlenmeyer flask.

Sonicate the soil once more with 100 ml of methylene chloride-acetone and decant the extracts into the first erlenmeyer flask.

2. CONCENTRATION BY KUDERNA-DANISH METHOD for 8140;

Pour the extracts through filter paper in a filtering funnel into a K-D flask; a 10-ml concentrator tube attached to the 500-ml reservoir.

Allow the extract to drain. Rinse the sample flask with methylene chloride several times, and pour the rinsates through the filter paper each time into the KD flask.

Add several small teflon boiling chips and attach the 3-ball macro-Synder column.

Prewet the column with methylene chloride, and concentrate the extract to ca 6 ml on the steam bath at ca 80-85 C.

Remove the KD flask from the bath and allow it to cool on the ring support for a minimum of 10 minutes.

CAREFULLY disassemble the concentrator tube and rinse the lower glass joint with small amount of methylene chloride.

Quantitatively transfer the extract to a 16-ml test tube and adjust the volume to 15 ml with methylene chloride; 15g/15ml.



Method 8140 continued-

3. ADJUSTMENTS of 8140;

Aliquot 2.0 ml of the water extract into an 8-ml test tube.

Reduce the extracts under nitrogen and exchange the solvent to isooctane several times.

Adjust the final volume to 2.0 ml; 2g/2ml.

Ready for GC-NP(TSD).

4. QUALITY ASSURANCE/CONTROL of 8140;

The method blank is mandatory and is performed for each set of matrix, and for every 20 samples.

The matrix spike and the matrix spike duplicate is optional and must be requested. They are performed for each matrix and for every 20 samples.

METHOD 8140; ORGANOPHOSPHATE PESTICIDES in soil

Spike the MS and MSD with 1.0 ml of 614/8140 spiking standard to the 15 g soil to yield:

	STANDARD CONCENTRATION	SPIKE LEVEL
phosdrin	10 ug/ml	330 ug/Kg (ppb)
thimet	10	330
diazinon	10	330
di-syston	10	330
dimethoate	10	330
fenthion	10	330
chlorpyrifos	10	330
methyl parathion	10	330
malathion	10	330
ethyl parathion	10	330
DEF	10	330
ethion	10	330
trithion	10	330
guthion	100	3,300

No surrogates are added; However, the P-surrogate does not interfere with the 614/8140 analysis.

DEG 6/1/88  
• 8140

MOCAP (ETHOPROP) in soil/sediment

This method from the CDFA (rev. 11/2/87).

1. EXTRACTION;

Label the cal id with the suffix 'MOCAP'.

Weigh 50 grams of the well mixed soil into a cleaned 8-oz bottle.

Measure 100.0 ml of ethyl acetate, add to the soil, and close it with the teflon-lined screw cap.

Shake well to mix.

Add the spiking solution if applicable. No surrogates are added.

Place the extracts on the orbital shaker in horizontal position and shake for 1 hour at ca 250 rpm.

Remove from the shaker and allow it to settle.

Decant through Whatman 1 filter paper into a cleaned 8 oz jar. Do not rinse the filter paper.

Extract the soil once more with 100.0 ml of ethyl acetate on the orbital shaker for 30 minutes, and decant through the filter paper into the 8 oz jar. Again do not rinse the filter paper.

2. ADJUSTMENT;

No volume adjustments needed if the ethyl acetate was initially carefully measured.

Mix the solution well, and aliquot 16 mls into the 16-ml test tube: 50g/200ml. The excess may be discarded (check with the supervisor).

Ready for GC-NP(TSD). No screenings necessary.

4. QUALITY ASSURANCE/CONTROL of MOCAP;

The method blank is mandatory and is performed for each set of matrix, and for every 20 samples.

The matrix spike and the matrix spike duplicate is optional and must be requested. They are performed for each matrix and for every 20 samples.

MOCAP (ETHOPROP) in soil

Spike the MS and MSD with 0.8 ml of MOCAP spiking standard to the 50 g soil to yield:

	STD CONC	SPIKE LEVEL
mocap (ethoprop)	500 ug/ml	8,000 ug/Kg

MOCAP (ETHOPROP) in soil/sediment continued-

No surrogates are added; However, the P-surrogate does not interfere with the 614/8140 analysis (MOCAP is an organophosphate pesticide).

