

Report No. 03

Macropore Effects on Pesticide Transport to Groundwater

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SYNOPSIS

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SUMMARY OF RESEARCH PROJECT:

Problems and research objectives:

Movement of agricultural chemicals (herbicides, insecticides, etc.) through the soil profile has become a public concern since the increase in the reports of groundwater contamination. Knowledge of the mechanisms of solute transport and the soil parameters affecting the movement of chemicals is needed to predict potential contamination of groundwater reservoirs. Prediction of the rate of solute movement in the soil and the influences the soil has on this rate are useful from several points of view. Groundwater contamination is an important issue affecting the leaching of pesticides and other toxic chemicals. Other issues relating to the study of solute movement in the soil are: understanding nutrient cycling in the soil, designing management schemes to minimize fertilizer losses and maintaining certain solutes, such as nitrate, within acceptable water quality standards. The objective of this investigation was to evaluate the leaching and degradation characteristics of atrazine and bromide in a

field of alluvial soils under no-till management.

### Methodology:

The field experiment for this project was located near Hartsburg, Missouri. The soils were Sarpy (loamy, mixed, mesic Typic Udipsamments) with the surface texture varying from silt loam to loamy sand. The experimental site was 0.1 ha in size. The experimental field was divided into 49 plots having 4 x 4 m dimensions. Four plots were chosen as control plots which received no chemicals. In May 1987, atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) was applied at 2.2 kg/ha after sorghum was planted. Seven hours after application, 14 surface soil samples 225 cm<sup>2</sup> x 3.0 cm deep were collected to determine the uniformity and average concentration of atrazine. There was 14.2 mm irrigation before these samples were collected. Atrazine was chosen since it is a commonly used broadleaf herbicide. Bromide (NaBr) was applied at 115 kg/ha five days later. By this time the herbicide had killed the weeds, thus minimizing the uptake of bromide by plants. Twenty surface soil samples 225 cm<sup>2</sup> x 3.0 cm deep were removed to determine the uniformity and average concentration of the bromide. Bromide was selected since it acts similar to nitrate. To minimize the degradation of atrazine due to light exposure and temperature, the samples were wrapped in aluminum foil and kept frozen while stored. They were later sent to the laboratory to be analyzed for atrazine concentration. Bromide samples were stored in plastic bags and kept at room temperature and later were analyzed for soil water content and bromide concentration. Samples were taken systematically for both chemicals during the summer using a truck-mounted hydraulic soil probe. Soil cores were extracted to a depth of 150 cm which were segmented into 7.5 cm increments. The size of each sample was 135.72 cm<sup>3</sup>. The dates for sampling were one week, one month, two months, three months, and four months after application of the chemicals. Measurement of the atrazine content (mg/kg) of the soil samples was done by the University of Missouri Trace Substances Laboratory. In this analysis, the soil sample was mixed with sodium sulfate to be dried. Then the sample was extracted with methylene chloride. The extract was then concentrated and fractionated on a Florisil column. Finally it was analyzed using a gas chromatograph unit interfaced with a mass spectrometer. The bromide content (mg/kg) measurement of the soil samples was done in the University of Missouri Soil Physics Laboratory. For this measurement the sample was mixed with distilled water in a 1:1 ratio. Then the bromide halide electrode, which was hooked up to a pH meter, was used to measure the activity of the bromide in millivolts which was an indication of bromide concentration. This measurement was done by direct reading from the soil-water mixture. The bromide concentration (mg/kg) was derived from the standard

curves constructed based on known samples.

Principal findings and significance:

The average atrazine concentration of the surface samples indicated that the application rate was 1.67 kg/ha with a coefficient of variation of 26%. This was lower than the application rate due in part to degradation of the atrazine and possible movement below the 3 cm depth with the initial irrigation. Atrazine was detected at a depth of 22.5 cm within the first week after application. The detection of atrazine to a depth of 22.5 cm within a week after application indicates that it moves much deeper than predicted from laboratory experiments. This is probably due to the presence of macropores (1-5 mm diameter holes) open to the soil surface. Bromide had moved to the 30 cm depth within the first week after application. This is explained by the lower retardation of bromide in the soil.

Publications and professional presentations:

Kazemi, H.V., and S.H. Anderson. Field variability of atrazine leaching under no-till management. ASAE Paper No. 88-\_\_\_\_, presented at the 1988 Winter ASAE Meeting, Chicago, Illinois.

M.S. theses: None.

Ph.D. dissertations:

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Macropore Effects on Pesticide Transport to Groundwater 1/

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## ABSTRACT

The objective of this investigation was to evaluate the leaching and degradation characteristics of atrazine and bromide in a field of alluvial soils under irrigated, no-till management. The experimental site was 0.1 ha in size. The soils were Sarpy (mixed, mesic Typic Udipsamments) with the surface texture varying from silt loam to loamy sand. Atrazine was applied at 2.2 kg/ha after sorghum (Sorghum bicolor) was planted. Bromide was applied at 115 kg/ha five days later. Soil cores were extracted to a depth of 150 cm which were segmented into 7.5 cm increments and were analyzed for each of the chemicals separately. The dates for sampling were one week, one month, two months, three months, and four months after application of the chemicals. As a result 1134 and 3542 soil samples were extracted for atrazine and bromide analysis, respectively. Atrazine was detected within the 15 to 22.5 cm depth increment one week after application. These data suggest that some of the atrazine can move to depth of 20 cm after one week which is probably due to the presence of macropores (1-5 mm diameter holes) open to the soil surface which were present in this field under no-till management. Atrazine was detected at very low concentrations at two and four months after application. Although extreme variability in atrazine concentrations occurred, the variations were not explained totally by differences in soil texture. The data in this study indicate some potential, although small, for atrazine contamination of groundwater.

## INTRODUCTION

Movement of agricultural chemicals (herbicides, insecticides, etc.) through the soil profile to groundwater has become a public concern since the increase in reports of groundwater contamination (Hallberg, 1986; Jury et al., 1987). Knowledge of the mechanisms of solute transport and the soil parameters affecting the movement of chemicals is needed to predict potential contamination of groundwater reservoirs.

Studies have been conducted evaluating the transport of solutes in soil (Rao and Jessup, 1983; Biggar and Nielsen, 1976; Jury and Stolzy, 1982; and Thomas and Phillips, 1979). Some of these studies have evaluated the effects of climate and soil and chemical properties on the movement of specific solutes. The conventional convection-dispersion equation (Biggar and Nielsen, 1967) describes most of the physical and chemical processes involved in the transport of solutes. The most important physical parameter is the velocity of water passing through the soil. Because the total flux of water moving through field soils is often small, the hydrodynamic dispersion and diffusion mechanisms should also be considered in the study of solute transport (Biggar and Nielsen, 1967). In the evaluation of the fate of organic contaminants, the adsorption characteristics, the rate of degradation, and the rate of volatilization are also important parameters.

Chemicals added to a soil profile from the surface may leave the zone of incorporation by one of three possible loss pathways



(Jury et al., 1987). The first pathway, known as leaching, takes place principally by mass flow and refers to the downward movement of dissolved chemicals. The second loss pathway, volatilization, refers to loss of chemical vapor to the atmosphere through the soil surface. The final loss pathway, degradation, refers to the biological or chemical transformation of the chemical to a different form with properties distinct from those of the chemical prior to transformation.

