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Movement and Aquifer-Contamination Potential of Atrazine and Inorganic Chemicals in Central Kansas Croplands

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Abstract

Two flooding experiments were conducted at two sites with different soils to study the transport and fate of the commonly used herbicide atrazine and inorganic chemicals in the Great Bend Prairie croplands. The instantaneous profile method supplemented by the use of an organic (atrazine) and an inorganic (bromide) tracer chemical were used to characterize in situ the hydraulic and chemical properties of the appropriately instrumented field sites. Atrazine readily degraded into hydroxyatrazine and biodegradation by-products and was not detected deeper in the soil profile and underlying shallow aquifer. The classical processes of chemical movement based on porous media–equilibrium–diffuse flow did not fit the data well at either site. Evidence that incompletely mixed, slug flow predominates at one of the sites and preferential flow at the other is documented. As a result of the observed slug movement, "piston-type" displacement of more saline solutions in

the soil profile to the shallow water table occurred. Relatively high nitrate concentrations both in the vadose and in the aquifer zones were observed in one of the sites, which is characterized by sandy soil. The nitrate data indicates a close relationship between N–fertilizer application, irrigation, and nitrate movement into the subsurface. Finally, recommendations for conducting related field studies based on our sampling experience are given, and suggestions for further research are outlined.

Statement of the problem

Recent incidents of chemical contamination of ground water by pesticides and other agricultural chemicals, such as nitrogen fertilizers, in surrounding states and in Kansas have increased concern for long-term environmental consequences of current agricultural practices on ground-water quality, especially regarding the high toxicity and health implications of such agrichemicals on both humans and animals. A recent epidemiological study of occurrences of non-Hodgkins lymphoma (NHL) in Kansas found farm herbicide use to be highly associated with NHL. The study suggests that NHL occurrence is associated with the number of days of exposure to herbicides per year (Hoar et al., 1986). A Kansas farmstead study (Steichen et al., 1988) indicated that of the 103 statistically representative samples collected statewide, 29 had nitrate levels above the maximum contaminant level for drinking water and 8 had detectable pesticides, atrazine being the only pesticide detected more than once (present in 4 wells). However, the sources of these contaminants have not been determined. Studies in Iowa indicate an increase in nitrate concentration from 3 mg/L to 10.3 mg/L NO_3–N from the 1950's to 1983 (Hallberg, 1985). Also, pesticides and elevated nitrate concentrations were present in all types of aquifers statewide in Iowa: glacial, alluvial, carbonate, and bedrock indicating a nonpoint source problem (Hallberg, 1985). Atrazine persisted in ground water year-round in both Iowa and Nebraska (Hallberg, 1985;

Wehtje et al., 1983). Pesticides were also detected in public water supplies, particularly those in shallow alluvial systems and surface waters (Kelley and Wnuk, 1986; Baker et al., 1985).

Table 1. Summary of Prominent Facts about the Constituents of Principal Concern in Ground Water Underlying Cropland (Adapted from CAST)

Constituent	Sources	Soil Processes Affecting the Amount Lost to Groundwater	Tendency to Move Downward through Soils in Percolating Water	Comments
Soluble salts	Irrigation water Organic materials Fertilizers Weathering of minerals Rainfall	Precipitation and dissolution of carbonates and sulfates Weathering of soil minerals Absorption/cation exchange	High	Must be leached from most irrigated soils to maintain crop production
Nitrate	Nitrogen fertilizers Organic materials Atmospheric nitrogen fixed by legumes Rainfall	Production and removal by microorganisms Removal by plants	High	Loss to groundwater is incidental to water movement and is a loss to crop production potential
Pesticides	Commercial products	Retention by soil Decomposition Volatilization Removal by plants	Varies widely among pesticides and soils	Principal occurrences in ground water result from pesticides that remain in solution in the soil, are not decomposed rapidly, and are applied to sandy soils with ground water near the surface and with much water movement through the soil to ground water

Recently discovered incidences of ground-water pollution from agrichemicals throughout the United States and the resulting series of environmental laws regulating the use or disposal of chemicals on land surfaces have created a new surge of interest in field-scale solute transport studies. Table 1 from the 1985 Agriculture and Groundwater Quality report by the Council for Agricultural Science and Technology (CAST), summarizes some facts about the constituents of principal concern in croplands overlying significant ground-water aquifers. The transport of dissolved chemicals with flowing water has been studied for many years under controlled laboratory conditions but has received relatively little experimental study under field conditions

(Biggar and Nielsen, 1967; Boast, 1973) until recently. As a result, most chemical transport models developed over the last decade for use in field-scale transport simulations use laboratory results to formulate transport equations (Anderson, 1979).

It is evident from the 1985 CAST report that our knowledge of the behavior of agrichemicals in the environment and specifically their potential for moving to ground water is mostly qualitative. The interactions of the various processes and factors are not well understood. The proposed study was designed to address some of these problems.

The Great Bend Prairie is a prime agricultural area in Kansas where the use of agrichemicals has been practiced for decades. However, until recently, no study has been conducted in that area to assess the impact of these practices on the Great Bend aquifer that yields water for irrigation, industrial, municipal, and domestic use.[1] Water resources of most of the Great Bend Prairie are locally managed by the Big Bend Groundwater Management District No. 5 (Fig.1), whose goal is to maintain adequate amounts of good quality water for present and future needs. Recent studies indicating aquifer pollution from agrichemicals in neighboring states with similar agricultural practices raised considerable concern in Kansas. Our initial conception was that, either the shallow aquifer of the region would contain appreciable amounts of various agrichemicals, such as nitrogen fertilizer derivatives and atrazine, or if the chemicals were not present in the aquifer, they would be held "in transit" in the unsaturated zone on top of the shallow clay layers in the region. This study was undertaken to provide some answers in this regard so that if significant concentrations of pesticides are found in the soils and ground water, proper measures, such as discontinued or limited use of certain agrichemicals in the affected area, could be taken.

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[1] The recently completed phase of the chemigation well water quality study in Kansas by the Kansas State Board of Agriculture (Anderson, 1989) included a 1988 summer survey of 38 wells from the Big Bend Groundwater Management District No. 5, but no pesticide was detected from that area. Also, according to the low sample density farmstead study (Steichen et al., 1988) no pesticide was detected in south-central Kansas.

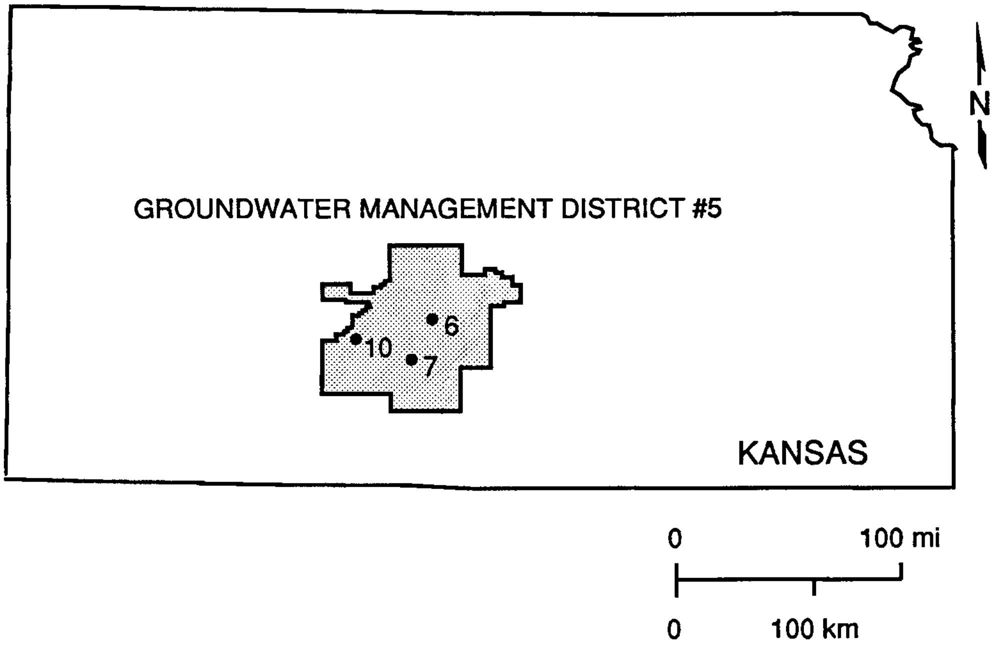

Figure 1. Location of field sites

Purpose and objectives

The purpose of this project is to determine the fate of agrichemicals commonly used in Kansas croplands in general and in the Great Bend Prairie in particular and to evaluate their potential to move through the soil profile into the underlying aquifer.

Atrazine is one of the most widely used herbicides in the Great Plains. According to the June 1987 issue of Chemical and Engineering News, about 36 million kilograms (79 million pounds) of atrazine active ingredient are used annually for weed control on corn and sorghum crops, and as a nonselective weed control herbicide on grain and pasture land. In Kansas it is the most commonly used herbicide, with nearly 2.5 million kilograms (5.5 million pounds) of atrazine or combinations including atrazine being applied to Kansas farmland in 1978 (Nilson and Johnson, 1980). Atrazine has been recently identified in ground water taken from aquifers underlying corn-growing areas in the Great Plains. It is also the most commonly detected pesticide in municipal and domestic wells in Kansas and Nebraska. Therefore this herbicide was chosen for further study under Kansas conditions.

The specific objectives of this project are: (1) to measure and evaluate the movement of a routinely applied agrichemical in the soil profile, the herbicide atrazine, and its ability to reach and pollute the underlying freshwater aquifer; (2) to test the validity and predictive capabilities of existing numerical simulation approaches to subsurface organic chemical transport; and (3) to assess the relationships among land use, ground-water recharge, and movement of agrichemicals in the unsaturated zone and aquifer.

Related research

For a detailed literature review, the reader is referred to Appendix A. A brief summary account on atrazine and nitrate is presented here.

Atrazine

The movement of atrazine and other herbicides is dependent on a variety of factors, for example, organic matter and clay content, pH of the soil and water, temperature, presence or absence of bacteria, and soil texture. Many of the studies that have been done in the past are laboratory studies that use repacked soil columns or small soil samples as medium. These studies are very useful for determining basic chemical processes that affect the movement of these chemicals. However, these studies cannot evaluate the field situation. In a farm field various other factors come into play, such as the presence or absence of routes of preferential flow (macropores caused by worms, plant roots, or small fractures), incompletely mixed parcels of water and chemical solutions, and slug and blob flow.

Degradation of atrazine is strongly dependent on the soil environment (Sheets, 1971). The physical characteristics of the soil, aeration, inorganic and organic nutrients, soil pH, quantity of clay and organic matter play a major role in the chemical and biological degradation of atrazine. Microbial degradation results in N-dealkylation of atrazine side chains (Fig. A1) to produce deethylated atrazine and/or deisopropylated atrazine (Kaufman and Kearney, 1970). Microbial degradation is temperature- and moisture-dependent, and increases with soil organic carbon and associated nutrients (Skipper and Volk, 1971) which are the major constituents of microbial food. Microbial community size in mineral soils has been directly relateto organic matter content (Alexander, 1977). Chemical degradation is characterized as a hydrolysis reaction at the number two carbon of the atrazine ring to produce hydroxyatrazine. Adsorption onto soil colloids is a prerequisite for hydrolysis (Armstrong et al., 1967). Atrazine adsoprtion onto clays and organic matter increases markedly as pH decreases below 6 (Bailey et al., 1968). Chemical hydrolysis of atrazine has been shown to be the predominant degradation route, especially at pH levels less than 6 (Skipper et al., 1978). Appendix A summarizes most aspects of atrazine degradation and movement in soils.

As the literature review (Appendix A) indicates, there is much controversy on the movement of herbicides through the soil to ground water. Many states, such as Nebraska and Iowa, are finding the chemicals in their alluvial aquifers but are only beginning to evaluate the role of soil in preventing or permitting the movement. Studies in Kansas indicate atrazine in surface waters as a result of attachment to soil particles and movement resulting from runoff from fields (Gilliom et al., 1985). The occurrence of atrazine in the ground water is limited, and the chemical has not been detected unless there was a spill or some other mitigating circumstance.

Nitrate

Studies of the movement of nitrate in soils and ground water indicate that there is a growing problem throughout the United States. Much of the research done on the occurrence and migration of nitrates through soil to ground water increasingly indicates that nitrate contamination is a nonpoint source problem. Much of the work cited in the literature review (Appendix A) suggests that fertilizer use in conjunction with excess precipitation and/or irrigation practices may be a primary source for the nitrate. Several states, such as Nebraska and Iowa, have shown that a combination of sandy soil conditions, fertilizer use, and irrigation has caused a widespread problem. Work in Kansas indicates that there is a trend toward increased nitrate in ground water.

Studies in Nebraska and California indicate that there is also the potential for contamination from oxidation of nitrogen bound up in rocks and sediments. Sediment type, potential for oxidizing conditions, and quantity of organically bound nitrogen are the major controls on the formation and movement of nitrate from sediments and rocks.

The occurrence of nitrate in ground water is a potential public health problem and a potential irrigation problem for economical crop management. In addition, occurrence of pesticides in ground water may mirror the nitrate problem. That nitrates move through the system may indicate that pesticides can also move in certain circumstances.

Site selection and instrumentation

A field approach was used to determine the in situ processes involved in the movement and fate of agrichemicals in soils and underlying aquifers. Three field sites in the Great Bend Prairie region were instrumented to monitor the movement and fate of agrichemicals (Fig. 1). Two sites [site 6 (T23S R12W Sec. 36 BDCA) and site 7 (T26S R14W Sec. 11 ADAB); Fig. 1] characterized by different soil types but used for growing the same crop (irrigated corn) were examined in detail. A third site [site 10 (T25S R19S Sec. 1 DDCD); Fig. 1], which is not cultivated (pasture land) and on which agrichemicals have never been used, was selected as the background (pristine) site.

All three sites were instrumented with a number of observation wells screened at different depth intervals, a neutron-access tube for monitoring soil moisture, tensiometers at various depths, and a recording rain gauge. This instrumentation was deemed the minimum necessary for characterizing soil-water movement (the agrichemical transporting vehicle) through the soil to the underlying aquifer. The two sites located on corn fields included additional instrumentation: a weather station, a number of suction lysimeters installed at 15, 30, 60, 90, 120, 150, and 180 cm (1/2, 1, 2, 3, 4, 5, and 6 ft) depths and 11 thermistors to measure soil temperatures from the near surface to 275 cm (9 ft) below ground surface. A schematic layout of the instrumentation at each site is shown in Figure 2.