---

Method modified 12/8/87: solvent changed from acetone to ethyl acetate.

DEG 12/8/87  
DFA.MOCAP

CALIFORNIA DEPT. OF FOOD & AGRIC.  
ENVIRONMENTAL MONITORING SECTION  
CHEMISTRY LABORATORY SERVICES  
3292 Meadowview Road  
Sacramento, CA 95832  
(916)427-4998

Date: 11/16/89

A Method for the Determination of Oxamyl and Oximino in Soil By  
Liquid Chromatography

PRINCIPLE:

Weigh 50 grams of soil into amber bottles. Add 80 ml 50:50 hexane/acetone, sonicate 10 minutes. Decant hexane/acetone into 250 ml flat bottom flask. Filter through #2 filter paper and a bed of anhydrous sodium sulfate. Add 60 ml hexane/acetone. Tumble 10 minutes. Decant into flask. Add 60 ml hexane/acetone. Sonicate 10 minutes. Decant into flask. Wash sodium sulfate with 5-10 ml of hexane/acetone. Evaporate on roto-evaporator to 2-3 ml. Transfer into 15 ml conical centrifuge tube. Wash flask 2-3 times with dichloromethane and transfer into centrifuge tube. Evaporate all dichloromethane under current of Nitrogen at low heat. Add 2 ml water. Sonicate for 5 minutes. Shake well. Filter through 0.2 micron filter paper. Analyze by HPLC.

HPLC CONDITIONS:

UV detector at wavelength 220 nm.

Solvent mobile phase: 12% ACN/H<sub>2</sub>O for 12 minutes, then increase to 80% ACN/H<sub>2</sub>O for 2 minutes in order to eliminate late eluting peaks.

Final volume: 20 microliters of 0.4 nanogram/microliter of oximino and 0.6 nanogram/microliter of oxamyl.

WRITTEN BY: Nirmal

TITLE: Agricultural Chemist III

CALIFORNIA DEPT. OF FOOD & AGRIC.  
ENVIRONMENTAL MONITORING SECTION  
CHEMISTRY LABORATORY SERVICES  
3292 Meadowview Road  
Sacramento, CA 95832  
(916)427-4998

DATE: 11/16/89

A Method for the Determination of Sulfocarb Residues in Soil By  
Liquid Chromatography

PRINCIPLE:

Weigh 100 grams of soil into amber bottles. Add 100 ml distilled water and shake for 30 seconds. Let it stay for 30 minutes. Shake again for 30 seconds. Let stay for another 30 minutes. Shake again for 30 seconds and leave it overnight. Decant the liquid portion into tubes and centrifuge. Filter through circular 0.25 micron filter paper and shoot in C18 reverse phase column.

HPLC CONDITIONS:

Column:

Sepralyte, 5 micron, 4.6mm i.d. X 25cm

Flow Conditions:

1.5 ml/minute

15% ACN/H<sub>2</sub>O for 2 minutes programmed to 50% ACN/H<sub>2</sub>O

Post column derivitization. Fluorescence detector.

Order of elution:

Aldicarb sulfoxide	4.36 min.
Aldicarb sulfone	6.57 min.
Aldicarb	13.94 min.

WRITTEN BY: Nirmal

TITLE: Agricultural Chemist III

APPENDIX B

SOIL TEXTURE DATA FOR SOIL CORE

Table B-1. Soil texture data for segments of one soil core from study location I.