The distance a chemical will travel through bulk soil will be determined by the tortuosity of the total path length it follows (Hillel, 1980). Because the degree of convection and diffusion vary for soils having different pore size distributions, the flow path for a chemical will not be the same between soils. Therefore, if the distribution of the chemical concentration is monitored over time, it will provide information about the mechanisms of how water is carrying solutes flowing through different soils (Wagenet, 1983).

Jury et al. (1982) found that under field conditions, the solute distribution is associated with the quantity and distribution of infiltrating water. They also found that the variability in the velocity of soil water could best be described as a stochastic process. This method may provide a better estimate of the earliest arrival times of chemicals to groundwater. This arrival time of chemicals to groundwater is critical in evaluating the potential contamination of groundwater.

Gish et al. (1986) conducted an experiment on simultaneous leaching of bromide and atrazine under nonirrigated field conditions. They assumed all of the atrazine not recovered in the field cores to have either degraded or moved beyond the depths sampled. Eventhough there was a poor agreement between predicted and observed atrazine concentration, atrazine was found more mobile than predicted. They were not successful in describing the convective component associated with atrazine movement using the bromide data due to the various pathways in which atrazine was lost. They attributed the early transit time of atrazine to preferential flow.

Since few studies have evaluated the fate and movement of organic chemicals under field conditions, it was proposed that additional work is needed in this area. The objectives of this study were to evaluate the leaching and degradation characteristics of atrazine and bromide under no-till, irrigated management. This work will be compared with similar work done on other soils under field conditions.

## MATERIALS AND METHODS

### Location of Experiment

The site of the field experiment was near Hartsburg, Missouri. The soil is on the flood plain of the Missouri River and is classified as Sarpy (mixed, mesic Typic Udipsamments). The soil surface texture varied from loamy fine sand to fine sandy loam (Fig. 1). The experimental site was 0.1 ha in size and was divided into 49 plots having 4 m x 4 m dimensions. Four plots were chosen as control plots which received no chemicals (Fig. 1). Scattered layers of clay were detected in the soil profile which were attributed to variability of deposits of the Missouri River. Another layer of clay exists in the soil profile at about the 3 m depth.

Rainfall and irrigation water (center pivot) were monitored using two weighing and recording precipitation gauges. One was installed at the experimental site to measure the total water added to the site. The second gauge was installed outside of the experimental site to measure the distribution and amount of natural rainfall. The crop at the time of experiment was grain sorghum (Sorghum bicolor) which was planted under no-till management right before the application of chemicals. The previous crop was soybean (Glycine max) and since soybean is sensitive to atrazine, no atrazine had been applied to this field for at least three years prior to the study.

### Chemical Application

On May 20, 1987 atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine) was sprayed at 2.2 kg/ha after sorghum was planted. Seven hours after application, 14 surface soil samples 225 cm<sup>2</sup> x 3.0 cm deep were collected to determine the uniformity and average concentration of atrazine. There was 14.2 mm of irrigation before these samples were collected. Atrazine was chosen since it is a commonly used broadleaf herbicide.

Sodium bromide (NaBr) was applied at 115 kg/ha five days later. By this time the herbicide had killed the weeds, thus minimizing the uptake of bromide by plants. Sodium bromide was used in the place of potassium bromide (KBr) to minimize the toxicity hazard to grazing animals since the site was in a farmer's field. Because the soils were coarse-textured, it was predicted that minimal dispersion would occur due to the sodium. Twenty surface soil samples 225 cm<sup>2</sup> x 3.0 cm deep were removed to determine the uniformity and average concentration of the bromide. Bromide was selected since it is a nonadsorbing chemical, does not degrade and acts similar to nitrate. Plant uptake was also assumed to be minimal (Gish et al., 1986).

### Soil Sampling for Chemical Analysis

Soil cores were removed using a truck-mounted hydraulic soil probe. Samples were taken systematically at 20 plots for atrazine and 49 plots for bromide (Fig. 2). Soil cores were extracted from different depths at each date and segmented into

7.5 cm increments. Samples were taken at one week, one month, two months, three months, and four months after application of the chemicals. Details for sampling data are presented in Table 1.

#### Storage of Samples

To minimize the degradation of atrazine due to light exposure and temperature, the samples were wrapped in aluminum foil and kept frozen while stored. They were later sent to the laboratory to be analyzed for atrazine concentration. Bromide samples were stored in plastic bags and kept at room temperature and later analyzed for soil water content and bromide concentration.

#### Sample Analysis

Atrazine. Soil samples are first mixed with sodium sulfate to dry. Then the sample is leached with methylene chloride to extract the atrazine. The extract is concentrated and fractionated on Florisil. Finally it is analyzed using gas chromatography/mass spectrometry. This is the standard atrazine analysis done in the laboratories (Lopez-Avila et al., 1985; Davoli et al., 1987; and Deleu and Copin, 1987). This analysis was done at the University of Missouri Trace Substances Laboratory.

Bromide. Soil samples are mixed with distilled water using a 1:1 ratio (Adriano and Doner, 1982). Then, the bromide halide electrode which is hooked up to a pH meter, is used to measure

the activity of the bromide in millivolts which is an indication of bromide concentration. This measurement is done by direct reading from the soil-water mixture. The bromide concentration (mg/kg) is derived after the standard curves are constructed based on the known sample readings.

#### Measurement of In Situ Water Content

A neutron meter was used weekly to monitor the water content of the soil profile throughout the growing season at selected locations of the experimental site (Fig. 2). Also gravimetric water content measurements were performed on all bromide samples.

## RESULTS

The average atrazine concentration of the surface samples indicated that the application rate was 1.67 kg/ha with a coefficient of variation of 26%. This was lower than the application rate due in part to degradation of the atrazine and possible movement below the 3 cm depth with the initial irrigation. Some of this variation might have been caused by the irrigation water applied before the surface samples were collected. The mean concentration of bromide application measured in the surface samples was 113.7 kg/ha with a coefficient of variation of 18.5%.

Average atrazine concentrations as a function of soil depth for the four sampling dates are shown in Figs. 3, 4, 5, and 7. Atrazine concentration in the surface 7.5 cm is highest in soil 3 and lowest in soil 1, seven days after application (Fig. 3). However, as the number of days after application increases, atrazine concentration in the 7.5 cm depth increment decreases largely due to degradation and leaching (Figs. 4, 5, and 7). Although atrazine leaching was minimal, some atrazine was detected at soil depths below 7.5 cm. Atrazine concentration was always highest in the 7.5 cm depth increment due to the retardation of this organic chemical which is attributed to adsorption by organic matter content of the soil.

Since atrazine concentrations were not found to be significantly different between the three soils, the average concentration for the entire field was calculated as a function

of time and plotted (Fig. 8). It is noticed that the degradation rate of atrazine in the surface samples was greater between 7 and 30 days and was lower between 60 and 120 days (Fig. 8). This is due to the fact that later in the season there is much less atrazine available to degrade. Degradation is linearly related to available atrazine. Atrazine was detected at a depth of 18.75 cm within the first week after application which indicates that atrazine moves much deeper than predicted from laboratory experiments. This is probably due to the presence of macropores (1-5 mm diameter holes) open to the surface. Atrazine was detected at the 26.25 cm depth one month after application. At two and four months after application, the atrazine concentration was minimal, especially in the lower depths. This is probably due to low concentration of atrazine available for leaching.