Methodology

Because of their chemical nature, organic chemicals interact with soil, water, and biota when applied to farmland. It is generally useful to study simultaneously the behavior of both reactive and nonreactive or conservative chemicals, such as bromide to contrast and elucidate this interactive behavior. Bromide is superior to other halogens as a tracer in soil-water systems (Jester and Uhler, 1974). Some of its advantages are its low background levels in the environment and its

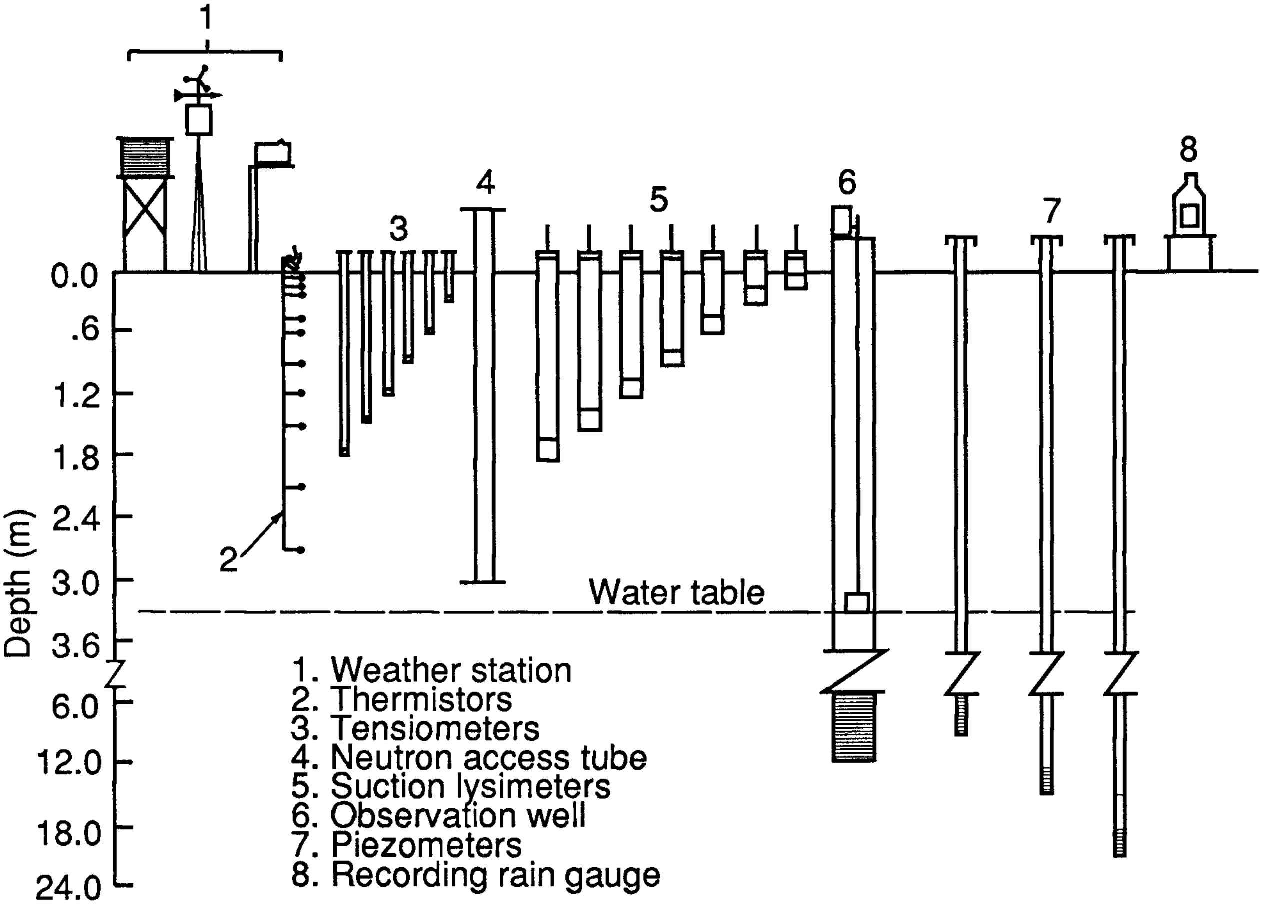

Figure 2. Schematic layout of site instrumentation

low toxicity to plants and animals. Therefore we studied the simultaneous movement of both an organic and a conservative inorganic tracer by running flooding experiments in each of the two sites designated for detailed study. For each experiment a commonly used organic chemical (atrazine) and a suitable conservative tracer (bromide) were used with the flooding water. The purpose of the flooding experiments was not necessarily to simulate actual field conditions (although flood irrigation may be reasonably simulated with our flooding experiments) but to evaluate the potential of atrazine leaching to the water table under highly favorable conditions.

Because of the importance of the soil environment in controlling the movement and degradation of atrazine, a detailed study of the soil profiles of the selected sites was conducted before the flooding experiments. Trenches for detailed soil sampling and analysis were excavated to at least 2 m (~ 7 ft) depth next to the test sites. With the assistance of the Soil Conservation Service (SCS) Lincoln Laboratory, we determined the following soil- and water-related properties: detailed and complete soil description, textural analysis, organic carbon, cation exchange capacity, bulk density, water content at various applied pressures, extractable ions, soil pH, electrical conductivity, clay mineralogy, and various other physical and chemical soil analyses

The flooding experiments had a dual purpose: (1) to study the relative movement of a conservative tracer and an organic chemical in two different soil profiles, and (2) to derive the hydraulic conductivity function of the soil profile through the instantaneous profile method.

We used the following procedure for the flooding experiments. The grassy area around the tensiometers, suction lysimeters, thermistors and neutron access tube was mowed as close to the ground as possible. Planks 244 cm (8 ft) by 40 cm (1.3 ft) were connected with door hinges to form a hexagonal (site 6) or rectangular (site 7) shape. The structure was secured by a 5–8 cm (2 –3 in.) groove dug around the inner perimeter and wooden stakes at the outside of the planks at the mowed site, forming a diked enclosure of 14–15 m^2 (150–160 ft^2) around the instrumentation and shallowest observation well. The planks were covered with 3–5-ml thick plastic sheeting. The outer perimeter of the diked area, which was also mowed, was wetted to reduce subsurface lateral fluid movement from the area to be flooded and covered with heavy black plastic. Then the diked area was flooded with the prepared chemical solution (site 7) or preflooded with municipal water from Stafford, Kansas, the nearest city, followed by the chemical solution (site 6). When the readings from the deepest tensiometers [150–180 cm (5–6 ft) deep] indicated near steady-state conditions, addition of the chemical solution to the diked area was stopped. At that time the chemical solution ponded to 5 to 10 cm (2 to 4 in.). As soon as the ponded solution infiltrated, the planks were removed and the flooded area was covered with heavy black plastic to prevent evapotranspiration and infiltration of rain.

Before, during, and especially immediately after covering the site with plastic, frequent instrument readings and sampling were conducted for a period of two to three months. Soil cores 2.3-cm (1 in.) in diameter and 30-cm (1 ft) long were collected periodically for measurement of atrazine concentrations. The surface 30 cm (1 ft) core was divided into four 7.5–cm (3–in) core increments, and all the rest into 15–cm (6–in) long increments for analysis. Field measurements of water conductance, temperature and pH accompanied most water sampling. For logistics reasons, the flooding experiments were initiated on September 9, 1987, for site 6, and on October 7, 1987, for site 7 right after the corn had been harvested. The plastic cover was removed from both sites in December 1987, after snow had already covered the sites.

Installation and calibration procedures

Observation wells

Observation wells at the sites consisted of two types: 5–cm (2–in) water-quality monitoring wells, and 13–cm (5–in) water-level monitoring wells. Extra precautions were taken during installation of the water-quality monitoring wells to prevent contamination through drilling procedures. A hollow-stem auger rig was used to drill all 5 cm (2 in.) wells. Clean rubber gloves were used to handle PVC casing and auger flights. Each auger flight section was washed with potable water, then acetone, and rinsed with potable water (the potable water tested negative for atrazine). During augering, cuttings were removed from the edge of the augered hole. Both PVC well-screen and casing were washed with potable water, scrubbed inside and outside with acetone, and thoroughly rinsed with potable water. When the desired well depth was reached, the screen and casing were lowered inside the hollow auger stem using thoroughly cleaned vise grips to hold the casing. The hollow stem auger was then filled with potable water to prevent sand from lodging between the casing and the hollow stem once the stainless steel plate at the bottom of the auger was knocked out. The auger flights were then pulled out of the hole leaving the well casing in place. The hole was then gravel packed using coarse sand to 1.5 m (5 ft) above the top of the screen. From the top of the gravel pack to the surface, the hole was filled in with Volclay. Well development was achieved by bailing using a 0.9–m (3–ft) Teflon or a 1.8–m (6–ft) PVC bailer for the shallower wells or a PVC Brainard-Kilman hand pump. The bailers and hand pump were cleaned with acetone and water between sampling of different wells.

The 13–cm (5–in) water-level observation wells were constructed using a mud rotary drilling rig. After reaching the desired depth, the mud was flushed out of the hole by pumping fresh water down through the drill stem, forcing the mud out through the annular space of the drilled 20–cm (8–in) hole. The drilling mud was then pumped out of the mud pit. The 13–cm (5–in) PVC screen and casing were then set to the proper depth, followed by dumping fine gravel into the water-filled hole, thus displacing the water up and out of the well. The gravel packing continued until the gravel reached approximately 1.5 m (5 ft) above the top of the screen. Bentonite pellets were then inserted around the casing on top of the gravel pack, followed by bailing a few casing volumes so as to pull the bentonite plug down on top of the gravel pack. Volclay grout was then pumped in through a tremie pipe until it reached the ground surface. After letting the grout settle for a few days, the well was completely developed by bailing, by pumping water out of the well, or by air lifting.

Table 2 summarizes all the well information at the three sites. It should be noted that these sites are part of a larger network of sites monitored year-round for ground-water recharge estimation.

Table 2: Summary data on observation wells at the three study sites.

Site	Observation well diameter cm	(in.)	Total depth m	(ft)	Screen interval m	(ft)	Water Level Recorder
6	5	(2)	6.1	(20)	4.6 – 6.1	(15–20)	
6	5	(2)	10.1	(33)	8.5 –10.1	(28–33)	
6	5	(2)	13.7	(45)	12.2 –13.7	(40–45)	
6	13	(5)	16.5	(54)	10.4 –16.5	(34–54)	yes
7	5	(2)	9.1	(30)	6.1 – 9.1	(20–30)	
7	5	(2)	15.2	(50)	12.2 –15.2	(40–50)	
7	5	(2)	21.3	(70)	18.3 –21.3	(60–70)	
7	13	(5)	12.0	(39.5)	5.9 –12.0	(19.5–39.5)	yes
7	13	(5)	24.4	(80)	21.3 –24.4	(70–80)	yes
10	5	(2)	13.7	(45)	10.7 –13.7	(35–45)	
10	5	(2)	18.3	(60)	15.2 –18.3	(50–60)	
10	13	(5)	16.8	(55)	10.7 –16.8	(35–55)	
10	13	(5)	19.8	(65)	13.7 –19.8	(45–65)	
10	13	(5)	27.4	(90)	24.4 –27.4	(80–90)	yes

Neutron probe access tubes

A 5–cm (2–in) galvanized steel pipe with its bottom rubber stopper sealed using adhesive sealant (to prevent water from entering the pipe) was used as an access tube for the neutron probe at each site. The access tube installation and probe calibration were performed simultaneously, as described in what follows:

A Madeira bulk-density sampler was driven at 15–cm (6–in) intervals into the ground. At each 15–cm (6–in) depth interval, the sampler was pulled out and putty knives were inserted into the sampler slots, thus isolating a known volume of soil (60 cm^3). Excess soil from both ends of the sampler were discarded, the putty knives were pulled out, and the known-volume soil sample was inserted into a plastic bag and weighed immediately so that soil-moisture loss from the sample was minimized. The 15–cm (6–in) hole depth interval was cleaned out with a 5–cm (2–in) hand auger, and the Madeira sampler was reinserted for another 15–cm (6–in) deep sampling. The process was repeated until the required depth was reached. For site 6 the augered depth was 320 cm (10.5 ft), and for site 7 it was 455 cm (15 ft). The access tube was then inserted into the 5–cm (2–in) hole with a tight fit and pushed down with a twisting motion, creating a snug fit. The neutron probe was then inserted into the access tube and three half-minute field neutron readings were taken at a depth interval of 15 cm (6 in.). A set of 10 standard count neutron readings were taken before inserting the probe in the access tube. The collected access tube soil samples were subsequently oven-dried, and the bulk density and moisture content on a dry weight basis were calculated, from which the volumetric water content was determined. The ratios (R) of field to standard neutron counts for all 15–cm (6–in) depth intervals were regressed against the corresponding measured volumetric moisture content values, and thus a regression equation was derived to convert neutron count readings to soil moisture content ($\underline{\theta} = -0.0672 + 0.2695\underline{R}$). A common calibration curve was developed by combining the calibration results from each site, as shown in Fig. 3, so as to increase significantly the number of data points in the regression analysis. A linear least-squares curve was fitted through the data with a correlation coefficient of 0.9507.

Tensiometers

Tensiometers were constructed in-house from Soil Moisture Corporation 100 kPa (1–bar) ceramic cups (part no. 655X1-B1M1) epoxied to 1.9–cm (3/4–in) PVC pipe. A 15–cm (6–in) clear acrylic tube snugly fitting inside the 1.9–cm (3/4–inch) pipe was also epoxied on top, and a rubber septum provided a sealing cap. A pressure transducer needle probe (tensimeter) inserted into the tensiometer rubber septum was used to read the capillary pressure. All tensiometers were checked before being inserted into the soil by filling them with water and letting them stand for 24 hours in plastic buckets with water covering the ceramic cups, to ensure that no water was being lost. Readings were taken to ensure proper working order. After these checks the tensiometers,

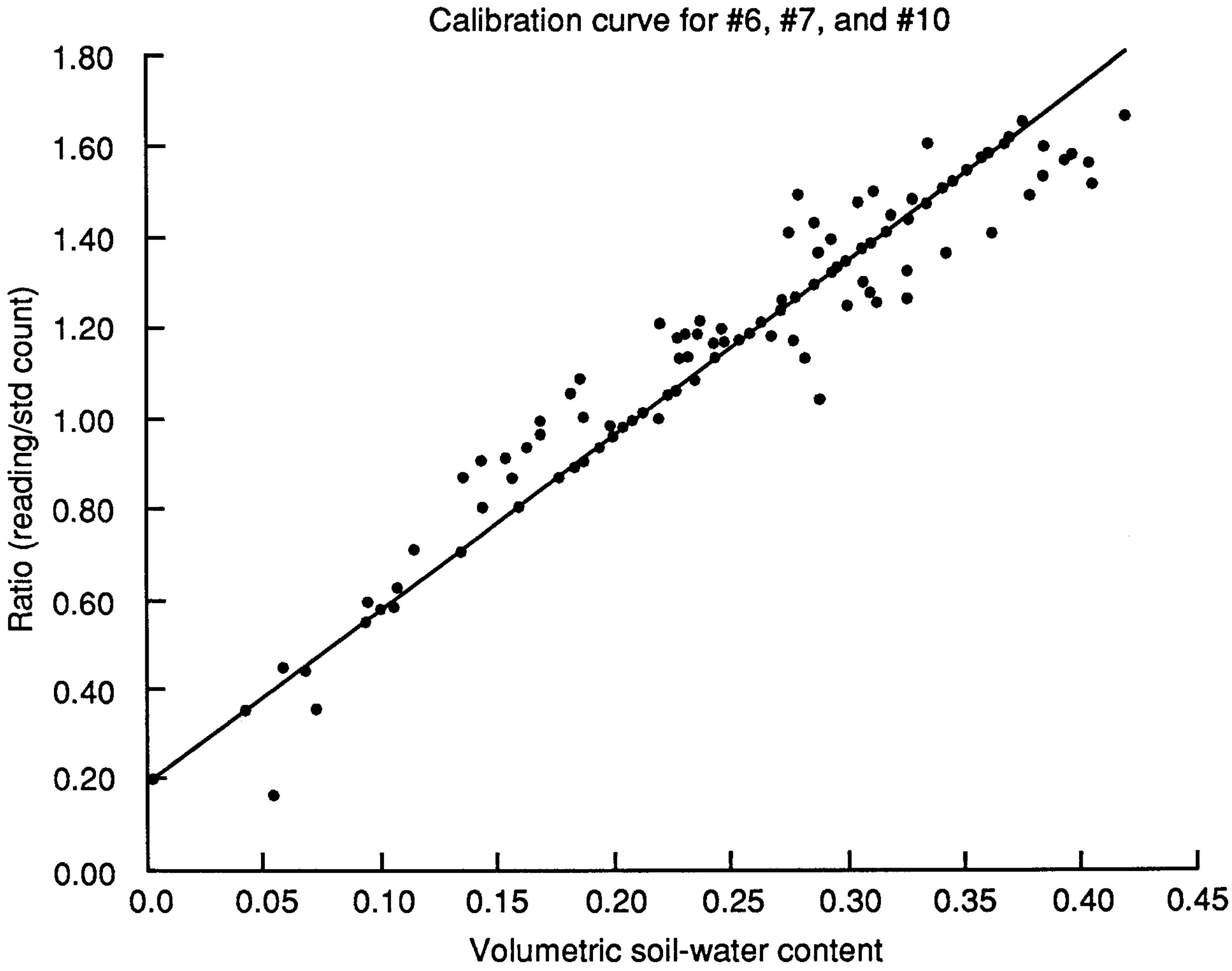

Figure 3. Field calibration curve for neutron probe

filled with deaired deionized water, were installed near the neutron access tube as follows: A hole was dug with the 5–cm (2–in) hand auger, down to 15 cm (6 in.) above the required depth. A hollow tube, a few millimeters smaller in diameter than the tensiometer ceramic cup, was used to core the final 15 cm (6 in.). The collected soil from the bottom of the hole was mixed with water to form a slurry, which was then poured into the hole. The tensiometer was then inserted into the hole to a snug fit. The rest of the hole was then backfilled with the augered soil while spraying water into the hole at the same time. The septum was protected from exposure to weather elements by covering the above-ground portion of the tensiometer with a 2.5–cm (1–in) capped PVC pipe.