Depth inches	Soil texture			Depth inches	Soil texture		
	% sand	% silt	% clay		% sand	% silt	% clay
0-6	82.4	13.0	4.6	260-266	----	---	---
6-12	82.4	12.0	5.6	266-272	----	---	---
12-18	84.4	a 10.0	5.6	272-278	43.4	38.0	18.6
20-26	----	----	---	280-286	----	---	---
26-32	86.4	8.0	5.6	286-292	----	---	---
32-38	87.4	8.0	4.6	292-298	5.4	81.0	13.6
40-46	----	---	---	300-306	33.4	61.0	5.6
46-52	92.4	3.0	4.6	306-312	12.4	60.0	27.6
52-58	91.4	4.0	4.6	312-318	17.4	63.0	19.6
60-66	----	---	---	320-326	----	---	---
66-72	92.4	4.0	3.6	326-332	36.4	56.0	7.6
72-78	95.4	1.0	3.6	332-338	41.4	53.0	5.6
80-86	98.4	1.0	0.6	340-346	94.4	2.0	3.6
86-92	93.4	3.0	3.6	346-352	89.4	7.0	3.6
92-98	96.4	0.0	3.6	352-358	68.4	29.0	2.6
100-106	94.4	2.0	3.6	360-366	----	---	---
106-112	97.4	1.0	1.6	366-372	84.4	12.0	3.6
112-118	95.4	1.0	3.6	372-378	77.4	19.0	3.6
120-126	96.4	0.0	3.6	380-386	59.4	37.0	3.6
126-132	96.4	2.0	1.6	386-392	62.4	34.0	3.6
132-138	96.4	1.0	2.6	392-398	61.4	35.0	3.6
140-146	96.4	2.0	1.6	400-406	75.4	21.0	3.6
146-152	98.4	0.0	1.6	406-412	96.4	0.0	3.6
152-158	97.4	0.0	2.6	412-418	65.4	31.0	3.6
160-166	----	---	---	420-426	42.4	48.0	9.6
166-172	98.4	1.0	0.6	426-432	18.4	76.0	5.6
172-178	98.4	1.0	0.6	432-438	19.4	72.0	8.6
180-186	----	---	---	440-446	3.4	72.0	24.6
186-192	----	---	---	446-452	3.4	49.0	47.6
192-198	62.4	26.0	11.6	452-458	2.4	58.0	39.6
200-206	78.4	17.0	4.6	460-466	40.4	52.0	7.6
206-212	71.4	23.0	5.6	466-472	39.4	52.0	8.6
212-218	89.4	7.0	3.6	472-478	62.4	32.0	5.6
220-226	87.4	9.0	3.6				
226-232	90.4	6.0	3.6				
232-238	97.4	0.0	2.6				
240-246	93.4	5.0	1.6				
246-252	95.4	1.0	3.6				
252-258	96.4	1.0	2.6				

a Lost sample.

APPENDIX C

PESTICIDE RESIDUES IN SOIL COLLECTED WITH VEIHMAYER TUBE



Table C-1. Concentrations of aldoxycarb in segments of soil cores collected on three dates with a Veihmeyer tube at varying distances from the dripline emitter.

<u>Aldoxycarb residues (ppm, dry wt.) in soil segments taken 8, 16, or 24 inches from emitter</u>										
Sample date	Depth (inches)	Associated with shallow core 1			Associated with shallow core 2.			Associated with deep core		
		8 inches	16 inches	24 inches	8 inches	16 inches	24 inches	8 inches	16 inches	24 inches
6/6/85	0 - 12	ND <sup>a</sup>	ND	ND	ND	0.09	0.03	ND	0.15	ND
	12 - 24	ND	ND	ND	ND	0.07	ND	ND	ND	ND
	24 - 36	0.13	0.02	ND	0.07	ND	ND	0.18	0.12	0.05
	36 - 48	0.10	0.08	0.08	ND	ND	ND	0.20	0.08	ND
95 11/17/85	0 - 12	0.02	ND	ND	0.01	0.02	0.04	ND	0.02	0.01
	12 - 24	0.03	0.01	ND	0.01	0.01	0.08	0.01	0.06	0.01
	24 - 36	ND	0.03	0.01	ND	0.03	0.02	0.11	0.04	ND
	36 - 48	0.13	ND	ND	ND	ND	0.03	0.10	ND	0.01
12/19/85	0 - 12	ND	ND	0.06	ND	ND	ND	ND	ND	ND
	12 - 24	ND	0.02	0.02	ND	ND	ND	ND	0.01	0.03
	24 - 36	0.02	0.05	0.01	ND	ND	ND	0.02	0.05	0.05
	36 - 48	ND	0.01	0.03	ND	ND	0.02	0.07	0.07	0.03

a None detected, minimum detectable level was 0.01 ppm.

