MONITORING DICAMBA AND PICLORAM MOVEMENT AND FATE IN THE VADOSE ZONE FOR GROUNDWATER QUALITY PROTECTION IN WYOMING

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Executive Summary

Extensive use of the herbicides dicamba and picloram in Wyoming, along with the large volumes of irrigation water used in some areas, has created a concern for the potential contamination of surface and ground water by these herbicides. Persistence and mobility of dicamba and picloram were investigated in batch adsorption, soil column, and field studies of both agricultural and rangeland soils. The objectives of this study were to characterize soil chemical and physical properties that affect herbicide transport, examine herbicide sorption, estimate degradation rate constants and model herbicide movement.

Soil chemical and physical properties that influence pesticide fate and mobility were examined in soils and substrata within three areas of Wyoming. Deep core incremental sampling was employed for pesticide analysis and was used as material for sorption studies to determine the potential extent of pesticide movement. Soil/substrata chemical and physical properties were also used in conjunction with results from the sorption studies to predict pesticide transport.

Essentially no sorption of dicamba was detected in laboratory studies; however, picloram sorption was found to be greater in soils containing increasing organic carbon contents. In saturated column (5.90, 2.96, and 0.82 kg ha^{-1} dicamba and 1.85, 0.97 and 0.47 kg ha^{-1} picloram) and unsaturated column (2.76 and 1.00 kg ha^{-1} dicamba and picloram, respectively) experiments, both herbicides and a Br tracer were displaced through soils using distilled water applied daily (60 ml d^{-1}). Herbicide and tracer breakthrough curves were obtained from the column experiment. Degradation rate constants were calculated using both a simple recovery fraction technique and by matching LEACHP-generated breakthrough curves to experimental data. For the two columns receiving intermediate application rates, anaerobic picloram dissipation was more rapid ($t_{1/2}$ = 19 d) than for aerobic conditions ($t_{1/2}$= 87 d). The rate of dicamba dissipation was approximately the same under aerobic and anaerobic conditions ($t_{1/2}$ = 15 and 17 d in the saturated and unsaturated columns, respectively). Picloram and dicamba dissipation was more rapid at the lowest application rates, with $t_{1/2}$ of 13 and 10 days. Both herbicides were found to be highly mobile, with the mobility of picloram increasing at the higher pore-water velocities.

Soil collected at the Torrington experiment station prior to herbicide application, did not, for the most part, contain any dicamba. Concentrations below the detection limit (8 ug/kg) were found at the 3 conventional tillage sites at all depths. The highest dicamba content was found at the 60-90 cm depth for some no-till-injection and chisel-broadcast sites with different tillage and fertilizer treatments. All samples from no-till sites with fertilizer injection treatment contained trace amounts of dicamba at all depths. Results also suggest dicamba leached to depths of 60-90 cm (trace content) and deeper after 80 days. The highest persistence of dicamba was in the no-till sites with fertilizer injection treatment.

The results of picloram concentrations in soils from the Sundance area (Crook County) were variable with respect to its movement and degradation rate. An initial application rate of 0.25 lb a.i./ac was equivalent to 250 ppb of picloram in the top 15-20 inches of soil. In some sites, picloram was present in the top 15 cm of soil at 8.5 mg/kg one to six months after application of 1 lb a.i./ac. Fourteen months after an application of 1 lb a.i./ac, picloram content was highest at the 40-100 cm depth. Results indicate that picloram

residues were limited to the top 100 cm with the highest concentration in the upper 40 cm. At one site, 10% of the applied picloram remained after 34 months.

Field studies were performed at an irrigated pasture site equipped with 64 soil water extractors installed at four depths. Samplers extract solution from 15, 30, 60 and 90 cm depth, with four replicated per plot at each depth. Two different herbicide application rates were applied to a total four plot. The highest application rates for picloram and dicamba were 2.9 kg ha^{-1} and 9.4 kg ha^{-1} respectively, and the lower application rate was 0.9 kg ha^{-1} for both picloram and dicamba each. Plots were irrigated weekly with 5 cm of water for a total of 20 weeks.

Mean herbicide concentrations as a function of time were determined because of the spatial variability in contaminant movement that was evident both between neighboring samplers and plots. For plots, with lower herbicide application rates, herbicide disappearance was relatively quick, especially for dicamba. Dicamba concentrations approached the detection limit (0.0015 pm) in 96 days at the depth of 15 cm and in 57-89 days at the depth of 30 cm. Maximum concentration at the depth of 60 cm (0.01-0.02 pm) was reached in 29 days and was below the detection limit in 43 days after application. Dicamba was not detected at the 90 cm depth during the entire experiment.

Picloram remained in the profile longer, but did not penetrate into the vadose zone as deeply as dicamba into the vadose zone. Picloram was not detected in any solution samples collected from 60 and 90 cm samplers. However, picloram was detected on 327th day at the depth of 60 cm. This is consistent with column study results in which picloram was adsorbed by all the soil materials.

For plots with higher herbicide application rates, dicamba content within the profile decreased more rapidly than picloram. Concentration peaks of picloram and dicamba diminished and spread with increasing depth. Picloram concentration peaks moved throughout the profile at a slower rate than dicamba peaks. The highest measured concentration of picloram and dicamba was reached 15 days after application at the depth of 15 cm; the peak reached a depth of 30 cm two weeks later and a depth of 60 cm six weeks later. Picloram content at the 90 cm depth was still increasing 327 days after herbicide application.

Modeling pesticide movement in a vadoze zone proved to be a useful research tool. LEACHP provided modeling parameters of solute movement in repacked soil columns. However, comparing model-predicted and field contaminant movement was more difficult due to spatial variability. Hydraulic conductivity was found to be highly variable, and would have the greatest effect on contaminant movement.

Additional studies are being conducted on the field site used for this project. Ground water monitoring wells have been installed at 10 locations throughout the research site. Both dicamba ($\approx$9.4 kg ha^{-1}) and Br- (225 kg ha^{-1}) have been applied to plots 1 and 2, and a Cl$^-$ tracer (50,000 mg L^{-1}) added to one of the ground water monitoring wells. Results of this additional study will provide information on pesticide and tracer characteristics in both vadose zone and ground water environments.

Introduction

Several pesticides used extensively in Wyoming on agricultural and rangeland soils have the potential for leaching into the soil/substrata environment that contain ground waters that are utilized for human, animal, and irrigation needs. Many of these pesticides have been detected in water supplies of states throughout the United States. Little information is available to determine if there is a problem, and to what extent pesticide contamination occurs in Wyoming; however, the herbicides dicamba and picloram have been detected in surface and ground waters of Wyoming (Lym and Messersmith, 1988; Druse et al., 1989). In 1983, picloram was detected in approximately 30% of Wyoming water samples with a maximum concentration of about 1 ppb (Hittle, 1983). Recent sampling has shown that picloram concentrations ranged between 2 and 18 ppb (Druse et al., 1989).

The results of the above studies indicates dicamba and picloram can be persistent in different Wyoming environments. Extensive use of picloram and dicamba, especially in irrigated areas, may result in the leaching of these pesticides into the vadose zone, and possibly a shallow subsurface aquifer. Information on the mobility and fate of dicamba and picloram can be used to identify causes of contamination as well as be used to find methods or practices which might reduce the problem. Leaching of pesticides represents not only a potential source of contamination but also an economic loss when pesticides are transported prematurely from the effective surface zone.

Wyoming has a diverse agricultural base with areas of intensive short season crop production. Coupled with the arid Wyoming climate, many of the agricultural areas rely heavily on irrigation as a source of the water necessary for crop growth. With the scope of pesticide usage in cultivated crop production, along with the volumes of irrigation water used, leaching of pesticides becomes a potential concern for contamination of the underlying ground water. Water table depths in irrigated basins of Wyoming can be shallow (e.g., 2-4 m) during the growing season, causing pesticides which migrate through the vadose zone into the saturated zone to undergo slow biodegradation. There is also sufficient evidence to indicate that even properly applied pesticides may leach into ground waters. Much of the potable water supply for several regions of Wyoming comes from wells in aquifers that may be affected by pesticides leached from agricultural practices. For Wyoming, water supplies for 61% of the residents comes from subsurface sources with 89% of the rural population depending on ground waters (Canter et al., 1987).

Pesticide contamination of water supplies has become a national issue (Moody, 1990). Many crop production and range/pasture areas of Wyoming have a history of pesticide use (Taylor et al., 1986; Legg et al., 1992). Dicamba and picloram have been used in area specific cropping patterns for a number of years. These pesticides have been listed for restricted use by the EPA due to their high potential for leaching in soils and for their persistence in ground waters (U.S. EPA, 1987). The long term use of these pesticides in Wyoming thus represents an excellent opportunity to study both long term and seasonal fate of pesticides in this (Nofziger and Hornsby, 1986).

A multitude of pesticide contamination and fate studies have been conducted throughout most of the United States (MacDonald et al., 1976; Melancon et al., 1986; White et al., 1986; Lym and Messersmith, 1988). Although these studies have

encompassed a range of conditions including laboratory and field studies of many soil/chemical systems, most have been conducted in areas with one of the following traits: vast agricultural production, pronounced vulnerability to contamination, intensive use of problem pesticides, or proximity to densely populated areas. Very few have had direct application in semi-arid and arid states such as Wyoming, where a combination of a persistent or mobile pesticide and its use on extensive areas of rangeland and irrigated crops may potentially lead to contamination.

The focus of this study was to examine Wyoming agricultural and rangeland soils to determine the movement and fate of dicamba and picloram by analyzing soil/substrata characteristics and pesticide concentrations before and after pesticide application. Physical and chemical characteristics of the soil/substrata materials were studied in order to model the potential for pesticide transport. Sorption studies were performed to determine pesticide interaction with the soil/substrata materials. Specific objectives of this research project were to:

- Analyze pesticide levels in soils/substrata, soil solutions, and ground waters from different areas in Wyoming.
- Characterize soil/substrata chemical and physical properties to determine which of these factors are important in controlling pesticide transport.
- Examine pesticide sorption by soil/substrata for correlation to chemical and physical characteristics. Batch studies were used to examine the extent of pesticide sorption for those pesticides determined at a particular site.
- Evaluate pesticide transport models for estimating potential ground water contamination based on experimental data from column studies and soil solution collectors.

Materials and Methods

Soil samples were collected from three study sites. They include sites in Albany, Goshen and Crook counties. The Albany county site is located at the University of Wyoming College of Agriculture's experimental farm west of Laramie. This site is primarily used for pasture, and was utilized for an intensive soil-solution sampling study due to its close proximity to the University. Soil-water collectors were installed and herbicide movement was measured. Soil from this site was also used for several column studies. Another site, the University of Wyoming's experiment station located northwest of the city of Torrington (Goshen County), was selected because of the recorded use of dicamba on different agricultural crops under various tillage practices. The third field location was in Crook county and was located within the Leafy Spurge research study area operated by the University of Wyoming in cooperation with the Wyoming Department of Agriculture. This site was selected to specifically examine the use of picloram on rangelands.

Properties of herbicides that affect their mobility in soil, and their associated threat to reach and impair groundwater, are primarily related to solubility, adsorption, and persistence. The persistence, as noted by the length of time a herbicide remains active in a soil system after application, was determined for soil samples collected in Goshen and Crook County. Adsorption studies using picloram and dicamba were performed on samples

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from Goshen, Crook and Albany County. Soil hydraulic properties, such as moisture retention and permeability, were also determined in the Albany county soils.

Pesticide analysis

Soil and water samples were analyzed to determine the presence and quantity of dicamba and picloram. Herbicide analysis was performed using high pressure liquid chromatography (HPLC) with solid phase extraction (SPE) for concentrating and purifying samples. Our technique "Solid phase extraction of dicamba and picloram from water and soil samples for HPLC Analysis" was accepted for publication in the Journal of Agricultural and Food Chemistry (Appendix 1).

Adsorption Study

Soil samples collected from each of the study sites were used for standard batch adsorption studies. This is an indirect method which determines the quantity of sorbed pesticide by measuring the change in solution concentration resulting from pesticide sorption. The quantity of sorbed solute is assumed to equal the quantity lost from solution. Adsorption isotherm parameters for picloram and dicamba were calculated from the Freundlich equation, which has been used extensively in pesticide adsorption studies (Grover 1971, Davidson and Chang 1972, Grover and Smith 1974, Farmer and Aochi 1974, Murray and Hall 1989, Grover and Cessna 1991). The Freundlich equation is as follows:

$$x/m = K*C^{1/n} \qquad [1]$$

where x/m = the amount of herbicide adsorbed per unit weight of adsorbent (mg/kg) and C is the equilibrium concentration (mg/l). Freundlich constants, K and $1/n$, are obtained by the least square regression method after linearly transforming the initial Freundlich equation by logarithmic transformation. The constant K is equal to the amount of pesticide adsorbed in equilibrium with a unit concentration of pesticide and therefore is taken as an index of adsorption. The best predictor of the sorption coefficient is soil organic carbon content, which was measured in our study by a modified Walkley-Black wet oxidation and titrimetric method. Sorption coefficients were calculated (Rao and Davidson 1981, Green and Karickhoff 1990) from the equation:

$$K_{oc} = (Kd/\%org.C)*100 \qquad [2]$$

Several adsorption studies were performed on soils collected at depths of 0-30; 30-60 and 60-90 cm from the University of Wyoming experiment station in Goshen County. Concentrations of added dicamba solution ranged from 0.5 to 10 mg/l with the final equilibrium pH range 7.3-7.8. All adsorption isotherms were done in triplicate. The ratio of soil to solution was 1:2 (20 g soil and 40 ml solution). Samples were shaken on a wrist action shaker for 10 hours and centrifuged at 2,000 RPM for 30 min and 8,000 RPM for 15 min. Solutions were stored in glass bottles and analyzed by using the solid phase

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extraction-HPLC technique described in Appendix 1.

Adsorption studies were also performed on soils collected from Sundance (Crook County) at three depths (0-30, 30-60, and 60-90 cm), using picloram concentrations ranging from 0.05 to 2.0 mg/l at pH 5.0. The ratio of soil to solution was 1:2 and triplicates for each concentration were shaken on a wrist action shaker for 10 hrs, centrifuged at 2,000 RPM for 30 min and 8,000 RPM for 15 min.

The adsorption studies, for soil collected near Laramie (Albany County), were performed on soil from three horizons (0-20, 20-35 and 35-50 cm) using pesticide concentrations of 0.2 to 5.0 mg/L picloram and 0.5 to 3.0 mg/L dicamba.

Column Experiment

A soil column experiment was used to study herbicide displacement in soil collected at the Albany County agricultural experiment station. Soils (sandy clay loam) were collected from depths of 0-20, 20-35, and 35-50 cm. Bulk density was measured in the field by the sand-cone method. Disturbed soil profiles were assembled in 3 glass columns, 8 cm in diameter and 52.5 cm high (Figure 1). The soil columns were constructed by assembling 5-cm glass segments glued together with silicon. A 2.5 cm layer of silica sand (baked at 500° C for 3 hrs), fine metal screen and buchner ceramic funnel were placed at the bottom of the column to retain the soil. An impact-lift method was used to obtained desired bulk density of soil at each horizon (ASTM Standards 1990). Each soil was mixed, sieved through a 4 mm sieve, brought up to a water content of about 20% (II and III horizon) and added to columns in 6 lifts (150 g dry soil each lift). Ten impacts were imparted to each lift for dry soil from the first horizon to obtain a 1.34 g/cm^3 density and 9 impacts to each lift for moist soil from the second horizon (1.52 g/cm^3) and 10 impacts to each lift of moist soil from the third horizon (1.54 g/cm^3). Initially, 60 ml of varying herbicide concentrations were applied to different columns. Each solution contained KBr as a tracer and pH was adjusted to 6.1. Every day, 60 ml of water was applied to each column. Columns reached a steady flow after 3 days of applying water. Chemical migration was monitored by analyses of daily effluent solutions using the solid-phase/HPLC method. At the end of the column leaching study the column segments were disassembled and soil was analyzed as a function of depth.

Field Studies

Field studies included collection and analysis of soils from soil profiles from sites in Albany, Goshen and Crook counties where herbicides have been applied. Soil solutions from soil water collectors were collected at the site in Albany county and analyzed for dicamba, picloram, and the Br⁻ tracer.

Soil core analysis

The content of herbicides in soil was determined by sampling soil profiles as follows:
- Goshen County (Torrington), before and after applying 1/4 lb a.i./ac dicamba (30th of April 1992)
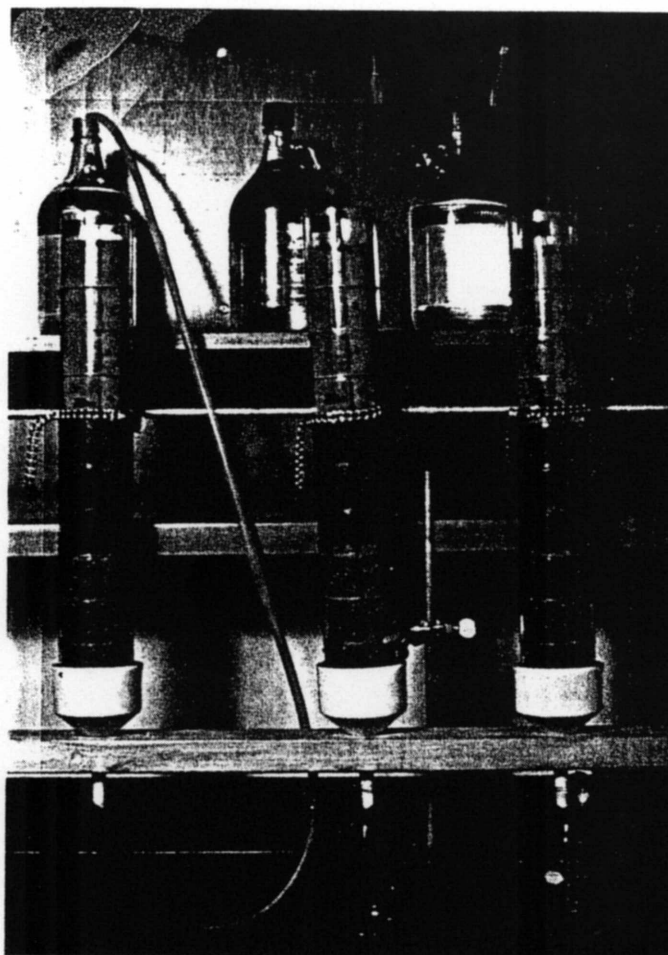
Figure 1. Examples of the soil columns used in the herbicide leaching studies. Columns contain reconstructed soil profiles representative of the Albany county study site.

- Crook County near Sundance, from sites receiving different application rates of picloram over a five year period (1987 to 1992).

Samples from Torrington were collected on the 17th of April, 1992 using a soil auger. Samples were taken from depths of 0-30 cm; 30-60 cm and 60-90 cm from conventional, chisel plow and no-till sites (27 soil samples). Sites of soil profiles collections on the 18th of July were located at conventional, chisel plow and no till type of tillage with different type of fertilizer application: full rate injection, broadcast and control (45 samples). Samples were refrigerated and analyzed for the dicamba content within two days of collection.

Samples from Crook County were collected from 9 profiles to the depth of 120 cm (42 samples). Samples were taken from sites differentiated by rate and date of picloram application (0.25, 1 and 2 lb a.i./ac). Samples were stored in a freezer and analyzed for the picloram content within two weeks of collection.

Field investigation using soil-water collectors

Soil water collectors were installed in June, 1993, at the University of Wyoming College of Agriculture's experimental farm located approximately 4 mile west of Laramie (Figure 2). The study area was equipped with soil water extractors installed at 4 depths. Samplers extract solution from depths of 15, 30, 60 and 90 cm, with four replicates per plot at each depth (Figure 3). Two different herbicide application rates were applied to a total of four plots. The highest application rate for picloram, 2.9 kg/ha, and dicamba, 9.4 kg/ha, was applied to plots no.3 and 4, the lowest application rate of picloram and dicamba, 0.9 kg/ha, was applied to plots no.1 and 2 (Figure 4). In addition, a control plot was delineated where no herbicides were applied. The five plots were irrigated weekly during the growing season from June 23rd until September 25th and biweekly until October 25th. During each irrigation event, 5 cm of water was applied to each plot. Soil solutions were collected two days after irrigation by applying vacuum to the soil water collectors. Samples were frozen and analyzed as soon as possible for picloram and dicamba content. Neutron probe access tubes were installed (3 per plot) to estimate water flux and moisture profiles. The hydrological conditions of the experimental site were checked by measuring the moisture of 3 horizons before and after watering using the neutron probe (20 times during the season). Saturated conductivity was measured using the auger-hole method and ring infiltration test (Amoozegar and Warrick, 1986).

