SOIL DISTRIBUTION OF SIMAZINE, DIAZINON AND BROMIDE IN SANDY SOIL AFTER EXPOSURE TO 1985—1986 WINTER RAINS IN FRESNO COUNTY

January 1988

ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM

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EH—88—2

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JANUARY 1988

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ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM

ABSTRACT

Rainfall has been implicated in the movement of pesticides to ground water in the northern coastal county of Del Norte in California. However, the importance of rainfall in other agricultural areas is unknown. Rainfall in the Central Valley, an area where pesticide residues have also been detected in ground water, occurs mainly during the winter months. This study sought to identify the influence of winter rainfall on movement of two pesticides in sandy soil located in Fresno County.

The soil distributions of simazine, diazinon, and bromide were determined after exposure to winter rain in 0.15 m increments of soil down to the 3.05 m depth. The herbicidal action of simazine inhibited growth of vegetation on that plot but dense weed growth was prevalent on the diazinon-treated plot. Bromide was also applied to each plot because it had historically been used to trace water movement through soil. Pesticide was applied on 11/22/85 and soil cores were taken on 5/6/86, 164 days after pesticide application. During that period, rainfall was recorded on 37 days and it totalled 25.2 centimeters (cm) with approximately 80% of the events below 1.0 cm in volume.

No diazinon was recovered from the cores. This probably resulted from its short soil half-life which ranges from 7 to 32 days. Simazine, on the other hand, was recovered down to the 1.906 meter (m) mean segment depth but according to mass balance calculations, 69% of the residue was recovered in the surface 0.15 m sample. A small peak in simazine soil distribution was observed between the 0.737 and 1.392 m mean segment depths. The amount of simazine recovered from the cores corresponded to a soil half-life of 56 days

which was very close to reported field dissipation values. Thus, the dissipation of simazine could have been attributed to microbial and chemical degradation processes.

The soil distribution of bromide, the water tracer, differed greatly from the simazine distribution. Most of the bromide was recovered in a peak between the 1.245 and 2.108 m mean segment depths which was deeper than the location of the peak measured for simazine. The bromide distribution also differed between the pesticide treatments. In the simazine-treated plot, very little bromide was detected in the surface 0.15 m segment and then it was not detected until the 0.889 m mean segment depth. In contrast, the bromide peak in the diazinon-treated plot was located in the first 0.15 m surface soil segment with a smaller amount recovered between the 1.245 and 2.108 m mean segment depths. Apparently, the presence of the weed vegetation affected the soil distribution of bromide by physically removing bromide from the soil into plant tissues and/or by affecting the soil distribution of water through transpiration.

The total cumulative amount of winter rainfall (25.2 cm) was enough to solubilize all of the applied simazine. But many events were 1.0 cm and below in volume which would have limited the depth of water penetration between events. Also, simazine's water solubility value is around 5 ppm so a single 1 cm rainfall event would be able to solubilize only 0.5 kg/ha or 11 % of the applied amount of simazine. Hence, in most events only a small amount of simazine would be available for movement as a solute. The pattern of bromide tracer indicated that water was available for deep movement which may have been mainly due to the few larger volume rain events. Penetration of simazine

residues below the first 0.15 m soil segment may also have been solely due to those few larger volume rainfall events. The retardation in movement noted in the simazine distribution when compared to the bromide distribution may, in part, have been due to soil adsorption differences.

This study indicated pesticide and soil properties that may mitigate pesticide movement in areas of low rainfall and sandy soils.

1. The results with diazinon indicated that pesticides with short soil-half lives will be rapidily degraded if kept near the surface and hence unavailable for movement.
2. The results with simazine indicated that in areas of low rainfall the water solubility of a pesticide will determine potential for movement from the surface sites. Soil adsorption properties may affect the shape of the pesticide soil distribution curve relative to that observed for water.
3. The results for the bromide tracer indicated that the presence of vegetation restricted the movement of the tracer. Thus, movement of pesticides could also be greatly modified by the presence of vegetation.

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INTRODUCTION

The recharge of ground water by surface water is the vector for movement of pesticides through soil to ground water. Large amounts of winter rain occur in the northwestern coastal plains of California and they are believed to be associated with pesticide contamination of well water (Lee, 1984). In the Central Valley, where heavy irrigation occurs during periods of crop growth, the relative contribution of winter rain and irrigation events on the movement of pesticides is not known. This study sought to identify the effect of winter rainfall on pesticide movement in an area of the Central Valley where the percolation rate of water through soil was high.

MATERIALS AND METHODS

EXPERIMENTAL DESIGN

The study was conducted at Fresno State University on a sandy soil of the Hanford series. The movement caused by winter rain of simazine, a herbicide, and diazinon, an insecticide, was investigated. Two 9.14 x 9.14 meter square plots were used, one for each pesticide. Both pesticides were applied at a rate of 4.48 kg active ingredient per hectare (kg ai/ha). Simazine was used because it was known to leach through soil. Diazinon was used in order to obtain data on its potential for movement and because its reported soil half-life was shorter than for simazine (Rao et. al., 1985). Each plot was divided into 4 quadrants and potassium bromide (KBr) tracer was added to 2 of the 4 quadrants (Figure 1). Bromide had previously been used as a tracer for water movement (Bruce et. al. , 1985) but its potential influence on pesticide leaching was unknown. Thus, a second objective was to determine any effect of bromide on pesticide movement by comparing the soil distribution of pesticide between bromide treated and untreated plots.

A background core was taken on 10/26/85 to determine whether or not residues of simazine, diazinon or bromide were present in the soil. There had been no recent historical record of application of either pesticide. No simazine, diazinon or bromide was detected at minimum detection limits of 1.0 and 3.0 ppb for simazine and diazinon, respectively, and at 0.5 ppm for bromide (Table 1). Pesticides were broadcast on 11/22/85 and potassium bromide was broadcast

Figure 1. Plot design denoting the pattern of pesticide and tracer application in the winter rain study.

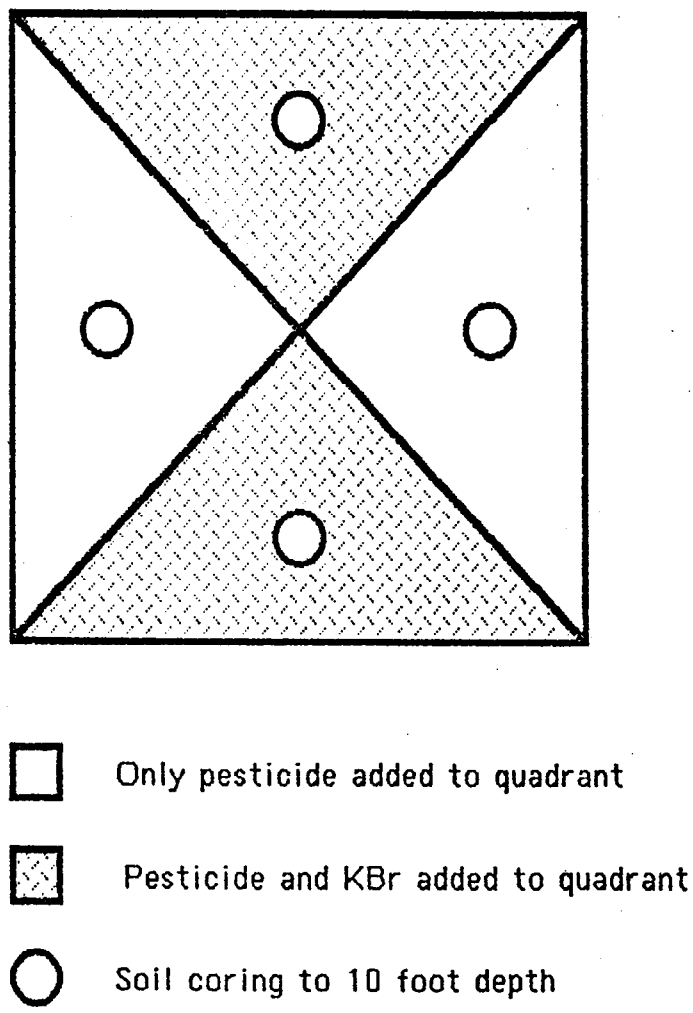


Table 1. Analyses of background core for the presence of simazine and diazinon at minimum detection limits of 1.0 and 3.0 ppb, respectively.