Table C-2. Concentrations of fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone in segments of soil cores collected with a Veihmeyer tube on June 4, 1985 at varying distances from the dripline emitter.

Fenamiphos residue (ppm) as total of fenamiphos (F), sulfoxide (SO), and sulfone (SO2)													
Associated Core	Depth (inches)	8 inches from emitter				16 inches from emitter				24 inches from emitter			
		Total	F	SO	SO2	Total	F	SO	SO2	Total	F	SO	SO2
Shallow Core 1	0 - 12	1.11	ND <sup>a</sup>	0.87	0.24	0.38	ND	0.27	0.11	0.37	ND	0.28	0.09
	12 - 24	0.36	ND	0.25	0.11	ND	ND	ND	ND	ND	ND	ND	ND
	24 - 36	ND	ND	ND	ND	0.05	ND	0.03	0.02	ND	ND	ND	ND
	36 - 48	ND	ND	ND	ND	0.09	ND	0.06	0.03	ND	ND	ND	ND
Shallow Core 2	0 - 12	0.81	ND	0.63	0.18	1.11	ND	1.00	0.11	0.60	ND	0.43	0.17
	12 - 24	0.12	ND	0.10	0.02	0.07	ND	0.07	ND	ND	ND	ND	ND
	24 - 36	0.04	ND	0.04	ND	ND	ND	ND	ND	0.02	ND	0.02	ND
	36 - 48	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Deep Core	0 - 12	1.27	ND	1.00	0.27	1.27	ND	0.97	0.30	ND	ND	ND	ND
	12 - 24	0.16	ND	0.14	0.02	0.02	ND	0.02	ND	ND	ND	ND	ND
	24 - 36	0.02	ND	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND
	36 - 48	0.02	ND	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND

a. None detected, minimum detectable limit was 0.01 ppm.

Table C-3. Concentrations of fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone in segments of soil cores collected with a Veihmeyer tube on November 5, 1985 at varying distances from the dripline emitter.

		Fenamiphos residue (ppm) as total of fenamiphos (F), sulfoxide (SO), and sulfone (SO <sub>2</sub> )											
Associated Core	Depth (inches)	8 inches from emitter				16 inches from emitter				24 inches from emitter			
		Total	F	SO	SO <sub>2</sub>	Total	F	SO	SO <sub>2</sub>	Total	F	SO	SO <sub>2</sub>
Shallow Core 1	0 - 12	0.60	0.09	0.39	0.12	0.55	0.05	0.40	0.10	0.33	0.20	0.09	0.04
	12 - 24	0.20	0.02	0.16	0.02	L.S. <sup>a</sup>	-- <sup>b</sup>	--	--	0.03	0.02	0.01	ND <sup>c</sup>
	24 - 36	ND	ND	ND	ND	0.10	0.05	0.04	0.01	ND	ND	ND	ND
	36 - 48	L.S.	--	--	--	ND	ND	ND	ND	ND	ND	ND	ND
Shallow Core 2	0 - 12	0.79	0.02	0.52	0.25	0.60	0.07	0.38	0.15	0.38	0.17	0.09	0.12
	12 - 24	0.40	ND	0.40	ND	L.S.	--	--	--	0.01	0.01	ND	ND
	24 - 36	0.31	ND	0.21	0.10	0.17	0.10	0.07	ND	0.01	0.01	ND	ND
	36 - 48	L.S.	--	--	--	0.29	0.16	0.11	0.02	ND	ND	ND	ND
Deep Core	0 - 12	1.63	0.08	0.67	0.88	0.53	ND	0.26	0.27	1.14	0.67	0.19	0.28
	12 - 24	0.22	0.01	0.21	ND	L.S.	--	--	--	ND	ND	ND	ND
	24 - 36	0.23	ND	0.23	ND	0.08	0.06	0.02	ND	0.01	0.01	ND	ND
	36 - 48	L.S.	--	--	--	0.16	0.07	0.08	0.01	ND	ND	ND	ND

a Sample lost, soil compacted or fell out of collection cylinder.

b No data.

c None detected, minimum detectable limit was 0.01 ppm.