Modeling

Modeling is increasingly being used as a tool for evaluating the fate of pesticide in soil-water systems. Sorption, leaching, degradation, volatilization and other processes are integrated through the use of simulation modeling techniques. An extensive review of recent types of pesticide simulation models was performed by Wagenet and Rao (1990). These models were evaluated and categorized according to their purpose and complexity as: research, screening, management and instructional models (Table 1). The present study is using a research type of model, which is the most sophisticated and quantitative,
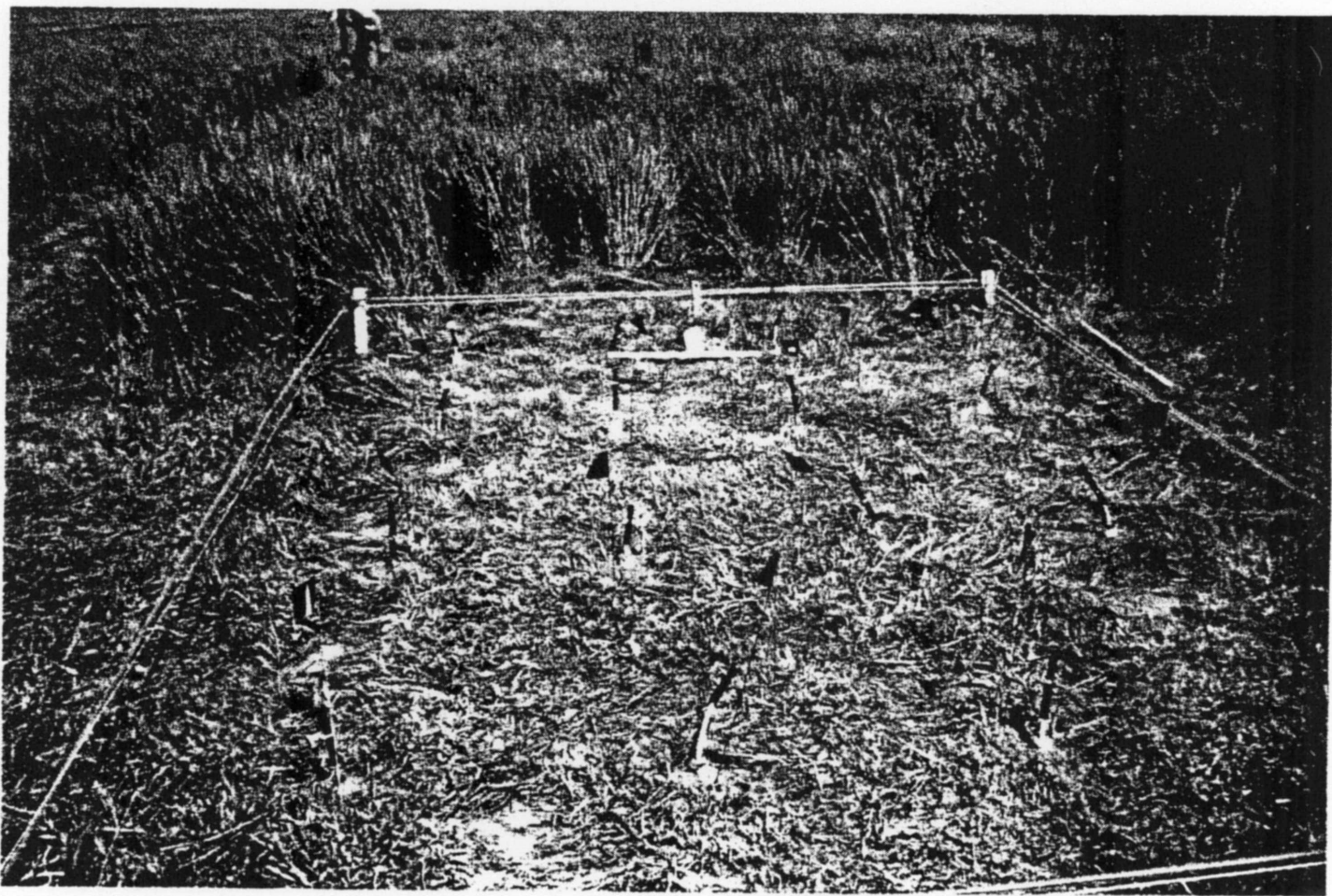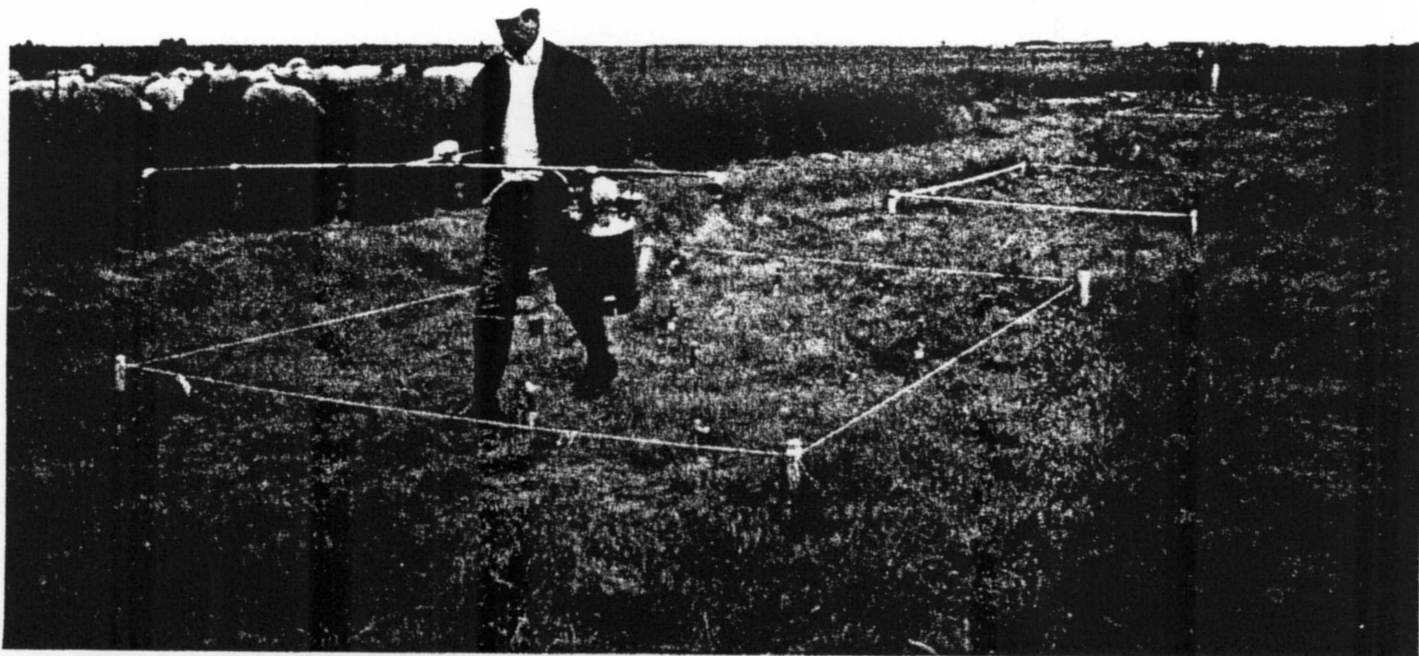
Figure 2. Application of dicamba and picloram (upper figure) to the Albany county research site. Lower figure is a view of the16 lysimeters installed at each plot (total of four plots).

Fig. 3 Arrangement of Plots and Location of Soil Solution Collectors at the Experimental Site
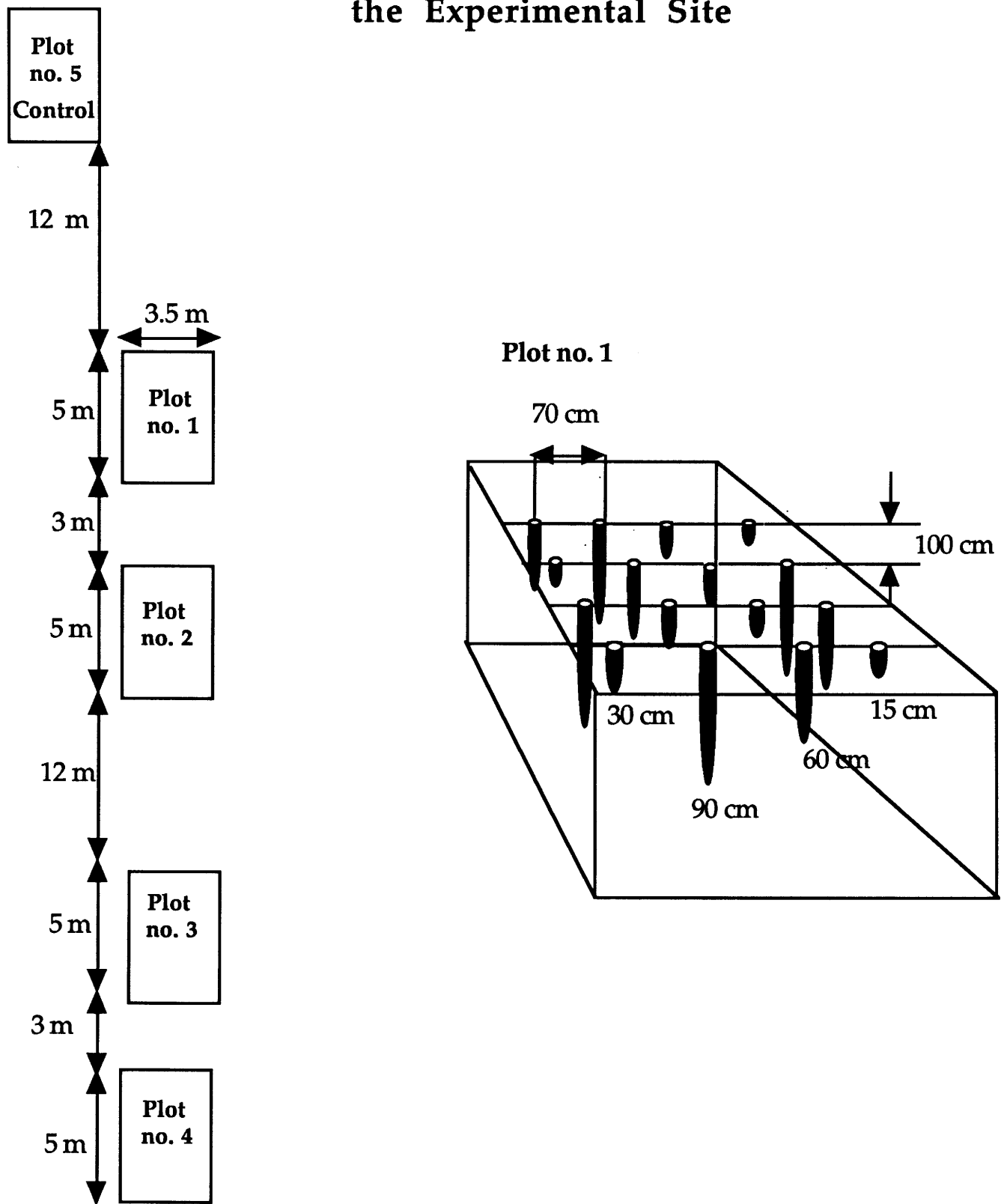
Fig. 4 Location and depths (cm) of soil water collectors

Plot no.1

1/4 60cm	1/3 90cm	1/2 30cm	1/1 15cm
1/5 15cm	1/6 60cm	1/7 30cm	1/8 90cm
1/12 90cm	1/11 30cm	1/10 15cm	1/9 60cm
1/13 30cm	1/14 90cm	1/15 60cm	1/16 15cm

Plot no.3

3/4 15cm	3/3 30cm	3/2 60cm	3/1 90cm
3/5 60cm	3/6 15cm	3/7 90cm	3/8 30cm
3/12 30cm	3/11 60cm	3/10 15cm	3/9 90cm
3/13 90cm	3/14 30cm	3/15 60cm	3/16 15cm

Plot no.2

2/4 90cm	2/3 60cm	2/2 15cm	2/1 30cm
2/5 15cm	2/6 30cm	2/7 90cm	2/8 60cm
2/12 30cm	2/11 90cm	2/10 60cm	2/9 15cm
2/13 60cm	2/14 15cm	2/15 30cm	2/16 90cm

Plot no.4

4/4 90cm	4/3 60cm	4/2 30cm	4/1 15cm
4/5 15cm	4/6 30cm	4/7 60cm	4/8 90cm
4/12 60cm	4/11 15cm	4/10 90cm	4/9 30cm
4/13 30cm	4/14 90cm	4/15 15cm	4/16 60cm

N →

and require the most input data. LEACHP is one of the four models in LEACHM and simulates pesticide degradation, transportation and movement (Hutson and Wagenet, 1992). The most important parameters for the LEACHP model are those defining solubility, retardation, volatility, transformation and degradation. Predicted herbicide transport is less sensitive to changes in dispersion and diffusion. Parameters required by the LEACHP model were obtained from sorption characteristic of the pesticides, hydraulic properties of the soil, bulk density of the soil, and characteristic of pesticide application. Parameters characterizing sorption (Kd) were obtained from the batch study.

Table 1   Simulation models developed or useful for pesticide fate assessment.

Model	Acronym	Purpose	Reference
Behavior Assessment Model	BAM	screening	Jury et al., 1982
Leaching Estimation And Chemistry Model	LEACHM	research	Wagenet and Hutson 1986
Pesticide Root Zone Model	PRZM	management	Carsell et al., 1984
Chemical Movement in Layered Soil	CMLS	instructional	Nofziger and Hornsby, 1986
Pesticide Analytical Solution	PESTAN	screening	Enfield et al., 1982
Chemicals, Runoff and Erosion from Agricultural Management Systems	CREAMS	management	Nyhan 1990
Seasonal Soil compartment model	SESOIL	management	Hetrick et al., 1989

Results and Conclusions

An analytical method for the determination of picloram and dicamba in water and soils was developed in the first year of the project (Appendix 1). Results of our column studies were also presented in a publication titled "Assessment of the fate of two herbicides in Wyoming rangeland soil: Column studies" which was accepted by the Journal of Environmental Quality (Appendix 2). Results of soil water collectors experiment are currently being prepared as a publication titled "Assessment of the fate of two herbicides in Wyoming rangeland soil: field simulation" which will be submitted to the Journal of Environmental Quality. Results which were not utilized in the above publications are presented below.

Adsorption Study

There was no adsorption of dicamba to soils collected from Goshen and Albany County which had equilibrium pH values ranging from 6.0 to 7.8. The adsorption of dicamba for similar soils (sandy loam or loam) was also zero for studies performed by Grover and Smith (1974).

Picloram adsorption isotherms were linear at concentrations of added picloram of 0.4 mg/1000 g soil and higher. Isotherms were not linear at concentrations of 0.02, 0.05 and 0.1 mg picloram /kg soil. This is consistent with the results of Green and Karickhoff (1990) who indicated that at high and low picloram concentrations, the value of Freundlich n constant decreases and the linear approximation becomes less and less satisfactory. The adsorption of picloram to soil from Albany County was highest at the 20-35 cm depth, which was attributed to its high organic carbon content. The adsorption of dicamba and picloram by the soils from Albany County is comparable to soils from other studies (Table 2).

Table 2.   Distribution coefficient value for different type of soil

Type of soil	Organic matter	Kd		Reference
	%	Picloram	Dicamba	
loam	6.0-10.0	0.07-0.08	-	Grover and Smith, 1974
heavy loam	4.5	0.00	-	
loam	4.0-10.0	0.1-0.49	0.03-0.3	Grover 1977
sandy loam	1.7	0.03	0.00-0.00	
loam	-	0.18	-	Davidson and Chang 1972
loam	6.5-12	0.29-0.75	-	Grover 1971
sandy loam	-	-	0.00-0.08	Grover and Smith 1974
silt	5.6	0.55-0.98	-	Farmer and Aochi, 1974
sandy clay loam	**2.1**	**0.00-0.26**	**0.00**	**present study**

Adsorption of pesticides is dependent on a number of factors, such as type and content of soil organic matter, pH of the media, temperature, and soil/solution ratio (Singh et al. 1990). The colloidal surface of most agricultural soils have a net negative charge and thus have an affinity for positively charged molecules, but not much affinity for negatively charged molecules (Khan 1991). Therefore, acidic pesticides such as picloram and

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dicamba are not readily adsorbed by clay minerals, but are adsorbed in limited amount by organic matter. Results of our studies showed that the effect of different organic carbon contents was evident for picloram adsorption with soils from Albany County. The effect of pH (values between 6-7) on adsorption coefficients for picloram and dicamba, however, was insignificant. Adsorption of the molecular species alone occurs at suspension pH values 1 to 2 units below the pKa of herbicides (Green and Karickhoff 1990).

Column Study

Results of the column study are presented in Appendix 2.

Field Studies

Field studies results are presented below for picloram and dicamba concentrations in soil profiles collected from Goshen and Crook counties, and results of the field experiment performed at the University of Wyoming's experimental farm, west of Laramie (Albany county).

Soil core analysis

Soil collected at the Torrington experiment station, prior to herbicide application, did not, for the most part, contain any dicamba. Concentrations below the detection limit (35 ug/kg) were found at the 3 conventional tillage sites at all depths. The dicamba content in soil about 80 days after application was also very low. The highest content was found at the 60-90 cm depth for some no-till-injection and chisel-broadcast sites with different tillage and fertilizer treatments. All samples from no-till sites with fertilizer injection treatment contained trace amounts of dicamba at all depths. Dicamba, after 80 days, was leached to depths of 60-90 cm (trace content) and deeper. This is consistent with other observations about the mobility, solubility, and persistence of dicamba in irrigated soil environments (Murray and Hall 1989, Grover and Smith 1974, Smith 1974). The highest persistence of dicamba was in the no-till sites with fertilizer injection treatment.

The results of the concentration of picloram in soil from the Sundance area (Crook County) did not indicate any consistent rate of movement or trend in degradation. An initial application rate of 0.25 lb a.i./ac was equivalent to 250 ppb of picloram in the top 15-20 inches of soil. In some sites, picloram was present in the top 15 cm of soil at 8.5 mg/kg one to six months after application of 1 lb a.i/ac (site 902/106). Fourteen months after an application of 1 lb a.i./ac, picloram content was highest at the 40-100 cm depth (Table 3). Results indicate that picloram residues were limited to the top 100 cm with the highest concentration in the upper 40 cm. At site 603/117, a surprising 10% of the applied picloram remained after 34 months.

Field investigation using soil-water collectors

The soil water collector studies represent results for picloram and dicamba concentrations in soil solutions from 64 lysimeters, collected on 15, 29, 43, 57, 67, 74, 81,

Table 3. Content of picloram in soil samples from Sundance area collected on 7/31/1992

| Plot #	Depth (cm)	Content of picloram (g/kg)	Rate of picloram application (lb a.i/ac)	Year of treatment
202/115	0-20 20-40 40-60 60-105 105-120	tr. 9.422 n.a. n.a. n.a.	2	5/28/1987
203/108	0-20 20-40 40-60 60-100 100-115	21.368 tr. tr. tr. b.d.l.	2 0.5 0.5	5/28/1987 1991 1992
502/106	0-20 20-45 45-60 60-105 105-115 115-120	b.d.l. b.d.l. b.d.l. b.d.l. b.d.l. b.d.l.	2	8/27/1988
603/117	0-15 15-40 40-60 60-80 80-100	tr. 108.0 88.2 8.92 n.a.	2	5/24/1989
603/120	0-15 15-45 45-60 60-100	tr. tr. 12.42 tr.	2 0.25	1989 6/10/1992
701/117	0-15 15-45 45-60 60-100 100-120	b.d.l. b.d.l. b.d.l. b.d.l. b.d.l.	2	6/1/1989
704/113	0-15 15-40 40-50 50-80 80-120	b.d.l. b.d.l. b.d.l. b.d.l. b.d.l.	2	6/6/1990
901/106	0-15 15-40 40-60 60-100 100-120	b.d.l. tr. 34.24 29.81 tr.	1	9/11/1991
902/106	0-15 15-35 35-60 60-120	8.54 tr. tr. tr.	1	6/9/1992

tr.-concentration <8 ug/kg; n.a. - not analyzed; b.d.l. - below detection limit

89, 96, 117, 123 and 327 days after herbicide application. The highest application rate of picloram (2.9 kg/ha) and dicamba (9.4 kg/ha) was applied to plot no.3 and 4, the lowest application rate (0.9 kg/ha) of picloram and dicamba was applied to plots no.1 and 2 (Figures 3 and 4).