MEAN DEPTH OF SEGMENT (METERS)	PESTICIDE	
	SIMAZINE	DIAZINON
0.076	0.0	0.0
0.229	0.0	0.0
0.381	ND[a]	ND
0.584	0.0	0.0
0.737	0.0	0.0
0.889	0.0	0.0
1.092	0.0	0.0
1.245	0.0	0.0
1.397	0.0	0.0
1.600	0.0	0.0
1.753	0.0	0.0
1.906	ND	ND
2.108	0.0	0.0
2.261	0.0	0.0
2.413	0.0	0.0
2.616	0.0	0.0
2.769	0.0	0.0
2.921	0.0	0.0

[a]Analyses Not Determined for that sample.

on 12/4/85 at a rate of 112 kg Br^-/ha. Soil cores were taken after the winter season on 5/6/86, 164 days after application of pesticides. One core to 3.05 meters was taken near the center of each quadrant in each plot. The effect of winter rain on movement was graphically determined. Tracer and plot effects were compared by Analysis of Variance (ANOVA) and regression analyses. The amount of rainfall was collected and recorded daily.

SOIL SAMPLING AND CHEMICAL ANALYSES

Undisturbed soil cores were collected with a truck-mounted soil drilling device. Procedures established in previous soil coring studies for sample collection and preparation for laboratory analyses were followed (Zalklin et. al.). According to this method, a 0.50 m sample of soil was obtained with a split-barrel sampler. This sample was partitioned into three separate 0.15 m samples, contained in stainless steel sleeves, and a 0.05 m segment of soil from the tip of the cutting head that was discarded. The soil in each sleeve was further split into three samples, one for determination of water content, one for chemical analyses, and one for soil texture analysis. Some difficulty was experienced in obtaining the first split-barrel sample in some cores: owing to compaction of the soil, 2 out of 3 samples were occasionally retrieved. Additional surface soil samples were obtained to provide data for missing surface segments. Soil texture, moisture, and organic carbon analyses were conducted as described in Zalkin et. al. (1984).

EPA method 3540 was used for the extraction of simazine and diazinon from the soil samples (EPA, 1986a). And EPA instrumentation methods 619 and 8140 were

used for the detection of simazine and diazinon, respectively (EPA, 1982; EPA, 1986b).

STATISTICAL METHODS

The effects of winter rain were determined from visual inspection of the data and from mass balance calculations of the amount of pesticide recovered from the cores. The effect of tracer addition on location of pesticide within the cores was determined by regression analysis. An R-square analysis was first conducted on the amount of pesticide recovered as a function of the first- through sixth-order terms with depth. Depth was determined as the mean of the upper and lower depth of a soil segment. A full model of the highest order that gave the best fit per model degrees of freedom, as determined by Mallow's C(p) statistic, was used in subsequent analyses. A split-plot ANOVA, with the regression on depth considered as a subplot, was then conducted to measure interactive effects of tracer addition on the spatial location of pesticide. The same procedure was used to compare the bromide distributions between pesticide-treated plots.

Pesticide and bromide concentrations were reported on a soil wet weight basis, so the amount recovered in each segment was determined according to equation 1:

Eq 1. (Bromide Concentration x (1+Water Content) x Volume of Segment x Bulk Density of Soil

The volume of soil taken in a stainless steel sleeve was 434 cc. The bulk density was determined for 0.15 m segments from three separate 3.05 m cores taken from the area adjacent to the winter rain site. The mean value from these three cores represented the bulk density at each depth (Table 2).

Missing values for concentration or moisture data were estimated by averaging the values obtained from segments located directly above and below the missing segment. In the case of missing data for moisture in the surface segment, an estimate was supplied from additional cores taken with a bucket auger.

The pesticide soil half-life was determined by equations 2.1-2.3:

Eq 2.1. $C=C_o e^{-rt}$

Eq 2.2. $r=Ln(C_o/C)/T$

Eq 2.3. $1/2\text{-life}=Ln2/r$

C_o was the theoretical amount of pesticide applied to the surface area of the core which was 1.308×10^{-3}g applied to 28 cm^2. C was the average amount of pesticide recovered in the cores to the 3.05 m depth. T was the time from pesticide application to soil coring which was 164 days.

Table 2. Bulk density measurements used to calculate the mass balance of pesticides recovered at each depth.

MEAN DEPTH OF SEGMENT (METERS)	BULK DENSITY (g/cc)			
	CORE 1	CORE 2	CORE 3	MEAN
0.076	1.48	1.58	1.53	1.53
0.229	1.47	1.52	1.51	1.50
0.381	1.54	1.49	1.53	1.52
0.584	1.50	1.54	1.52	1.52
0.737	1.59	1.57	1.61	1.59
0.889	1.62	1.58	1.62	1.61
1.092	1.60	ND[a]	1.51	1.56
1.245	1.58	1.54	1.58	1.57
1.397	1.57	1.56	1.59	1.57
1.600	ND	1.58	1.68	1.63
1.753	1.50	1.68	1.72	1.63
1.906	1.75	1.66	1.64	1.68
2.108	1.65	1.59	1.49	1.58
2.261	1.65	1.56	1.57	1.59
2.413	1.68	1.58	1.61	1.62
2.616	1.56	1.56	1.46	1.53
2.769	1.62	1.56	1.56	1.58
2.921	1.62	1.57	1.60	1.60

[a]Bulk density Not Determined for that sample.

RESULTS AND DISCUSSION

SITE DESCRIPTION

Soil texture analyses were conducted on cores taken from the simazine-treated plot. Sand was the predominant component throughout the soil column (Tables 3-6). Clay content was low near the surface but it averaged over 10% between the 1.753 and 2.108 m mean segment depths (Figure 2). The organic carbon content was around 0.5% in the first 0.15 m segment but it decreased rapidly to below 0.1% in subsequent segments.

Total rainfall at the site from 11/22/85 to 5/6/86 was 25.2 cm (Table 7). Most rain events (81%) were 1.0 cm or below in volume. The water content measured in the cores at 5/6/86 appeared to increase with depth concommittantly with the clay content of the soil (Tables 8 and 9). In the simazine-treated plot, the average percent moisture in the segments was positively correlated with the average clay content (Figure 3). A comparison of the water profile between pesticide treatments indicated greater percent moisture values in the simazine-treated plot down to around the 1.906 m mean segment depth (Figure 4).

EFFECT OF BROMIDE ON PESTICIDE MOVEMENT

The effect of bromide on pesticide distribution in the soil was first explored because in the absence of a significant effect, the data could be pooled from

Table 3. Soil texture and organic carbon analyses measured on individual soil segments taken from core 1 in the simazine-treated plot where potassium bromide had not been added to the soil.