Suction lysimeters

The suction lysimeters (Soil Moisture Corporation soil-water samplers 1900 series) were first filled with deionized water to a level above the ceramic cup to wet the capillary pores. A 5–cm (2–in) hand auger was used to auger the holes to the appropriate depth, ranging from 15 cm to 180 cm (6 in. to 6 ft). A silica flour slurry was mixed with water, the hole was wetted and the slurry was poured down the hole. The water was dumped out of the lysimeter and the lysimeter was inserted into the hole with a twisting motion. The rest of the hole was grouted with a slurry made of the augered soil and water. The surface portion of the hole was filled with bentonite. Vacuum was then applied to the lysimeter.

Soil temperature thermistors

A hole was hand augered with the 5–cm (2–in) auger down to 275 cm (108 in.) below ground surface. A 3–m (10–ft) wooden dowel was prepared by taping thermistors (YSI series 400 general purpose probes) at the following depths: 7.5, 15, 23, 30, 45, 60, 90, 120, 150, 210, and 275 cm (3, 6, 9, 12, 18, 24, 36, 48, 60, 84, and 108 in., respectively). The thermistor dowel was then inserted into the hole. A slurry made of the cuttings and water was poured around the dowel and packed. The thermistor cables at the surface were covered in a plastic bag and further protected by covering the protruding dowel with a 15–cm (5–in) capped PVC casing. A YSI telethermometer was used to read the thermistor temperatures.

Chemical formulation of applied solutions

Farmers in the Great Bend region normally apply 2.24 kg of atrazine per hectare, or 0.22 g/m^2 (2 lb of atrazine per acre for corn) using ground-spray equipment, center-pivot irrigation systems, or occasionally, aircraft. The atrazine is incorporated into the upper 15 cm (6 in.) of soil. One acre-foot of soil (~1233 m^3) weighs approximately 4 million pounds or ~1814 metric tons (Richards, 1969); thus 1 acre-half foot of soil (616 m^3) weighs approximately 2 million pounds (907 metric tons). Thus the atrazine concentration usually applied by farmers is 2 lb atrazine per 2 x 10^6 lb soil, or 1.0 mg/kg (ppm) atrazine. We increased the quantity of atrazine in the flooding experiment solution to 1.5 mg/L (which for site 6 amounted to 0.45 g/m^2 and for site 7 to 1.0 g/m^2) to ensure that enough atrazine was available for possible downward leaching during one field application. To prepare that concentration, liquid Atrazine 4L herbicide (Platte Chemical Co., Inc.) was used. It contained 4 lb (1.814 kg) of active ingredient per gallon (3.785 L), or 40.8% active ingredient, which translates to 479 g/L of atrazine active ingredient. A concentration of 1.5 mg/L of atrazine equals 5.68 x 10^{-3} g/gal atrazine, and because the active ingredient in Atrazine 4L was 40.8%,

$$\frac{5.68 \times 10^{-3}}{.408} = 1.39 \times 10^{-2} \text{ g/gal}$$

of Atrazine 4L was required. Since a 500 gal (1.89 m^3) tank was available for mixing the chemical solution, 6.96 g of Atrazine 4L was mixed in the 500–gallon (1.89–m^3) tank filled with city of

Stafford water (which tested negative for atrazine) to obtain the 1.5 mg/L required concentration of atrazine active ingredient.

The concentration of bromide tracer (5 meq/L or 400 mg/L) was selected to be high enough to exceed by several times the background levels after more than 100-fold dilution by soil solutions. The tracer solution was prepared with NaBr because sodium is the most common of the monovalent cations in the soil solution. The solution was prepared by adding NaBr to the same water to which the atrazine was added in the 500–gallon (1.89–m^3) tank. This required 973.7 g NaBr (514.5 mg/L NaBr) to 1.89 m^3 (500 gal) water. The measurement of the water volume in the tank was inexact; thus samples of the final solution as prepared were collected and analyzed to determine the exact concentrations of both bromide and atrazine.

At site 6 a quantity of 1.89 m^3 (500 gal) of chemical solution containing atrazine and bromide was applied after the soil profile was nearly saturated with city of Stafford water. At site 7 a quantity of 3.79 m^3 (1000 gal) of chemical solution of the same concentration as in site 6 was directly applied without presaturating the site.

Chemical analysis methodology

Atrazine was determined in soil extract solutions and water samples at the Kansas State Board of Agriculture Pesticide Laboratory using a Hewlett Packard 5890A Gas Chromatograph with an HP5470 mass selective detector. Atrazine extraction efficiencies from soil samples were 95 to nearly 100 percent. Bromide was determined at the Kansas Geological Survey by automated colorimetric methods on a Technicon Autoanalyzer. The atrazine degradation by-products were determined by a commercial analytical laboratory using gas chromatography for the biodegradation products and high-performance liquid chromatography for hydroxyatrazine determination. Additional analytical methodology is described in Appendix B.

Vadose zone and Pleistocene aquifer profile

The Great Bend Prairie is characterized by mostly sandy soils underlain by relatively thin, widespread clayey layers at shallow depth [generally 1–2 m (4–8 ft) deep] and by a shallow water table, generally 4–9 m (15–30 ft) deep.

The deepest observation well at each site was gamma-ray logged. Gamma radiation generally increases as the clay content increases. Figure 4 displays the gamma-ray log traces and drill-cuttings lithology for all three study sites, where a generally fining upward sedimentary sequence can be recognized.

Site 6: The soil profile and its physical and chemical characteristics

The soil profile at this site—not a designated soil, but a fine-loamy, mixed, thermic Typic Argiustoll—consists of grayish brown silt loam down to 40 cm (15.75 in. or 1.31 ft), comprising the A horizon; the upper portion of this horizon is characterized by a medium granular structure, and the lower part by a weak, medium subangular blocky structure. Underlying that layer is an 8–cm–thick grayish brown E horizon of silt loam texture and weak medium platy structure. A relatively hard brown to yellowish brown silty clay loam layer follows down to 77 cm (30.3 in. or 2.53 ft), comprising the soil Bt horizon, characterized by moderate medium prismatic and subangular blocky structure with many fine platelike soft masses of lime and common fine irregular salt masses; this Bt horizon exhibits strong effervescence. Underlying this soil is another light yellowish brown soil of moderate medium subangular blocky structure; this soil is characterized by only a Bt horizon, which can be subdivided into three Bt subhorizons down to 147 cm (57.9 in. or 4.82 ft). The texture of this second soil is clay loam characterized by many rounded carbonate nodules with strong effervescence. A third light brown buried soil is also present, consisting also of a Bt horizon of subangular blocky structure and a transition BC layer

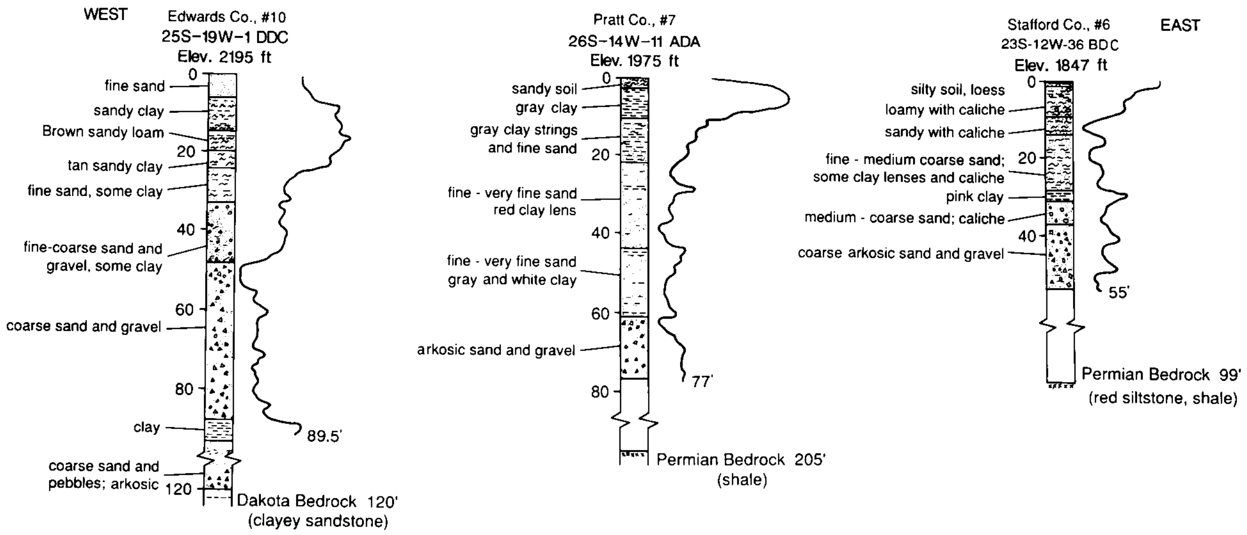

Figure 4. Geologic logs for each site based on drill cuttings and gamma-ray geophysical logs

down to the maximum analyzed depth of 230 cm (90.5 in. or 7.5 ft). This third soil is also of clay loam texture and is characterized by many rounded carbonate nodules with strong effervescence.

The specific detailed soil horizons and their grain size distribution (texture) as determined by the Soil Conservation Service (SCS) are shown in Figure 5. It can be seen from the figure that the clay fraction increases significantly in the 45–90 cm (1.5–3 foot) depth interval, whereas the sand fraction decreases. As the fine-grained fraction increases, the surface area per unit volume of soil increases markedly, thus making the soil more chemically active because of its greater surface charge per unit volume and its capacity to hold greater amounts of water by adsorption. The significance of these observations as related to organic chemical movement through the soil will be shown later.

According to SCS, the clay fractions of all soil horizons analyzed (A1, A3, Bt, 2Bt, 2Bt3, and 3BCK) exhibit only "medium" mica and montmorillonite peaks, with kaolinite and quartz peaks being in the "small" and "very small" range.

The organic carbon content of the site 6 soil profile (Fig. 6) is much higher in the upper 40 cm (1 ft) than in the rest of the soil profile. Organic carbon makes up over one-half of the organic matter, and therefore organic carbon content is commonly used to characterize the amount of organic matter in soils. Generally, the percentage of organic matter in a soil is considered to be approximately 1.72 times the percentage of organic carbon (Birkeland, 1984). Soil organic matter considerably increases both the water-holding capacity and the cation-exchange capacity of soils. The organic acids that are produced from organic matter form chelating compounds that increase the solubility of some ions in the soil environment. The CO_2 gas that is evolved during humus formation (the bulk of the soil organic matter) builds up to reach concentrations higher than those in the atmosphere; this results in the formation of abundant carbonic acid, which lowers the soil pH.

The cation-exchange capacity (CEC) of the soil profile is also shown in Figure 6. In addition to a relatively high proportion of organic matter, this figure shows that the upper foot of

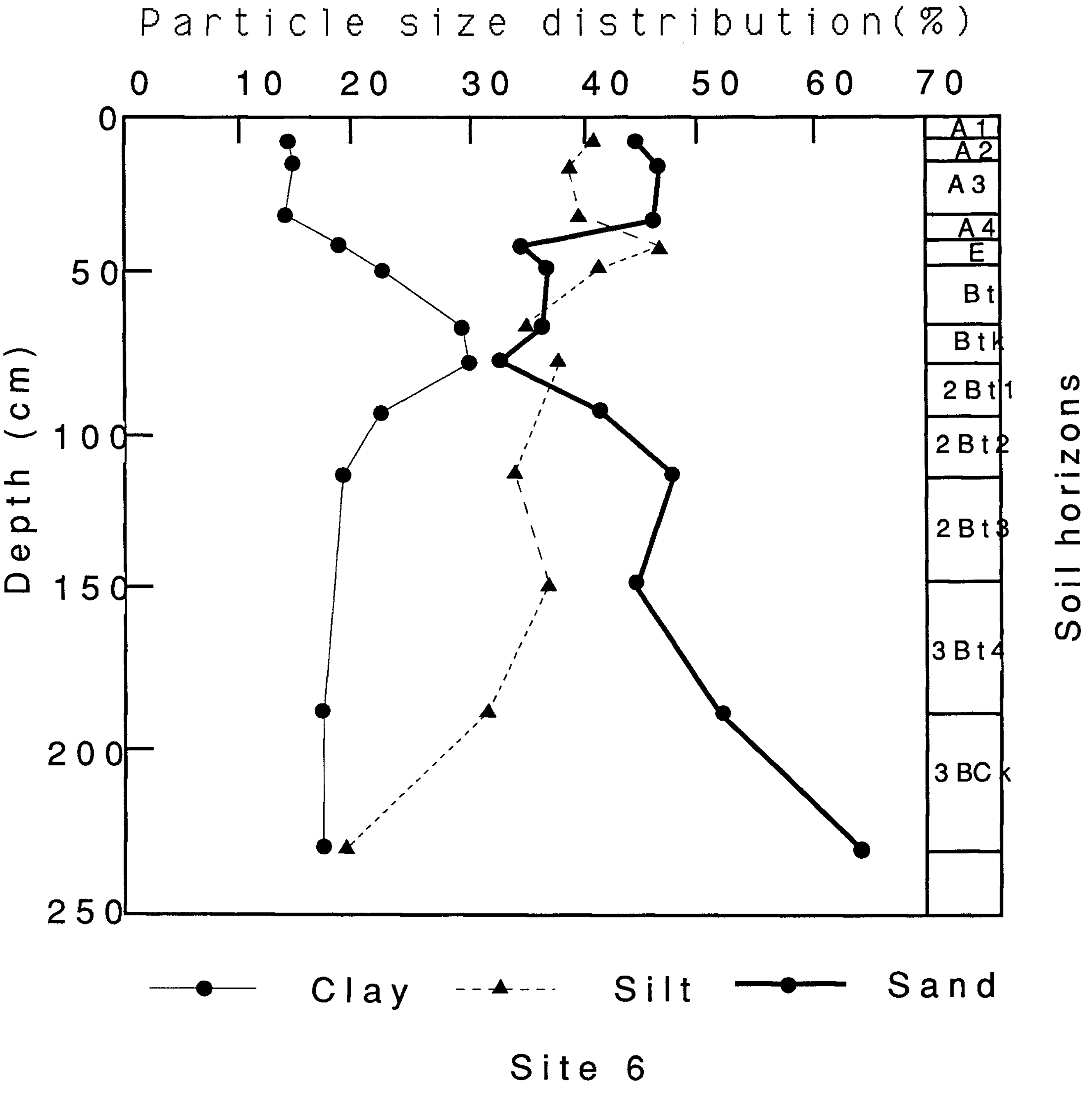

Figure 5. Grain-size distribution and soil horizons for site 6

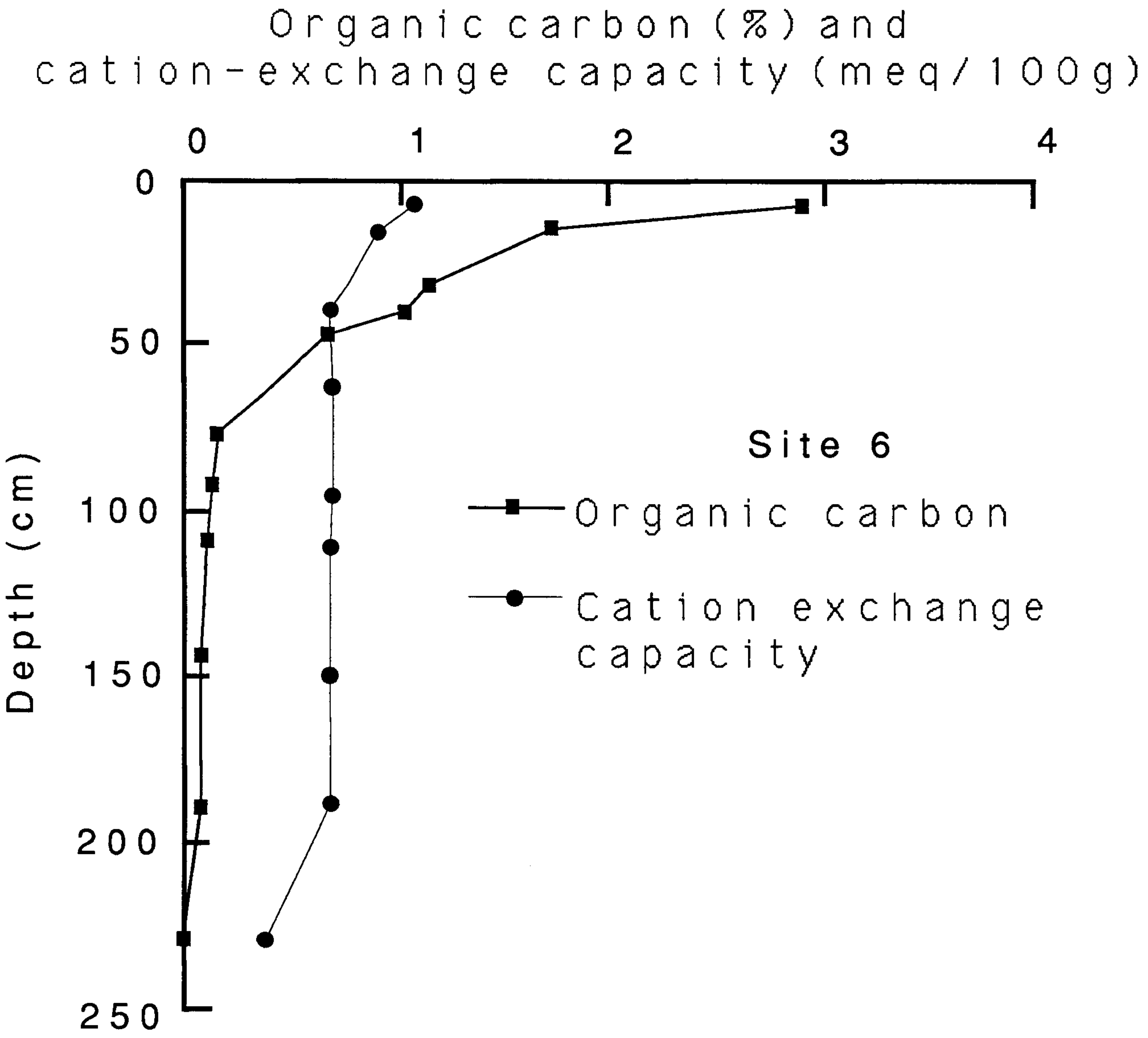

Figure 6. Organic carbon content and cation exchange capacity profiles for site 6