DISTRIBUTION OF PICLORAM: The distribution of herbicide content in soil water collectors at the plot no.1 was similar to the plot no.2 (Figure 5). The highest picloram concentration at the 15 cm depth in plots 1 and 2 was reached on the 29th and 15th day after herbicide application, respectively. The interpretation of the mean picloram content in the 30 cm depth collectors was more difficult, because solutions from two of the collectors (no. 2/15 and 1/2) had consistent levels of picloram through the whole period of experiment. The other four 30 cm depth collectors also indicated that the highest concentration (0.22 mg/l) was obtained 15 days after pesticide application. Higher picloram concentrations were observed at the 15 cm depth as compared to the 30 cm depth for the first 57 days (plot no.1) or 43 days (plot no.2) after application. After this time the amount of picloram decreased to 0 in the 15 cm depth collectors, and was more prominent in the 30 cm depth collectors (Figure 6 and 7). The picloram content at the 60 and 90 cm depths was below the detection limits (0.01 mg/L) for 123 days of the experiment. The following spring, 327 days after herbicide application, picloram was present in the 60 cm deep collectors with concentrations of 0.07 mg/l (plot no. 1) and 0.14 mg/l (plot no.2) (Figure 6 and 7). This indicates picloram leached over time and is not rapidly degraded. With time, we can expected the movement of picloram to the lower 90 cm horizons later in a season.

The distribution of picloram content in solutions from soil water collectors of plot no.3 indicated almost twice as much picloram was applied to this plot as compared to plot no.4. Therefore, the results for plots no.3 and no.4 are treated separately (Figure 8). The different distribution was probably due to more pesticide being applied during the application process for plot no.3 as compared to plot no.4, or there are major macroenvironmental differences between the two plots. The highest concentration of picloram in plot no.3 at the 15 cm depth was reached 15 days after application; at the 30 cm depth the highest concentration was reached two weeks later, and at the 60 cm depth six weeks later (Figure 8). Results of picloram in soil water collectors of plot no.4 did not indicated such consistent trends as results from plot no.3. The highest concentration of picloram at the 15 cm depth was reached on the 57th day after application and at the 30 cm depth 74 days after application. At the 60 and 90 cm depths, the highest picloram concentration was obtained on the 96th day after herbicide application (Figure 8). In plot no.3, picloram concentrations were higher at the depth of 30 cm for the first 81 days (11 weeks after application), afterwards the highest concentration was observed at the 60 cm depth (Figure 9). Soil at the 60 cm depth (plot no.3 and 4) obtained the highest concentration of picloram 57 days after herbicide application (e.g. four weeks later compared to soil at the depth of 30 cm in plot no.3). Results of the deepest collector (90 cm) in both plots indicated there was an increasing trend in the concentration of picloram during the experimental period, and 327 days after the herbicide application, the content was 0.36 mg/L for plot no.3 and 0.34 mg/L for plot no.4, which was the highest value detected for this depth in plot no.4 (Figure 10).

9

Picloram content at 15, 30, 60 and 90 cm depths, plot no.1
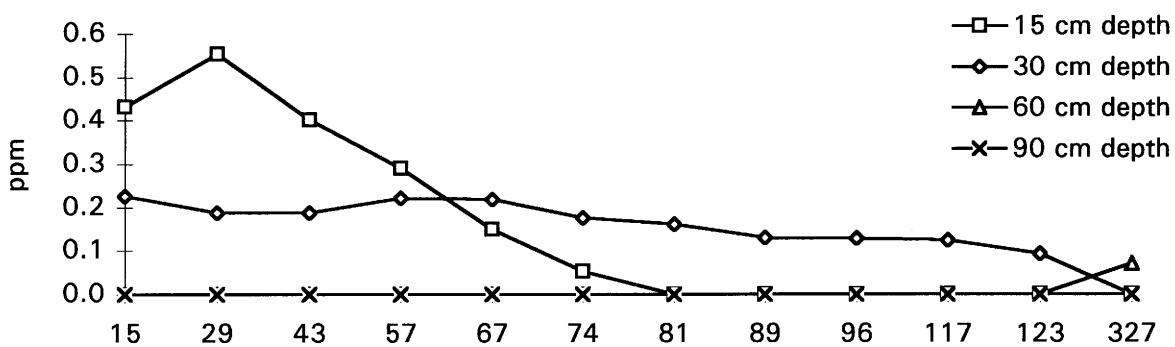
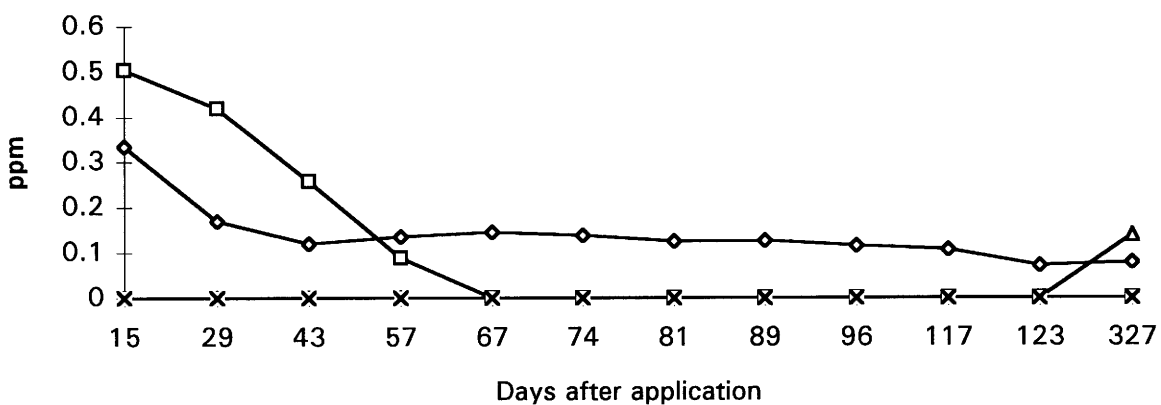**Picloram content at 15, 30, 60 and 90 cm depths, plot no.2**

Figure 5   Mean concentration of picloram in soil water collectors, plot no.1 and 2 (0.9 kg/ha picloram)

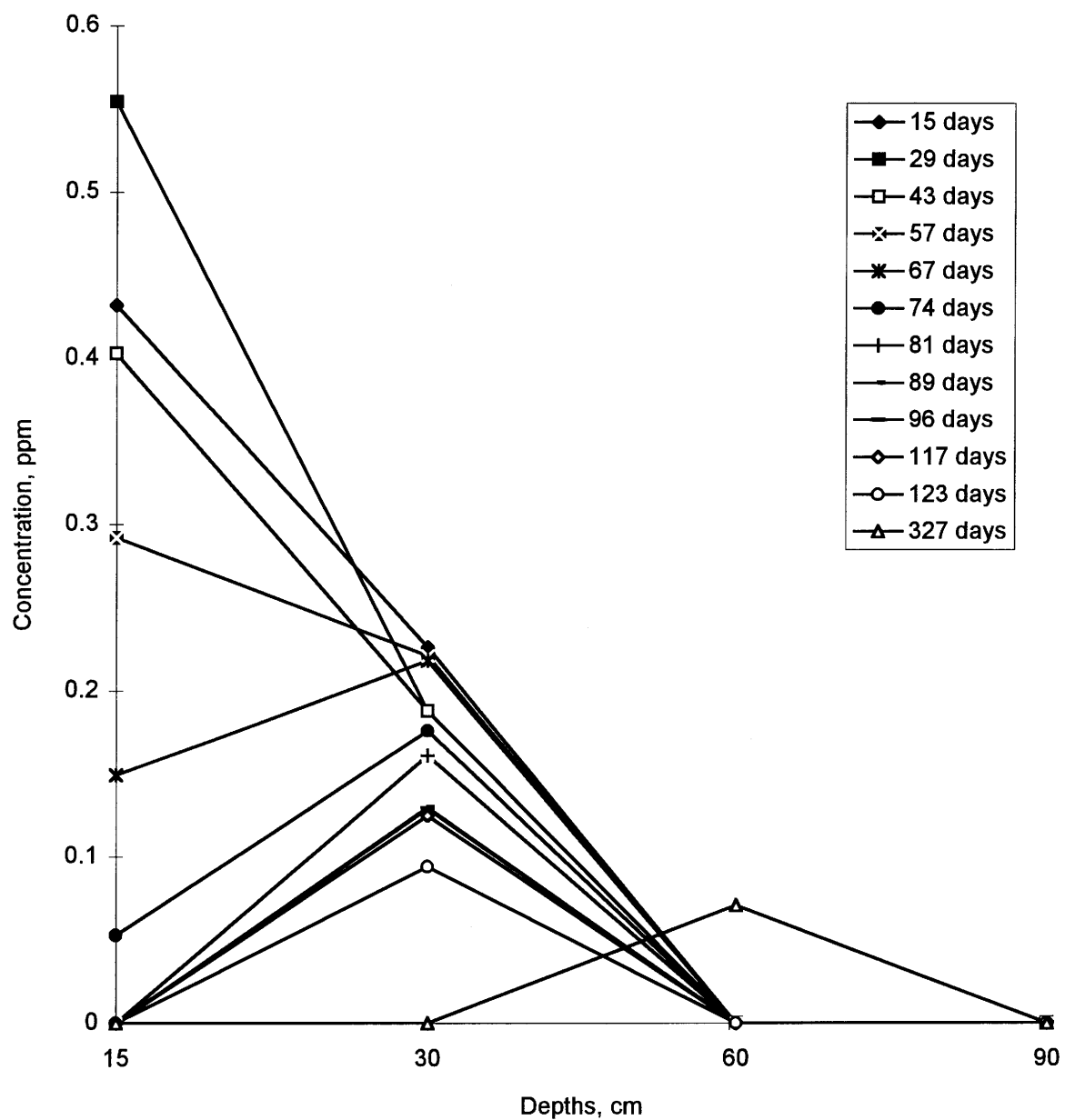Fig. 6 Mean picloram content at different days after herbicide application, plot no. 1

Legend:
- 15 days
- 29 days
- 43 days
- 57 days
- 67 days
- 74 days
- 81 days
- 89 days
- 96 days
- 117 days
- 123 days
- 327 days

Y-axis: Concentration, ppm
X-axis: Depths, cm

Fig. 7 Mean picloram content at different days after herbicide application, plot no.2

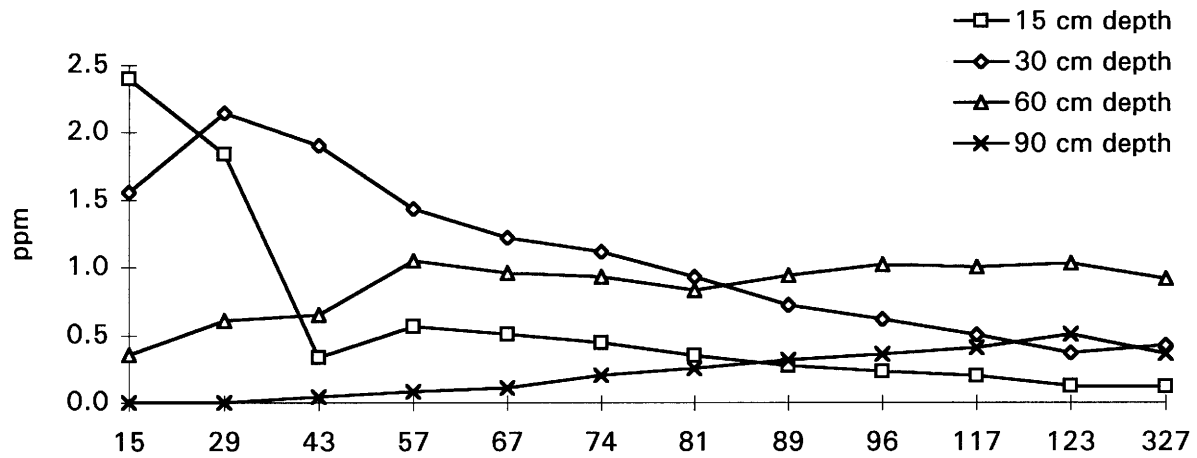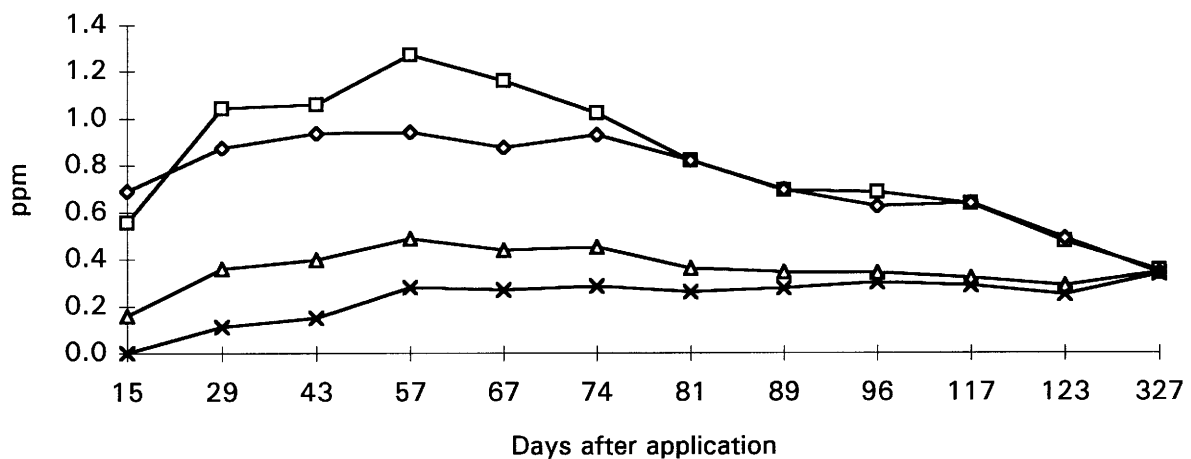**Figure 8   Mean concentration of picloram in soil water collectors, plot no.3 and 4 (2.9 kg/ha picloram)**

Fig. 9   Mean picloram content at different days after herbicide application, plot no.3
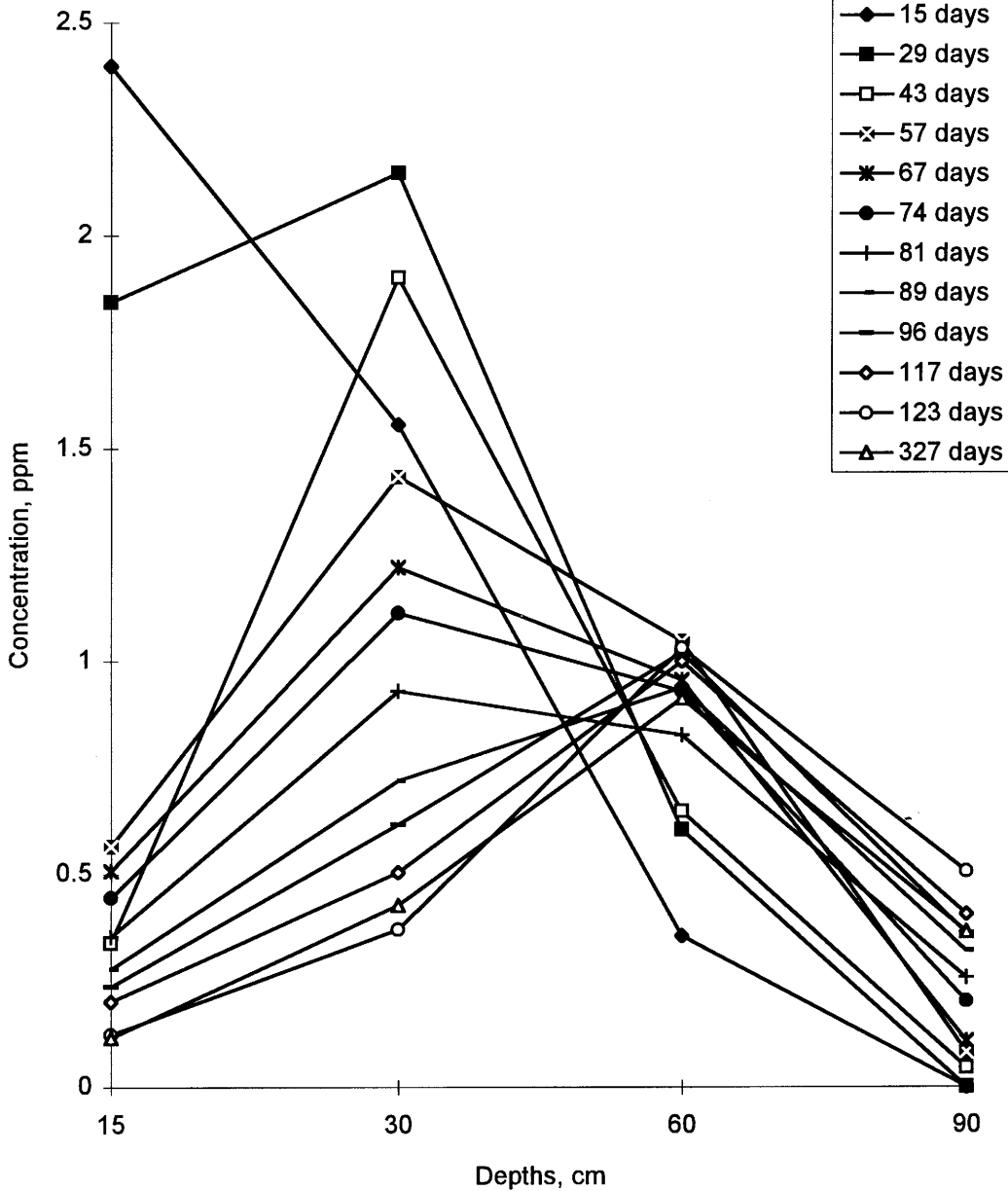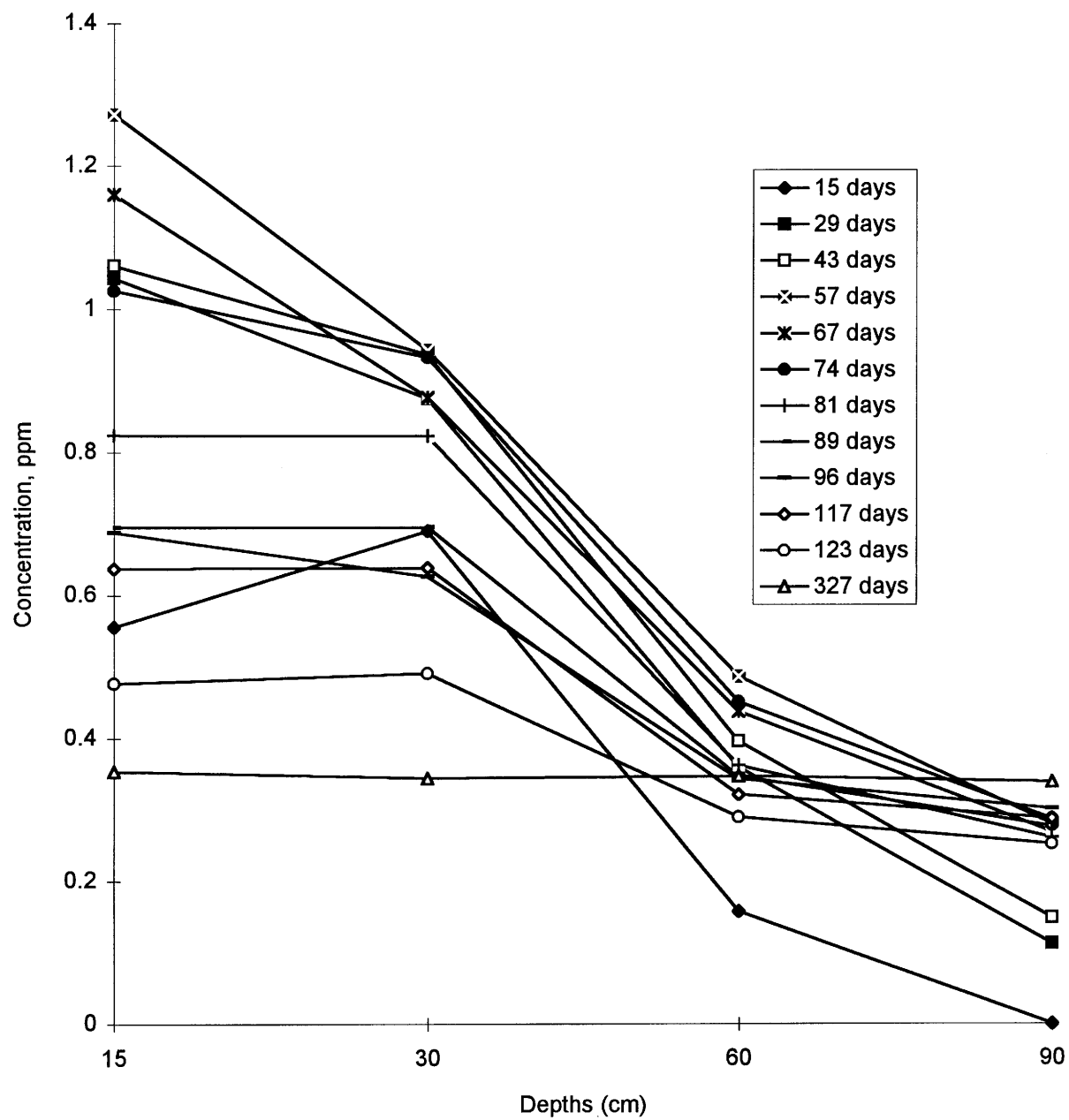
Fig. 10   Mean picloram content at different days after herbicide application, plot no.4

DISTRIBUTION OF DICAMBA: Concentrations of dicamba in the soil-water collectors in plot no.1 and 2 were very similar (Figure 11). The highest concentration at the 15 cm (0.31 and 0.46 mg/L) and 30 cm (0.13-0.20 mg/L) depths were observed two weeks after herbicide application (Figure 11). Dicamba content was below the detection limit by the 96 day for the 15 cm depth and in 57-89 days at the 30 cm depth. Maximum concentration at the 60 cm depth (0.01-0.02 mg/L) was reached in 29 days and decreased below the detection limit (0.0015 mg/L) 43 days after application (Figure 12 and 13). Dicamba in the 90 cm depth collectors was below the detection limits during the entire experiment, except for the collection on 327th day in plot no.1.