Average bromide concentrations as a function of soil depth for the five sampling dates are shown in Figs. 3-7. Bromide moved to the 30 cm depth within the first week after application. After one month after application, bromide was detected at a depth of 80 cm. This is explained by the lower retardation of bromide relative to atrazine in the soil.

The highest concentration (peak concentration) of bromide seven days after application is at the soil surface (Fig. 3). At 30 days after application, the peak has moved down to the 40 cm depth, and at 60 days after application to the 60 cm depth. All soils have similar results for the first 60 days. However, on later dates, there are variations in the depth at which the peak concentration occurs. At 90 days after application, the peak



concentrations were at about 95 cm, 80 cm, and 60 cm for soils 1, 2, and 3, respectively. At 120 days after application, the peak concentrations were at about 110 cm, 80 cm, and 60 cm for soils 1, 2, and 3, respectively. The depth of peak concentration was highest in soil 1 and least in soil 3. These differences could be due to differences in the water holding capacity of the soils. Soil 1 had a lower water holding capacity due to a coarser texture compared to soils 2 and 3. Therefore, a given amount of precipitation could have penetrated to a deeper soil depth in soil 1. Another reason for these differences could have resulted in poorer plant growth and subsequent lower transpiration in soil 1 compared to soils 2 and 3.

## DISCUSSION

There are several factors related to the persistence of atrazine in soils. Some knowledge of these factors is needed in order to be able to describe the process of atrazine movement in soils. One of the most important of these factors is probably the organic matter content of the soil. Huang et al., (1984) found that the rate of adsorption of atrazine by soils decreases significantly after the removal of the organic matter. This might be a reason for atrazine to be retarded in the upper horizons and subsequently degraded due to higher temperatures and higher availability of light in the shallow soil layers of this experiment.

Harris and Warren (1964), and McGlamery and Slife, (1966) reported that the influence of temperature on the adsorption of atrazine by soils seems to be quite variable with the nature of the soil components. Atrazine was allowed to be adsorbed on selected particle size fractions ranging from very coarse sand (1 to 2 mm) to fine clay particles ( $<0.2 \mu\text{m}$ ). The particle size fractions of 5 to 20, 2 to 5, 0.2 to 2, and  $<0.2 \mu\text{m}$  were important in the adsorption of atrazine. The adsorption of atrazine molecules by soil components involve van der Waals forces, hydrogen bonding, ion-dipole and coordination types of interaction (Bailey and White 1970). Therefore, finer-textured soils would cause greater retardation of atrazine. In this study, there was not a great range in soil textures and therefore the results were similar in all soils.

Acidity is another factor influencing the degradation of atrazine in soils. Hydrolysis of atrazine is highly controlled by soil pH and organic matter content of the soil (Armstrong et al., 1967). The most rapid rate of atrazine degradation occurred in the most acid soil in the investigation by Armstrong et al. (1967) and for soils with similar pH, atrazine degradation rates increased with increased atrazine adsorption. Since the pH decreases with soil depth in the present study, significant hydrolysis of atrazine could occur which would lower the atrazine concentration at deeper soil depths.

It was found that the atrazine concentration was always highest in the upper soil layers. One reason for this is probably no-till management. Under no-till system, like that used in this study, less mechanical dilution of herbicides occurs and soil covered by stubble is heated less rapidly thus reducing degradation. Also greater surface soil compaction under reduced tillage may decrease herbicide leaching. However, higher soil water content in weed-free, no. till areas should enhance degradation (Wicks and Smika, 1973). Ghadiri et al. (1984) found that the persistence of atrazine is greater under a no-till system as compared to conventional tillage. Dissipation of atrazine was found to be similar in conventional-till and no-till systems and the half life of atrazine in the surface 10 cm of soil was estimated by linear regression to be approximately 42 and 50 days in conventional-till and no-till plots, respectively. The half life of atrazine in this experiment, which was estimated to be 40 days at most, was less than 68 days which was reported

by Jury et al., (1984). This suggests that atrazine was lost at a higher rate during this study.

Atrazine moved to a depth of 22.5 cm and 30 cm, seven days and 30 days, respectively, after application. This indicates that under suitable environmental conditions, atrazine has the potential to contaminate groundwater. There are several factors directly involved in relation to the study of the environmental fate of atrazine. A better and detailed information of these factors is very important in predicting the potential for atrazine to contaminate groundwater.

## SUMMARY AND CONCLUSIONS

This study was conducted to evaluate the leaching and degradation characteristics of atrazine and bromide under no-till irrigated management. Atrazine moved to the depth of 22.5 cm and 30 cm depth, seven days and 30 days, respectively, after application. Atrazine was detected at very low concentrations at two months and four months after application. Although extreme variability in atrazine concentrations occurred, the variations were not explained totally by differences in soil texture. Bromide moved to a depth of 35 cm and 80 cm, seven days and 30 days, respectively, after application. The soil depth with the highest concentration of bromide within 60 days after application was similar in all soils. However, there were differences in the depths where the peak concentrations occurred between the different soils of this study.

Based on the data of the present study, atrazine does appear to have some potential for groundwater contamination. However, a better knowledge of the factors influencing atrazine leaching in soil is needed to better predict the potential for atrazine contamination of groundwater.

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## LIST OF TABLES AND FIGURES

- Table 1. Number of samples removed from the experimental site for atrazine and bromide analysis as a function of sampling date.
- Table 2. Monthly and seasonal irrigation and rainfall data for the experimental site during 1987.
- Figure 1. Distribution of soils, designated by differences in surface texture, at the experimental site.
- Figure 2. Diagram of the experimental site outlining plots, atrazine and bromide sampling locations, and locations of access tubes.
- Figure 3. Mean solute concentration vs. soil depth measured 7 days after application.
- Figure 4. Mean solute concentration vs. soil depth measured 30 days after application.
- Figure 5. Mean solute concentration vs. soil depth measured 60 days after application.
- Figure 6. Mean solute concentration vs. soil depth measured 90 days after application.
- Figure 7. Mean solute concentration vs. soil depth measured 120 days after application.
- Figure 8. Mean atrazine concentration vs. time after application at four selected depths.



Table 1. Number of samples removed from the experimental site for atrazine and bromide analysis as a function of sampling date.

Date	Maximum Soil Depth		# of Samples	
	Atrazine	Bromide	Atrazine	Bromide
May 20	3.0*	3.0*	14	14
May 27	60	60	160	392
June 20	90	90	160	588
July 20	120	120	240	784
August 20	***	120	***	784
September 20	150	150	400	980
Total			1134	3542

\* Surface samples

\*\*\* No atrazine samples were removed on this date.

Sample size: 7.5 cm diam. x 4.8 cm long.

Table 2. Monthly distribution of irrigation and rainfall for the experimental site during 1987.