soil has the highest cation-exchange capacity of the whole soil profile. Most soil colloids (inorganic and organic) have a net negative surface charge, thus attracting cations. The strength of cation attraction varies with the colloid and the particular cation, and some cations may exchange for others. The total negative charge on the surface is the cation-exchange capacity, expressed in milliequivalents per 100 g oven-dry material.

The soil bulk density, as determined by the core method using the Madeira sampler and by the clod method (as determined by SCS), is shown in Figure 7. An increase in bulk density with depth is evident from the figure. This apparently results from a lower organic matter content (Fig. 6), less aggregation and root penetration, and compaction caused by the weight of the overlying layers.

Figure 8 depicts the available water-holding capacity of the soil profile of site 6. The available water-holding capacity is the difference between field capacity (specific retention) and permanent wilting point (at which the moisture is so tightly held by the particles that the roots can no longer extract it). Soil water and chemical retention and movement are strongly related to the surface area per unit volume of the soil mass, and this, in turn, is related to the clay fraction (Fig. 5) and the organic matter content (Fig. 6).

The soil pH distribution of the soil profile based on a 1:1 soil to water extract and a 1:2 soil to 0.01 m $CaCl_2$ solution is depicted in Figure 9. The soil approaches acidic conditions just below the upper 30 cm (1 ft), whereas below the 60–cm (2–ft) depth it approaches alkaline conditions. Soil pH is often related to dissociation, adsorption, and chemical alteration of organic chemicals, as well as to the concentration of inorganic ions in the soil solution and the mineral character of the soil. The two principal controlling factors are the organic matter, and the type and amount of carbonate minerals and dissolved carbonate anions. Large amounts of organic matter induce acidity, except when counterbalanced by high concentrations of soluble carbonates.

The soil profile contains an appreciable amount of salts, especially in the lower horizons below 120 cm (~4 ft), and in the upper 30 cm (1 ft), as shown by the electrical conductivity of the

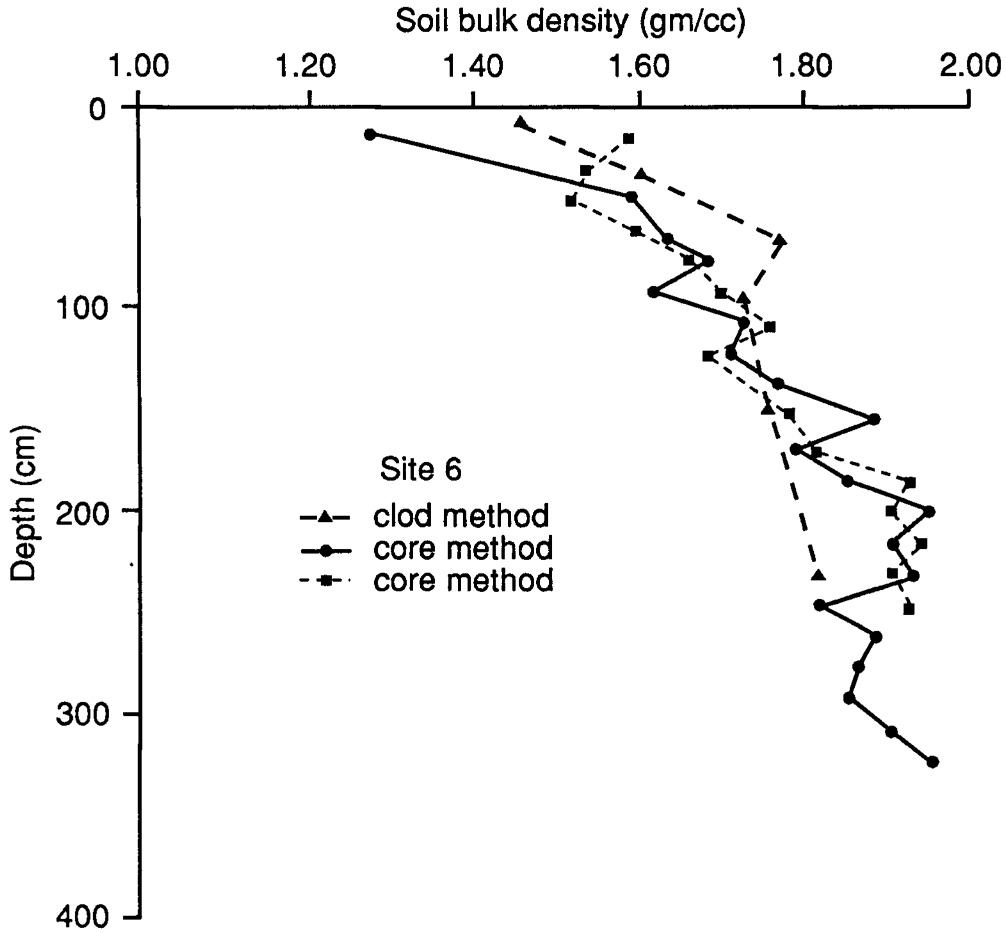

Figure 7. Bulk density distributions determined by the two methods indicated for soil profile at site 6

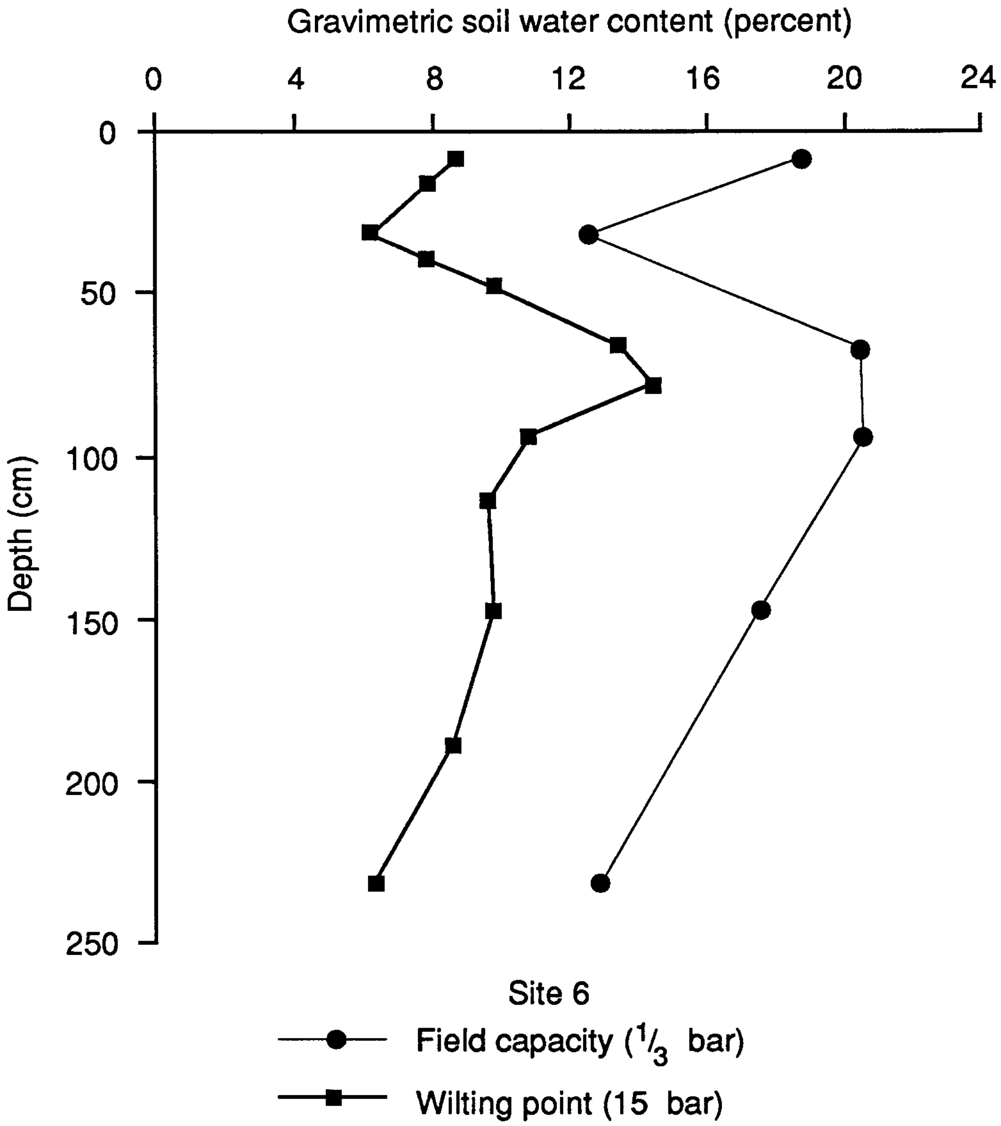

Figure 8. Available water-holding capacity of the soil profile at site 6.

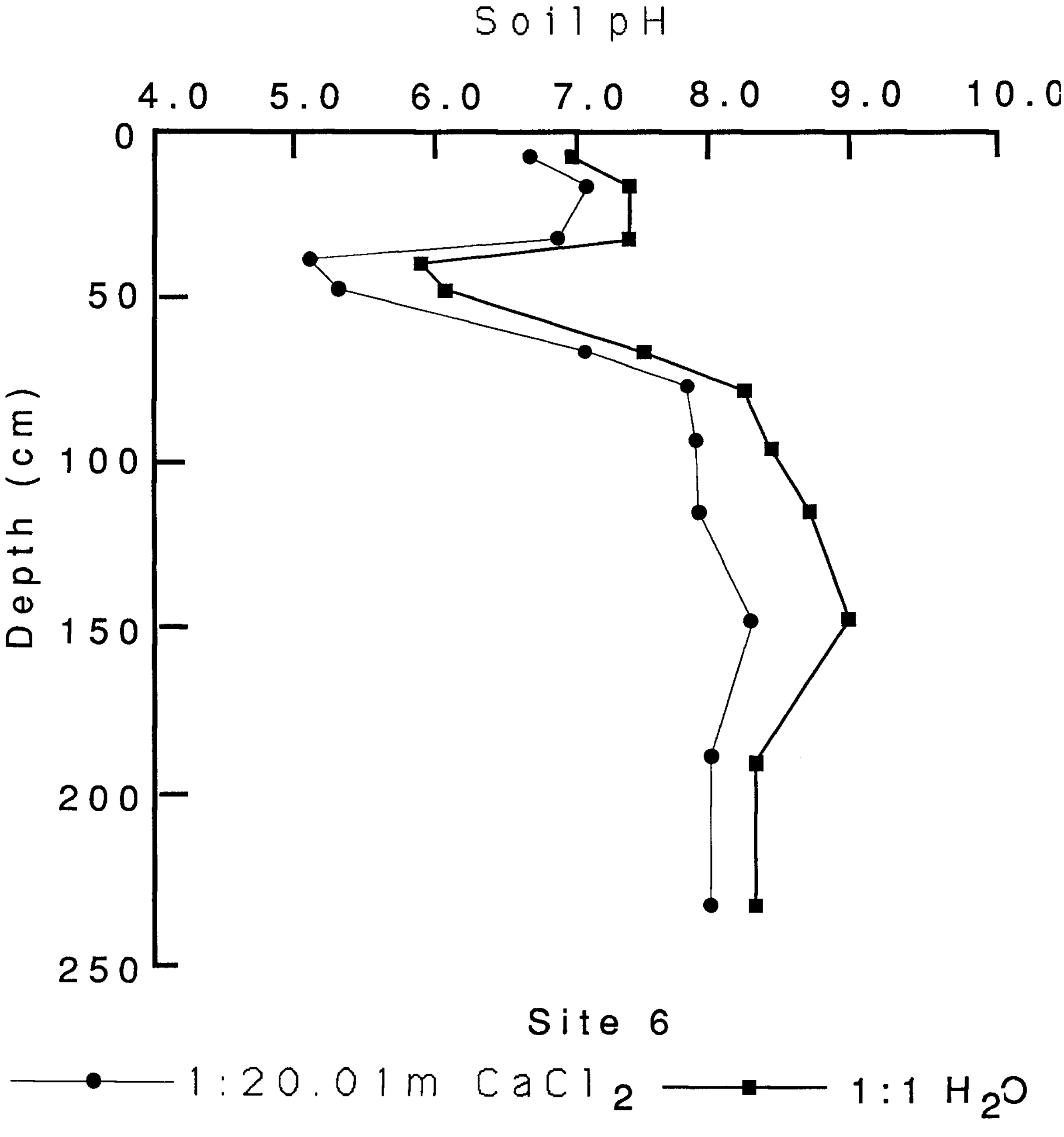

Figure 9. Soil pH profile determined by the methods indicated for site 6.

water extracted from saturated soil pastes (Fig. 10). The exchangeable sodium percentage, which indicates the degree of saturation of the soil-exchange complex with sodium, is also shown in Figure 10. The lower part of the soil profile below 120 cm (4 ft) contains a significant amount of sodium, enough to influence hydraulic conductivity. However, in the 2Bt1 [77–93 cm (2.53–3.05 ft)] and 2Bt2 [93–113 cm (3.05–4.82 ft)] horizons the salt content is low enough (Fig. 10) to keep the clay in a dispersed state, given the relatively high sodium content of these horizons.

Water chemistry of site 6

Site 6 in Stafford county is located at the edge of a flood-irrigation field used for growing corn during the period of study. Average precipitation in the area is approximately 61 cm/yr or 24 in/yr (Sandyland Agricultural Experiment Station,1983). The site has a zone of concentrated salts within the upper 6 m (20 ft) of the soil, as shown by the background specific conductance measurements collected from the 6.1, 10.1, and 13.7 m (20, 33, and 45 ft) wells before the test (Table C.1), the observed salt accumulations within the soil profile (below the A and E horizons), and the electrical conductivity of the water extracted from the soil pastes (Fig. 10). The specific conductance measurements from the 6.1–m (20–ft) well are considerably higher than those from either the 10.1– or 13.7–m (33– or 45–ft) well (Table C.1). Drilling logs of these wells show the presence of clay layers between the 6.1 m and 10.1 m (20 ft and 33 ft) wells (Fig. 4). These layers may prevent movement of salts to the lower aquifer zones.