MEAN DEPTH OF SEGMENT (METERS)	SOIL TEXTURE SAND (%)	SILT (%)	CLAY (%)	ORGANIC CARBON (%)
0.076	93.0	6.0	1.0	0.12
0.229	93.0	4.0	3.0	0.06
0.381	91.0	5.0	4.0	0.06
0.584	86.0	4.0	10.0	0.06
0.737	85.0	2.0	13.0	0.06
0.889	87.0	4.0	9.0	0.06
1.092	89.0	4.0	7.0	0.06
1.245	89.0	2.0	9.0	0.06
1.397	89.0	5.0	6.0	0.06
1.600	87.0	7.0	6.0	0.0
1.753	85.0	6.0	9.0	0.0
1.906	ND[a]	ND	ND	ND
2.108	87.0	4.0	9.0	0.06
2.261	91.0	2.0	7.0	0.0
2.413	91.0	2.0	7.0	0.0
2.616	90.0	5.0	6.0	0.0
2.769	90.0	4.0	6.0	0.0
2.921	89.0	5.0	6.0	0.0

[a]Values Not Determined for that segment.

Table 4. Soil texture and organic carbon analyses measured on individual soil segments taken from core 2 in the simazine-treated plot where potassium bromide had not been added to the soil.

MEAN DEPTH OF SEGMENT (METERS)	SOIL TEXTURE SAND (%)	SILT (%)	CLAY (%)	ORGANIC CARBON (%)
0.076	90.2	5.0	4.8	0.46
0.229	90.2	4.0	5.8	0.06
0.381	91.2	5.0	3.8	0.06
0.584	90.2	6.0	3.8	0.06
0.737	90.2	1.0	8.8	0.06
0.889	88.2	2.0	9.8	0.06
1.092	88.2	2.0	9.8	0.06
1.245	86.2	4.0	9.8	0.06
1.397	88.2	2.0	9.8	0.06
1.600	86.2	6.0	7.8	0.06
1.753	80.2	6.0	14.0	0.06
1.906	87.2	3.0	9.8	0.06
2.108	90.2	2.0	7.8	0.06
2.261	90.2	3.0	6.8	0.0
2.413	90.2	4.0	5.8	0.0
2.616	90.2	2.0	7.8	0.0
2.769	90.2	2.0	7.8	0.0
2.921	84.2	6.0	9.8	0.0

[a]Values Not Determined for that segment.

Table 5. Soil texture and organic carbon analyses measured on individual soil segments taken from core 1 in the simazine-treated plot where potassium bromide had been added to the soil.

MEAN DEPTH OF SEGMENT (METERS)	SOIL TEXTURE SAND (%)	SILT (%)	CLAY (%)	ORGANIC CARBON (%)
0.076	91.0	6.0	3.0	0.23
0.229	91.0	7.0	2.0	0.06
0.381	ND[a]	ND	ND	ND
0.584	89.0	2.0	9.0	0.06
0.737	91.0	2.0	7.0	0.06
0.889	91.0	2.0	7.0	0.06
1.092	90.0	1.0	9.0	0.06
1.245	89.0	2.0	9.0	0.06
1.397	91.0	4.0	5.0	0.0
1.600	83.0	6.0	11.0	0.06
1.753	83.0	6.0	11.0	0.06
1.906	83.0	6.0	11.0	ND
2.108	87.0	2.0	11.0	0.0
2.261	89.0	2.0	9.0	0.0
2.413	89.0	2.0	9.0	0.0
2.616	89.0	2.0	9.0	0.0
2.769	90.0	2.0	9.0	0.0
2.921	89.0	2.0	9.0	0.0

[a]Values Not Determined for that segment.

Table 6. Soil texture and organic carbon analyses measured on individual soil segments taken from core 2 in the simazine-treated plot where potassium bromide had been added to the soil.

MEAN DEPTH OF SEGMENT (METERS)	SOIL TEXTURE SAND (%)	SILT (%)	CLAY (%)	ORGANIC CARBON (%)
0.076	92.4	5.0	2.6	0.93
0.229	91.4	8.0	0.6	0.46
0.381	91.4	6.0	2.6	0.06
0.584	91.4	6.0	2.6	0.06
0.737	91.4	1.0	8.8	0.06
0.889	87.4	4.0	8.6	0.06
1.092	ND[a]	ND	ND	ND
1.245	ND	ND	ND	ND
1.397	90.4	3.0	6.6	0.0
1.600	89.4	3.0	7.6	0.06
1.753	77.0	9.0	14.0	0.06
1.906	80.4	8.0	12.0	0.06
2.108	90.4	3.0	6.6	ND
2.261	91.4	2.0	6.6	0.0
2.413	ND	ND	ND	ND
2.616	91.4	2.0	6.6	0.0
2.769	90.4	2.0	7.6	0.0
2.921	ND	ND	ND	0.0

[a]Values Not Determined for that segment.

Figure 2. Physical characteristics of the soil profile in the winter rain plots.

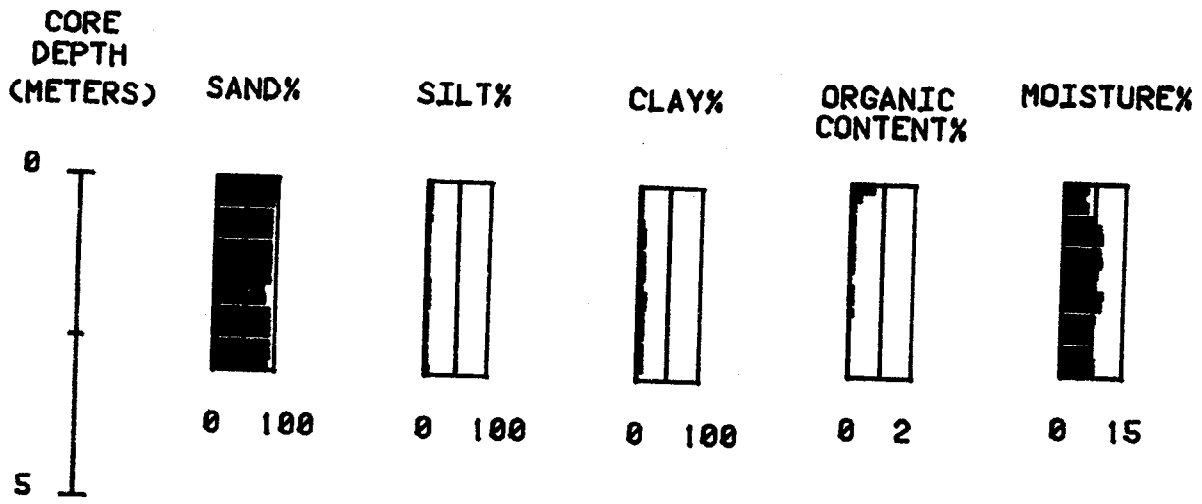


Table 7. Date and amount of rainfall recorded between application of pesticide on 11/22/85 and soil coring on 5/6/86.

Date	Amount (cm)	Date	Amount (cm)
11/24/85	0.80	2/12/86	4.70
11/25/85	0.60	2/13/86	0.70
11/27/85	0.10	2/14/86	0.70
11/28/85	1.00	2/15/86	0.90
11/29/85	1.90	2/16/86	1.60
11/30/85	0.10	2/17/86	0.60
12/2/85	1.20	2/18/86	0.20
12/14/85	0.10	2/19/86	0.40
12/17/85	0.10	3/1/86	0.10
12/27/85	0.20	3/13/86	1.70
12/29/85	0.30	3/14/86	0.10
1/4/86	0.10	3/15/86	2.70
1/5/86	0.30	3/16/86	0.50
1/9/86	0.10	3/27/86	0.10
1/13/86	0.10	3/28/86	0.20
1/27/86	0.10	4/5/86	0.60
1/30/86	0.20	4/6/86	0.50
1/31/86	1.40	4/15/86	0.10
		5/3/86	0.10
		Total	25.20

Table 8. Percent moisture measured in each soil segment in cores taken from the simazine-treated plot in areas with and without potassium bromide added to the soil.