Type	Month					Season Total
	May	June	July	Aug.	Sept.	
Irrigation (mm)	12.2	53.3	105.7	64.0	20.3	255.5
Rainfall (mm)	21.8	29.2	40.9	3.48	16.0	142.7
Total (mm)	34.0	82.5	146.6	98.8	36.3	398.2

Fig. 1. Distribution of soils, designated by differences in surface texture, at the experimental site.

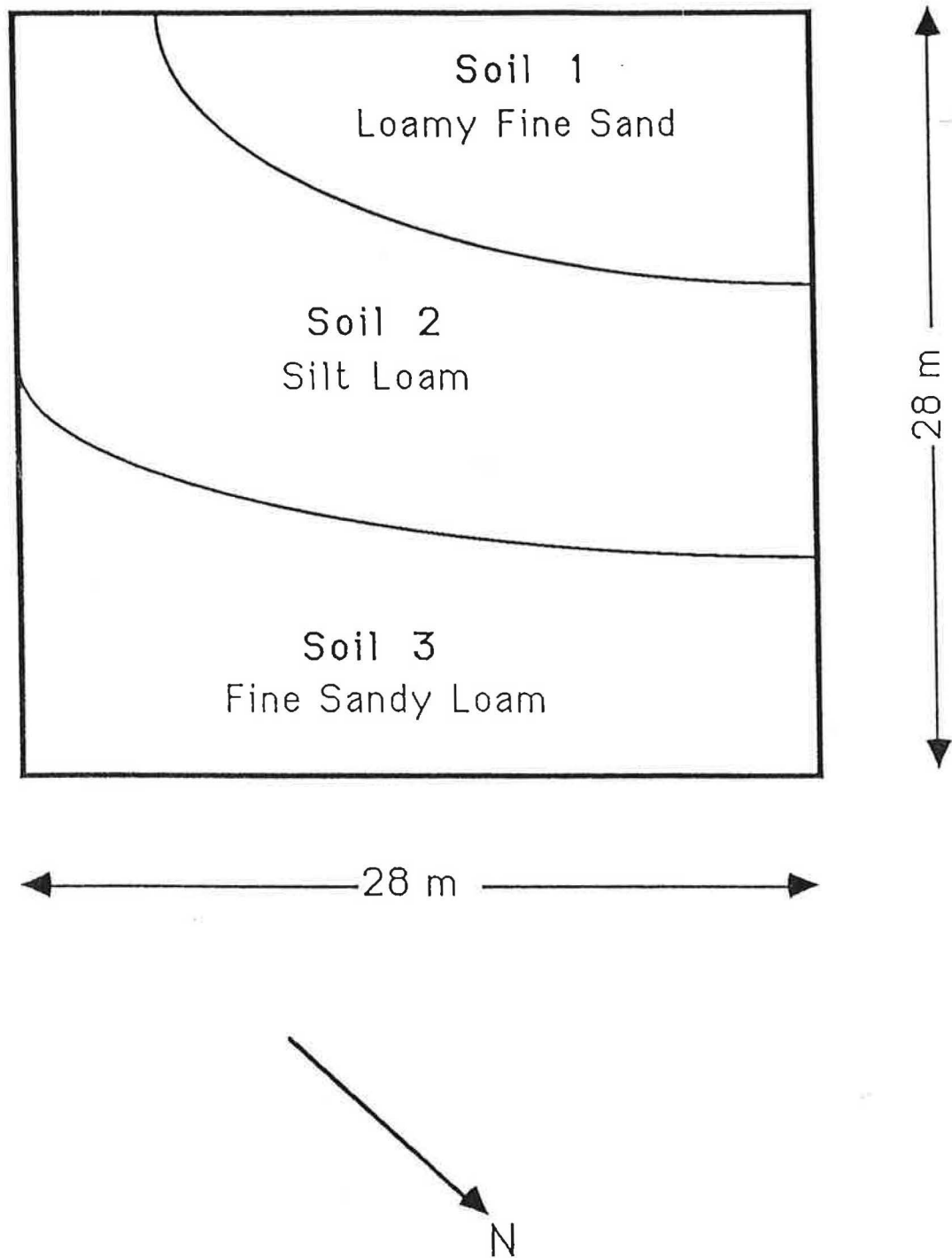
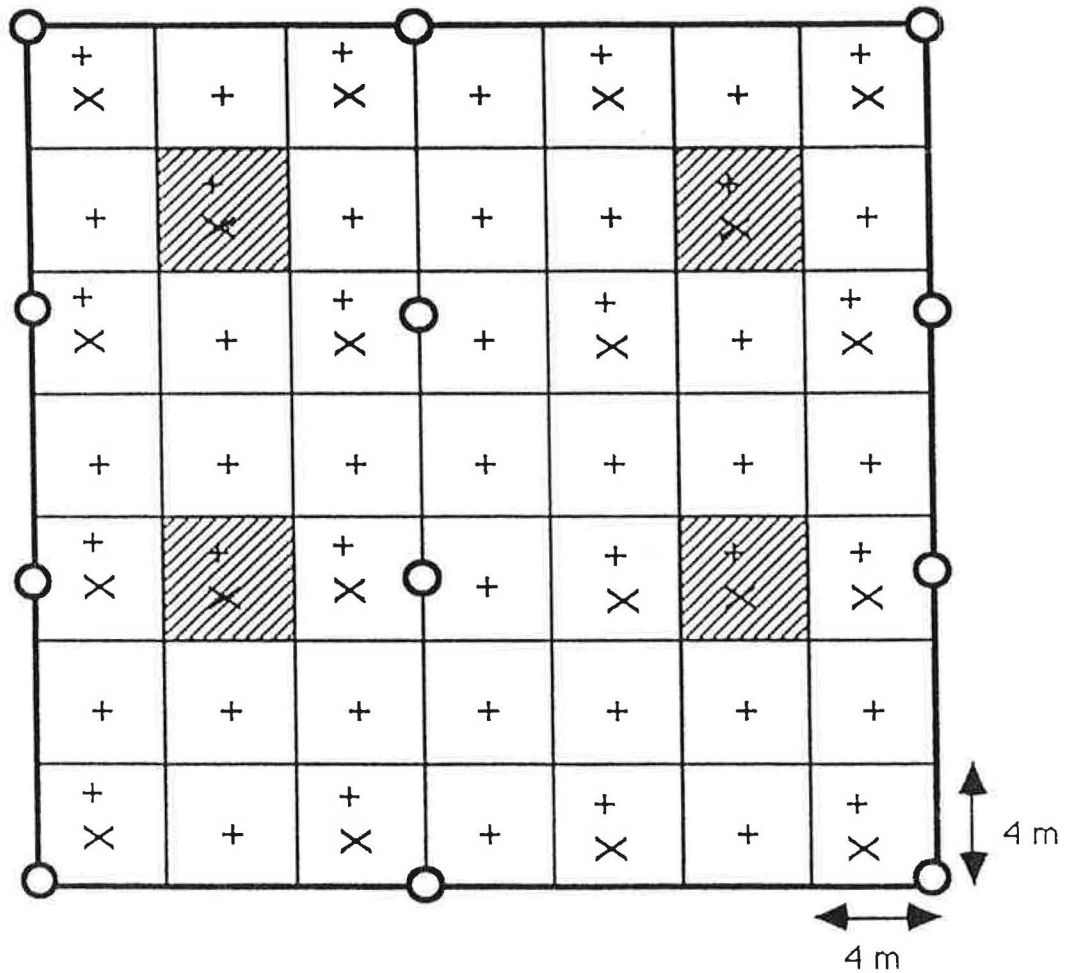


Fig. 2. Diagram of the experimental site outlining plots, atrazine and bromide sampling locations, and locations of access tubes.