Table C-4. Concentrations of fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone in segments of soil cores collected with a Veihmeyer tube on December 17, 1985 at varying distances from the dripline emitter.

		<u>Fenamiphos residue (ppm) as total of fenamiphos (F), sulfoxide (SO), and sulfone (SO2)</u>											
Associated Core	Depth (inches)	8 inches from emitter				16 inches from emitter				24 inches from emitter			
		Total	F	SO	SO2	Total	F	SO	SO2	Total	F	SO	SO2
Shallow Core 1	0 - 12	0.27	0.09	0.12	0.06	0.32	0.12	0.17	0.03	0.36	0.11	0.12	0.13
	12 - 24	0.23	0.13	0.09	0.01	0.31	0.11	0.18	0.02	0.09	0.03	0.03	0.03
	24 - 36	0.05	0.02	0.02	0.01	0.18	0.09	0.09	ND <sup>a</sup>	0.04	0.01	0.03	ND
	36 - 48	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Shallow Core 2	0 - 12	0.65	0.38	0.20	0.07	0.67	0.28	0.29	0.10	0.28	0.08	0.11	0.09
	12 - 24	0.30	0.11	0.17	0.02	0.64	0.18	0.42	0.04	0.18	0.06	0.11	0.01
	24 - 36	0.14	0.06	0.08	ND	0.35	0.09	0.25	0.01	0.06	0.02	0.04	ND
	36 - 48	ND	ND	ND	ND	0.05	0.01	0.04	ND	ND	ND	ND	ND
Deep Core	0 - 12	0.51	0.32	0.11	0.08	0.56	0.39	0.10	0.07	0.25	0.08	0.17	ND
	12 - 24	0.29	0.13	0.14	0.02	0.41	0.11	0.26	0.04	0.18	0.07	0.07	0.04
	24 - 36	0.74	0.70	0.04	ND	0.57	0.15	0.39	0.03	0.12	0.09	0.03	ND
	36 - 48	0.05	0.05	ND	ND	0.06	0.02	0.04	ND	ND	ND	ND	ND

a None detected, minimum detectable limit was 0.01 ppm.

Table C-5. Concentrations of oxamyl and oxamino in segments of soil cores collected on three dates with a Veihmeyer tube at varying distances from the dripline emitter.

Sample date	Depth (inches)	Oxamyl residues (ppm,dry wt.) in soil segments taken 8, 16, or 24 inches from emitter								
		Associated with shallow core 1			Associated with shallow core 2			Associated with deep core		
		8 inches	16 inches	24 inches	8 inches	16 inches	24 inches	8 inches	16 inches	24 inches
6/5/85	0 - 12	0.50 <sup>a</sup>	0.12	0.09	0.19	0.04	ND <sup>b</sup>	0.68 <sup>a</sup>	0.10	ND
	12 - 24	0.08	0.12	0.02	ND	ND	ND	ND	ND	ND
	24 - 36	ND	ND	ND	ND	ND	ND	ND	ND	ND
	36 - 48	ND	ND	ND	ND	ND	ND	ND	ND	ND
11/6/85	0 - 12	ND	0.32 <sup>a</sup>	ND	ND	ND	ND	ND	ND	0.03 <sup>a</sup>
	12 - 24	ND	0.05 <sup>a</sup>	0.06	ND	0.14 <sup>a</sup>	ND	ND	ND	ND
	24 - 36	ND	ND	0.03	ND	ND	ND	ND	ND	ND
	36 - 48	ND	ND	ND	ND	ND	ND	ND	ND	ND
12/18/85	0 - 12	ND	0.03	ND	0.02	0.03	0.02	0.03 <sup>a</sup>	ND	ND
	12 - 24	0.04 <sup>a</sup>	ND	0.02 <sup>a</sup>	0.05 <sup>a</sup>	0.03	ND	ND	ND	ND
	24 - 36	ND	ND	ND	ND	ND	ND	ND	ND	ND
	36 - 48	ND	ND	ND	ND	ND	ND	ND	ND	ND

a Includes oxamyl plus oxamino residue.

b None detected, minimum detectable level was 0.02 ppm.