A definite source for the salts in the sampled soil solutions and ground water originates from the paleosols at depth. Continuing evapotranspiration losses may be responsible for concentrating salts in the upper soil zone of the field. Plants are capable of absorbing fairly fresh water but leave most of the dissolved solids from the water in the soil zone (Bower, 1978). Continuous flood irrigation for a considerable length of time may also result in movement of salts from the upper root zone into the deeper lower permeability horizons. The bromide/chloride ratios for the soil background solutions (collected from the suction lysimeters), and for the ground water

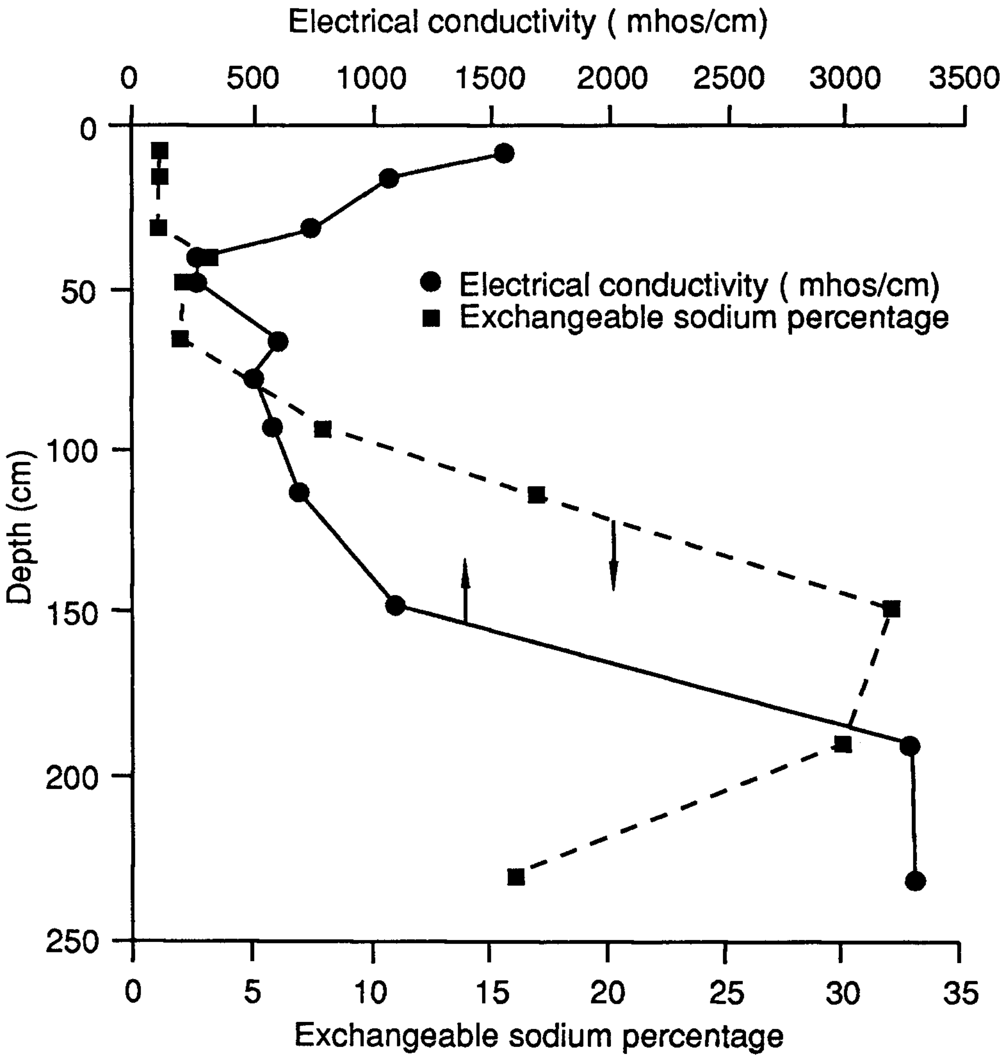

Figure 10. Electrical conductivity and exchangeable sodium percentage for soil profile at site 6.

at the site were generally too low to be from oil-brine disposal in the Great Bend region (Whittemore, 1984).

The dominant water type at this site is in the Ca-Na-HCO_3-Cl range (Fig. 11). As stated previously, this is probably due to the movement of a slug of salts from the soil zone downward to the shallower water table. The location of the 60– and 90–cm (2– and 3–ft) lysimeters on the trilinear plot (Fig. 11) illustrates the effects of salt movement through the soil zone. The lysimeters show a Na-Ca-HCO_3 water, which may indicate concentration processes by plants and cation-exchange processes with clays in the soil zone. The presence of carbonate nodules below a depth of 50 cm (19.5 in.) appears to substantiate the idea of concentration and precipitation of constituents from the soil solution.

At site 6 the low level of nitrate in the soil zone is probably due to the lack of nitrogen fertilizer application on the test plot (Table C.1). The concentrations of nitrate in the 20– and 33–ft wells are similar to the levels recorded for the 38–ft GMD5 ground-water quality network well (26 mg/L as nitrate in the quarter section east of our test site (Table C.1). This implies that the water in the monitoring wells is reflective of the overall ground-water flow from the farm.

Site 6: Water and chemical flooding

The soil moisture profile at the site just before the initiation of flooding (Fig. 12) indicates dry conditions throughout most of the soil profile. To reduce lateral water movement from the area to be flooded to the surrounding area, we used 3.79 m^3 (1000 gallons) of Stafford municipal water on September 9, 1987, to increase the soil water content of the perimeter strip of the area to be flooded. We covered the wetted perimeter area with plastic immediately after wetting it and then flooded of the enclosed area with 9.52 m^3 (2250 gal) of Stafford municipal water at a rate that ponded the water to a depth of 5–10 cm (2–4 in.) for 6 days (September 9–15, 1987) We then flooded the area with a 1.89–m^3 (500–gal) chemical solution (atrazine and sodium bromide) for

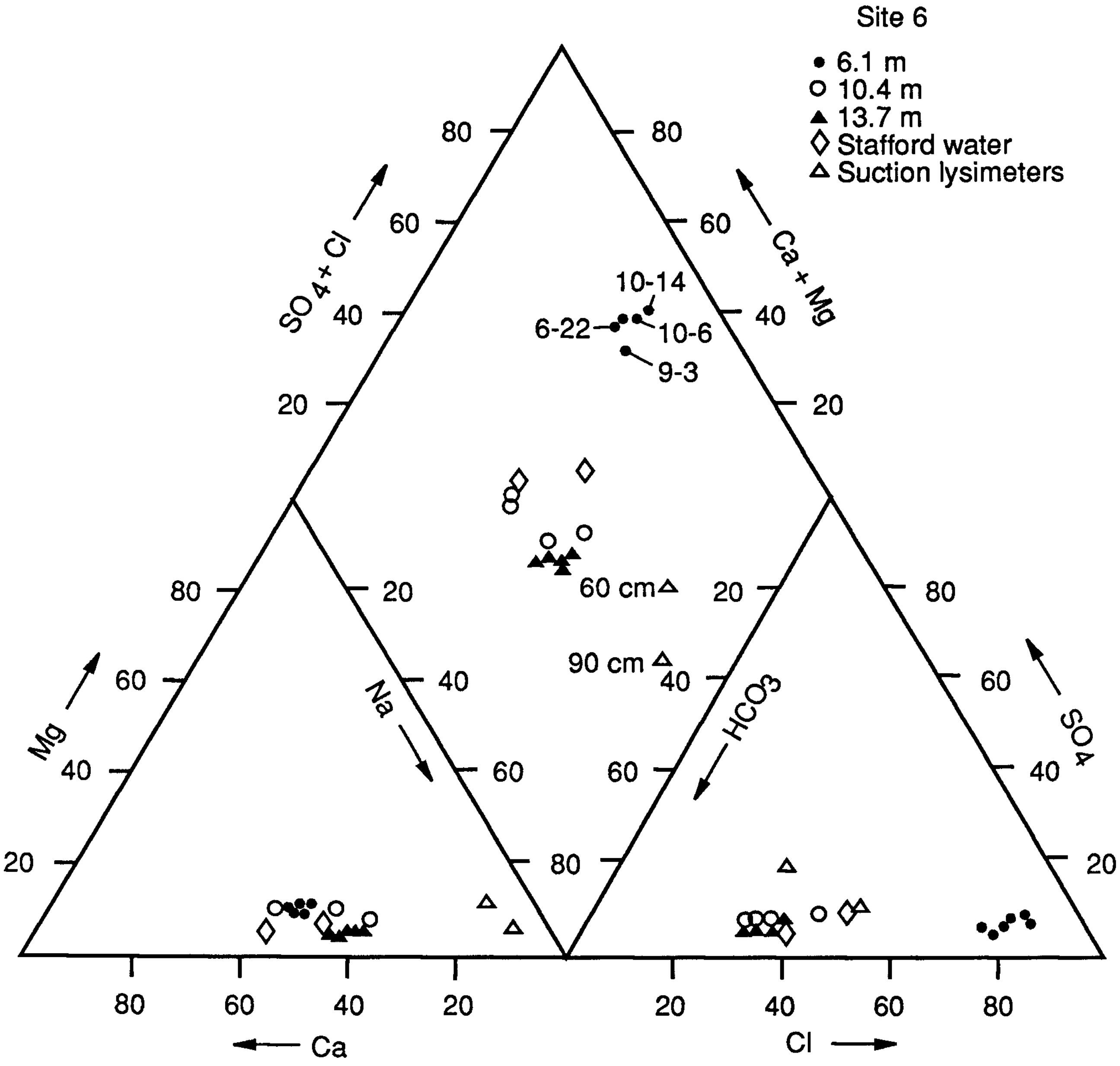

Figure 11. Trilinear diagram showing water chemistry data for three wells, two suction lysimeters, and Stafford city water (used for flooding) at site 6.

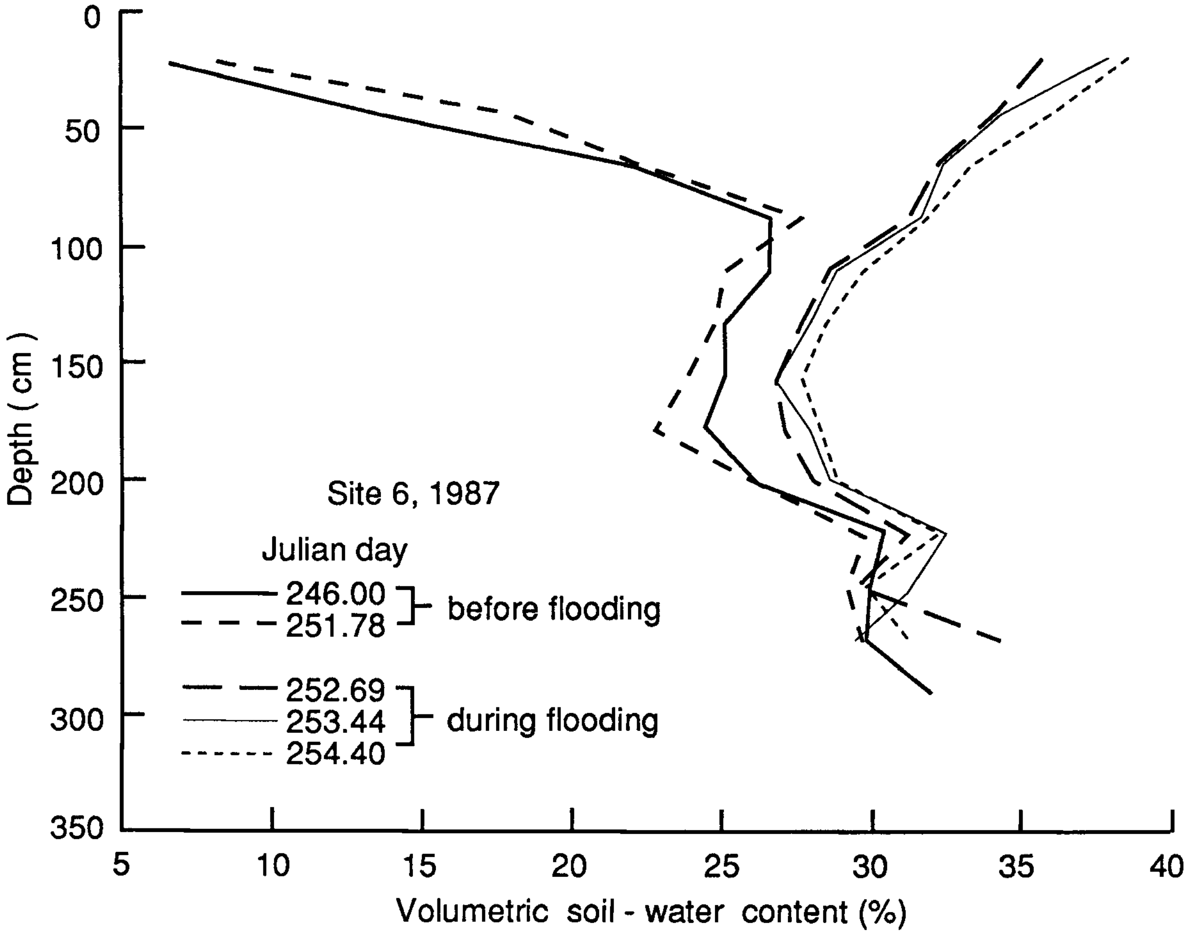

Figure 12. Soil-water content profiles before and during flooding at site 6.

approximately 1 day. The chemical flooding was identical with water flooding with respect to application rate and ponding depth. The flooded area was hexagonal in shape, enclosing 15.42 m^2 (166 ft^2) of soil. As soon as the chemical slug seeped into the soil (Sept. 16, 1987), we covered the site with heavy black plastic and a thin layer of soil to minimize evaporation losses. The soil-moisture profiles before and during the flooding period (Fig. 12) show that the soil became nearly saturated down to approximately 270 cm (9 ft). Soil-moisture drainage curves for 15-cm (6-in.) depth intervals since covering the site with plastic are shown in Figure 13, where soil water drainage down to the 230-cm (90-in.) plotted depth can be recognized.

During water flooding but before chemical flooding we sampled the suction lysimeters on various dates and analyzed the samples for chloride, bromide, and in some samples concentrations of other dissolved inorganic constituents. The distribution of dissolved chloride with depth, plotted in Figure 14, suggests that the flooding freshwater (containing a chloride content of 157 mg/L) displaced naturally existing salts downward within much of the soil profile (see section on the soil profile, especially Figure 10). However, there is also evidence of some preferential movement of flood waters through the profile. Flood solutions appeared to dissolve salts at the 120–cm depth, but the high chloride contents were not displaced to soil horizons immediately underlying this depth. Instead, the results suggest that the variations at the underlying depths are caused by water bypassing the 120–cm level. The high content of chloride in samples from the 120–cm depth could have accumulated at the base of the root zone by evapotranspiration. The presence of carbonate nodules below a depth of approximately 60 cm (23 in.) appears to substantiate the idea of concentration and precipitation of constituents from the soil solution. Such salt concentrations would then be available for dissolution and deeper penetration during prolonged wet periods or excessive irrigation as simulated by the flood experiment.