- + Bromide Sampling Site
- × Atrazine Sampling Site
- Neutron Meter Access Tube
- ▨ Control Plot

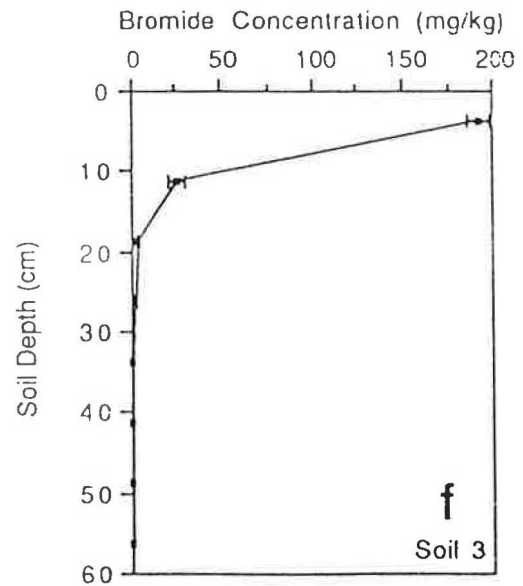
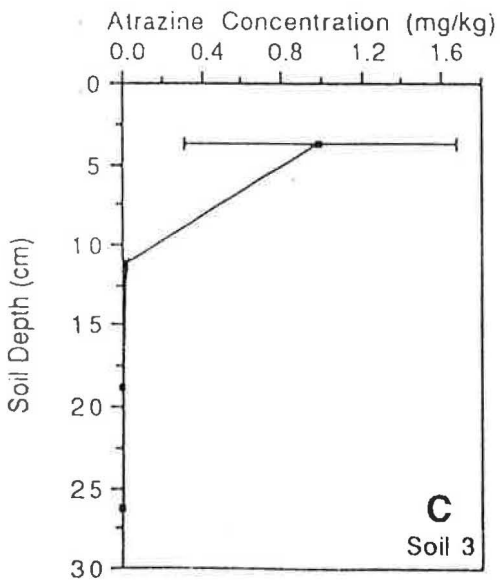
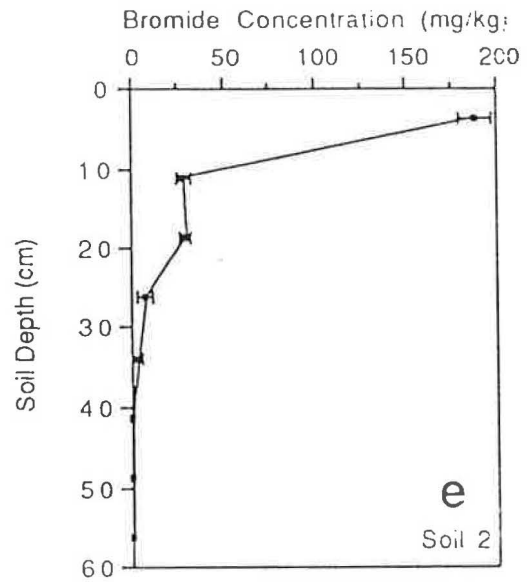
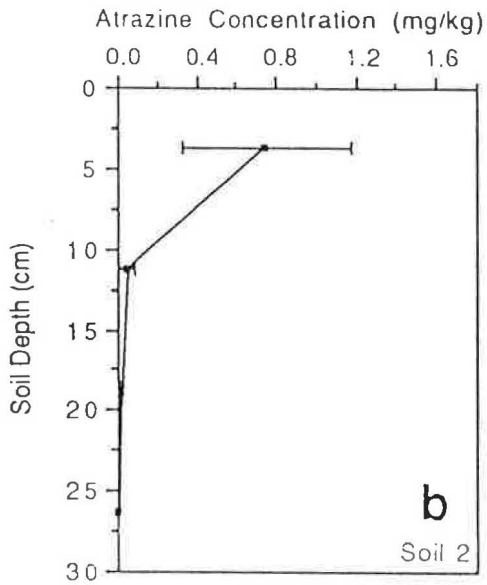
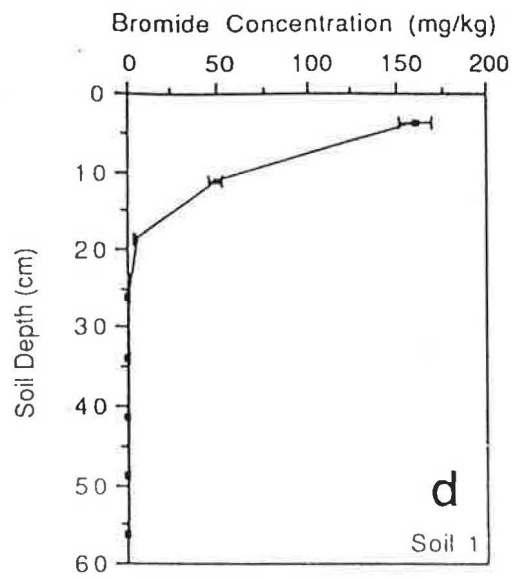
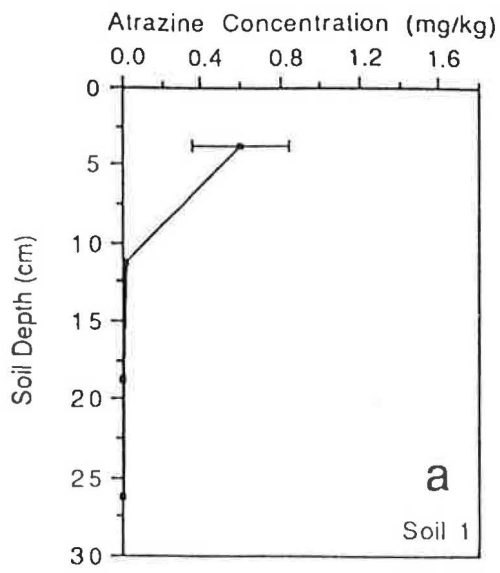


Fig. 3. Mean solute concentration vs. soil depth measured 7 days after application: (a) atrazine in soil 1, (b) atrazine in soil 2, (c) atrazine in soil 3, (d) bromide in soil 1, (e) bromide in soil 2, and (f) bromide in soil 3. Standard deviations are represented by horizontal lines.