APPENDIX D

SOIL MOISTURE CONTENT OF SOIL CORES FROM KEARNEY FIELD STATION

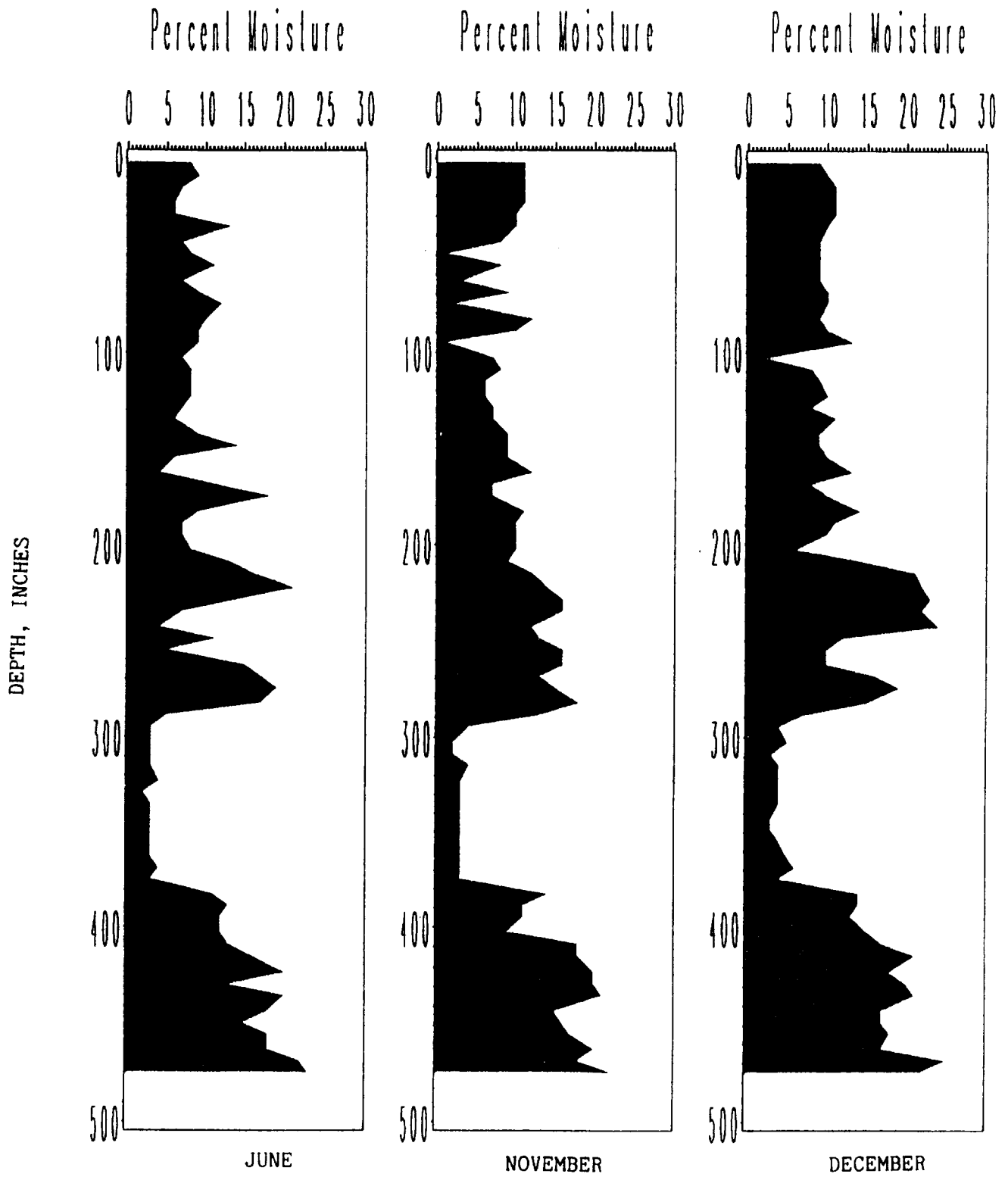


Figure D-1. Soil moisture content in deep soil cores collected on three sampling dates from the aldoxycarb plot in the Kearney Field Station study.