For the plots with higher dicamba application rates, the highest concentration (2.4-5.6 mg/l) at the 15 cm depth was observed on the 15th day; at the 30 cm depth (2.2-9.7) on the 29th day; at the 60 cm depth (1.1-1.7) on the 43rd day (Figure 14). In the 90 cm depth collectors, dicamba decreased on the 327th day after application to the value of 0.12 mg/l in plot no.3 and no.4 (Figure 15 and 16). Dicamba was below the detection limit in the 15 cm depth by the 57th day (plot no.3) and 89th day (plot no.4), at the 30 cm depth on the 89th day (plot no.3 and 4), and at the 60 cm depth on the 117th day (plot no.3) or 96 day (plot no.4) (Figure 14). Dicamba content at the 90 cm depth was higher than the 15, 30 and 60 cm depths 43 days after herbicide application, which is an indication of leaching and accumulation processes.

SUMMARY OF SOIL WATER COLLECTORS RESULTS: Although considerable spatial variability in contaminant movement was evident between neighboring samplers and between plots, mean herbicide concentrations as a function of time were found to represent realistic outputs that have been used in model simulation efforts. For plots no. 1 and 2, with low herbicide application rates, herbicide disappearance was relatively quick, especially for dicamba (Figure 11). Dicamba concentrations approached the concentration below the detection limit (0.0015 ppm) in 96 days at the depth of 15 cm and in 57-89 days at the depth of 30 cm. Maximum concentration at the depth of 60 cm (0.01-0.02 ppm) was reached in 29 days and decreased below the detection limit in 43 days after application. Dicamba was not detected at the 90 cm depth during the entire experiment.

Picloram remained in the profile longer, but did not penetrate as deeply as dicamba into the vadose zone (Figure 5). Picloram was not detected in any solution samples collected from 60 and 90 cm depth samplers during 1993. Picloram was detected in solutions collected in 1994, 327th day after application at the 60 cm depth. This is consistent with column study results in which picloram was strongly adsorbed and leached at a slower rate than dicamba.

For plots 3 and 4, with the higher herbicide application rates, dicamba content within the profile decreased more rapidly than picloram (compare Figures 8 and 14). Unlike plots 1 and 2, dicamba was present throughout the profile. Concentration peaks of picloram and dicamba diminished and spread with increasing depth. Picloram concentration peaks moved throughout the profile at a slower rate than dicamba peaks. The highest measured concentration of picloram and dicamba was reached 15 days after application at the depth of 15 cm; the peak reached a depth of 30 cm two weeks later and a depth of 60 cm six weeks later. Picloram content at the 90 cm depth was still increasing 327 days after herbicide application (Figure 8).
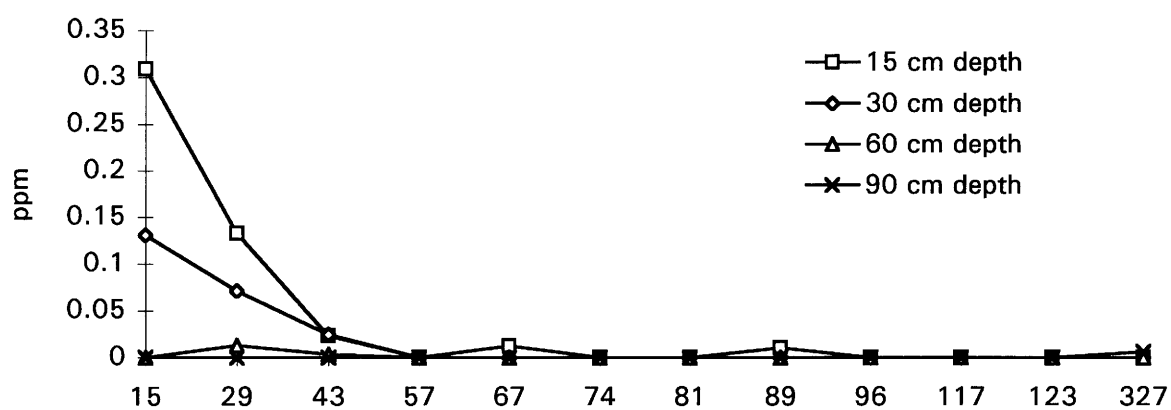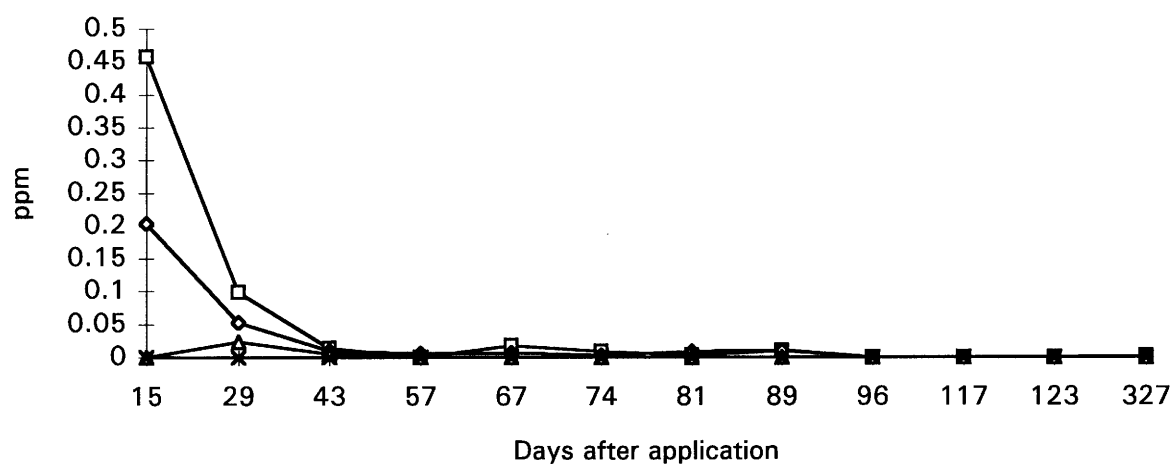
Figure 11 Mean concentration of dicamba in soil water collectors, plot no.1 and 2 (0.9 kg/ha dicamba)
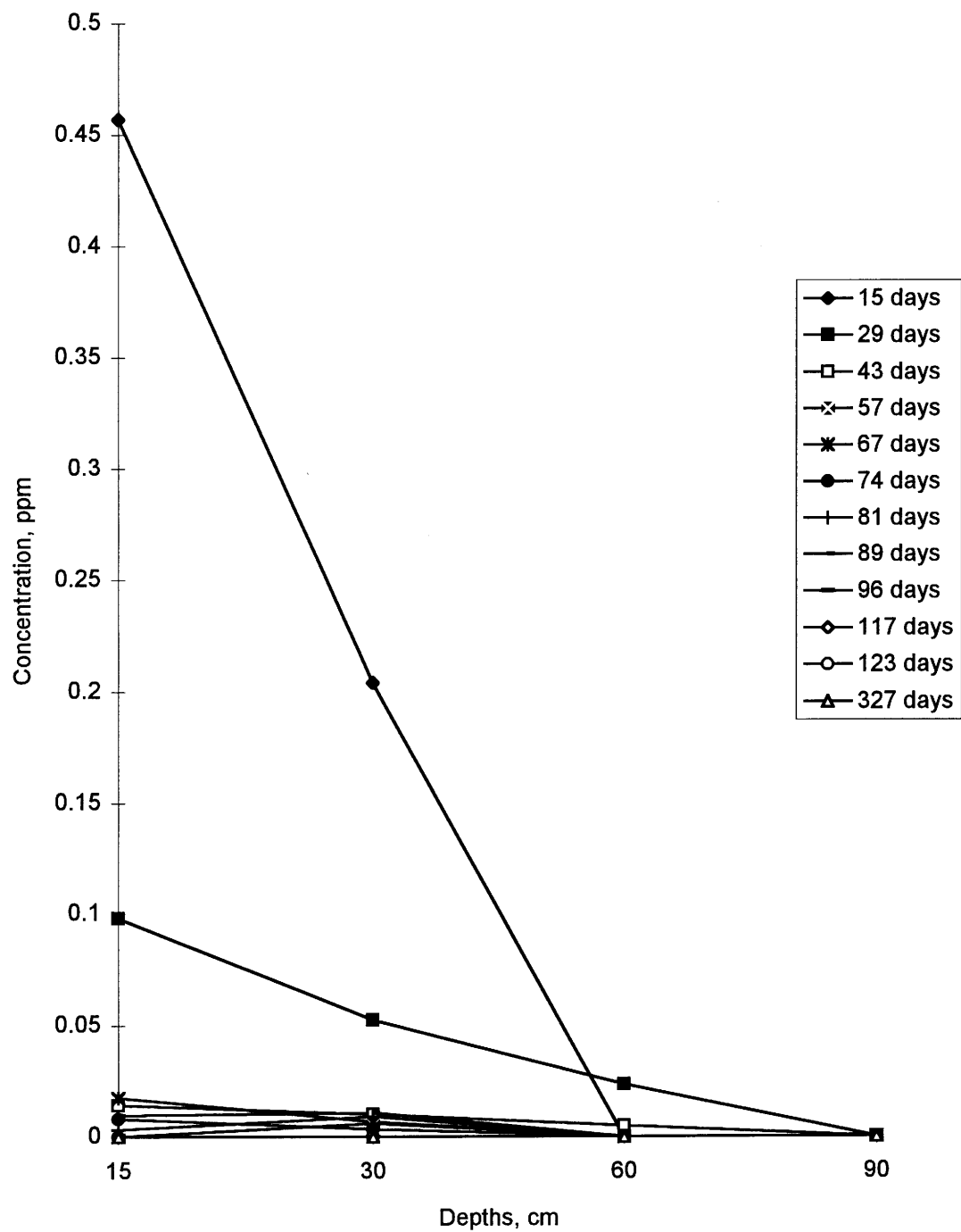
Fig. 12   Mean dicamba content at different days after herbicide application, plot no.1

Fig. 13 Mean dicamba content at different days after herbicide application, plot no.2
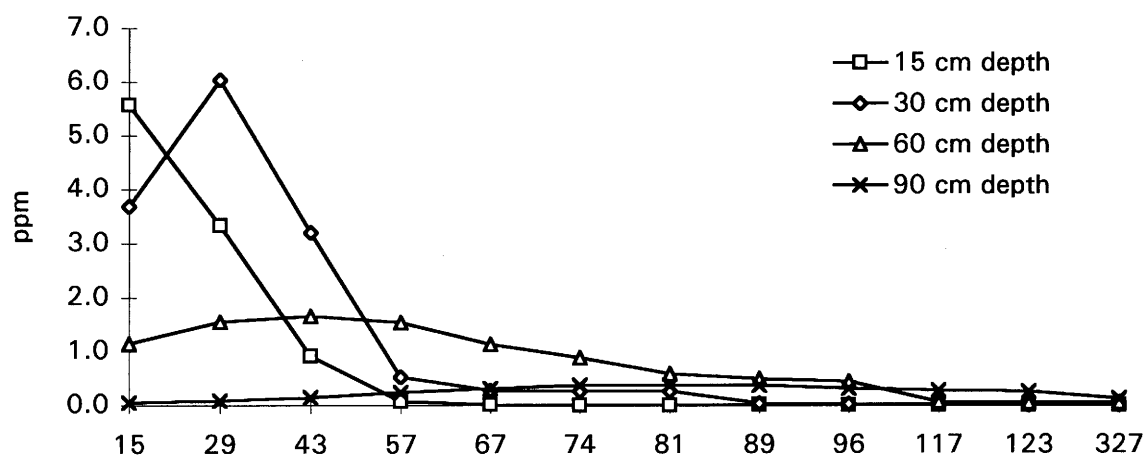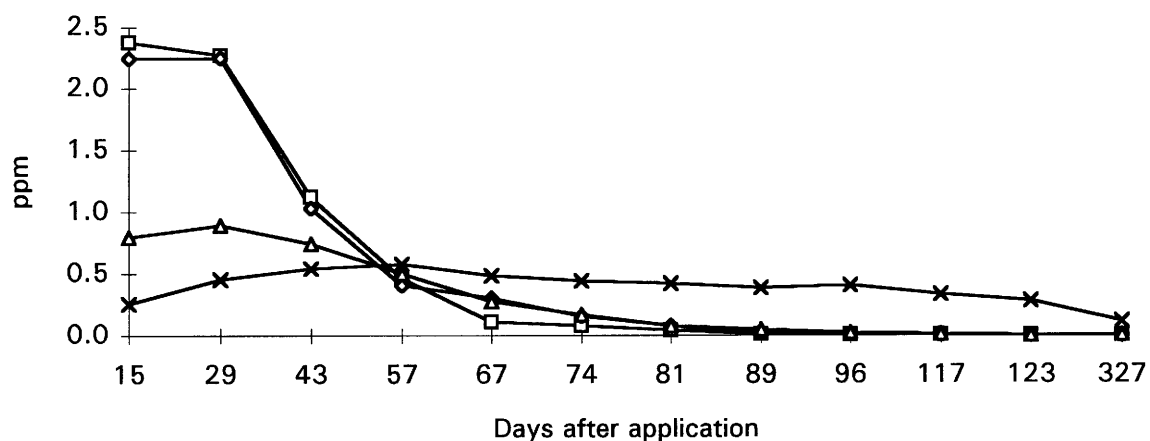
Figure 14   Mean concentration of dicamba in soil water collectors at different depths, plot no.3 and 4 (9.4 kg/ha dicamba)

Fig. 15 Mean dicamba content at different days after herbicide application, plot no.3

Legend:
- 15 days
- 29 days
- 43 days
- 57 days
- 67 days
- 74 days
- 81 days
- 89 days
- 96 days
- 117 days
- 123 days
- 327 days

Y-axis: Concentration, ppm

X-axis: Depths, cm

Fig. 16 Mean dicamba content at different days after herbicide application, plot no.4
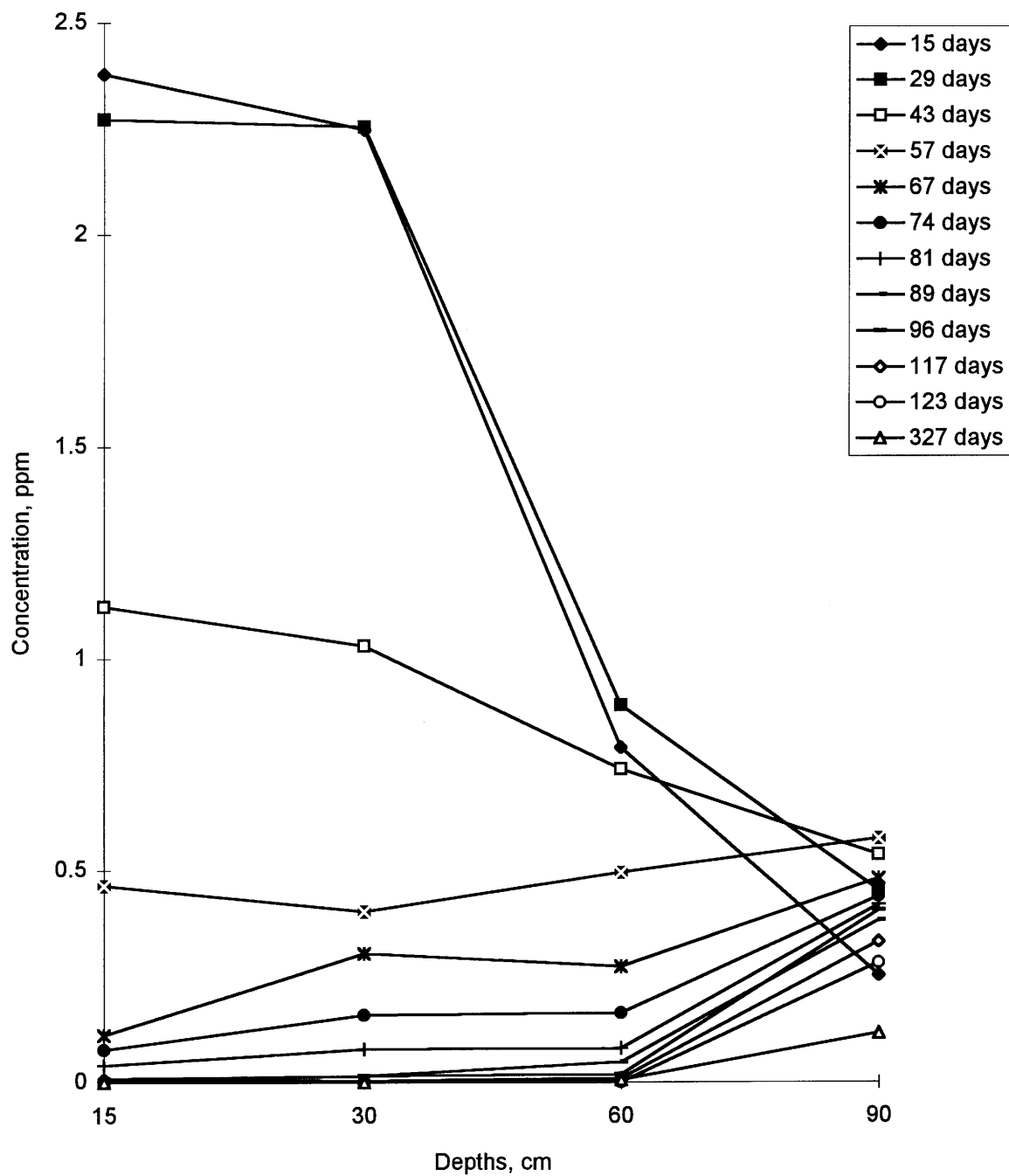
Hydrological Tests

Soil moisture did not vary much during the experiment and averaged approximately 22% for most of the growing season, drying to about 18% at the end of season. Soil moisture varied within the profile by about 6% (maximum). Results of 16 measurements on the saturated hydraulic conductivity for the 0-30 cm depth ranged from 1 to 28 m/day with an average flow rate of 2 m/day.

Modeling

Contaminant movement in plots 3 and 4 was simulated using two modeling techniques. LEACHP, a numerical finite-difference model, was employed for plot 3. A transfer function model was utilized for plot 4. The intent of the modeling was to estimate and verify soil properties controlling contaminant movement and fate.