The source of the high conductivity water is probably the observed abundant irregular salt masses and rounded carbonate nodules which increased with depth throughout the soil profile below the A and E soil horizons (Fig. 5). Measured electrical conductivity of water extracted from

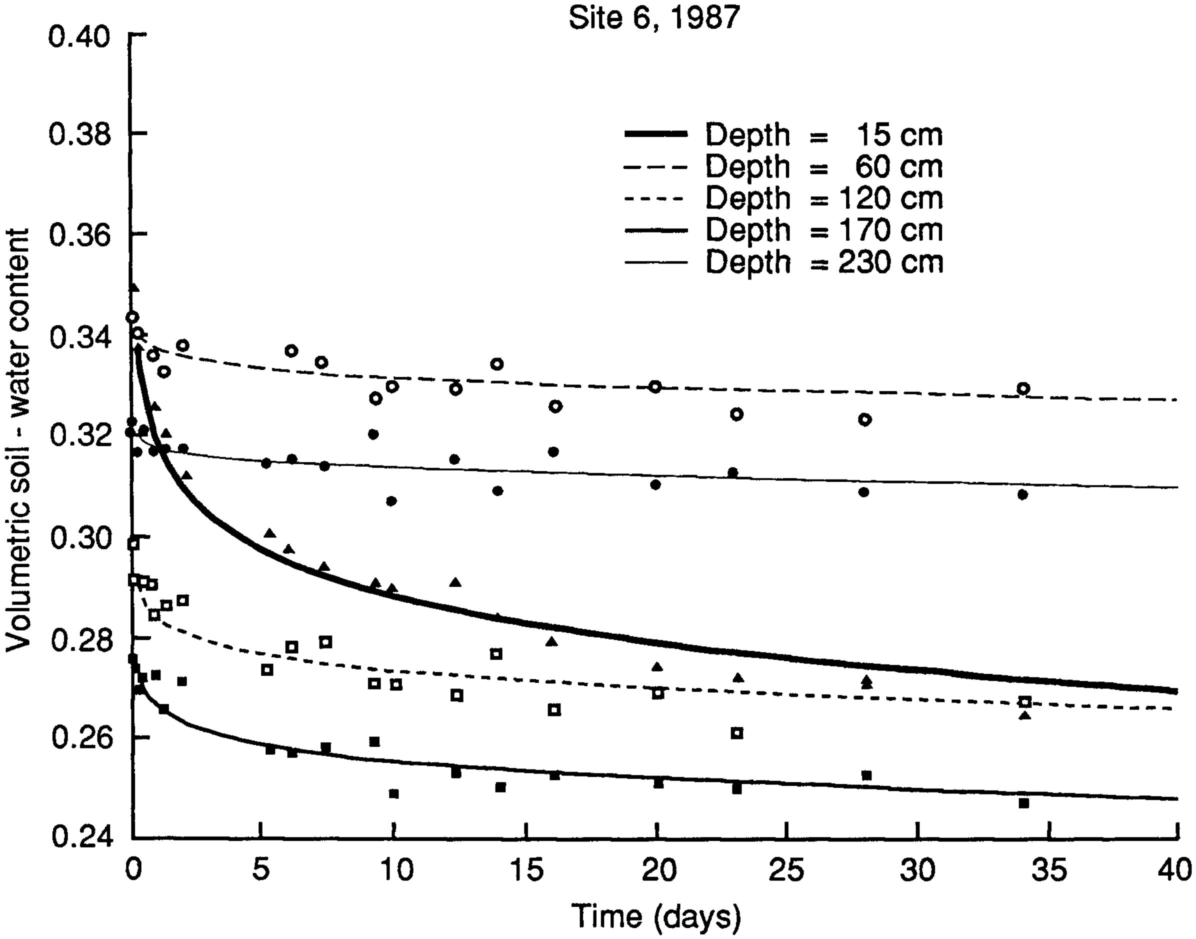

Figure 13. Soil water-drainage curves for five depths at site 6. Least-squares fit curves using a drying model are also shown.

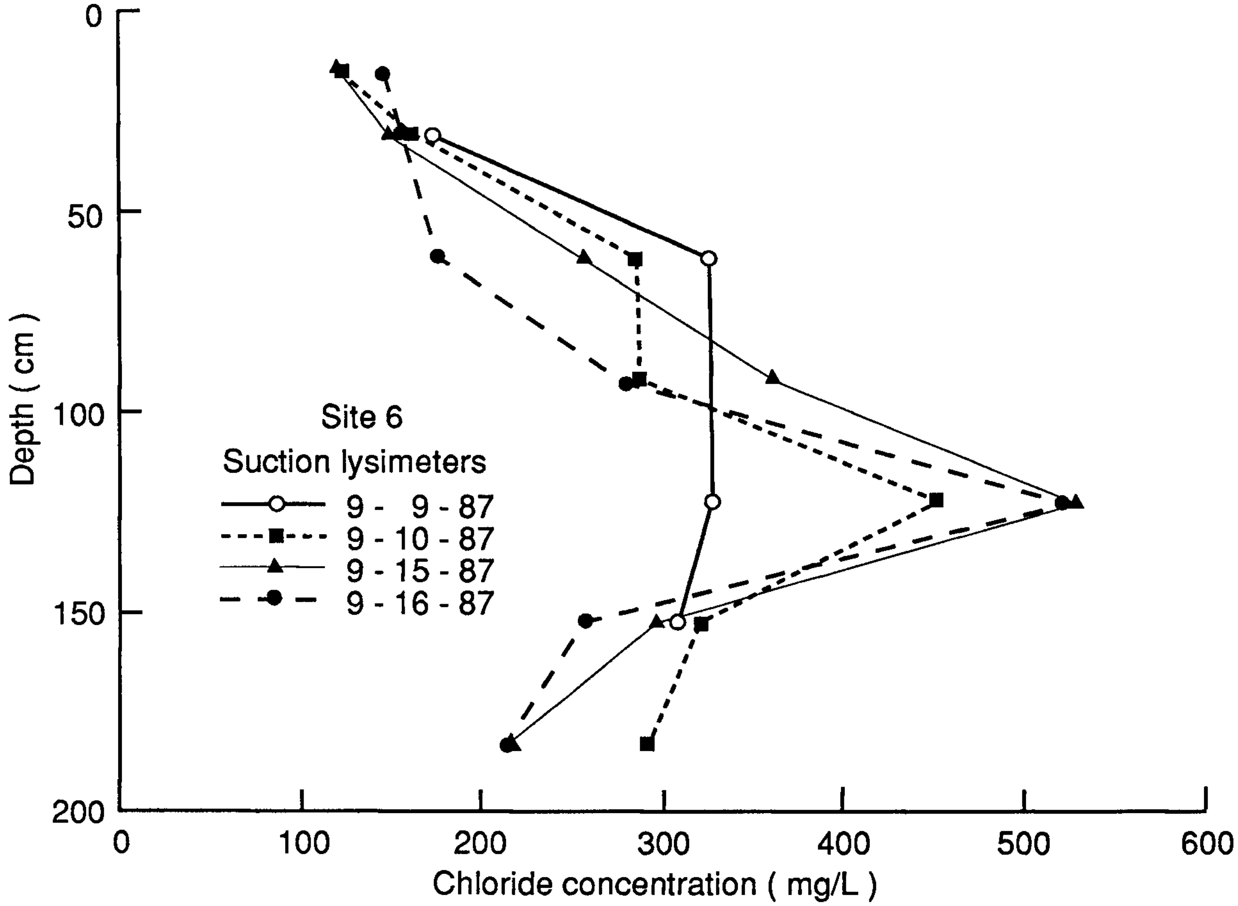

Figure 14. Profiles of dissolved chloride sampled from suction lysimeters during flooding at site 6.

saturated soil pastes prior to the flooding experiments generally increased with depth and ranged from more than 2,000 to more than 3,000 µmhos/cm below the 120 cm depth; specific conductance of suction lysimeter samples ranged from 2,300 to 4,300 µmhos/cm over the sampled depth intervals of 90 to 150 cm during flooding (Table C.1). Data from drillers' logs indicate increasing "caliche" presence from the near surface down to almost 9m, while the unconsolidated sediments became sandier with depth below 1.5 m. Although the upper 75 cm of the soil profile were dry prior to the flooding experiment, the profile below 2 m was relatively wet (Fig. 12). The sandier and wetter nature of the deeper sediments would facilitate transmission of saline solutions to the shallow (3.4 m deep) water table. To nearly saturate the unsaturated soil profile within the diked area at this site, approximately 3.83 m^3 of water would be required, assuming no displacement of native pore water, and no lateral flow. Thus, the remaining 6.58 m^3 of chemical solution and flooding water (representing ~38% of the pore water within the flooded pore volume above the water table) would have displaced an equal amount of pore water. Assuming a combination of displacement and mixing with the 2.7 m water column (based on the 6.1 m well and 3.4 m depth-to-water), the concentration of the leaching solution needed to raise the ground-water conductance from 2,500 to almost 4,200 µmhos/cm (Fig. 8) would be approximately 5,800 µmhos/cm, a plausible estimate given the abundance of salt masses and carbonate nodules in the deeper soil profile.

After several days of suction lysimeter sampling, the performance of the lysimeters deteriorated such that many, especially those at shallower depths, could not hold a vacuum long enough to collect sufficient pore fluid for analysis. Careful cleaning of the rubber stoppers in the lysimeters (as supplied by the manufacturer) and wrapping with Teflon tape did not markedly improve the performance. Subsequent freezing conditions rendered all suction lysimeters inoperable during the winter.

The displacement of more mineralized soil water by the fresher flooding water is also reflected in the specific conductance and chloride concentration in the 6.1–m (20–ft) observation well, as shown in Figure 15, whereas the deeper observation wells remained practically unaffected. The dissolved solids content increased markedly in the ground water, as indicated from the shallow observation well (6.1 m) after the onset of water flooding at the surface. Thereafter the amount of dissolved solids decreased steadily, but to levels appreciably higher than before the experiment. The salt movement to the water table is probably the result of pistonlike displacement of more saline soil solutions in the soil profile.

The significance of the observations from site 6 to agricultural chemical movement is that during periods of unusually high rainfall and ponding in the area or during excessive flood irrigation, downward movement of chemicals concentrated in soils could be triggered, thus affecting the quality of the shallow ground water.

We used the instantaneous profile technique (Rose et al., 1965; Watson, 1966; Hillel et al., 1972) to analyze the results of the flooding experiment. We wrote a set of FORTRAN 77 computer programs to analyze and graphically display the field data. To summarize the results of the flooding experiment, we depict in Figures 16 and 17 the field-obtained water characteristic or water-retention curves (which express the ability of the soil to retain water as a function of its energy status) and the hydraulic conductivity curves (which express the ability of the soil to transmit water as a function of its degree of water saturation) for various depths. Because of the clayey nature of the soil profile, the observed water characteristic and retention curves do not show a significant decrease in water content with an increase in capillary pressure or suction (Fig. 16). The resulting Darcy water fluxes for various depths as a function of elapsed time since the site was covered with plastic (to prevent evapotranspiration losses) are shown in Fig. 18, in which an exponential-type decrease with time can be readily recognized.

The soil profile temperatures during the flooding experiment (September to November 1987) are shown in Figure 19, in which a progressive soil temperature decrease with time at all

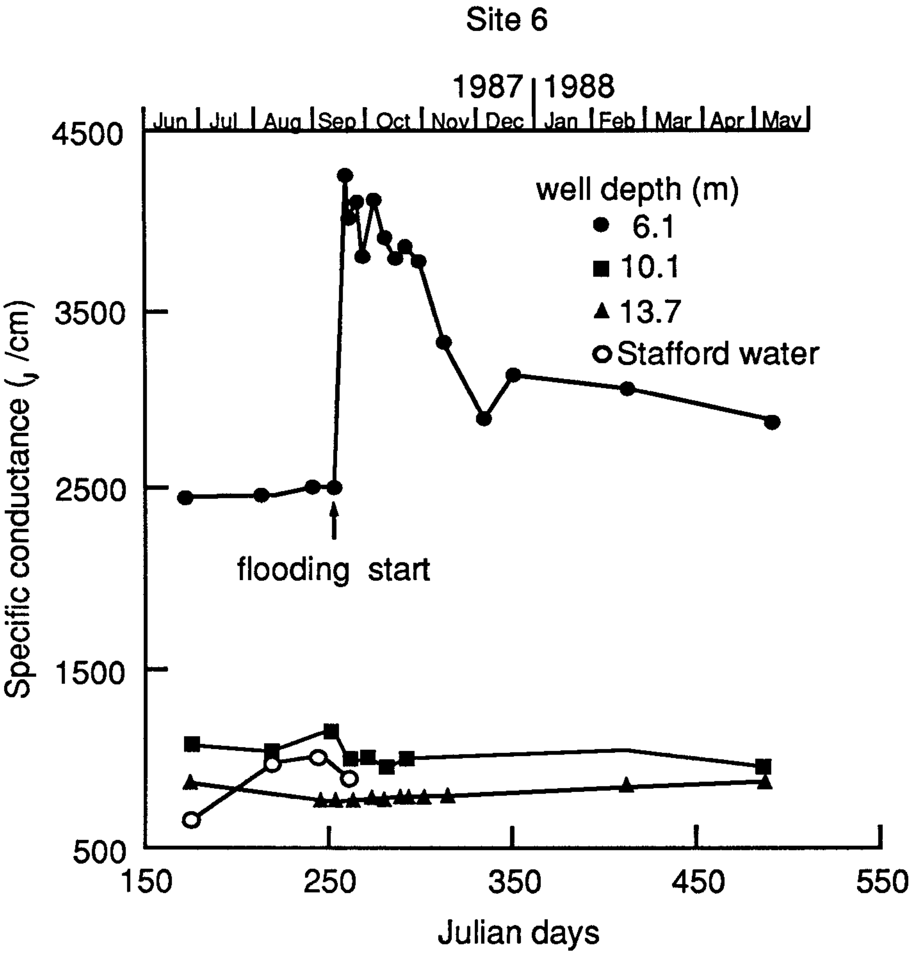

Figure 15. Specific-conductance time-series distribution of observation wells and of Stafford water used for flooding at site 6.

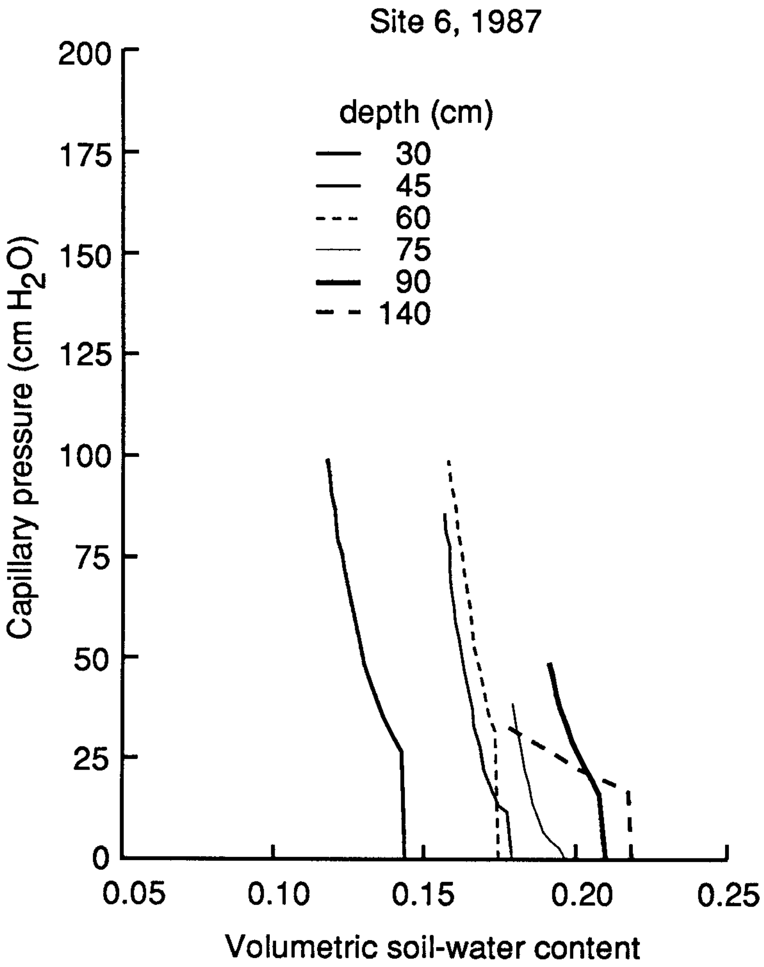

Figure 16. Field-measured water retention curves for site 6.