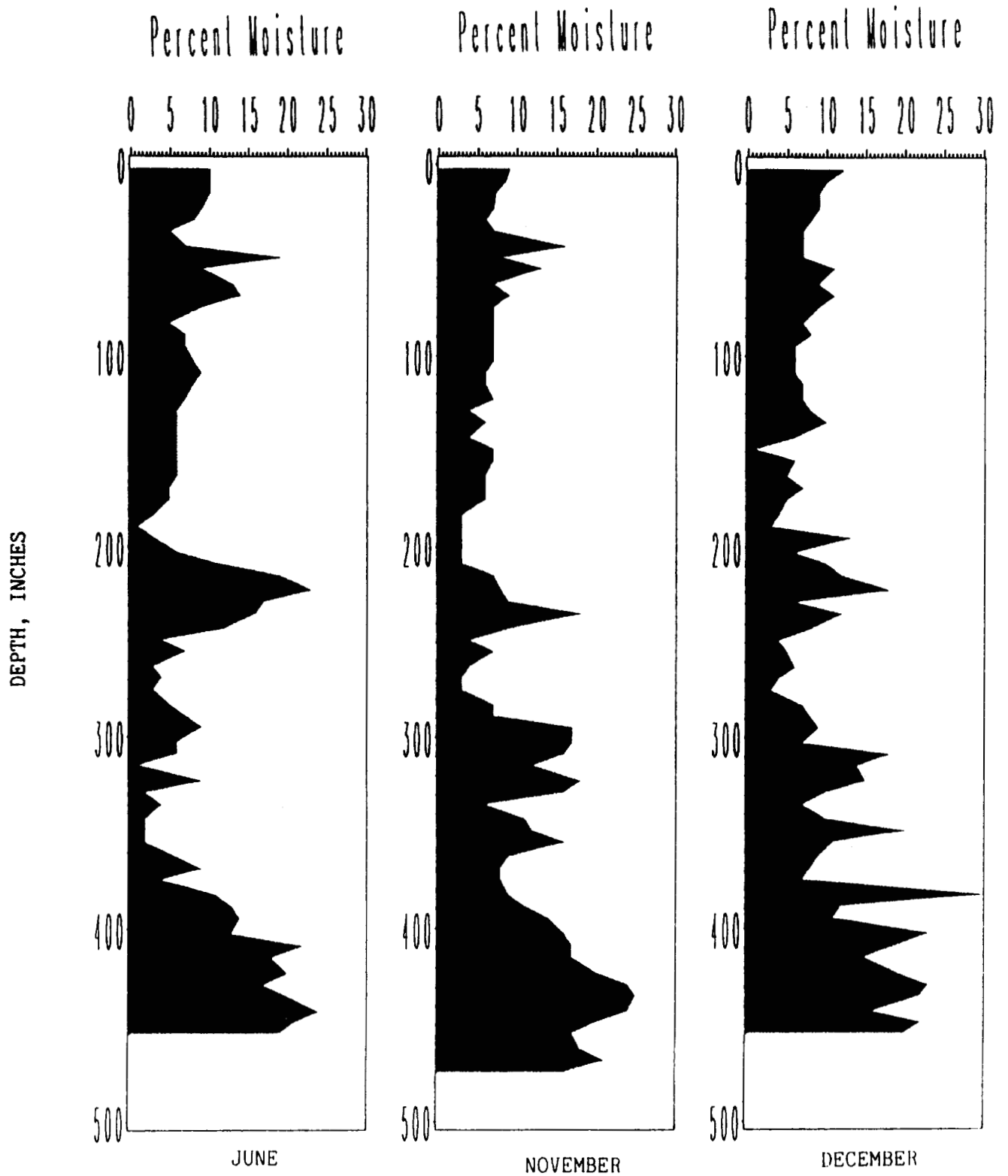


Figure D-2. Soil moisture content in deep soil cores collected on three sampling dates from the fenamiphos plot in the Kearney Field Station study.