LEACHP results

Modeling parameters for LEACHP were determined from the previously mentioned column study, ring infiltration measurements of saturated hydraulic conductivity, and neutron probe measurements of volumetric water content. Modeled profiles were assumed homogeneous: average values of modeling parameters were used as inputs. LEACHP-generated concentration profiles closely approximated the plot's mean concentration profiles at several points in time. LEACHP-generated profiles are in relatively close agreement with measured profiles in both general shape and in the magnitude of concentration peaks (Figure 17 and 18).

Transfer functions results

An alternate way to represent process models of solute transport is by the use of transfer functions based on a probability density function of the travel time of solute molecules. The probability density function characterizes the distribution of travel time that a solute molecule experiences in migrating from point A (pulse input) to point B (soil-water collectors). More recently, transfer functions have been applied to model complex systems in a simple way by characterizing the output flux as a function of the input flux. The transformation of an arbitrary input signal into an output signal for a linear system is achieved be means of the impulse response function, which defines the response of the system to a narrow pulse input. The transfer function has been used to model solute transport under field conditions by fitting the mode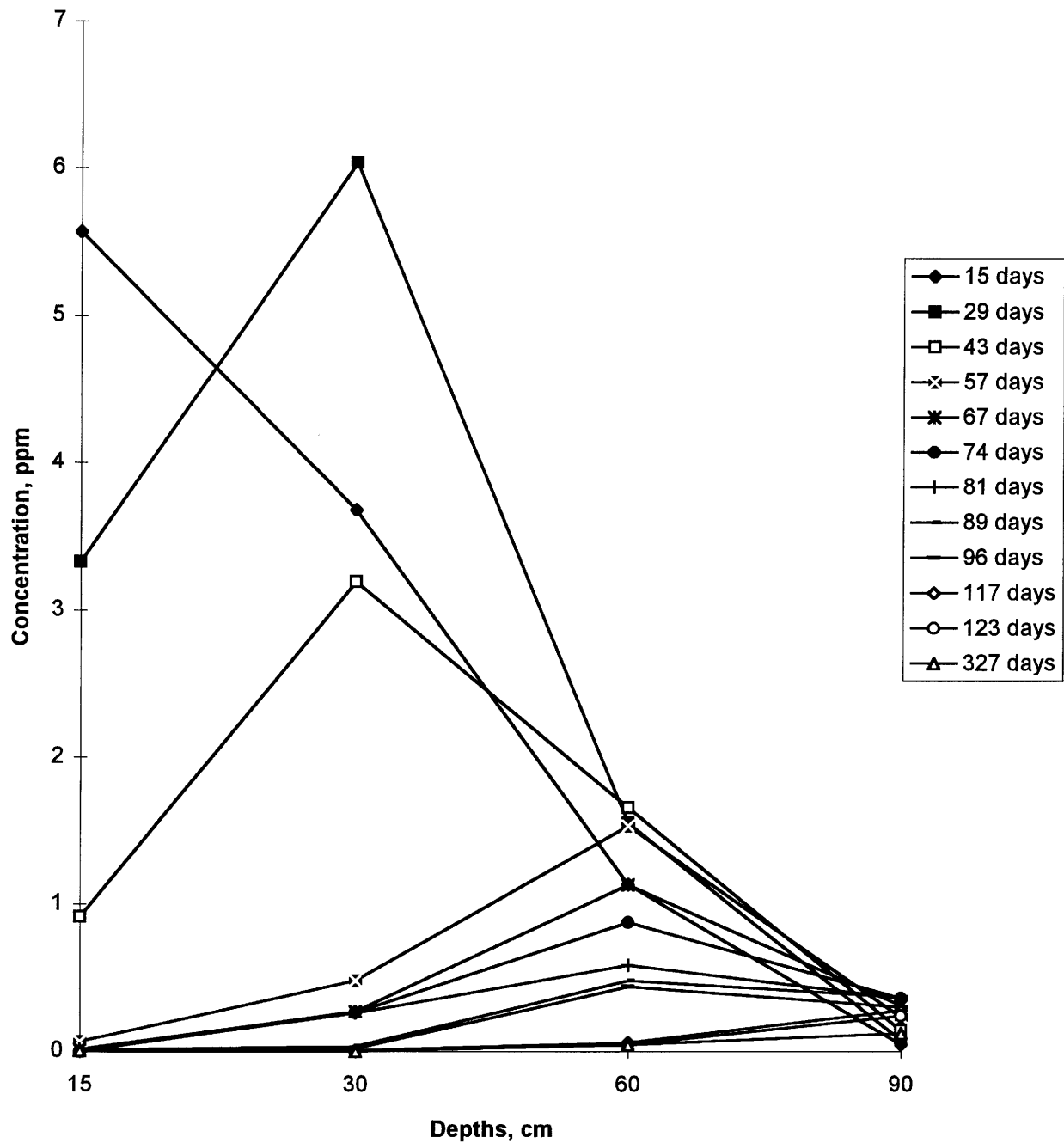l with the field experimental data. As shown in Figure 19, the transfer function may be a promising tool to describe contaminant movement in a field setting.

Preliminary modeling results, while cautiously positive, illustrate a high degree of spatial variability in contaminant movement. Ring infiltration tests performed at the site indicated saturated hydraulic conductivity was highly variable, even when test locations differ by only a few feet. Additional modeling is proposed that will more adequately describe contaminant movement at this site.

11
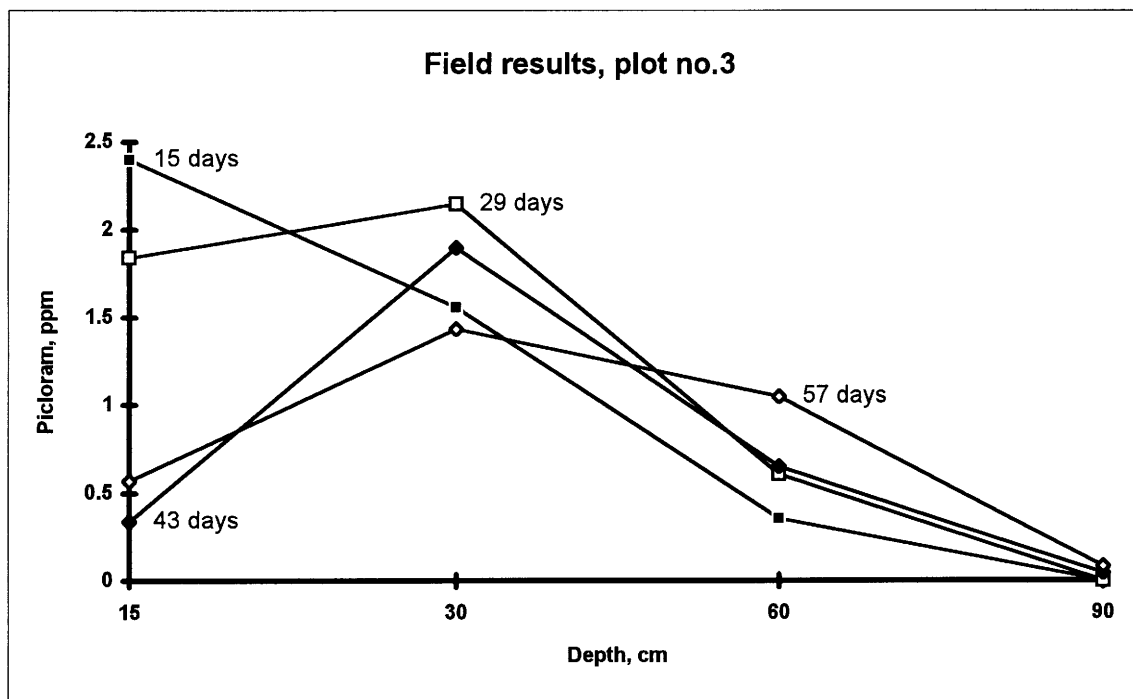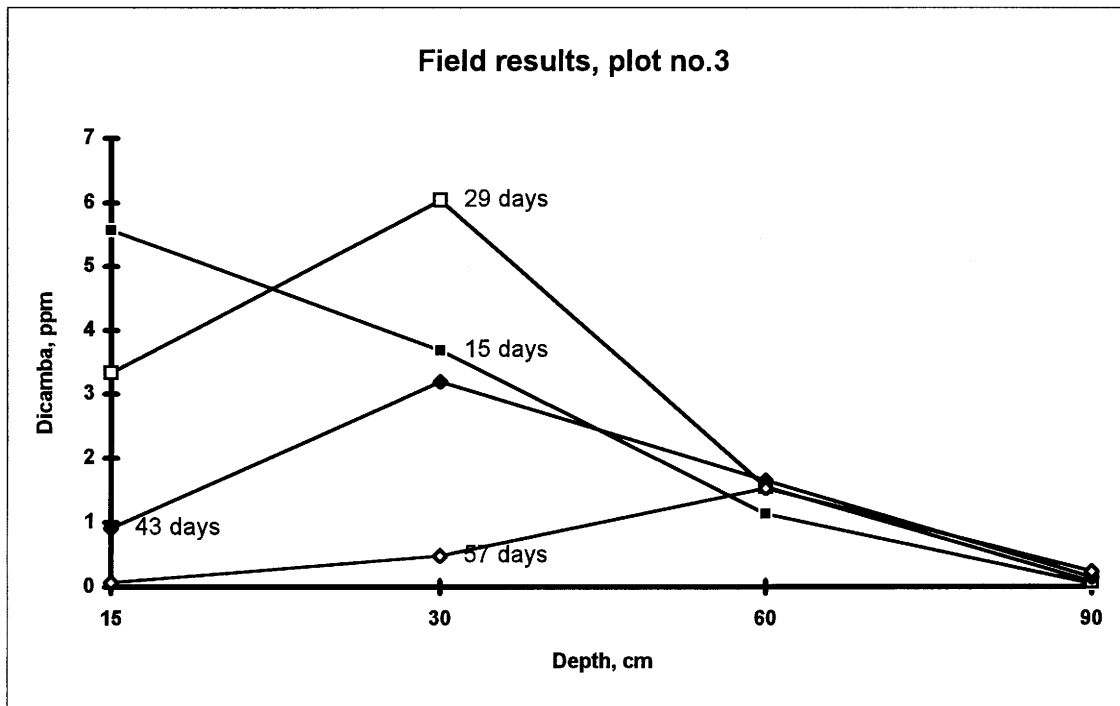
**Figure 17 Field results of picloram and dicamba content at different depths
at 15, 29, 43 and 57 days after herbicide application**

LEACHP model results, plot no.3

Dicamba, ppm vs Depth, cm

15 days

29 days

43 days

57 days

LEACHP model results, plot no.3

Picloram, ppm vs Depth, cm

15 days

29 days

43 days

57 days

Figure 18 Simulation of dicamba and picloram content, plot no.3 (LEACHP model)

Figure 19 Simulation of dicamba content, plot no.4 (transfer function model)
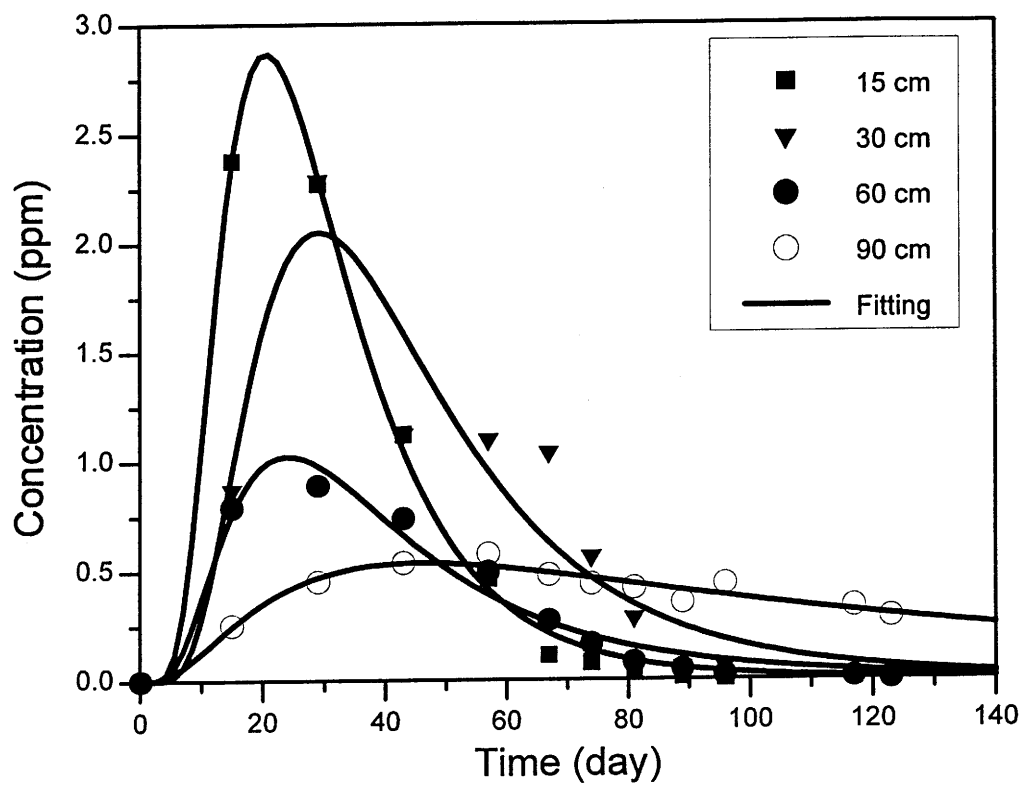
Summary and Conclusion

The pesticide picloram has been proven to be persistent under many soil conditions while dicamba has been recognized as being a particularly mobile pesticide. Picloram transport and fate has been studied in laboratory columns and under field conditions with detection occurring over a year after application. In one of our studies, picloram content was detected 327 days after pesticide application and at that time the highest concentration reached the 60 cm depth (application rate 0.9 kg/ha), probably due to the slow rate of leaching which is influenced by greater adsorption of picloram especially in the upper horizons with higher organic matter contents. Higher application rates (such as with the 2.9 kg/ha application rate used in our study), picloram content can still be present at depths of 60-90 cm one year after application, while simultaneously decreasing in upper horizons due to leaching.

A simulation of dicamba movement showed the pesticide moving well below the root zone of the sandy clay loam soil used in this study. Experimental monitoring in laboratory columns verified dicamba's tendency to be highly mobile and easily leached which results in high effluent concentrations. Travel times through our columns were about 3 days shorter for dicamba than for picloram. Dicamba first appeared in the effluent on the 8th day after application, which was five days earlier than for picloram. This difference is even greater in field situations. Dicamba content within the profiles decreased more rapidly, especially in upper horizons (0-30 cm) than picloram. Dicamba was below the detection limit at the 30 cm depth on the 89th day after application and between 89th and 117th day for the 60 cm depth; however, picloram was still present at all four depths within plots 3 and 4 after 327 days. Field results indicated dicamba was more mobile than picloram, but was not as easily leached as column study results would have predicted. Dicamba was still present 327 days after pesticide application at the depth of 90 cm in plot no. 3 and 4. The highest concentration of picloram and dicamba was reached at the depth of 15 cm in a period between 15 and 29 days after pesticide application. Below the 30 cm depth, herbicide concentrations become more distributed.

The lower application rate plots of 0.9 kg/ha picloram and dicamba were found to have 0.07-0.14 mg/l picloram at the 60 cm depth and 0.01 mg/l dicamba at the 90 cm depth 327 days after application. The higher applic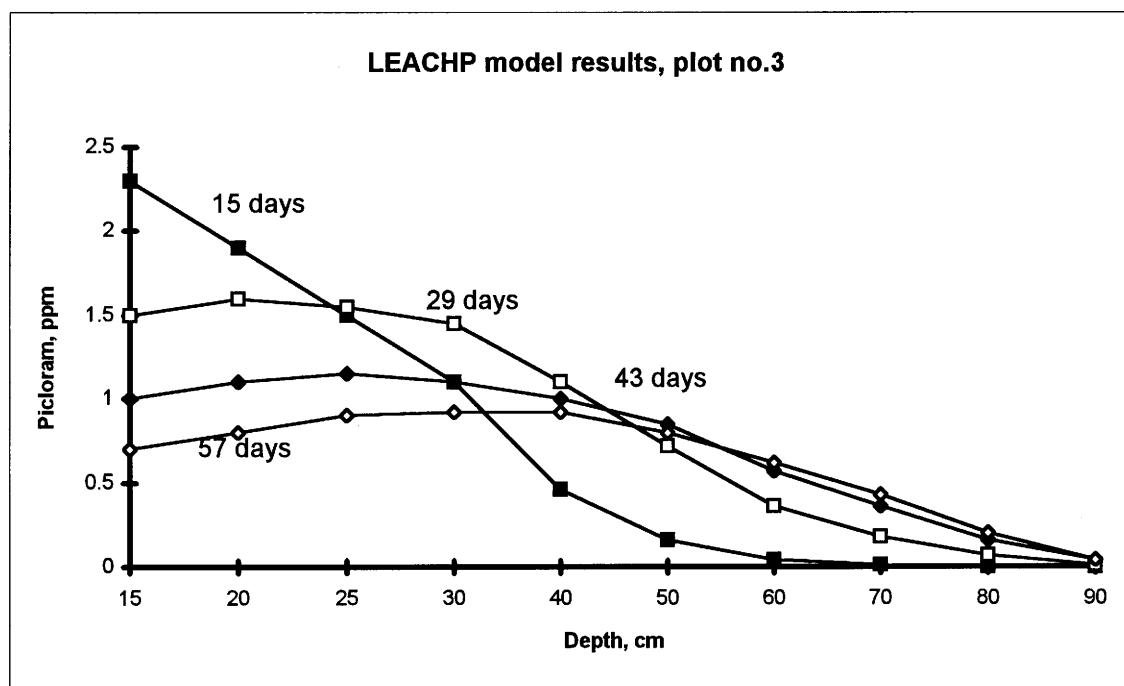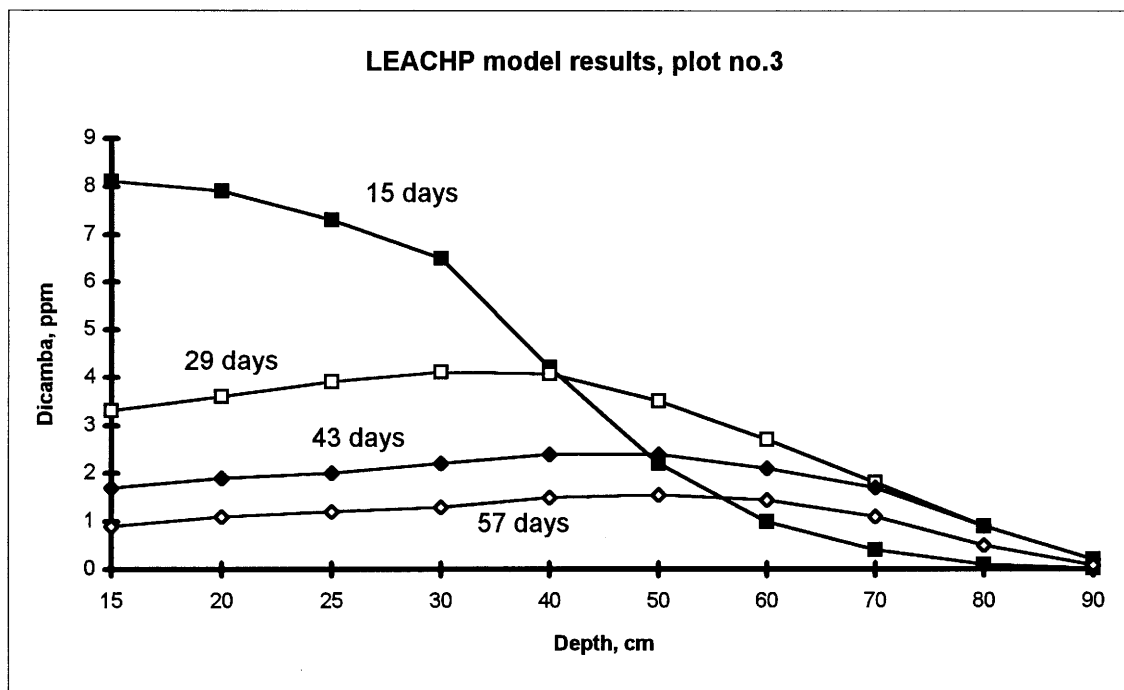ation rate of picloram (2.9 kg/ha) resulted in an increase in the content of picloram in horizons below the 30 cm depth after 327 days. Dicamba content decreased with time, but still was present at the 90 cm depth 327 days after application.