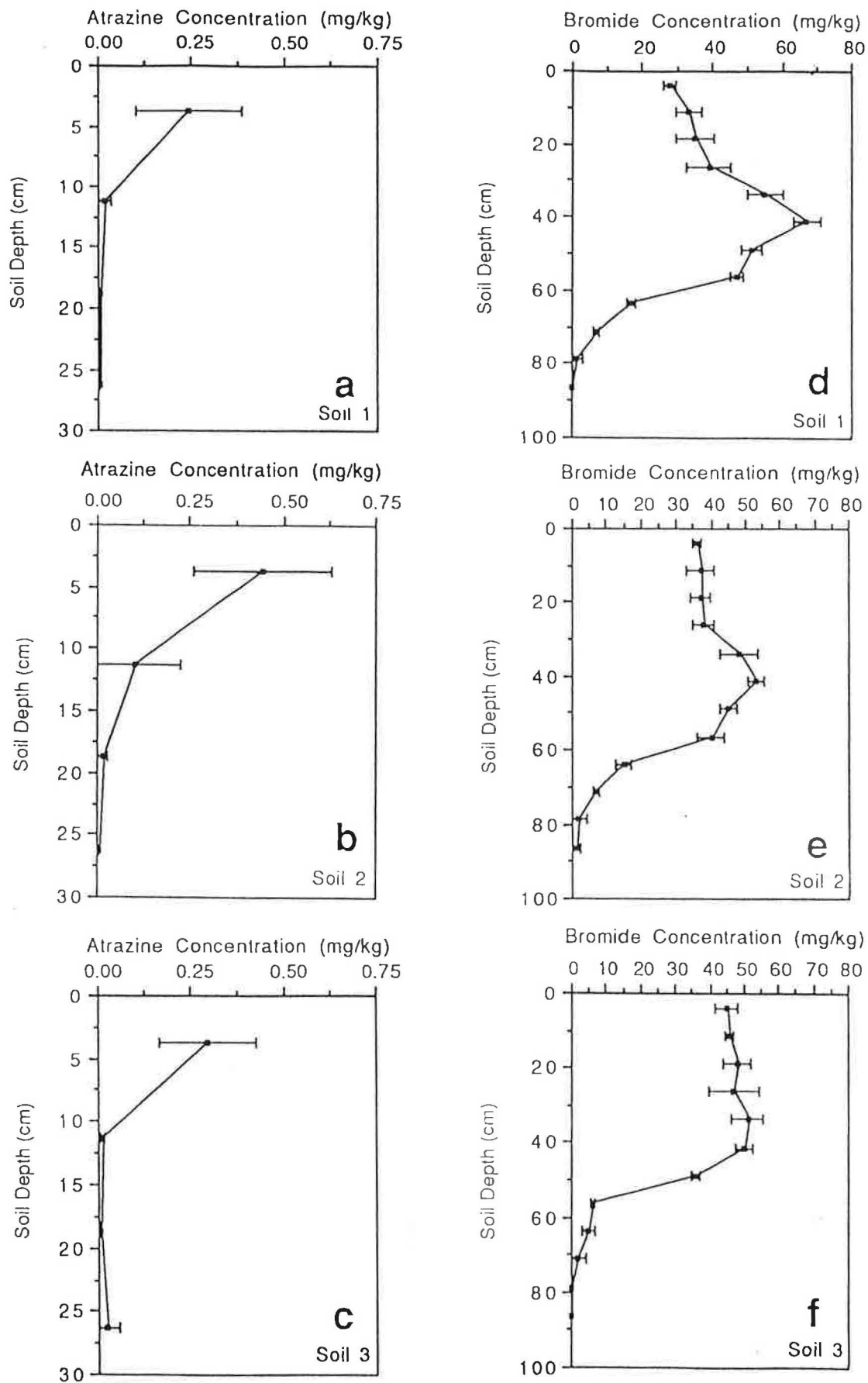


Fig. 4. Mean solute concentration vs. soil depth measured 30 days after application: (a) atrazine in soil 1, (b) atrazine in soil 2, (c) atrazine in soil 3, (d) bromide in soil 1, (e) bromide in soil 2, and (f) bromide in soil 3. Standard deviations are represented by horizontal lines.

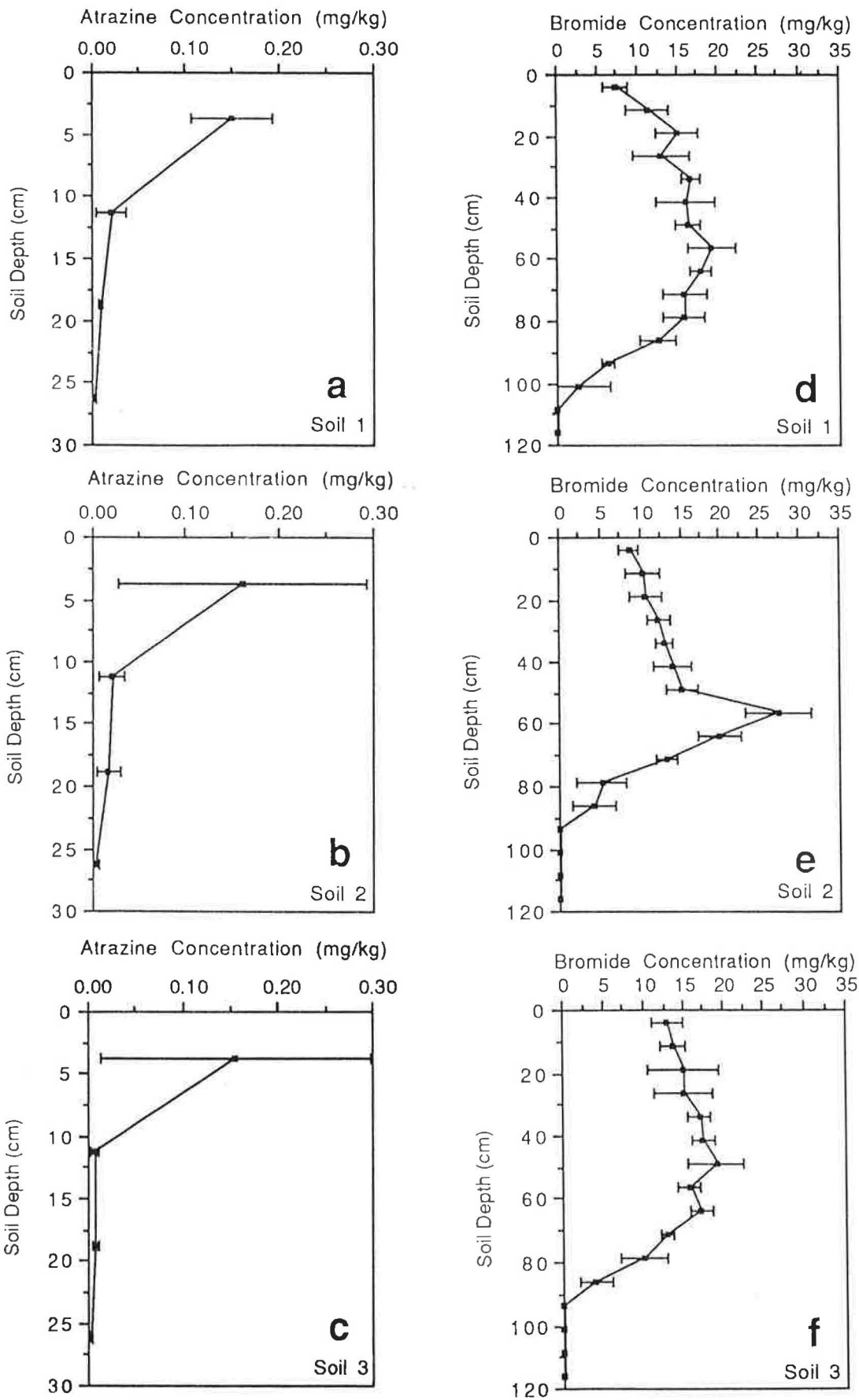


Fig. 5. Mean solute concentration vs. soil depth measured 60 days after application: (a) atrazine in soil 1, (b) atrazine in soil 2, (c) atrazine in soil 3, (d) bromide in soil 1, (e) bromide in soil 2, and (f) bromide in soil 3. Standard deviations are represented by horizontal lines.