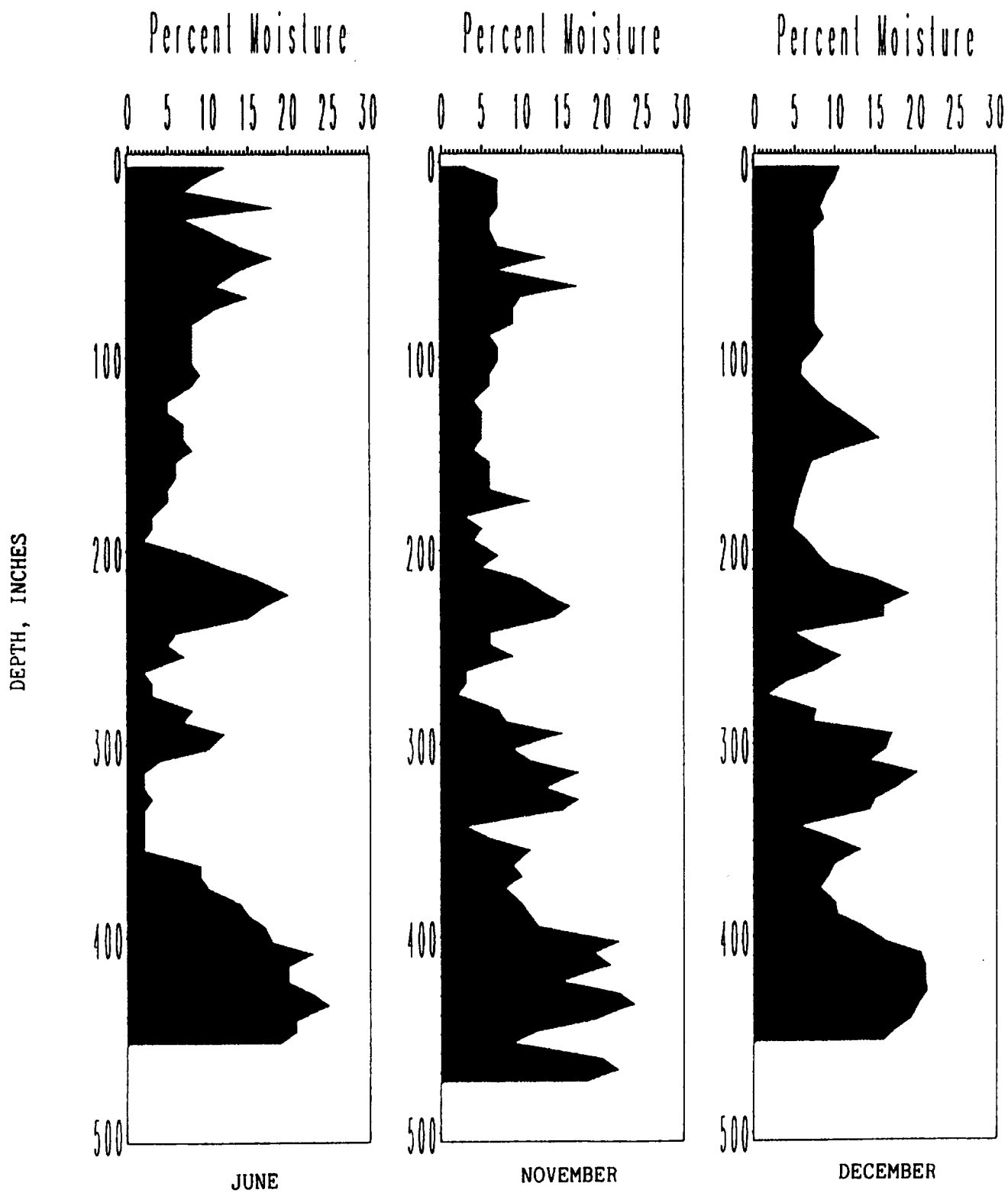


Figure D-3. Soil moisture content in deep soil cores collected on three sampling dates from the oxamyl plot in the Kearney Field Station study.