Modeling pesticide movement in a vadoze zone proved to be a useful research tool. LEACHP provided modeling parameters of solute movement in repacked soil columns. However, comparing model-predicted and field contaminant movement was more difficult due to spatial variability. Hydraulic conductivity was found to be highly variable, and would have the greatest effect on contaminant movement.

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Appendix 1

SOLID PHASE EXTRACTION OF DICAMBA AND PICLORAM FROM WATER AND SOIL SAMPLES FOR HPLC ANALYSIS

SOLID PHASE EXTRACTION OF DICAMBA AND PICLORAM FROM WATER AND SOIL SAMPLES FOR HPLC ANALYSIS.

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and

George F. Vance[*]

[*]Corresponding Author

ABSTRACT

Methods are presented for the analysis of two commonly used herbicides, dicamba and picloram, in water and soil samples. The methods utilize solid-phase extraction (SPE) and high-performance-liquid-chromatography (HPLC). For separation and concentration of the herbicides, two types of SPE cartridges were used - aminopropyl (NH_2) weak anion exchange adsorbent for dicamba and octadecyl (C-18) strong polar adsorbent for picloram. Detection limits for HPLC analysis of dicamba were 1 ppb for water samples and 10 ppb for soil samples. Recovery experiments for dicamba indicated 90 to 99% recovery for the concentration range of 10 to 60 ppb in water samples and 83 ± 6% recovery of 10 ppb dicamba added to soil samples. Detection limits for picloram were 8 ppb for water samples and 10 ppb for soil samples. Recovery of picloram from water samples was between 85 and 96% for the 10 to 60 ppb concentration range and 88 ± 6% recovery of 10 ppb picloram added to soil samples. The recovery of standard solutions by different brand name SPE cartridges was also tested. Differences in the efficiencies of various SPE cartridges were determined, not only among manufacturers, but also between lots. We suggest that one brand name of SPE cartridge, all of the same lot number, be used throughout a particular study, and caution against changing manufactures and lots without adequately evaluating the SPE cartridges for their ability to separate and concentrate the pesticide of interest.

INTRODUCTION

Herbicide residue analysis generally requires several steps, such as extraction of the pesticide from the sample of interest, removal of interfering co-extractives, and identification and quantification of the pesticide content (Das, 1981). There are many methods of analyzing herbicides in environment samples, the most common being gas chromatography and high-performance-liquid-chromatography (HPLC). Both liquid-liquid and solid-phase extraction of solution sample can be used to extract, concentrate, and purify herbicides (Majors, 1992). The advantages of solid-phase extraction (SPE) over liquid-liquid extraction include decreased use and

exposure to hazardous materials, less time consuming, and extraction that are not hindered by the formation of emulsions (Johnson et al., 1991).

With the SPE chromatography method, pesticides in aqueous samples can be isolated, concentrated, and purified. The following steps are generally required: sample preparation (mainly by pH adjustment); cartridge preparation (activation with strong solvent, e.g. methanol or acetonitrile followed by a rinse step which removes the activation solvent); sample application (controlled by flow rate); analyte elution (by strong solvent, e.g. 25% acetic acid or methanol); analyte concentration (mainly through evaporation). Solid-phase extraction using octadecyl-(C18)-bonded porous silica columns has been used for herbicide extraction and cleanup (Junk and Richard, 1988; Huang and Pignattelo, 1990). Herbicide extraction by SPE has also been reported for picloram in water and soil (Wells, 1986; Wells and Michael, 1987; Michael et al., 1989) and for dicamba in water (Arjmand et al., 1988).

The objectives of this study were to evaluate and improve upon methods used for the extraction of dicamba and picloram in water samples by using SPE followed by HPLC analysis. In addition, methods are presented for the extraction and analysis of dicamba and picloram from soils.

MATERIALS AND METHODS

Reagents and equipment

Organic solvents used in the SPE and HPLC studies were reagent grade quality suitable for trace pesticide analysis, which were obtained from Chem. Service Inc. (West Chester, PA). Stock solutions were prepared by dissolving 0.1031 g of dicamba (2-Methoxy-3,6-dichlorobenzoic acid) in methanol (1000 ppm), or by dissolving 0.0105 g of picloram (4-Amino-3,5,6-trichloropicolinic acid) in 25% glacial acetic acid (100 ppm). Appropriate amounts of each of these stock solutions were added to water to obtain desired final concentrations. Working standards were prepared weekly for dicamba and every two weeks for picloram. The SPE cartridges used in the final analysis of dicamba and picloram in this study were aminopropyl (500

3

mg) cartridges obtained from J.T.Baker Inc and C-18 (1000 mg) cartridges purchased from Burdick and Jackson Corp. Solvent reservoirs, adapters, and a vacuum manifold with 12 ports were purchased from Burdick and Jackson Corp. Pesticide quantification was performed on a high-performance liquid chromatography (HPLC) system (Beckman model 344 CRT-Based Gradient, with an 5 μ octadecyl column (25 x 0.46 cm) and a reversed phase guard column).

Sample preparation

Water samples to be analyzed for dicamba did not require any pretreatment. However, water samples containing picloram required the addition of 2.5 g NaCl to 50 ml samples followed by acidification to pH 2. Extraction of dicamba from soil was based on the method of K. Luong (personal communication) whereas extraction of picloram was by the method of Cheng (1969) (Table I). Fortified water samples used in the recovery studies were prepared by dissolving dicamba and picloram standards into separate water solutions. All soil samples used in this study were field-moist and passed through a 2.0 mm sieve.

Before extracting dicamba from soils, samples were first subjected to ultrasonic vibration (25 g of moist soil with 80 ml of methanol/water solution (50:50, v/v) for 40 min.). Soil extracts were centrifuged, and a 20 ml aliquot was decanted and diluted to 100 ml with deionized-distilled water. Extraction of picloram from soils was accomplished by shaking 100 g field moist soil with 100 ml of 2N KCl for 60 min. Soil extracts were centrifuged and the supernatants was decanted. The supernatant solutions were analyzed according to the methods applied to water samples using SPE cartridges. The extraction process for removing dicamba and picloram from soil is outlined in more detail in Table I.

SPE and HPLC Analysis

SPE cartridges were connected to 75 ml capacity polypropylene sample reservoirs and placed on a vacuum manifold system using adapters. Cartridge sorbents were conditioned to activate the packing materials before the extraction of samples. Aminopropyl SPE cartridges were conditioned using 1 N acetic acid and distilled water; octadecyl SPE cartridges were conditioned using methanol and 4% acetic acid. Cartridges, after conditioning and before

4

application of samples, were never allow to dry; 1 ml of solution always remained above the cartridge resin. Water samples (50 ml) were transfer to the SPE cartridge reservoirs and eluted through the cartridges at a flow rate of approximately 2 to 5 ml min^{-1}. After eluting samples containing picloram through the octadecyl SPE cartridges, the cartridges were washed with methanol; no post-treatment was necessary for octadecyl SPE cartridges. After eluting the water samples, and completing the post-treatment in aminopropyl cartridges, both types of cartridges were dried for 10-15 min. using vacuum. The aminopropyl cartridges were rinsed with 4 portion of 500 ul 0.1 N K_2HPO_4 and the octadecyl cartridges using 2 portions of 2 ml 25% acetic acid in water (Table II). We found that pesticide recovery was enhanced by about 10% when pesticides were eluted from the cartridges using several small aliquots as compared to one larger aliquot. Each aliquot remained in contact with the packing material for about 1 min. Dicamba and picloram were respectively collected in either 2 ml or 5 ml graduated glass vials, vortexed, and the volumes brought to 2 or 4 ml with the different mobile phases used for their HPLC analysis.

The mobile phase for dicamba analysis was 50/50 methanol/water with 0.005 M tetrabutylammonium phosphate at a flow rate of 1 ml/min. For picloram analysis, the mobile phase was 95/5 4% acetic acid in water/acetonitrile at a flow rate of 1.5 ml/min. (Table III). The mobile phase was never allowed to remain idle in the system; the columns were completely purged with acetonitrile or methanol every 24 hrs. The sample volume injected for dicamba analysis was 0.08 ml and for picloram analysis was 0.4 ml.

RESULTS AND DISCUSSION

Recently, pesticide extraction and concentration with SPE have been used to extract dicamba and picloram in water and soil samples (Wells, 1986; Wells and Michael, 1987; Arjmand et al., 1988; Michael et al., 1989). The method proposed here for the analysis of dicamba in water was modified after Arjmand et al., 1988. We found that the strong non-polar octadecyl C-18 reversed phase cartridges (500 mg) were not efficient for dicamba analysis. Previous results indicated the maximum percent recovery of dicamba from a 50 ppb water sample was only about

5

60 to 80%. In addition, Arjmand et al. (1988) recommended samples be acidified to approximately pH 1 before eluting through octadecyl SPE cartridges. Our studies showed that, at this low pH, octadecyl material was stripped off the silica stationary phase along with dicamba, as the eluted solutions contained colloidal substances that interfered in the analysis of dicamba. Using aminopropyl SPE cartridges (500 mg) resulted in improved recoveries of dicamba over the octadecyl SPE cartridges.

Our method for the analysis of picloram in water samples was modified after Wells et al. (1984). Water samples were made up to 1 N NaCl and acidified to pH 2 before passing through octadecyl SPE cartridges. Adding NaCl increased the percent recovery of picloram in water samples by up to 30%.

Water samples containing from 10 to 60 ug l^{-1} of dicamba and picloram in 50 ml of water were passed through individual SPE cartridges; average recoveries are summarized in Table IV. The percent recovery using a 25 ml sample was the same as for 50 ml; however, the percent recovery was dependent upon sample concentration. The recovery of dicamba from water samples varied from 90.3 ± 5.0% to 99.2 ± 13.2% for samples containing 50 and 20 ppb dicamba, respectively. Picloram recoveries from water samples ranged from 84.9 ± 13.0% to 96.4 ± 2.4% for 10 and 60 ppb picloram, respectively. The detection limits for pesticides in water samples subjected to direct HPLC analysis were 25 ppb for dicamba and 100 ppb for picloram. SPE cartridges used in our method decreased detection limits by a factor of 25 times for dicamba and 12.5 times for picloram. Therefore, the detection limits of dicamba and picloram in water using SPE cartridges were lowered to 1 and 8 ppb, respectively.

Comparison of water sample results of the present study with those obtained by others indicate that for picloram, we achieved a slightly higher detection limit with a comparable mean recovery, and for dicamba, a significantly lower detection limit with a comparable mean recovery (Table V).

Octadecyl SPE cartridges from Supelco (Envi and Supelclean) and Burdick and Jackson were tested to determine which gave the best recovery of picloram. The results indicated that the

recovery of 20 ppb picloram in water samples was only about 75 ± 10% (triplicate analyses) for the two Supelco octadecyl SPE cartridges. Aminopropyl cartridges from J.T. Baker and Burdick and Jackson were tested using a 500 ppb dicamba water sample. Approximately 10 to 20% greater recoveries were obtained when using the J.T. Baker cartridges. We also found that the difference in percent recoveries of either dicamba and picloram varied from between 10 and 20% among different lots of SPE cartridges from the same vendor.

Soil samples used for dicamba and picloram recovery studies contained less than 1.4% organic carbon, 23% clay content, and a pH of 8.0. In preliminary studies, soil samples for picloram analysis were extracted by the method of Cheng (1969) and Wells et al. (1984). We found that with the Wells et al. (1984) method, background noises interfered with the detection of picloram using the HPLC conditions listed in Table III. The method proposed by Cheng (1964) was originally developed for use on samples containing from 1 to 25 ppm of picloram. We modified this method so that soils containing picloram at concentrations below 1 ppm could be analyzed.

Results of the recovery studies involving soils amended with either dicamba or picloram indicated the detection limit and mean recovery were good or better than previous studies using SPE techniques (Table V). The detection limit for both dicamba and picloram extracted from soils was approximately 10 ppb; for picloram, comparable recoveries were obtained for soil samples fortified with 10 and 500 ppb picloram solutions. Examples of dicamba and picloram chromatographs of standards, solutions passed through SPE cartridges, and that which was recovered from fortified soil samples are presented in Figure I.

In summary, the SPE technique with HPLC analysis reported here is capable of measuring picloram and dicamba in water and soil samples at low ppb levels. The method is simple and much less time consuming than liquid-liquid extraction and derivatization. Approximately 24 water samples can be analyzed daily, starting from SPE cartridge preparation (using a 12-port vacuum manifold) to HPLC analysis. Extraction of dicamba or picloram from 24 soil samples takes approximately 8 hrs., after which another day is required for HPLC analysis. Once the

7

procedure is learned, a laboratory assistant should be able to process and analyze approximately 120 water samples or 50 soil samples for dicamba or picloram weekly. The estimated cost for cartridges and HPLC grade chemicals required to analyze 24 water samples is about $75.

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Figure Caption

Figure 1.   Examples of chromatographs for dicamba and picloram (a) 500 ppb standards, (b)

solutions that were passed through SPE cartridges, and (c) solutions that were recovered

from soil samples.

Table I.   **Extraction of dicamba and picloram from soil samples.**

Extraction	Dicamba (adapted from K. Luong, personal communication)	Picloram (adapted from Cheng, 1969)
Amount of soil (g)	25	100
Extraction solution	80 ml of methanol/water (50:50, v/v)	100 ml of 2N KCl
Process of extraction	- ultrasonic vibration for 40 min; - centrifuged at 2,000 RPM for 20 min and at 10,000 RPM for 30 min; - decanted 20 ml aliquot and diluted to 100 ml with distilled water.	- pH adjusted to 7 with 5 N KOH; - shake for 60 min; - centrifuged at 1,500 RPM for 10 min and 10,000 RPM for 15 min; - decanted 50 ml

Table II. Solid-phase extraction conditions for water samples.

Extraction conditions	Dicamba	Picloram
Cartridge Column Preparation	500 mg aminopropyl column - elute 18 ml 1N acetic acid at a rate of 5 ml/min; - passed 6 ml distilled water at rate of 5 ml/min. Keep 1 ml of solution above the packing material at all times.	1000 mg octadecyl C-18 column - elute with 10 ml methanol; - elute 10 ml of 4% acetic acid at a rate of 12 ml/min. Keep 1 ml of solution above the packing material at all times.
sample application	50 ml suction-filtered at 2-3 ml/min.	50 ml suction-filtered at 5 ml/min.
column wash	Rinsed with 3 ml methanol; Dry for 15 min. using the vacuum source.	Dry for 10 min. using the vacuum source.
analyte elution	Eluted with 2 ml of 0.1N K_2HPO_4.	Eluted with 4 ml of 25% acetic acid in water.

Table III.   High-Performance-Liquid-Chromatography conditions.

Conditions of analysis	Dicamba	Picloram
mobile phase	Methanol/water (50/50, v/v) and 0.005 M tetrabutyl-ammonium phosphate	4% acetic acid in water/acetonitrile (95/5, v/v)
flow rate ml/min.	1	1.5
wavelength nm	210	254
range of absorbance, AUI	0.1	0.01
retention time	7	17
width	5	20
attenuation	1	2
loop, ul	20	100

Table IV. Percentage recovery of dicamba and picloram from water and soil samples.

Pesticide added	Average recovery			
(ppb)	n*	Dicamba	n	Picloram
Water samples				
10	10	91.7 ± 22.0	8	84.9 ± 13.0
20	11	99.2 ± 13.2	20	90.7 ± 6.0
40	6	92.9 ± 10.0	6	92.3 ± 7.0
50	10	90.3 ± 5.0	10	91.4 ± 10.4
60	4	93.0 ± 3.5	4	96.4 ± 2.4
Soil samples				
10	4	83.2 ± 5.6	4	88.3 ± 6.0
100	-	-	4	79.4 ± 10.5
200	-	-	4	86.2 ± 11.3
500	4	85.8 ± 10.5	4	88.9 ± 9.0

* number of samples analyzed.

Table V. Detection limits and efficiencies using SPE and HPLC analysis for quantifying dicamba and picloram in water and soil samples.

Pesticide	Detection limit (ppb)	Recovery (%)	References
Water samples			
Dicamba	1	91	present study
	10	93	Arjmand et al. 1988
Picloram	8	91	present study
	2	92	Wells et al. 1984
Soil Samples			
Dicamba	10	83	present study
Picloram	10	89	present study
	10	61	Wells et al. 1984

Dicamba

(a)

Picloram

(a)

Recorder response

(b)

(b)

(c)

(c)

0   2   4   8   10.9

0   4   8   1 2   15.8

Retention   time   (min.)
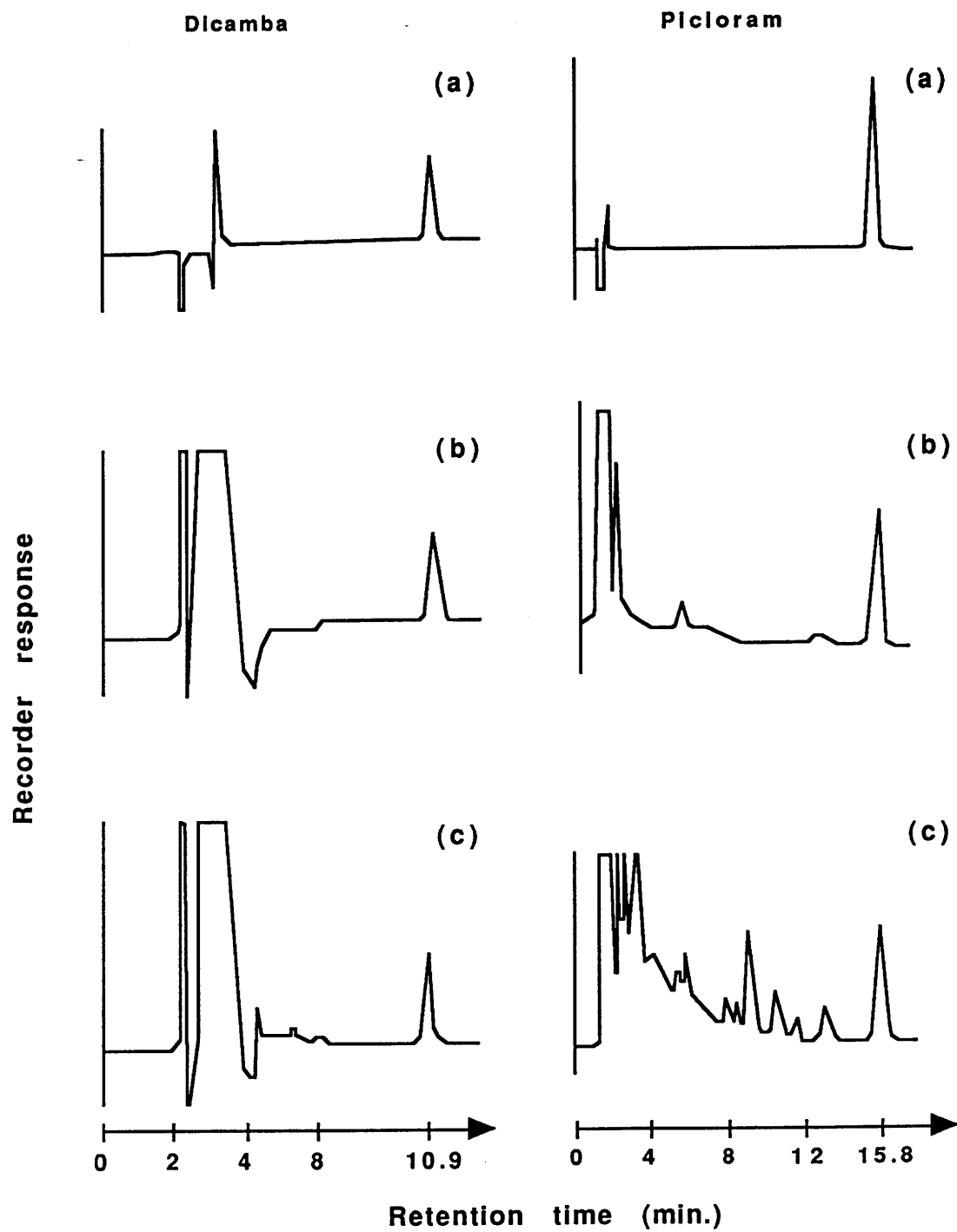
Appendix 2

ASSESSMENT OF THE FATE OF TWO HERBICIDES IN A

WYOMING RANGELAND SOIL: COLUMN STUDIES

ASSESSMENT OF THE FATE OF TWO HERBICIDES IN A

WYOMING RANGELAND SOIL: COLUMN STUDIES

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ABSTRACT

2   Extensive use of the herbicides dicamba and picloram in arid Wyoming, along with the

3   large volumes of irrigation water used in some areas, has created a concern for the potential

4   contamination of surface and ground waters by these herbicides. Persistence and mobility of

5   dicamba and picloram, were investigated in a Wyoming rangeland soil using batch adsorption and

6   soil column, both saturated and unsaturated, studies. The objectives of this study were to

7   characterize soil chemical and physical properties that affect herbicide transport, examine

8   herbicide sorption, model herbicide movement, and estimate degradation rate constants.