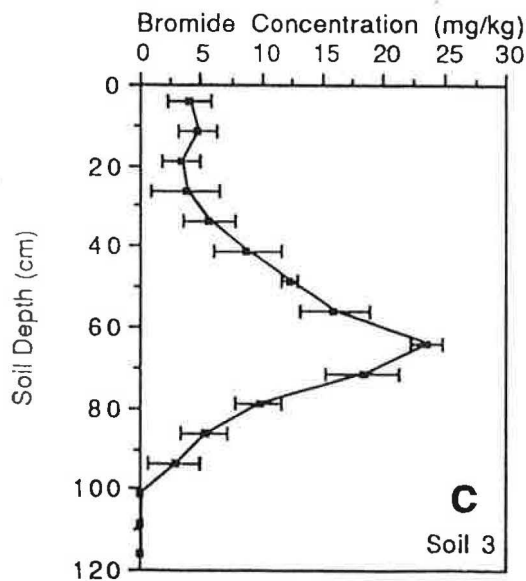
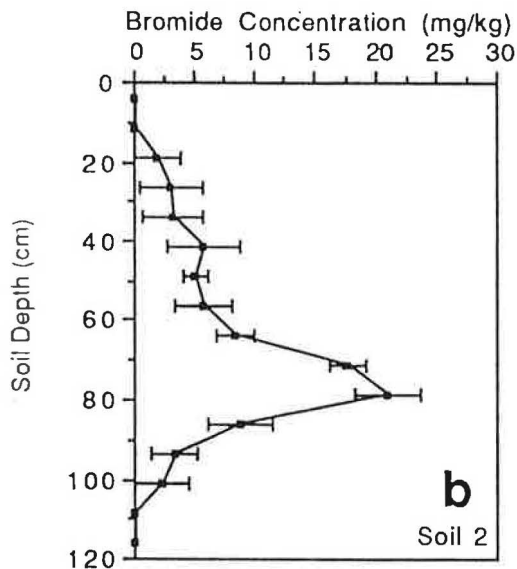
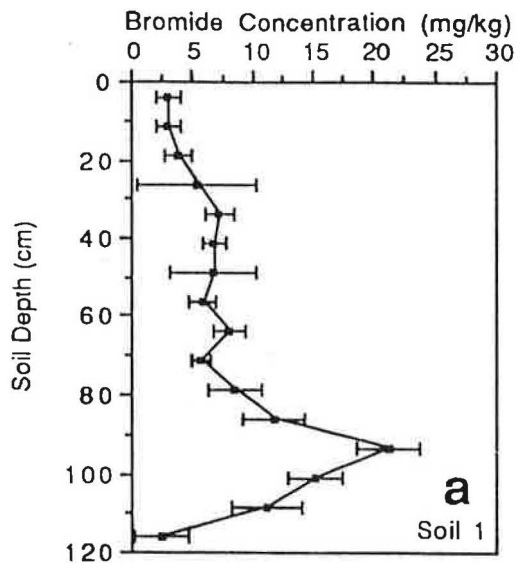


Fig. 6. Mean solute concentration vs. soil depth measured 90 days after application: (a). bromide in soil 1, (b) bromide in soil 2, and (c) bromide in soil 3. Standard deviations are represented by horizontal lines. (No atrazine samples were taken on this date.)



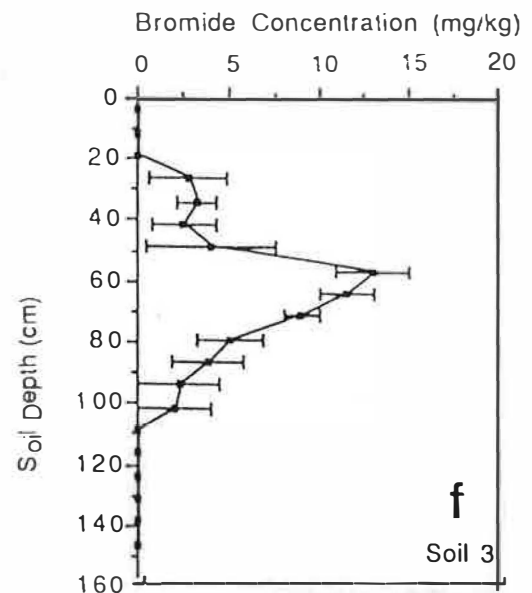
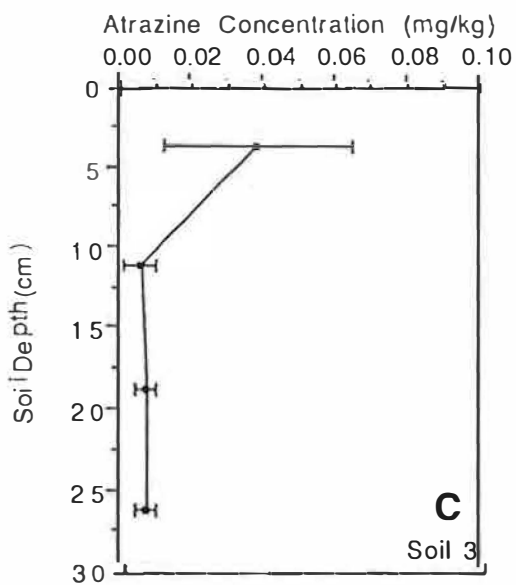
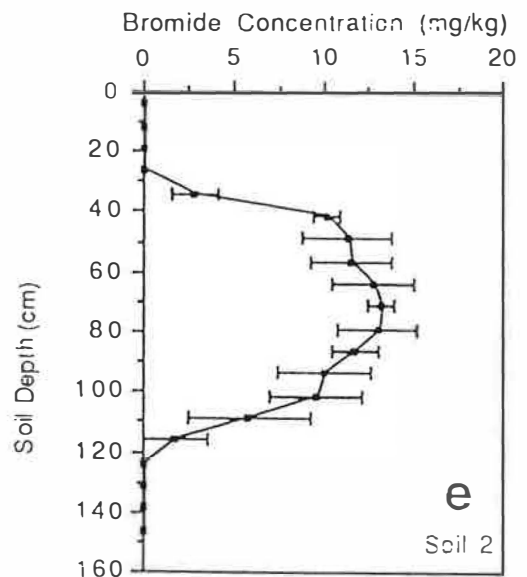
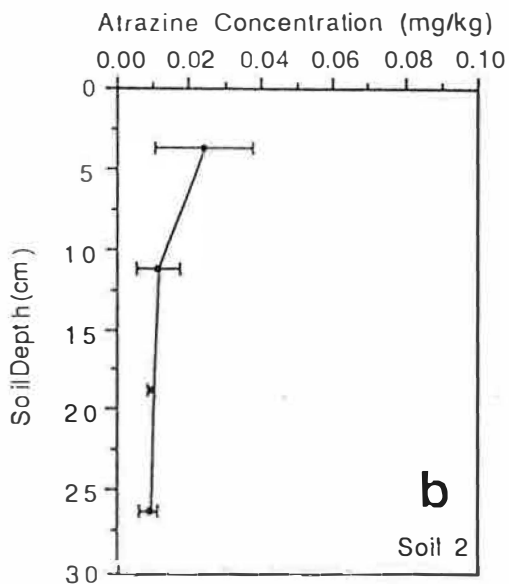
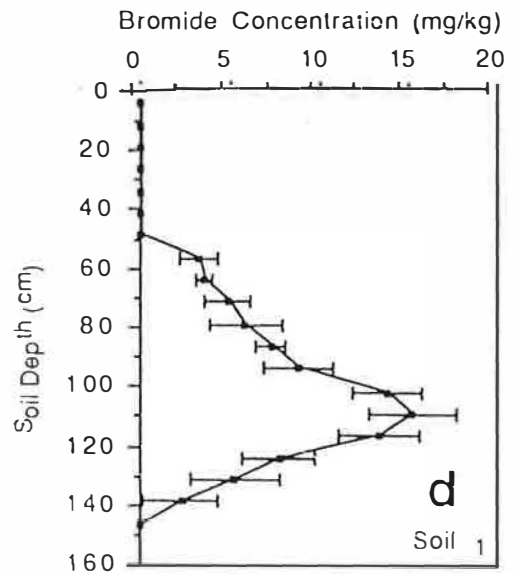
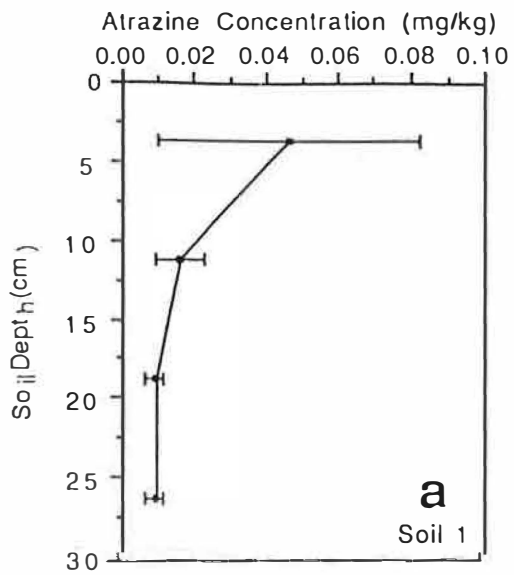