MEAN DEPTH OF SEGMENT (METERS)	-KBr		+KBR	
	CORE 1	CORE 2	CORE 1	CORE 2
0.076	1.8	6.4	8.8	(1.0)[a]
0.229	4.1	4.8	5.3	5.1
0.381	5.8	5.9	(6.0)	5.4
0.584	8.9	7.1	6.7	6.5
0.737	10.1	9.1	8.7	8.7
0.889	9.6	9.3	10.1	9.3
1.092	9.0	9.1	10.0	(8.7)
1.245	8.0	8.4	13.0	8.0
1.397	8.5	7.6	(10.5)	7.0
1.600	7.6	8.5	8.0	7.5
1.753	9.6	9.8	9.5	10.5
1.906	9.8	9.6	10.1	9.4
2.108	8.1	7.5	9.2	7.2
2.261	6.9	6.0	8.2	7.5
2.413	6.3	5.9	7.5	(7.3)
2.616	6.9	6.8	7.3	7.1
2.769	7.9	7.9	8.2	8.8
2.921	8.7	8.1	8.1	7.3

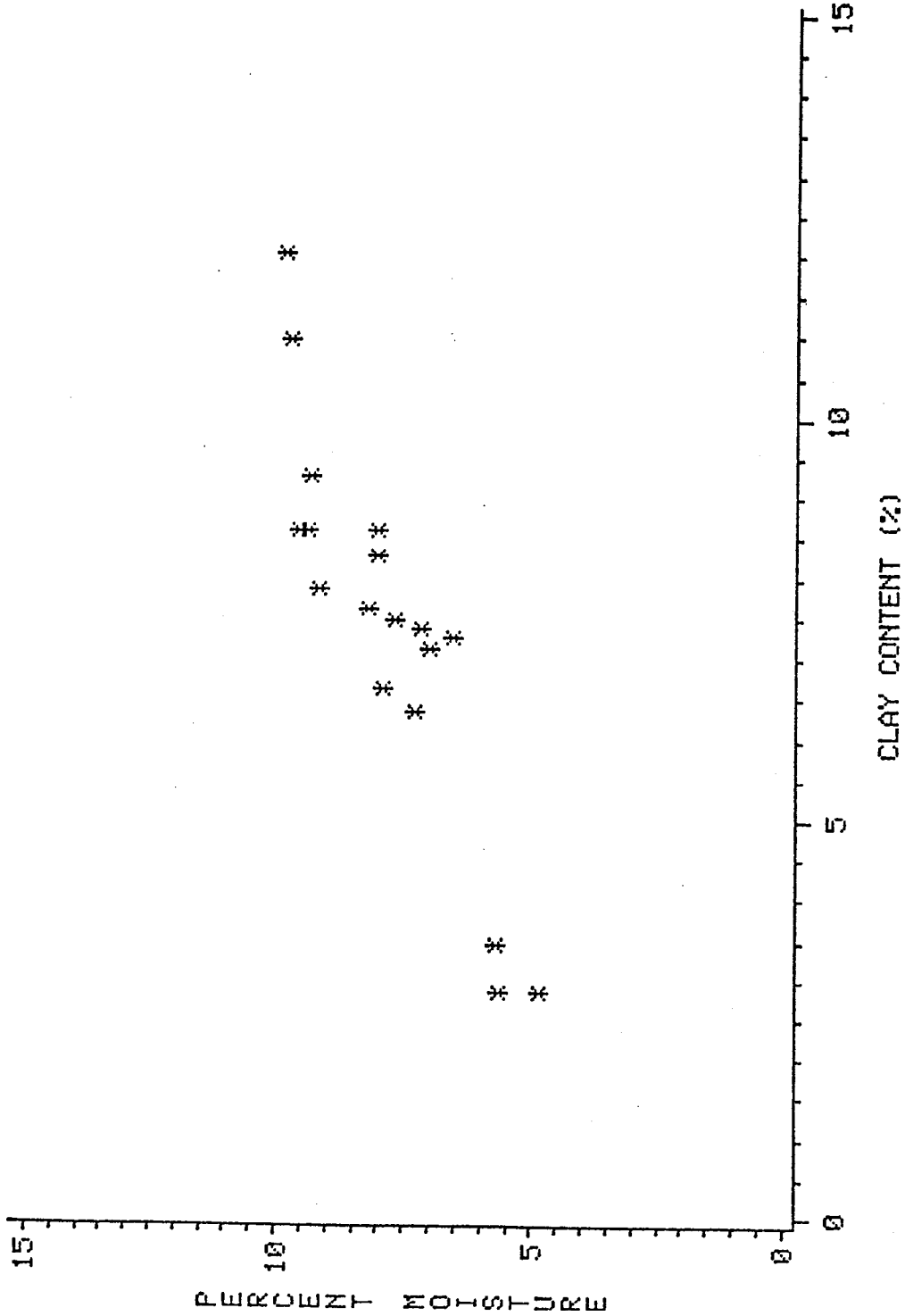
[a]The missing value for the surface segment determine from extra surface soil samples whereas missing values for subsequent segments averaged from the previous and posterior values in that core.

Table 9. Percent moisture measured in each soil segment in cores taken from the diazinon-treated plot in areas with and without potassium bromide added to the soil.

MEAN DEPTH OF SEGMENT (METERS)	-KBr		+KBR	
	CORE 1	CORE 2	CORE 1	CORE 2
0.076	ND[a]	1.1	(1.5)	(1.5)
0.229	2.2	1.6	0.7	1.1
0.381	ND	2.5	(2.2)	(1.9)
0.584	4.6	4.7	3.7	2.7
0.737	6.1	5.9	5.9	4.1
0.889	5.8	6.8	(7.0)	5.4
1.092	ND	6.7	8.1	7.1
1.245	5.8	5.9	8.0	7.4
1.397	5.3	5.8	(7.3)	6.6
1.600	5.6	6.1	6.5	7.1
1.753	5.4	8.3	8.5	8.3
1.906	8.7	10.3	8.2	9.6
2.108	ND	9.5	(7.9)	9.1
2.261	6.8	7.2	7.5	8.6
2.413	5.7	5.5	5.5	7.0
2.616	6.4	5.6	6.0	6.0
2.769	7.1	ND	6.9	7.2
2.921	7.5	7.5	8.2	8.0

[a]In cores where the mass balance of bromide was not derived, missing values are denoted Not Determined. In cores where the mass balance of bromide was derived, missing values for the surface segments were estimated from data from an additional core and missing values for deeper segments were estimated as the average of the previous and posterior values.

Figure 3. Relationship between the average percent moisture and average clay content in soil segments obtained from the simazine-treated plot.