9   Essentially no sorption of dicamba was detected in any of the three horizons studied, however,

10   picloram sorption was found to be greatest in the horizon with the highest organic carbon content.

11   For saturated column experiments, herbicide applications, along with a bromide tracer,

12   corresponding to 5.90, 2.96, and 0.82 kg ha^{-1} for dicamba and 1.85, 0.97, and 0.47 kg ha^{-1} for

13   picloram, respectively. In an unsaturated column, an application rate of 2.76 and 1.00 kg ha^{-1}

14   for dicamba and picloram, respectively, was used. The herbicides and Br tracer (34, 38, 69, and

15   137 mg l^{-1}) were displaced through the soil columns using distilled water which was added in

16   daily increments (60 ml d^{-1}). Herbicide and tracer breakthrough curves were obtained from the

17   column experiment. Degradation rate constants were calculated using both a simple recovery

18   fraction technique and by matching LEACHP-generated breakthrough curves to experimental data.

19   Differences in herbicide degradation rates apparently resulted from variations in application rates

20   and the degree of saturation. For the two columns receiving intermediate application rates,

21   anaerobic picloram dissipation was more rapid ($t_{1/2}$ = 19 d) than for aerobic conditions ($t_{1/2}$ = 87

22   d). The rate of dissipation of dicamba was approximately the same under aerobic and anaerobic

23   conditions ($t_{1/2}$ = 15 and 17 d in the saturated and unsaturated columns, respectively). Picloram

and dicamba dissipation was more rapid at the lowest application rates, with $t_{1/2}$ of 13 and 10

2 days. At the highest application rates, $t_{1/2}$ of 23 and 17 days were measured for picloram and

3 dicamba, respectively. Both herbicides were found to be highly mobile, with the mobility of

4 picloram increasing at higher pore-water velocities.

5

6   **INTRODUCTION**

7   Pesticide contamination of surface and/or ground water supplies has become a national

8 issue (Moody, 1990). Many crop production and range/pasture areas of Wyoming have a history

9 of pesticide use (Taylor et al., 1986; Legg et al., 1992). Two herbicides, dicamba and picloram,

10 have been used extensively for specific rangeland and crop weed control for a number of years.

11 These herbicides have been listed for restricted use and are on the EPA priority pesticide list due

    to their high potential for leaching in soils and for their persistence in groundwater. Little

13 information exists on the fate of dicamba and picloram applied to rangeland and crop ecosystems

14 in Wyoming. The long term use of these herbicides in Wyoming thus represents an excellent

15 opportunity to study both long term and seasonal fate of pesticides in this region through a

16 window of several years of experimental monitoring and modelling (Nofziger and Hornsby,

17 1986).

18   Dicamba and picloram have been detected in surface and groundwater of Wyoming (Lym

19 and Messersmith, 1988; Druse et al., 1989). In 1983, picloram was detected in approximately

20 30% of Wyoming water samples with a maximum concentration of about 1 ppb (Hittle, 1983).

21 Recent sampling has shown that picloram concentrations ranged between 2 and 18 ppb (Druse

22 et al., 1989).

Picloram has been proven to be persistent under a variety of soil conditions (Michael et

2   al., 1989; MacDonald et al., 1976) and dicamba is recognized as being a particularly mobile

3   pesticide (Murray and Hall, 1989). Picloram transport and fate has been studied in laboratory

4   columns (Davidson and Chang, 1972; Davidson and McDougal, 1973) and under field conditions

5   (MacDonald et al., 1976; Michael et al., 1989) with detection occurring over a year after

6   application. A simulation of dicamba movement showed the herbicide moving well below the

7   root zone of both a clay and sandy soil (Nofziger and Hornsby, 1987). Experimental monitoring

8   in laboratory columns verified dicamba's tendency to be highly mobile and easily leached which

9   resulted in high concentrations in the effluent (Smith, 1973; Murray and Hall, 1989; Melancon

10   et al., 1986). Few studies, however, have considered environments such as found in semi-arid

11   and arid states of Wyoming and other western states, where a combination of a persistent and/or

     mobile pesticide and its use on extensive areas of rangeland and irrigated crops may potentially

13   lead to contamination of our environment (Fairchild, 1987).

14   Wyoming has a diverse agricultural base with areas of intensive short season crop

15   production. Coupled with the arid Wyoming climate, many of the agricultural areas rely heavily

16   on irrigation as a source of the water necessary for crop growth. With the scope of pesticide

17   usage in cultivated crop production, along with the volumes of irrigation water used, leaching of

18   pesticides becomes a potential concern for contamination of the underlying groundwater. Water

19   table depths in irrigated basins of Wyoming can be shallow (e.g., 2-4 m) during the growing

20   season. Much of the potable water supply for several regions of Wyoming comes from wells in

21   aquifers that may be affected by pesticides leached from agricultural activities. For Wyoming,

22   water supplies for 61% of the residents comes from subsurface sources with 89% of the rural

     population depending on groundwater (Canter et al., 1987).

3

Modeling is increasingly being used to evaluate the fate of pesticides in soil-water

2   systems. Sorption, leaching, degradation, volatilization and other processes are integrated through

3   the use of simulation modeling techniques. An extensive review of recent types of pesticide

4   simulation models was performed by Wagenet and Rao (1990). These models were evaluated

5   and categorized according to their purpose and complexity as: research, screening, management

6   and instructional models.

7   The focus of this study was to examine a Wyoming rangeland soil to quantify the

8   movement and fate of dicamba and picloram. Results and data from this research should provide

9   insight into dicamba and picloram reactivity and persistence in Wyoming rangeland environments,

10   and the associated threat to groundwater quality. The corresponding data for transport modeling

11   will aid in prediction of site and management characteristics that influence transport and

       contamination. The specific objectives of this research included:

13   1) Characterization of soil/substrata chemical, physical, and hydraulic properties for each

14   horizon to determine their importance in controlling herbicide transport.

15   2) Examination of herbicide sorption at different soil/substrata depths for correlation to

16   chemical and physical characteristics.

17   3) Modeling of herbicide movement in soil columns using LEACHP to assess parameters

18   determined in items 1 and 2, and estimate degradation rate constants.

19   Both batch adsorption and column studies were performed as an initial assessment of herbicide

20   persistence and mobility to aid in the preparation and design of a field investigation.

21

MATERIALS AND METHODS

2   Soil samples (Borollic Haplargid) for column and adsorption studies were collected from

3   the University of Wyoming's experiment farm located west of Laramie, in Albany County,

4   Wyoming. This soil type represents a significant portion of the soils in Wyoming and Colorado

5   high elevation rangelands and is used primarily for grazing, hayland and wildlife habitat

6   (Wyoming Agricultural Experiment Station, 1977). Bulk samples were taken from three soil

7   horizons collected at depths of 0-20, 20-35, and 35-50 cm, and bulk densities were measured in

8   the field by the sand-cone method. Some chemical and physical properties of the soils are listed

9   in Table 1.

10   Adsorption Study

11   Soil samples collected from the study site were used for standard batch adsorption studies.

Adsorption isotherm parameters for dicamba and picloram were calculated from the Freundlich

13   equation, which has been used extensively in pesticide adsorption studies (Grover, 1971;

14   Davidson and Chang, 1972; Grover and Smith, 1974; Farmer and Aochi, 1974; Murray and Hall,

15   1989). The Freundlich adsorption equation is:

16    $$x/m = K*C^{1/n}$$

17   where x/m equals the amount of herbicide adsorbed per unit weight of adsorbent (ug g^{-1}), and C

18   is the equilibrium concentration (mg L^{-1}). Constants K and 1/n are obtained by the least square

19   regression method on the linearized form (logarithmic) of the Freundlich equation. K is equal

20   to the amount of herbicide adsorbed in equilibrium with a unit concentration of herbicide and

21   therefore is taken as an index of adsorption. The best predictor of herbicide sorption is often soil

22   organic C content, which in this study was measured by a modified Walkley-Black wet oxidation

method (Greweling and Peech, 1960). Sorption coefficients (K_{oc}) were calculated (Rao and

2   Davidson, 1981; Green and Karickhoff, 1990) from the equation:

3    $$K_{oc} = (K / \%org.C) * 100$$

4   The adsorption studies were performed on soil from the three horizons using herbicide

5   concentrations of 0, 0.5, 1.5, 3.0, 10.0 mg L^{-1} for dicamba and 0, 0.2, 0.5, 1.0, and 5.0 mg L^{-1}

6   for picloram. A soil/solution ratio of 1:2 was used for all the adsorption studies.

7   <u>Column study</u>

8   Soil columns were prepared by reconstructing the soil profile in glass columns that

9   measured 8 cm in diameter and 52.5 cm high (Figure 1). Soil columns were constructed by

10   assembling 5 cm segments joined together with silicon adhesive sealant. Each horizon was

11   throughly mixed and sieved through a 4 mm sieve. All horizons were added to the columns in

     lifts (150 g dry soil each lift) using an impact-lift method that was developed to obtained a

13   desired bulk density for each horizon. This packing method was developed by trial using a

14   cylinder (8 cm dia.) mounted on a base plate. With this device, the compacted volume and

15   density of each lift were measured relative to the number of impacts and water content. Ten

16   impacts were imparted to each lift for dry soil from the A horizon to obtain a 1.34 g cm^{-3} density,

17   whereas 9 impacts to each lift for moist soil (water content = 20%) from the Bt horizon (1.54

18   g cm^{-3}) and 10 impacts to each lift of moist soil (water content = 20%) from the 2Btk1 horizon

19   (1.52 g cm^{-3}). A 2.5 cm layer of silica sand (baked at 500° C for 3 hrs), fine metal screen and

20   Buchner ceramic funnel were placed at the bottom of the column to retain the soil. After

21   saturation from the bottom up, columns reached steady flow after 3 days of applying 60 ml water

22   daily. Initially, 60 ml of water containing varying herbicide concentrations were applied to the

     different columns. Herbicide concentration corresponding to 5.90 (47.8 mg l^{-1}), 2.96 (24.0 mg

l^{-1}), and 0.82 (6.6 mg l^{-1}) kg ha^{-1} for dicamba and 1.85 (15.9 mg l^{-1}), 0.97 (8.4 mg l^{-1}), and 0.47

2   (4.0 mg l^{-1}) kg ha^{-1} for picloram were applied to separate columns, respectively (Table 2). Each

3   solution was adjusted to pH 6.0 and contained KBr (Br added at 137, 69, 34, 38 mg L^{-1} for

4   columns 1, 2, 3, and 4, respectively) as a tracer. Following herbicide application, 60 ml of

5   distilled water was applied daily to each column for 28 days.

6   An additional soil column (unsaturated) identical to those described above was maintained

7   at a lower water content by attaching a vacuum source to a filter flask at the bottom of the

8   column. An intermediate application rate (2.76 kg ha^{-1} of dicamba and 1.0 kg ha^{-1} of picloram)

9   was applied to this column and a flow rate of 60 ml day^{-1} was maintained for the duration of the

10   experiment.

11   For saturated columns, capillary rise was greater than column length. Therefore, once

     columns were saturated from the bottom up, water drained from columns only when water was

13   applied to top of column and acted to displace water from the bottom. In this saturated

14   condition, steady flow was quickly reached (3 days) and herbicides were applied. For the

15   unsaturated column, where a constant vacuum source was applied to the side-arm flask supporting

16   the column, approximately 2 weeks were required before a steady flow rate was achieved and

17   herbicides were applied.

18   <u>Analytical methods</u>

19   Upon completion of solute displacement, column segments were disassembled and soil

20   from the column with the highest application rate was analyzed for pesticide content as a function

21   of depth. Soil and effluent sample analyses were performed by high performance liquid

22   chromatography (HPLC) using solid phase extraction methods for concentrating and purifying

     samples. The solid phase extraction methods for picloram and dicamba extraction were a

7

modification of methods presented by Arjmand et al. (1988) and Michael et al. (1989). Two

2 different types of sep-pak cartridges were used: C-18 octadecyl strong polar for picloram and

3 NH$_2$-aminopropyl weak anion exchange sorbent for dicamba.

4 Herbicide measurements of column effluent did not require any pretreatment for dicamba

5 analysis, whereas effluent samples for picloram analysis were bought to 1N NaCl and acidified

6 to pH 2. Soil samples were passed through a 2.0 mm sieve and, after extraction, were analyzed

7 following the effluent protocol. Dicamba was extracted from the soils (25 g) using a 50:50

8 (volume:volume) mix of methanol/water (80 ml) and ultrasonic treatment for 40 min. Soil

9 extracts were centrifuged at 14,000 rpm for 20 min. and 20 ml of the supernatant diluted to 100

10 ml with deionized-distilled water. Picloram was extracted from 100 g moist soil by addition of

11 100 ml 2N KCl and shaking for 60 min (Cheng, 1969).

Dicamba and picloram were analyzed using a Shimadzu model SPD-MGA photodiode

13 array UV-VIS detector system equipped with a 5 μ C-18 column (150 mm in length) and

14 reversed phase guard column. The mobile phase for dicamba analysis was methanol/water

15 (50/50) and 0.005 M tetrabutyl-ammonium phosphate using a flow rate 1 ml min^{-1} and detection

16 at 210 nm. Mobile phase for picloram analysis was 4% acetic acid in water/acetonitrile (95/5)

17 using a flow rate 1.5 ml/min and detection at 254 nm. The detection limit for dicamba analysis

18 was 1 and 10 ppb, and for picloram 5 and 8 ppb in water and soil samples, respectively.

19 Bromide and nitrate concentrations in effluent samples were measured using ion chromatography

20 (Dionex 2000i, Sunnyvale, CA).

21 <u>Modeling</u>

22 For this study a "research model" LEACHP was used. LEACHP is one of the four

submodels in LEACHM and numerically simulates pesticide degradation, transformation and

movement (Hutson and Wagenet 1992). LEACHP was employed in conjunction with the soil

2   column study to obtain estimates of modeling parameters by a curve-fitting technique (Mishra

3   and Misra, 1990). Specifically, values were assumed for dispersivity and degradation rate

4   constants until the experimentally-measured breakthrough data matched the simulated

5   breakthrough curves generated by LEACHP. The relative width (spreading) of a tracer

6   breakthrough curve is proportional to the dispersivity of the porous medium. The area under the

7   herbicide breakthrough curve is a function of the degradation rate. Rate constants indicate

8   average rates of disappearance for the profile, and no distinction was made between

9   transformation and degradation, either biological or chemical. Other significant modeling

10   parameters affecting pesticide movement such as soil hydraulic properties, normalized distribution

11   coefficients, % organic C, and bulk density were determined by separate experiments or obtained

     from references.

13   Herbicide transport is inseparable from water movement; therefore, it was necessary to

14   adequately define the soil hydraulic properties. Important parameters are saturated conductivity

15   and the moisture-retention relationship. Saturated conductivity was measured by the constant-

16   head method (ASTM Standards, 1990). The moisture-retention data (volumetric water content

17   as a function of matrix potential) was obtained using porous and pressure plate apparatus (ASTM

18   Standards, 1990). The moisture-retention data determined for each horizon was fitted using the

19   RETFIT program within LEACHM (Hutson and Wagenet, 1992). From these two parameters,

20   LEACHP estimates unsaturated conductivity and specific water capacity for any water content

21   or matrix potential.

22   Several simplifying assumptions were incorporated into the modeling of herbicide

     movement in soil columns to obtain estimates of degradation rate constants. The overall picloram

distribution coefficient for the profile was calculated by averaging each horizon's K_{oc} relative to

2   its fraction of the profile depth (i.e., depth of horizon 1 was 40% of the profile and its K_{oc} made-

3   up 40% of the overall K_{oc}). The steady-state option was invoked for this simulation: a constant

4   water flux and an average moisture content were specified.

5

6   **RESULTS AND DISCUSSION**

7   <u>Adsorption study</u>

8   No adsorption of dicamba was found for any of the soil horizons over a pH range of 6.0

9   to 7.8. Studies performed by Grover and Smith (1974) also indicated that both sandy loam and

10   loam soils had essentially no affinity for dicamba. Picloram adsorption isotherms were linear at

11   concentrations higher than 0.2 ppm ($\geq$0.4 mg kg^{-1} soil) (Figure 2). Picloram adsorption was

     highest in the Bt horizon, which also had the highest organic C content (Table 1).

13   Adsorption of pesticides to soil depends on a number of factors such as type and content

14   of soil organic matter, pH, temperature, and soil/solution ratio (Singh et al., 1990). The colloidal

15   surface of most agricultural soils have a net negative charge and thus have an affinity for

16   positively charged species, but not much affinity for negatively charged species (Khan, 1991).

17   Therefore acidic pesticides, such as picloram and dicamba, are not readily adsorbed by clay

18   minerals, but are adsorbed (or partitioned) in limited amounts by organic matter. Although the

19   clay content was similar for each horizon, organic C content varied among soil horizons. This

20   study shows that the adsorption of picloram increased with an increasing content of organic

21   carbon. This is consistent with others studies that have found adsorption of picloram to be

22   correlated with organic C contents but not with clay content (Farmer and Aochi, 1974). The

                                                  10

effect of pH (values between 6-7.8) on adsorption coefficients for picloram and dicamba in the

2   present study was insignificant.

3   <u>Column study</u>

4   Travel times through columns (columns 1, 2 and 3) at a high water content (approaching

5   saturation) were 13 to 14 days for dicamba and 16 to 17 days for picloram (Figures 3). The

6   average travel time for the Br tracer was 13 days, which was roughly equal to that for dicamba.

7   For column 4 (lower water content), travel times of solutes were less, with a peak effluent

8   concentration occurring on day 11 for dicamba and day 13 for picloram (Figure 4). These data

9   are consistent with other studies on dicamba's tendency to be highly mobile and easily leached

10   (Melancon et al., 1986). The longer travel time for picloram was due to adsorption.

11   Effluent dicamba concentrations decreased fairly rapidly after the solute front reached the

     column outlet, with concentrations approaching zero after 27 days from the date of application.

13   Picloram breakthrough curves extended laterally out in time. Dicamba first appeared in the

14   effluent (columns 1 and 2) on the 8th day after application, which was five days earlier than for

15   picloram.

16   The amount of picloram and dicamba eluted from the columns is listed in Table 2. It

17   should be noted that the percent dicamba recovered was higher than that of picloram in the

18   saturated columns. Although dicamba has been reported to have a shorter half-life ($t_{1/2}$) (Smith,

19   1973; Overcash and Davidson, 1981; Michael et al., 1989)) and less recovery might be expected,

20   the recovery of picloram was more limited by the effects of adsorption. The one exception to

21   this trend was column 4, which was maintained at a lower water content during leaching. The

22   unrecovered herbicide fractions were presumably degraded chemically and biologically, or

     retained in the columns. Both dicamba and picloram are relatively nonvolatile (Foy, 1976), hence

this loss mechanism was considered to be negligible. The detection limits (5 and $1 \mu g \ l^{-1}$) and

2   percent recovery (90 to 99%) for picloram and dicamba from water samples was determined in

3   a separate study which developed the analytical methods used within this study (Krzyszowska

4   and Vance, 1994).

5   Herbicide leaching in the unsaturated column (column 4) was performed under different

6   operating conditions as compared to the other three columns. The main difference between

7   unsaturated and saturated columns was the low water content in the former columns; however,

8   volumetric flow rates (ml day^{-1}) were equivalent in all columns. This unsaturated soil-water

9   system resulted in a higher pore-water velocity, as indicated by the shorter residence time, and

10   ensured an aerobic environment. The average pore-water velocity in column 4 was greater than

11   in the saturated columns by a factor of approximately 1.3. For saturated columns (No. 1, 2, and

3), the residence time of picloram was 3 days more than for dicamba. However, for column 4,

13   the difference in residence times decreased to two days (Figure 4). This indicates that the

14   mobility of picloram increased because of a higher pore-water velocity or a lower water content.