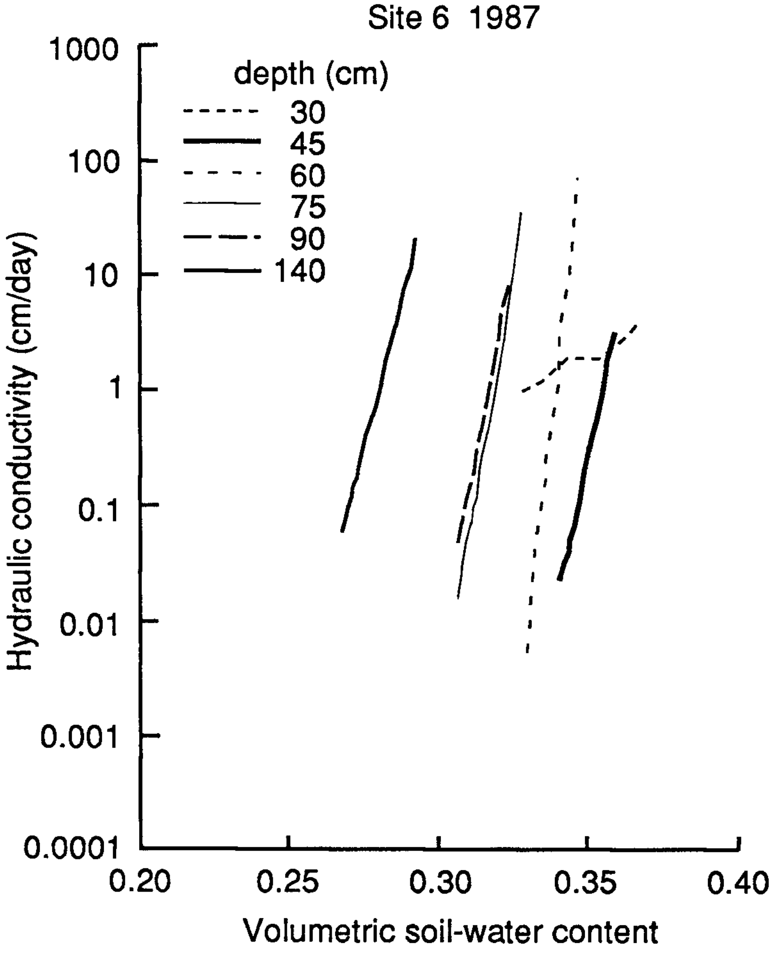

Figure 17. Hydraulic conductivity curves derived from the instantaneous profile technique for site 6.

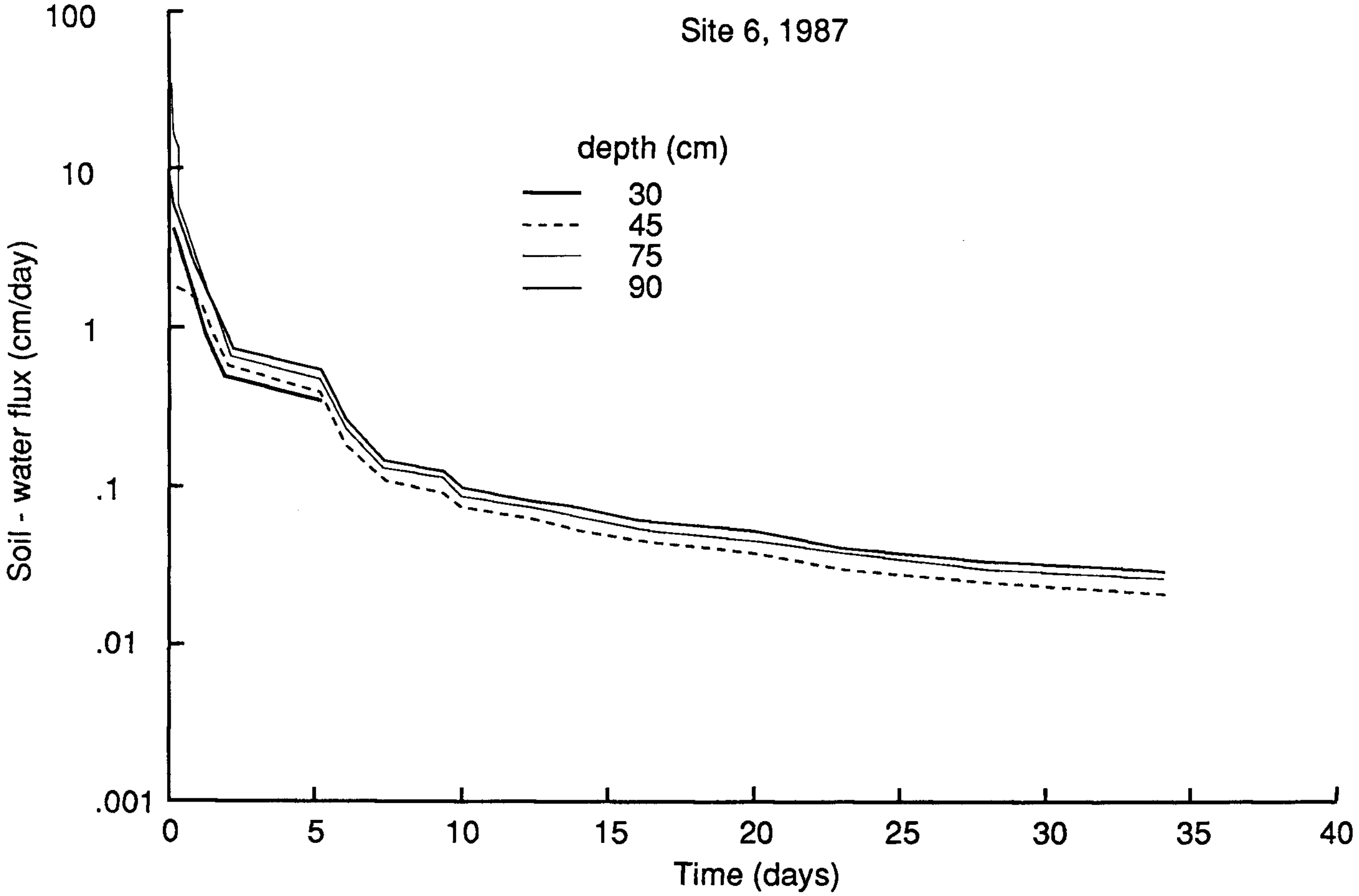

Figure 18. Soil-water flux time distributions derived from the instantaneous profile technique for site 6.

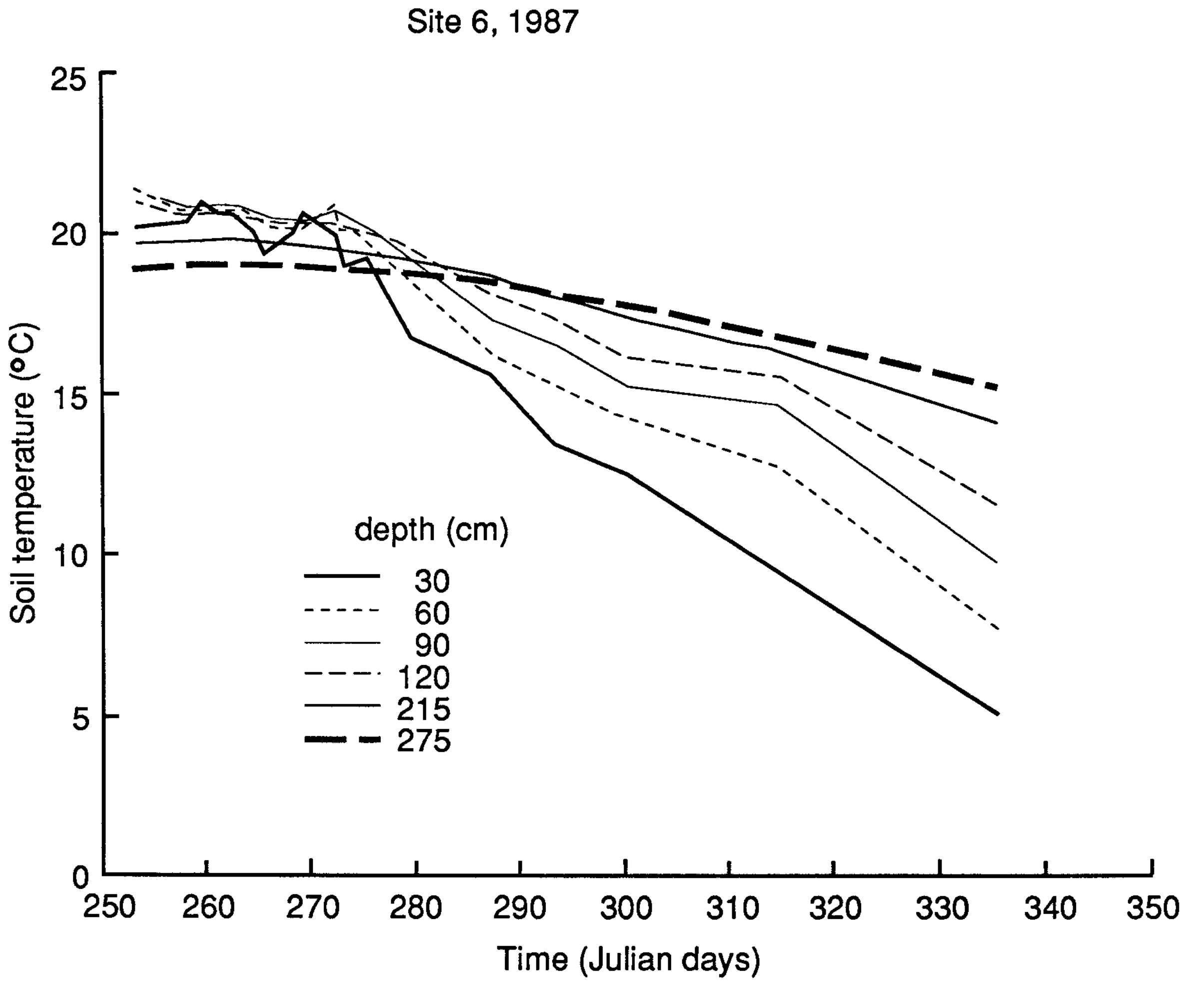

Figure 19. Soil-temperature time-series distribution for six depths at site 6.

measured depths is evident. The figure also shows that during September there was also a progressive temperature decrease with depth. However, from October onward there was a temperature-depth reversal; that is, deeper temperatures were higher than shallower temperatures. It is well established that the temperature of a soil greatly affects the physical, biological and chemical processes occurring in that soil. At low temperature (cold) soils, chemical and biological rates are slow, with absorption and transport of water and chemical species adversely affected.

Bromide. Bromide concentrations versus time after the start of chemical flooding are shown by the tracer breakthrough curves through the soil profile (Fig. 20) based on suction lysimeter sampling. Bromide concentrations (Fig. 20) were corrected by subtracting the small background values at each depth (mostly ranging from 0.1 mg/L to 0.2 mg/L). The actual bromide content of the chemical solution applied was 376 mg/L. The added bromide penetrated to the 150–cm (6–ft) level in concentrations appreciably above background within 2–3 days after the beginning of chemical flooding. Conclusive penetration of tracer bromide to levels substantially higher than the highest background content occurred after about 2 weeks at the greatest lysimeter depth of 180 cm (6 ft). However, conclusive penetration of tracer bromide to the 120–cm (4–ft) depth was not detected until about 9 months after addition, corroborating the observation of some preferential flow based on chloride movement. The bromide concentration distribution in the soil profile after chemical flooding was initiated (September 15, 1987, 11:00 a.m.) is shown in Figure 21, where the bulk of the bromide solution is indicated in the top 30 cm (1 ft) of the soil profile. Before chemical flooding, the bromide concentration in the soil profile was within the thickness of the 0 bromide concentration line and thus not plotted in Figure 21. Lack of complete data at later times prevents the study of the bromide pulse decay. The bromide persistence observed at the 30–cm (1–ft) lysimeter is caused by the substantial decrease in hydraulic conductivity and water flux in the soil profile after the cessation of flooding (Figs. 17 and 18) and the existence of a clayey underlying soil zone (Fig. 5) The greater apparent penetration of the applied water was due to the infiltration of flood water without tracer before initiation of the chemical flood.

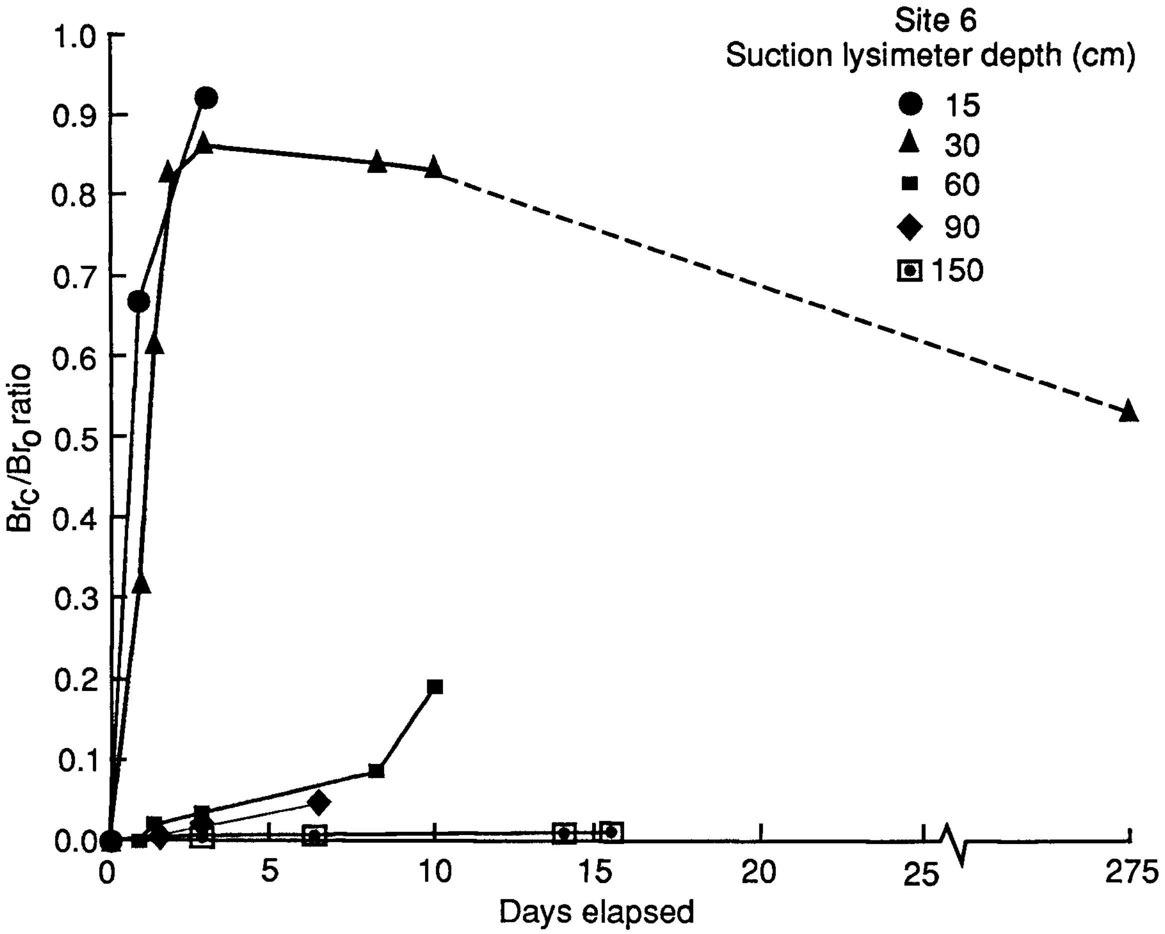

Figure 20. Bromide concentration breakthrough curves based on suction lysimeter sampling for site 6. Bromide is expressed as a ratio of bromide corrected for background levels (Brc), over bromide tracer concentration in the flooding solution (Br0).

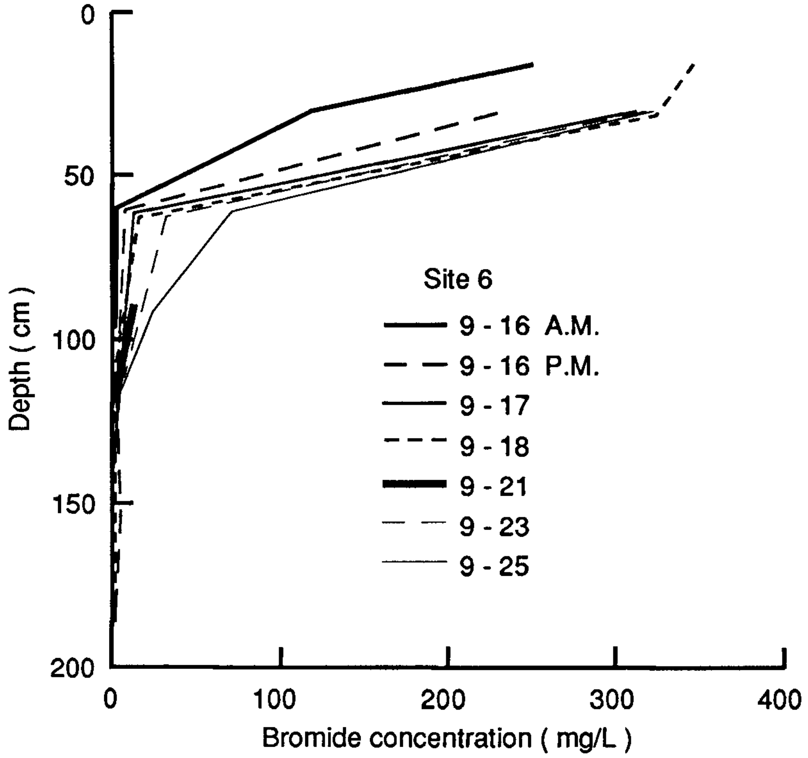

Figure 21. Bromide concentration profiles since chemical flooding was initiated at site 6.