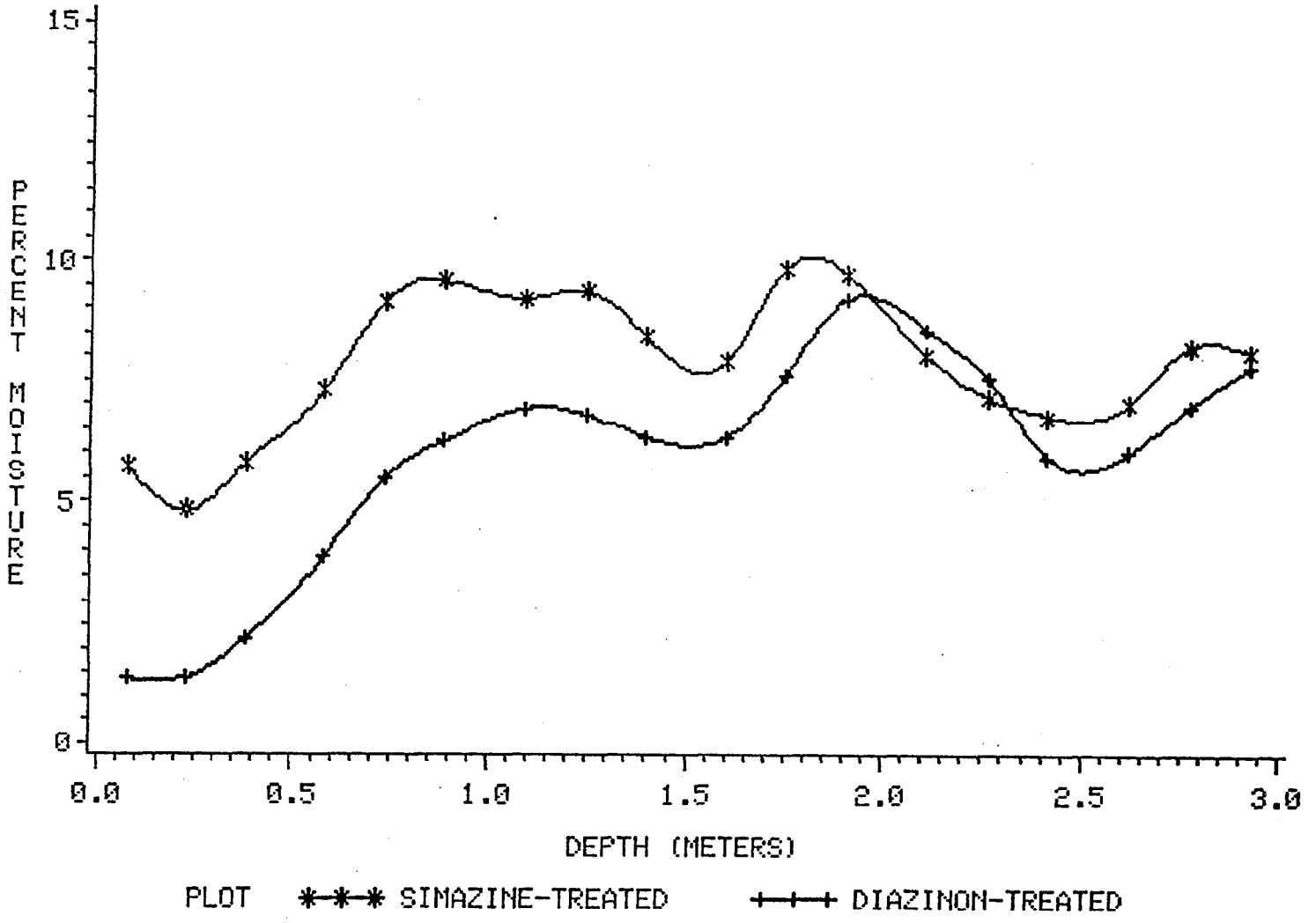


Figure 4. Comparison between simazine-treated and diazinon-treated plots of the change in the average percent moisture content of segments with depth.

the four cores. Since there was only 1 positive result for diazinon (MDL was 3 ppb), no effect of bromide could be determined in that plot (Table 10).

The results for simazine indicated no effect of tracer addition on the distribution of simazine in soil (Tables 11 and 12). R-square analyses by core indicated that a full rank sixth-order linear model efficiently described the distribution of simazine with depth. The split-plot ANOVA with the full rank model indicated a high level of significance for the first- through sixth-order terms and non-significance for the lack-of-fit test (Table 13). None of the interaction terms of depth with bromide treatment were significant. Thus, bromide did not affect the distribution of simazine so data from the cores could be pooled.

EFFECT OF WINTER RAIN ON PESTICIDE MOVEMENT

For simazine, a visual inspection of the data from the 4 cores indicated that simazine was detected down to the 1.906 m mean segment depth (Table 11). However, an average of 69% of the total amount of simazine recovered was located in the first 0.15 m of soil (Table 14). A small peak in the soil distribution of simazine was observed between the 0.737 and 1.397 m mean segment depths. The average amount of simazine recovered per 3.05 m core was 0.17 mg. Based on the application rate of 4.48 kg ai/ha, this recovery corresponded to a soil half-life of 56 days. This value was close to a reported soil half-life of 64 days, also obtained from a field study (Rao, et. al., 1980). Thus, although simazine was detected down to the 1.906 m

Table 10. Concentration of diazinon, expressed in ppb on a fresh weight basis, at each increment of depth in cores taken from plots with and without KBr added to soil.

MEAN DEPTH OF SEGMENT (METERS)	-KBr		+KBR	
	CORE 1	CORE 2	CORE 1	CORE 2
0.076	0.0	0.0	3.0	0.0
0.229	0.0	0.0	0.0	0.0
0.381	ND[a]	0.0	ND	ND
0.584	0.0	0.0	0.0	0.0
0.737	0.0	0.0	0.0	0.0
0.889	0.0	0.0	ND	0.0
1.092	0.0	0.0	0.0	0.0
1.245	0.0	0.0	0.0	0.0
1.397	0.0	0.0	ND	0.0
1.600	0.0	0.0	0.0	0.0
1.753	0.0	0.0	0.0	0.0
1.906	0.0	0.0	0.0	0.0
2.108	0.0	0.0	0.0	0.0
2.261	0.0	0.0	0.0	0.0
2.413	0.0	0.0	0.0	0.0
2.616	0.0	0.0	0.0	0.0
2.769	0.0	0.0	0.0	0.0
2.921	0.0	0.0	0.0	0.0

[a]Value Not Determined for that sample.

Table 11. Concentration of simazine, expressed in ppb on a fresh weight basis, measured at each increment of depth in cores taken from plots with and without KBr added to soil.

MEAN DEPTH OF SEGMENT (METERS)	-KBr		+KBR	
	CORE 1	CORE 2	CORE 1	CORE 2
0.076	220.0	100.0	100.0	210.0
0.229	10.0	5.0	4.0	20.0
0.381	10.0	4.0	(6.0)[a]	0.0
0.584	10.0	0.0	8.0	0.0
0.737	50.0	3.0	3.0	0.0
0.889	40.0	10.0	5.0	10.0
1.092	30.0	9.0	9.0	10.0
1.245	30.0	2.0	1.0	10.0
1.397	20.0	0.0	0.5	3.0
1.600	5.0	0.0	0.0	2.0
1.753	3.0	0.0	0.0	2.0
1.906	1.0	0.0	0.0	0.0
2.108	0.0	0.0	0.0	0.0
2.261	0.0	0.0	0.0	0.0
2.413	0.0	0.0	0.0	(0.0)
2.616	0.0	0.0	0.0	0.0
2.769	0.0	0.0	0.0	0.0
2.921	0.0	0.0	0.0	0.0

[a]Value averaged from the previous and posterior values in that core.