Fig. 7. Mean solute concentration vs. soil depth measured 120 days after application: (a) atrazine in soil 1, (b) atrazine in soil 2, (c) atrazine in soil 3, (d) bromide in soil 1, (e) bromide in soil 2, and (f) bromide in soil 3. Standard deviations are represented by horizontal lines.

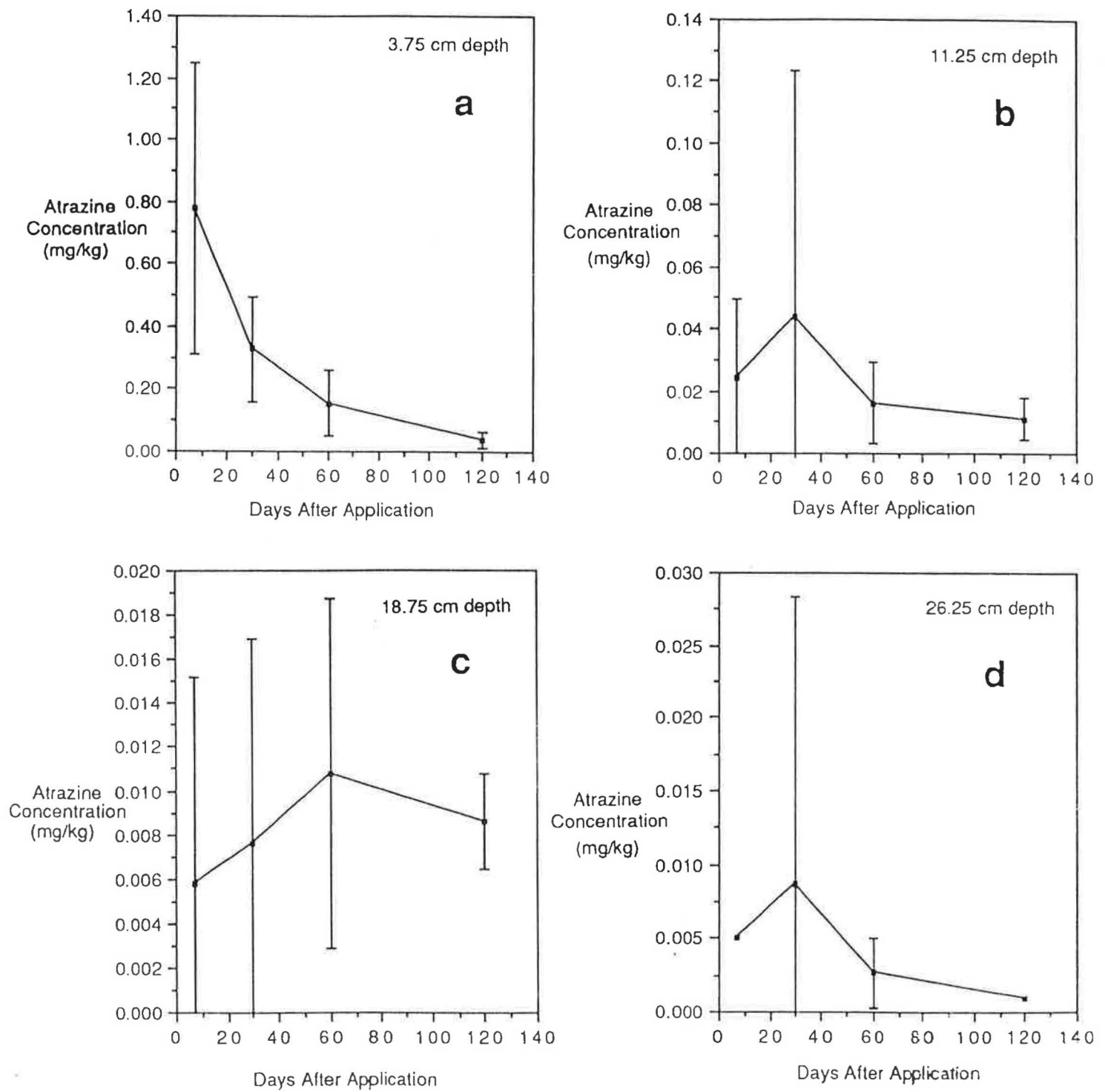


Fig. 8. Mean solute concentration vs. time after application at four selected depths: (a) 3.75 cm depth, (b) 11.25 cm depth, (c) 18.75 cm depth, and (d) 26.25 cm depth. Standard deviations are represented by vertical lines.