15   The content of picloram and dicamba recovered at the completion of the leaching

16   experiment from soil column 1 was insignificant. The highest amount of picloram (2 $\mu g \ kg^{-1}$

17   soil) was found 25 cm below the surface. The cumulative mass of picloram extracted from the

18   soil was 1% for picloram and 0.03% for dicamba when compared to the total amount added. No

19   degradation products were isolated from soil treated with picloram as indicated by the HPLC

20   chromatograph. A common degradation product of dicamba is 3,6-dichlorosalicylic acid, which

21   was not detected in this study.

22   The aerobic soil environment in column 4 was contrasted by the anaerobic conditions that

began to dominate in soil columns 1, 2, and 3 shortly after the experiment started, as indicated

by low effluent NO_3^- concentrations. Effluent samples soon developed a noticeable pungent odor.

2   Therefore, it was assumed that herbicide degradation was primarily a result of anaerobic activity;

3   however, no data was collected that could substantiate this hypothesis.

4   Seven days after herbicide application, and following six days of daily water applications

5   (60 ml day^{-1}), the effluent nitrate concentration in column 4 dropped and then began to increase

6   (Figure 4). The solute residence time (11 days for bromide and dicamba) suggests that

7   nitrification was affected by herbicide and tracer addition. In the vicinity of the solute front for

8   nonadsorbing solutes, i.e., bromide and dicamba, nitrification was inhibited. Nitrification

9   accelerated once the solutes were eluted. Under conditions of low microbial activity, nitrate is

10 thought to be a non-reactive solute, and a residence time identical to bromide would be expected

11 since it moves almost as quickly as the water (Bohn et al., 1985). The lowest content of NO_3-N

corresponded to the time where the highest content of bromide and dicamba were detected in the

13 effluent, suggesting dicamba may have inhibited the nitrification process (Bundy and Bremner,

14 1973); however, the amount of nitrogen resulting from the added picloram was insignificant when

15 compared to the mass of nitrate eluted. High herbicide concentrations may also kill existing

16 microbial biomass which could possibly contribute a readily available nitrogen source to

17 surviving bacteria or be leached from the columns. Effluent nitrate levels in saturated columns

18 remained low. This is expected since nitrification is an aerobic process.

19 Degradation rate determination

20 In addition to determining rate constants by curve fitting simulated breakthrough curves

21 to experimental data using LEACHP, another more approximate approach was utilized as well

22 (Table 3). Degradation rate constants were calculated using a recovery fraction method described

13

by Mishra and Misra (1990), which is based on the assumption of first-order kinetics. This

2   approach is best explained by the equation:

3   $$Ln \text{ (mass fraction eluted)} = -kT$$

4   where k is the degradation rate constant, and T is solute travel time or the mean residence time

5   in which solutes are exposed to degradation. The mass fraction eluted (fraction recovered) and

6   mean residence time were determined experimentally (Table 2). Because this mass balance does

7   not consider herbicides still within the profile, degradation rate constants may be overestimated.

8   Consequently, it gives better results when applied to non-adsorbing solutes like dicamba.

9   LEACHP-estimated rate constants are consistently lower because the model includes sorbed

10 herbicides in the mass balance. Therefore, the rate constants derived from the two methods agree

11 more closely for dicamba than for picloram.

The degradation rate constants obtained from LEACHP vary with application rate.

13 Columns 1 and 2, with high and intermediate application rates, had similar degradation rates;

14 values ranged from 0.030 to 0.036 day^{-1} for picloram and 0.040 to 0.041 day^{-1} for dicamba (Table

15 3). Column 3 (lowest application rates) exhibited the highest rate constants, i.e., the shortest half-

16 lives for both picloram and dicamba. Foy (1976) also observed picloram dissipation was faster

17 at low application rates which is contrary to the assumption of first-order kinetics. The same

18 appears to be evident for dicamba.

While rate constants for dicamba were relatively similar at the two water contents (column

20 1, 2 and 3 compare to column 4), the rate constants for picloram differed greatly. Picloram

21 degradation in column 4 (unsaturated-low water content) was unusually low when compared to

22 other values. This would suggest picloram degradation was affected by the degree of saturation.

As compiled by Nash (1991), soil moisture influences the rate of dissipation of most pesticides,

14

with dissipation more rapid in a wet soil. Furthermore, the degradation rate for picloram was found to be dependent upon soil moisture at a constant temperature (Meikle et al., 1973). However, dicamba degradation was not impaired at a low water content.

Best agreement was attained between experimental and simulated breakthrough curves for dicamba (Fig. 3). LEACHP, in all instances, predicted a slightly slower velocity (more retardation) for picloram. The residence time, as controlled by K_{oc}, is one day longer than experimental results in saturated columns. For column 4 with its higher pore-water velocity, the effect is much more pronounced. The residence time predicted by LEACHP exceeded the actual residence time by three days. At this higher velocity, picloram retardation was significantly overestimated by LEACHP.

If the velocity of an adsorbate is directly related to its distribution coefficient, then doubts arise as to the applicability of the equilibrium adsorption model for this dynamic flow system. Although batch adsorption tests, which are considered to be in equilibrium after a certain time, are the standard method to estimate retardation, laboratory soil columns may not be in equilibrium (Green and Karickhoff, 1990). Davidson and Chang (1972) reported that picloram sorption is a function of pore water velocity, as was suggested by decreasing pore-water velocity substantially reducing picloram mobility. For a higher pore-water velocity, time for diffusion of adsorbate to sorption sites was reduced. In simulating picloram movement in a field situation, however, the assumption of equilibrium is expected to be valid for porous media flow since pore-water velocities are normally much lower. On the other hand, when solute movement is dominated by macropore flow, the equilibrium assumption may not be acceptable.

Overall, LEACHP served as a useful laboratory research tool in the present study by effectively fitting breakthrough curves to estimate dispersivity and disappearance rates.

LEACHP's primary advantage is due to the increased versatility of LEACHP over analytical

2   models. The numerical solution technique used in LEACHP allows consideration of more

3   complex, transient, and variable soil-water-solute systems. Additionally, increased versatility also

4   arises from the variety of initial and boundary conditions which may be specified for a myriad

5   of experimental configurations. For example, as illustrated by the present experiment, bottom

6   boundary conditions of atmospheric pressure for tension-saturated columns and a constant

7   negative pressure for the saturated columns were both successfully represented with LEACHP.

8   The one disadvantage of LEACHP, however, is the additional time required to become proficient

9   in using LEACHP model.

10   Experimental results and environmental factors inherent in this rangeland system indicate

11   situations which may significantly increase herbicide longevity, especially for picloram. The

      short growing season, mild climate, and the large diurnal temperature fluctuation will increase

13   herbicide persistence. After the growing season, degradation rates are likely to decrease further

14   as the soil dries and the mean daily temperature drops. Consequently, the increased persistence

15   of picloram under dry conditions suggests picloram remaining at the end of the growing season

16   or applied late may persist until the soil thaws the following spring.

17

18   **CONCLUSIONS**

19   Batch adsorption and column studies were performed as an initial assessment of herbicide

20   persistence and mobility to aid in the preparation and design of a field simulation. Estimates of

21   herbicide degradation rates and adsorption were obtained under varying conditions that may occur

22   in an agricultural system. Experimental results suggest the potential for high picloram

      persistence. Specific findings are summarized as follows:

- Herbicide disappearance was found to depend upon application rate. At low application rates, dicamba and picloram were degraded more quickly than at high rates.

- Picloram adsorption was reduced with higher pore-water velocity. No adsorption of dicamba was evident.

- Degradation of picloram varied with water content and picloram disappearance was much slower in the unsaturated column.

- Predicted degradation rates obtained from the simulation model, LEACHP, were similar for dicamba at the intermediate application rate regardless of whether anaerobic or aerobic conditions dominated.

- LEACHP's successful use as an analytical research tool was demonstrated in estimating soil dispersivity and herbicide disappearance rates.

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FIGURE CAPTIONS

Figure 1. Schematic of soil columns used in the herbicide leaching studies.

Figure 2. Adsorption of picloram by the three soil horizon used in the column studies.

Figure 3. Comparison of experimental data and LEACHP-generated breakthrough curves for column 1, 2, and 3.

Figure 4. Herbicide and nitrate concentrations in the unsaturated column experiment (column 4).

Table 1. Some soil chemical and physical characteristics and Freundlich adsorption parameters for picloram.

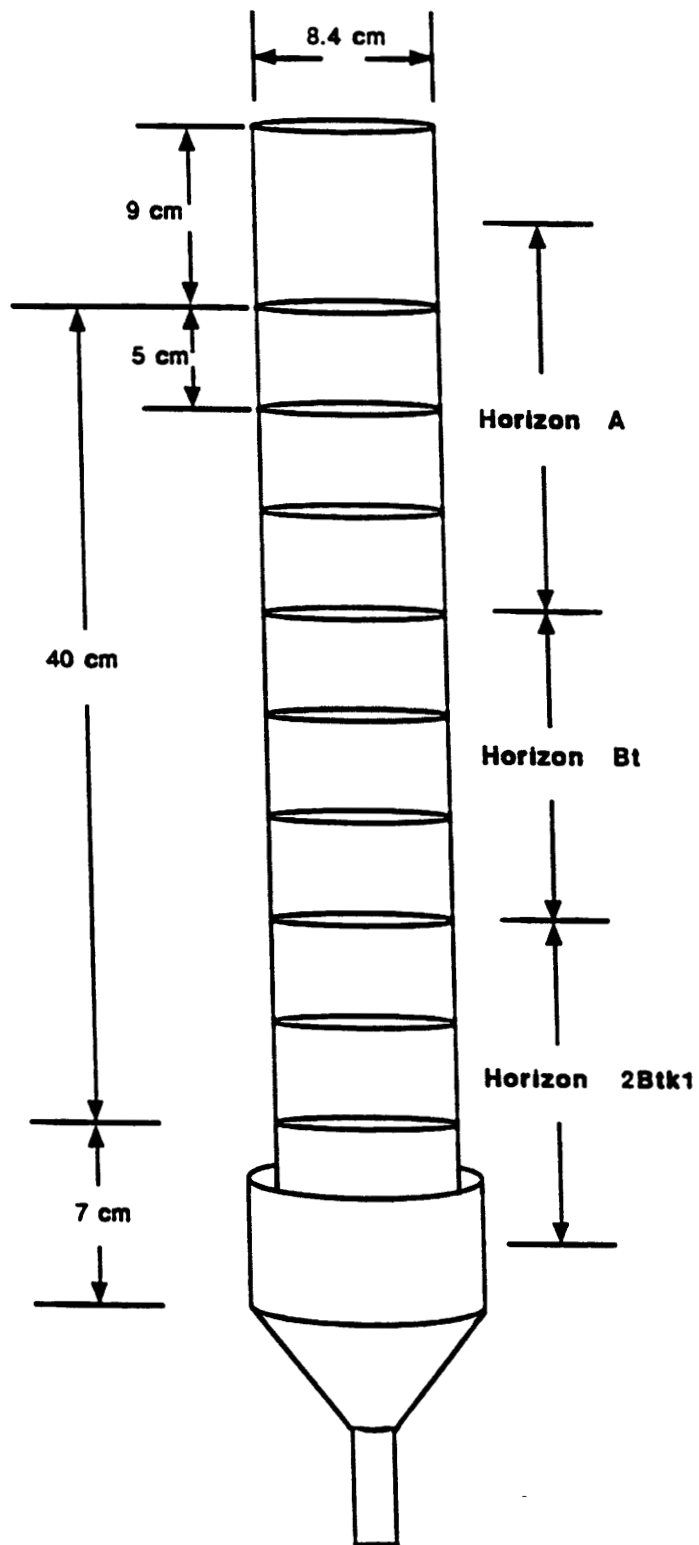| Horizon	Depth (cm)	Bulk Density (g/cm³)	Sat. hyd. conductivity (mm/day)	RETFIT constants		% Organic carbon	Freundlich constants	
				A (kpa)	B		1/n	K
A	0-20	1.34	140	-4.89	3.65	1.4	0.94	0.0765
Bt	20-35	1.54	19	-4.15	7.47	1.8	1.02	0.2580
2Btk1	35-50	1.52	24	-4.89	9.62	0.85	1.02	0.0001

Table 2. Herbicide application rates, residence times, and recovery of picloram and dicamba from the saturated (1, 2, and 3) and unsaturated (4) columns.
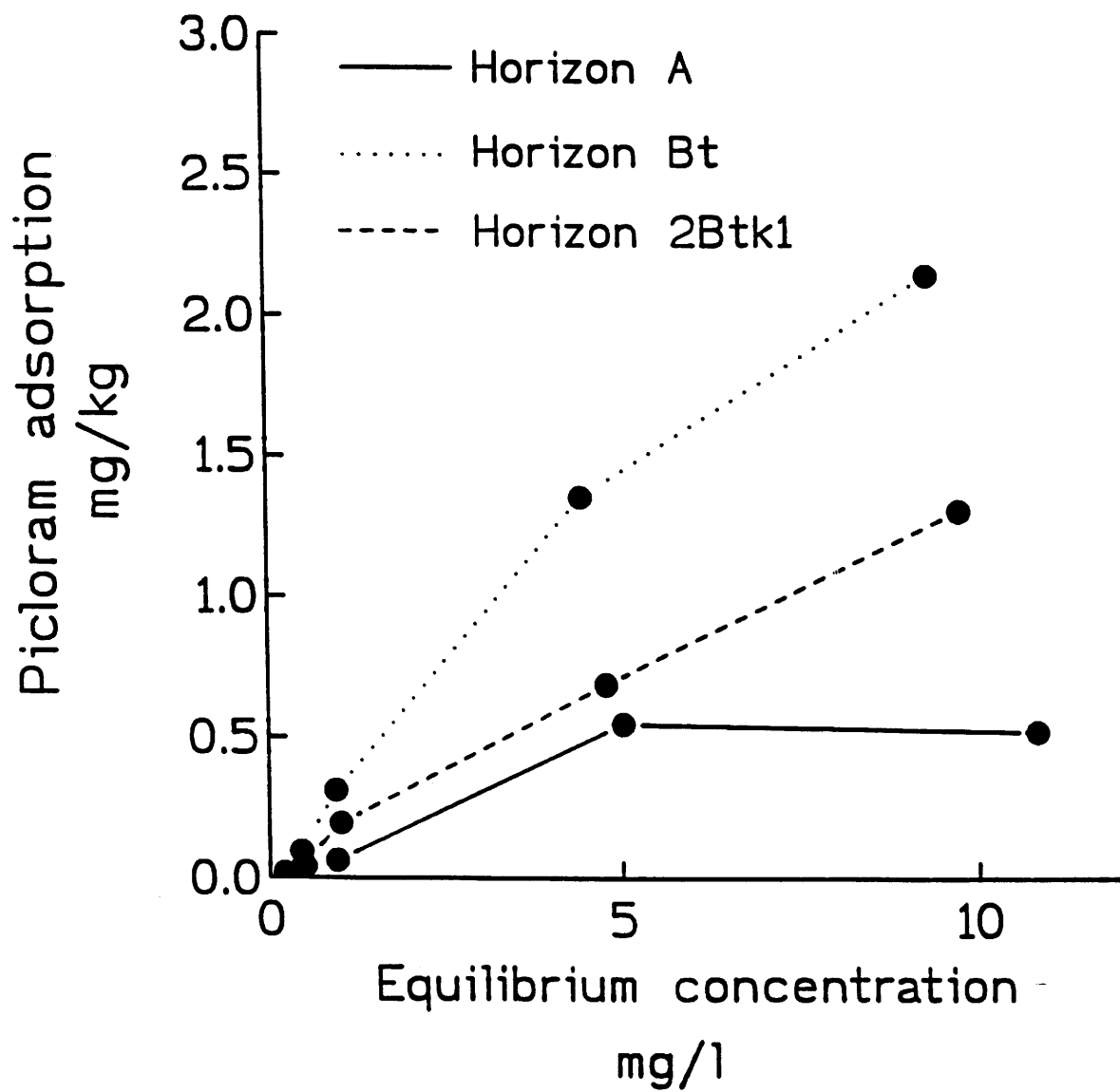
Parameters	Picloram column number				Dicamba column number			
	1	2	3	4	1	2	3	4
Application rate (kg ha^{-1})	1.85	0.97	0.47	1.00	5.90	2.96	0.82	2.76
Residence time (days)	17	16	17	13	14	13	14	11
Percent recovered in effluent[†]	51.9	49.1	35.7	72.6	54.0	62.9	37.0	56.2

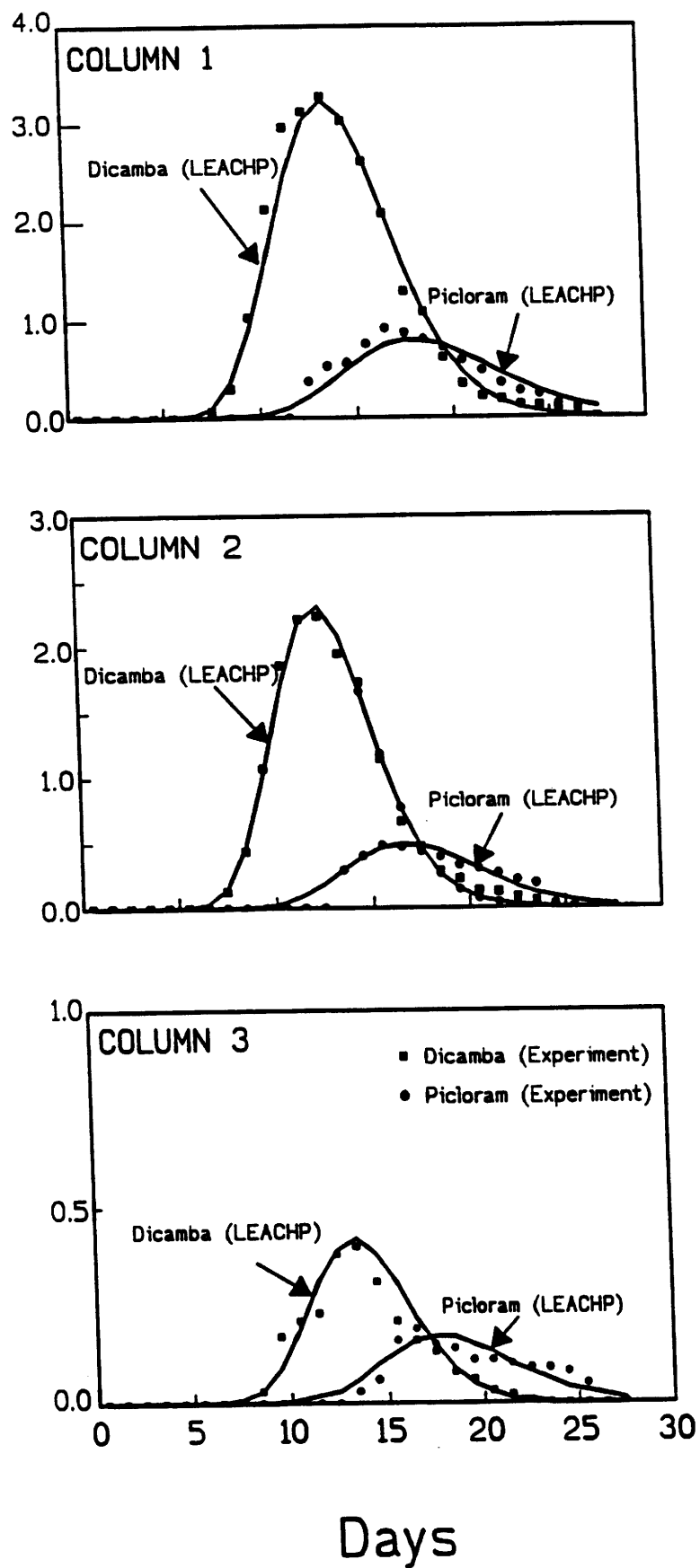[†] Percent recovery = (amount recovered in effluent solutions/initial amount added to columns) x 100.

Table 3. Degradation rate constants (day^{-1}) determined from experimental data and LEACHP and half-life for picloram and dicamba.

	Picloram column number				Dicamba column number			
	1	2	3	4	1	2	3	4
Degradation Rates								
Column Study	0.039	0.044	0.061	0.024	0.044	0.036	0.071	0.053
Model LEACHP	0.030	0.036	0.053	0.008	0.040	0.041	0.068	0.046
$t_{1/2}$ (days)	23	19	13	87	17	17	10	15

8.4 cm

9 cm

5 cm

40 cm

7 cm

Horizon A

Horizon Bt

Horizon 2Btk1

Fig 1

Fig 2

Fig 3

Fig 4