Table 12. Amount of simazine, expressed in micrograms, recovered at each increment of depth in cores taken from plots with and without KBr added to soil.

MEAN DEPTH OF SEGMENT (METERS)	-KBr		+KBR	
	CORE 1	CORE 2	CORE 1	CORE 2
0.076	148.7	70.7	72.3	147.5
0.229	6.8	3.4	2.7	13.7
0.381	7.0	2.8	(4.2)[a]	0.0
0.584	7.1	0.0	5.6	0.0
0.737	36.6	2.2	2.2	0.0
0.889	30.6	7.6	3.9	7.6
1.092	22.1	6.7	6.7	7.4
1.245	22.1	1.5	0.8	7.4
1.397	14.8	0.0	0.4	2.2
1.600	3.8	0.0	0.0	1.5
1.753	2.3	0.0	0.0	1.6
1.906	0.8	0.0	0.0	0.0
2.108	0.0	0.0	0.0	0.0
2.261	0.0	0.0	0.0	0.0
2.413	0.0	0.0	0.0	(0.0)
2.616	0.0	0.0	0.0	0.0
2.769	0.0	0.0	0.0	0.0
2.921	0.0	0.0	0.0	0.0
Total	302.7	94.9	98.8	188.9

[a]Value averaged from the previous and posterior concentration values in that core.

Table 13. Analysis of variance for the effect of potassium bromide addition on the distribution of simazine (ug/segment) with depth. Type I sums of squares are presented.

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Square	Level of Significance
Core	1	192.23	192.23	>0.10
Bromide Addition (Br)	1	168.15	168.15	>0.10
Error I (Core x Br)	1	1234.47	1234.47	
Depth	17			<0.01
Linear	1	10788.88	10788.88	<0.01
Quadratic	1	7092.84	7092.84	<0.01
Cubic	1	5631.69	5631.69	<0.01
Quartic	1	7106.37	7106.37	<0.01
Quinnic	1	7189.97	7189.97	<0.01
Sextic	1	4010.53	4010.53	<0.01
Lack-of-fit	11	1974.92	179.54	>0.10
Depth x Br	17			>0.10
Linear xBr	1	52.16	52.16	>0.10
Quadratic x Br	1	82.15	82.15	>0.10
Cubic x Br	1	163.70	163.70	>0.10
Quartic x Br	1	4.52	4.52	>0.10
Quinnic x Br	1	51.44	51.44	>0.10
Sextic x Br	1	43.77	43.77	>0.10
Lack-of-fit x Br	11	118.54	10.78	>0.10
Error II	34	5920.48	174.41	

Table 14. Percent of simazine recovered in each segment based on the total amount of pesticide recovered in each core.

MEAN DEPTH OF SEGMENT (METERS)	-KBr		+KBR	
	CORE 1	CORE 2	CORE 1	CORE 2
0.076	0.49	0.74	0.73	0.78
0.229	0.02	0.04	0.03	0.07
0.381	0.02	0.03	(0.04)[a]	0.00
0.584	0.02	0.00	0.06	0.00
0.737	0.12	0.02	0.02	0.00
0.889	0.10	0.08	0.04	0.04
1.092	0.07	0.07	0.07	0.04
1.245	0.07	0.02	0.01	0.04
1.397	0.05	0.00	0.00	0.01
1.600	0.01	0.00	0.00	0.01
1.753	0.01	0.00	0.00	0.01
1.906	0.00	0.00	0.00	0.00
2.108	0.00	0.00	0.00	0.00
2.261	0.00	0.00	0.00	0.00
2.413	0.00	0.00	0.00	(0.00)
2.616	0.00	0.00	0.00	0.00
2.769	0.00	0.00	0.00	0.00
2.921	0.00	0.00	0.00	0.00

[a]Value averaged from the previous and posterior concentration values in that core.

mean segment depth, the major portion of simazine was recovered in the first 0.15 meters of soil and any simazine lost from the initial application could be attributed to microbial and/or chemical degradation.

Diazinon was detected in only one surface soil segment at 3 ppb so essentially none was recovered (Table 10). Reported soil half-lives for diazinon range from 7 days (Sumner et. al., 1987) to 32 days (Rao et. al., 1985). At the application rate of 4.48 kg ai/ha, dissipation of diazinon could have been attributed to microbial and/or chemical degradation.

BROMIDE DISTRIBUTION IN SOIL

There was a difference in the soil distribution of bromide between the pesticide-treated plots, as indicated by the significant depth by plot interaction term in the ANOVA (Tables 15, 16 and 17). It should be noted that the magnitude of the mean sums of squares for interaction was approximately equal to the regression sums of squares. A description of the differences in bromide soil distribution was provided by a comparison of the cumulative amount of bromide recovered with each increment in depth (Figure 5). In the simazine-treated plot, most bromide was recovered between the 1.245 and 2.108 m mean segment depths with very little bromide recovered in the first 0.81 m of soil. In contrast, in the diazinon-treated plot, the greatest portion of bromide was recovered in the first 0.15 m of soil with a peak detected between the 1.397 and 2.108 m mean segment depths. Some bromide was measured in segments located after the subsurface peak in both plots down

Table 15. Concentration of bromide, expressed in ppm on a fresh weight basis, measured at each increment of depth in cores taken from simazine- or diazinon-treated plots.

MEAN DEPTH OF SEGMENT (METERS)	SIMAZINE-TREATED PLOT		DIAZINON-TREATED PLOT	
	CORE 1	CORE 2	CORE 1	CORE 2
0.076	0	0.11	7.24	11.20
0.229	0	0	0.31	0.33
0.381	(0)[a]	0	(0.32)	0.33
0.584	0	0	0.33	0.32
0.737	0	0.10	0.36	0.18
0.889	0.10	0.11	(0.26)	0.26
1.092	0.19	0.48	0.16	0.43
1.245	1.22	0.73	0.18	0.68
1.397	(2.07)	1.88	(0.48)	0.49
1.600	2.92	2.95	0.78	1.23
1.753	1.87	4.41	0.33	2.90
1.906	0.88	3.92	0.36	1.39
2.108	0.15	2.95	0.46	0.74
2.261	0.16	1.82	0.32	0.40
2.413	0.22	(1.54)	0.29	0.23
2.616	0.12	1.26	0.11	0.14
2.769	0	1.30	0.11	0.28
2.921	0	1.30	0	0.27

[a]Value averaged from the previous and posterior values in that core.

Table 16. Amount of bromide, expressed in milligrams, recovered at each increment of depth in cores taken from simazine- or diazinon-treated plots.

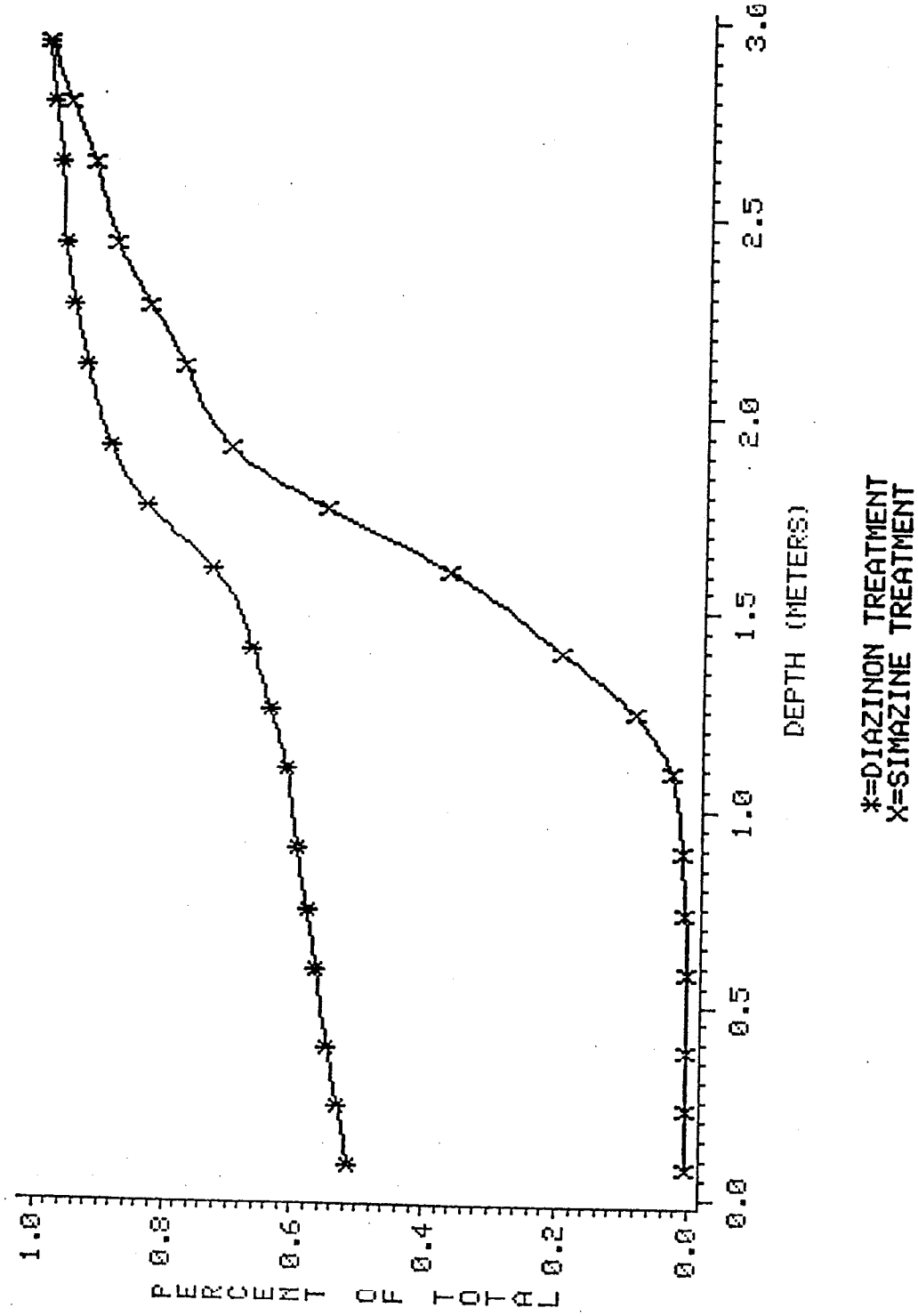
MEAN DEPTH OF SEGMENT (METERS)	SIMAZINE-TREATED PLOT		DIAZINON-TREATED PLOT	
	CORE 1	CORE 2	CORE 1	CORE 2
0.076	0	0.07	4.72	7.30
0.229	0	0	0.20	0.21
0.381	(0)[a]	0	(0.21)	(0.22)
0.584	0	0	0.22	0.21
0.737	0	0.08	0.26	0.13
0.889	0.08	0.08	(0.20)	0.19
1.092	0.15	0.36	0.12	0.32
1.245	0.95	0.54	0.13	0.50
1.397	(1.56)	1.37	(0.35)	0.36
1.600	2.09	2.11	0.55	0.87
1.753	1.33	3.17	0.23	2.04
1.906	0.74	3.26	0.30	1.16
2.108	0.12	1.94	0.36	0.58
2.261	0.12	1.40	0.25	0.31
2.413	0.17	(1.20)	0.22	0.18
2.616	0.09	0.90	0.08	0.10
2.769	0	0.99	0.08	0.21
2.921	0	0.99	0	0.21
Total	7.40	18.46	8.48	15.10

[a]Value averaged from the previous and posterior concentration values in that core.

Table 17. Analysis of variance for the effects of pesticide treatment on the distribution of bromide (mg/segment) with depth. Type I sums of squares are presented.

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Square	Level of Significance
Core	1	4362568	4362568	>0.10
Pesticidal Compound (Pest)	1	72436	72436	>0.10
Error I (Pest x Core)	1	279218	279218	
Depth	17	39566430	2327437	<0.01
Depth x Pest	17	43215996	2542117	<0.01
Error II	34	10679171	314093	

Figure 5. Comparison between simazine-treated and diazinon-treated plots of the cumulative distribution of the amount of bromide recovered with depth.



to the last sampled segment with a greater average amount detected in the simazine-treated plot (Tables 15 and 16).

The difference in the distribution of bromide between the pesticide-treated plots may be related to the pesticidal activity of the compounds. Simazine is a herbicide so the plot was free of vegetation allowing water and bromide to move freely through the soil column. Since diazinon is an insecticide with no herbicidal action, vegetation grew in that plot during the winter. This could have affected the bromide distribution in the soil either by influencing water movement due to transpirational requirements or by adsorption and accumulation of bromide from the soil water solution into plant tissue. Peaks in bromide distribution were measured at similar depths in the two plots, but the amount of water available for movement may have been less in the diazinon-treated plot. As previously noted, the water content was lower in the diazinon-treated plot from the surface down to around the 1.906 m mean segment depth indicating some depletion of water in those vegetated plots (Figure 4). Vegetation samples taken from the diazinon plot contained 465 and 755 ppm bromide for a dried and wet vegetation sample, respectively. Thus, the influence of vegetation on retaining the water tracer near the surface of the soil may have been from a combination of affecting either the mass of water available for movement or the adsorption of bromide from the soil solution.

CO-DISTRIBUTION OF SIMAZINE AND BROMIDE

In the simazine-treated plot, the cumulative frequency distribution of the relative amount of compound recovered with depth differed between bromide tracer and simazine. Bromide was detected down to the lowest sampled segment (2.921 m mean segment depth) in one core whereas simazine was detected only down to the 1.906 m mean segment depth in all 4 cores; Also, a bromide peak was detected between the 1.245 and 2.108 m mean segment depths whereas a simazine peak was detected between the 0.737 and 1.392 m mean segment depths; And, lastly, very little bromide was recovered in the first 0.81 m of soil whereas the major portion of simazine was recovered in the first 0.15 m of soil (Figure 6). If bromide was an indicator of water movement from winter rain, then simazine movement was greatly retarded with respect to the flow of water. The retention of simazine in the first soil segment may have been related to the water solubility of simazine. Most rain events were below 1 cm with a total rainfall of approximately 25.2 cm recorded between 11/22/85 and 5/6/86 (Table 7). Depth of water infiltration would be limited in such low volume rainfall events. But also the amount of pesticide that could move as a solute would be limited. For example, at simazine's water solubility of 5 ppm, a 1.0 cm event could solubilize 0.5 kg or 11 % of the 4.48 kg/ha application. Hence, movement of pesticide between low volume rainfall events would have been slight.

Any deep penetration of simazine may have been solely due to the few larger volume rain events because of deeper infiltration and the larger soluble pesticide content of the percolating water. Since the soils where high in sand content and low in organic carbon content, the soil adsorption of simazine should have been low but it may have contributed to the differences observed in the subsurface soil distribution between bromide and simazine.

events and some soil adsorption of simazine may have kept simazine residues in the upper 0.15 m of soil. A more water soluble compound may have moved to deeper depths, approximating the movement of bromide tracer.

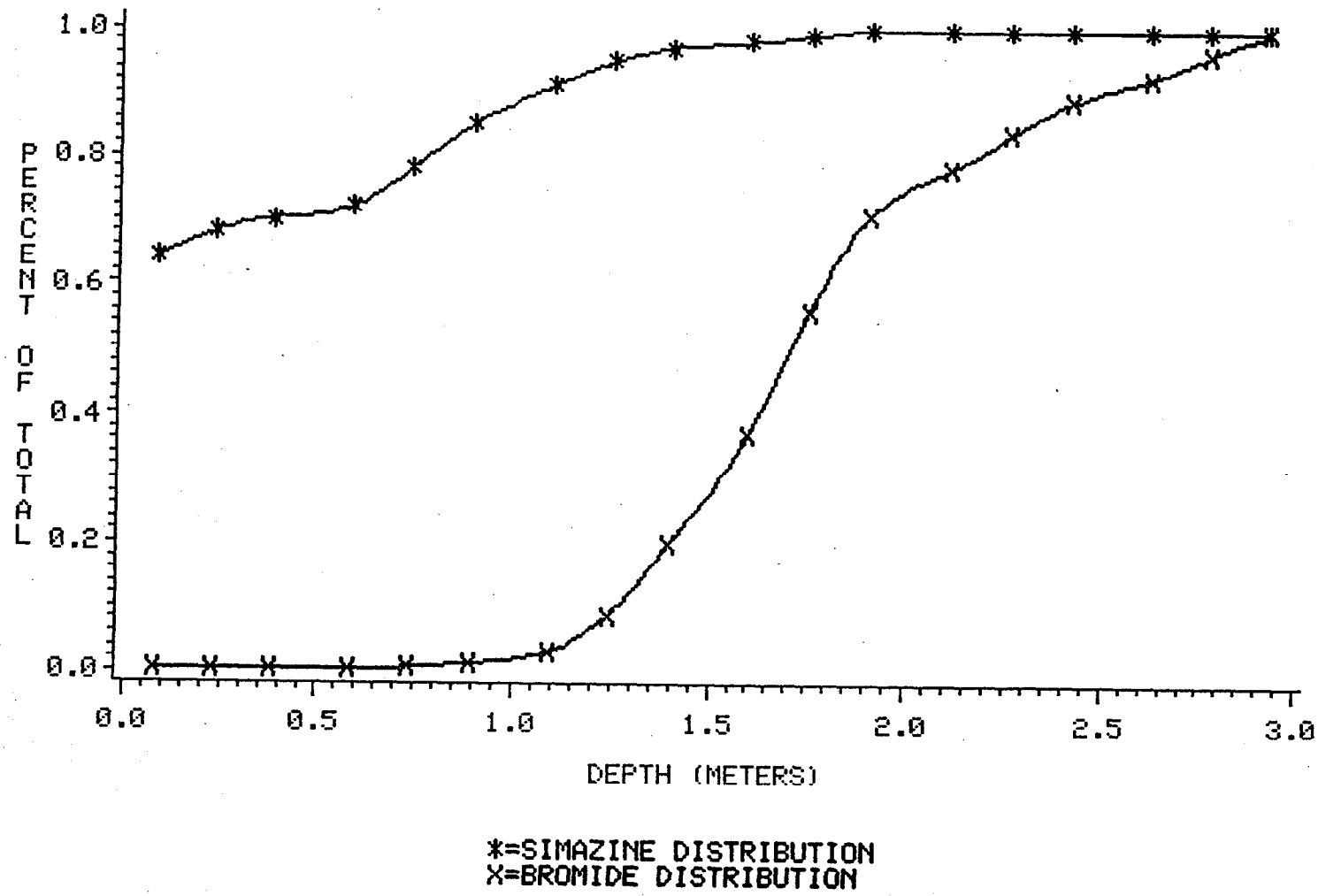


Figure 6. Comparison of the cumulative distributions with depth of bromide and simazine in cores taken from the simazine-treated plot.

CONCLUSIONS

1. Bromide, a tracer for the movement of water, was detected in the soil at the lowest sampling depth of 3.05 meters after exposure to 25.2 cm of winter rain. The bulk of the tracer in the simazine-treated plot was recovered between the 1.245 and 2.108 m mean segment depths whereas in the diazinon-treated plot the major portion of bromide was recovered in the first 0.15 meters of soil. Since diazinon is an insecticide, vegetative growth was prevalent on that plot whereas simazine inhibited plant growth. The growth of vegetation greatly affected the distribution of bromide in the soil either by affecting water transport or by physical accumulation of bromide in plant tissue.

2. Diazinon was not detected in soil after 164 days. The short soil half-life of diazinon, approximately 7 to 32 days, mitigated its potential for movement by winter rain.

3. Most of the simazine residue was recovered in the first 0.15 m of soil after exposure to 25.2 cm of winter rain. Low concentrations of simazine were detected down to the 1.906 m mean segment depth. A mass balance calculation indicated that the amount of simazine lost between application and soil coring dates were attributed to chemical and/or microbial degradation processes; simazine's soil-half life in the study was 56 days which was close to a reported value of 64 days. The low mobility of simazine observed in this study may have been due to its low water solubility in relation to the low volume of the majority of the winter rainfall events. Thus, the few larger volume events would have been

responsible for movement of simazine out of the surface 0.15 m of soil. The location of the simazine peak at a shallower depth than bromide may have been due to soil adsorption processes.

REFERENCES

1. Bruce, R.R., R.A. Leonard, A.W. Thomas, and W.A. Jackson. 1985. Redistrubution of bromide by rainfall infiltration into a Cecil Sandy Loam landscape. J. Environ. Qual, 14(3):439-445.

2. EPA. 1982. Determination of triazine in industrial and municipal wastewater, Method 619. EPA No. 600/4-82-007, NTIS No. PB82-156019. January,1982.

3. EPA. 1986a. Method 3540. EPA Hazardous Waste Manual, SW-846. September, 1986.

4. EPA. 1986b. Method 8140. EPA Hazardous Waste Manual, SW-846. September, 1986.

5. Lee, M. 1983. Aldicarb contamination of groundwater in Del Norte County. Internal Memo Sept. 21, 1983, PMAP program, California Department of Food and Agriculture, Sacramento, CA.

6. Rao, P.S.C., and J.M. Davidson. 1980. Estimation of pesticide retention and transformation parameters required in nonpoint source pollution movels. p. 23-29. In M.R. Overcash and J. M. Davidson (ed.) Environmental Impact of Nonpoint Source Pollution. Ann Arbor Science. Ann Arbor, MI.

7. Rao, P.S.C., A.G. Hornsby, and R.E. Jessup. 1985. Indices for ranking the potential for pesticide contamination of groundwater. Proceedings Soil and Crop Sci. Soc of Florida, 44:1-8.

8. Sumner, D.D., A.E. Keller, R.C. Honeycutt, and J.A. Guth. 1987. Fate of iazinon in the environment. p. 109-113. In J.W. Biggar and J.N. Seiber (ed.) Fate of Pesticides in the Environment. Agricultural Experiment Station, Division of Agriculture and Natural Resources, University of California, Publication 3320.

9. Zalkin, F., M. Wilkerson, and R.J. Oshima. 1984. Pesticide Movement to Groundwater. Volume II: Pesticide Contamination in the Soil Profile at DBCP, EDB, Simazine and Carbofuran Application Sites. California Department of Food and Agriculture, Sacramento, CA, 168pp.