The bromide time-series distribution from the shallow 6.1–m (20–ft) observation well shows a similar pattern as the specific conductance and chloride time series for the same well (Fig. 15). The water and chemical flooding displaced naturally existing bromide in the soil profile down to the water table, thus creating the relatively elevated bromide levels in the shallow ground water after the start of flooding (Fig. 22). The displaced bromide is interpreted as naturally existing in the deep soil because the accompanying rise in chloride in the well water kept the Br/Cl ratio in the range expected for concentration of natural soil waters by evapotranspiration (Whittemore, 1988). The deeper observation wells were not affected by the bromide displacement process (Fig. 22). More than a year after chemical flooding, no bromide concentrations related to tracer breakthrough to the water table were observed in any of the wells. All bromide data are tabulated in Tables C.1 and C.4.

Figures 15 and 22, referring to the upper (shallow) saturated zone, and Figure 14, referring to the vadose zone, demonstrate vertical displacement of pore fluids by the flooding water. Comparisons of water content with depth on the dates of bromide sampling (Fig. 23) indicate that the relative distribution of the bromide tracer with depth does not correspond with the water content distribution in the soil profile. This observation supports deduction from Figures 14, 15, and 22 that the applied chemical flood primarily displaces the initial pore fluids during the infiltration and percolation process; percolation through the soil profile by bypassing the existing pore fluid was minor. As a consequence of this displacement, the bromide tracer remained near the soil surface, thus probably explaining its persistence in the upper foot of soil.

Atrazine and atrazine metabolites. The atrazine versus time breakthrough curve based on suction lysimeter sampling is shown in Figure 24. The atrazine breakthrough curve based on soil core extraction is shown in Figure 25. Because each core sample comes from a different (random) location within the flooded area and because of natural soil heterogeneity, the atrazine breakthrough curve based on soil cores shows wide fluctuations resulting from random noise. Otherwise the breakthrough curves are similar to the ones based on suction lysimeters. The

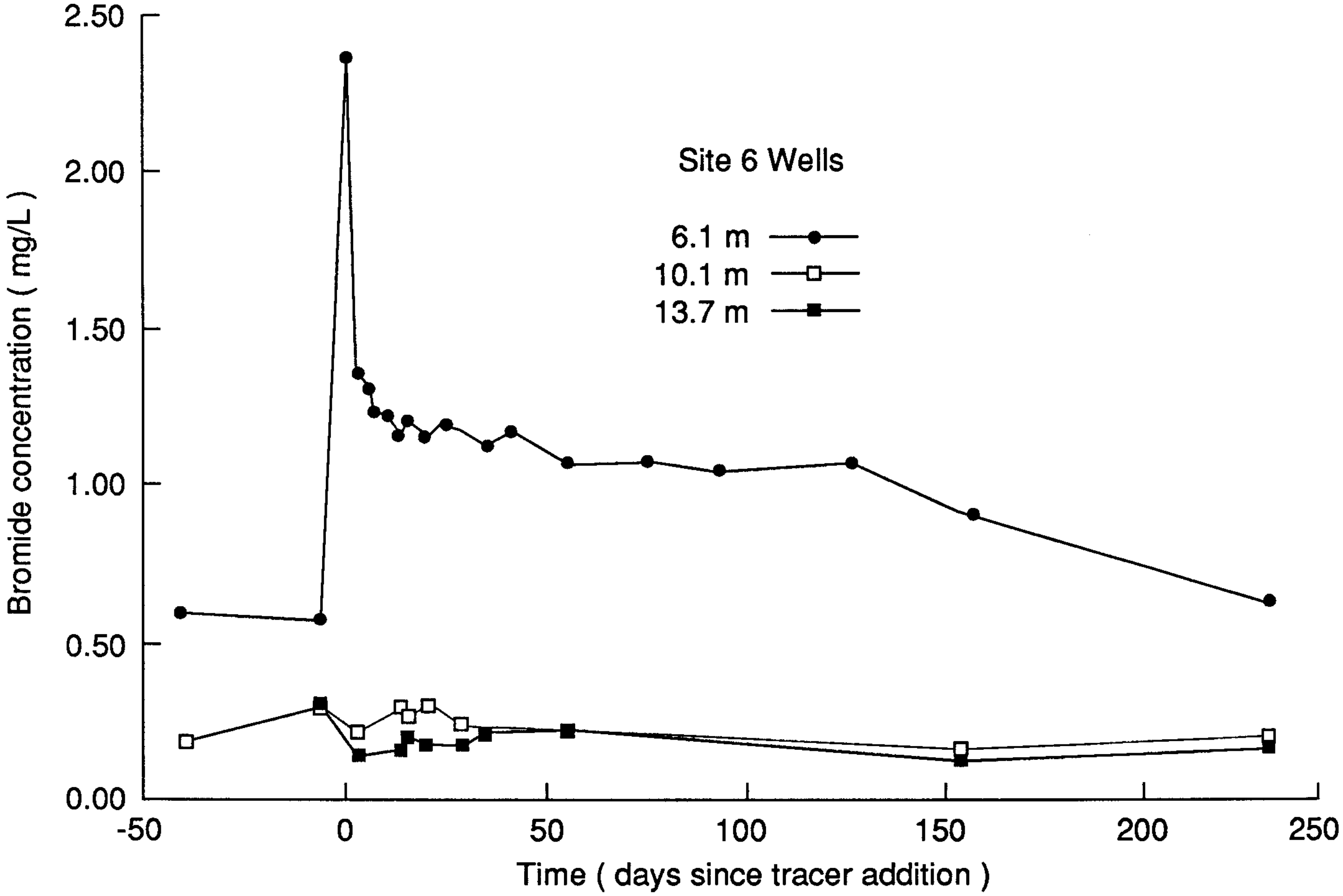

Figure 22. Bromide concentration time-series distribution from site 6 observation wells.

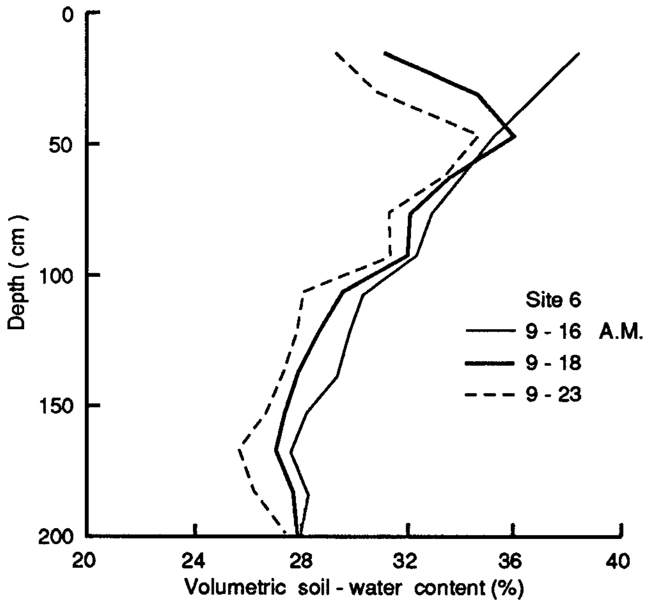

Figure 23. Soil-water content profiles since chemical flooding was initiated at site 6.

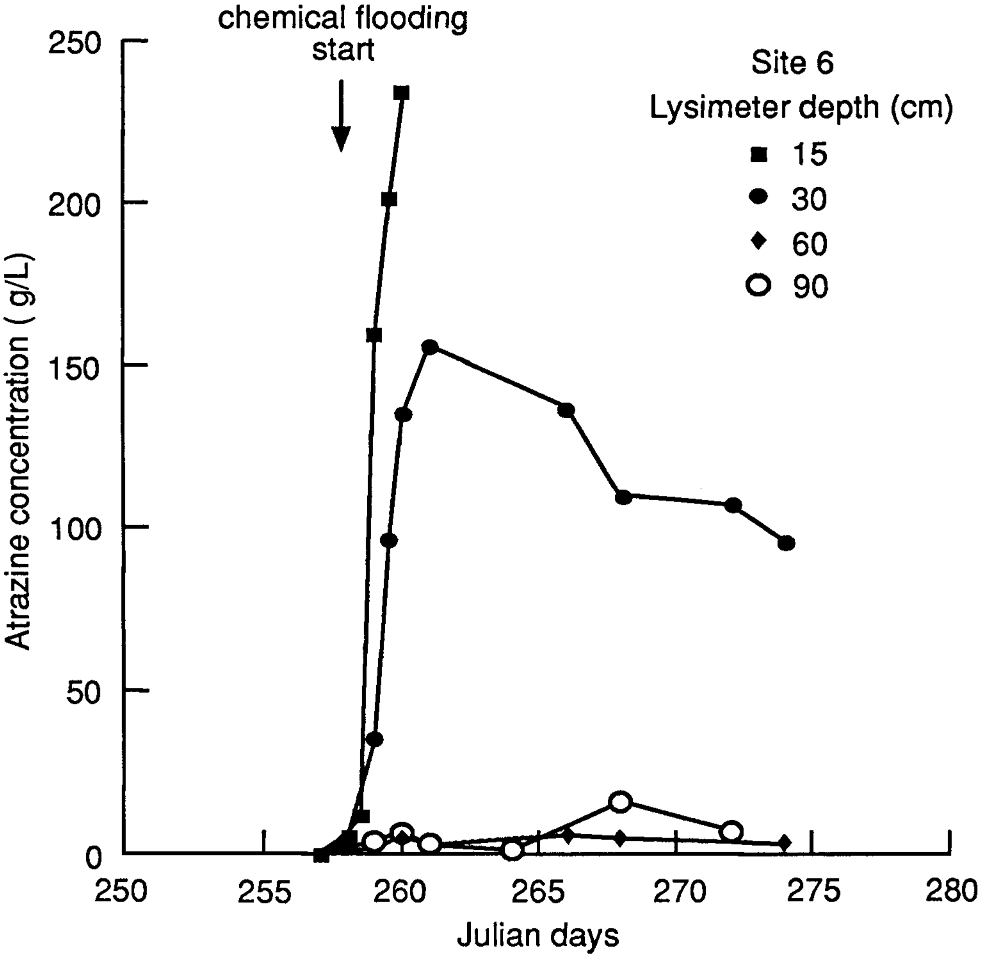

Figure 24. Atrazine breakthrough curves for site 6 based on suction lysimeter sampling.

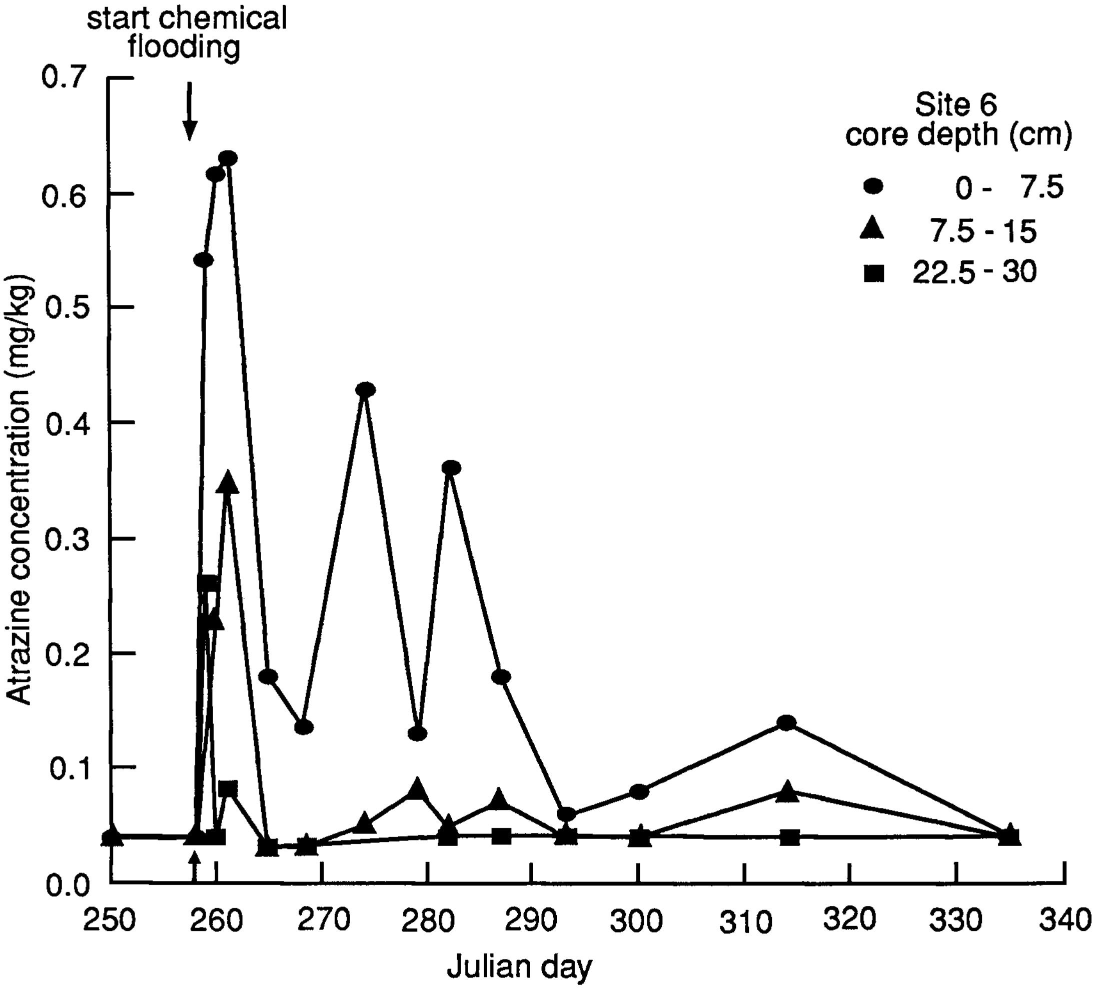

Figure 25. Atrazine breakthrough curves for site 6 based on soil cores. Detection limit is 0.04 mg/kg.

vertical distribution of atrazine in the soil shows an exponential-type decay with depth (Fig. 26). Atrazine did not penetrate below the top 30 cm (1 ft) of soil until December, approximately 3 months after flooding. However, during the February and May 1988 soil core samplings, some atrazine was detected to a depth of 75 cm (30 in.). However, this apparent deeper penetration of atrazine occurred after the plastic cover had been removed. Since then the field has been plowed and chemically treated with additional atrazine.

Given that the applied atrazine did not penetrate below the top 30 cm (1 ft) of soil as of December 1987, and that the calculated soil-water fluxes decreased drastically to a fraction of 1 cm/day within a few days of covering the site with plastic (Fig. 18), we calculated a mass balance for atrazine to check whether the atrazine measured in the soil cores before December, 1987 accounted for the amount of atrazine applied at the surface. During the first three days after the end of the chemical flood the mass balance accounted for 97% to more than 100% of the applied atrazine. However, after the first few days, only 10–50% of the atrazine mass could be accounted for (Fig. 27).

Physical-chemical properties of the soil profile essential for biological and chemical degradation of atrazine to daughter products could explain this apparent mass imbalance. Figure 6 indicates that the content of organic carbon is relatively high in the top 30 cm (1 ft) of soil and decreases rapidly with depth. The cation exchange capacity (CEC) of the soil in the top 30 cm also is the highest in the soil profile, and the soil pH reaches its minimum value of 5.9 just under the top 30 cm of soil, below which it rapidly increases to greater than 8.5 just below the 100–cm (3.5–ft) depth. The soil changes from silty loam to silty clay loam below 48 cm (19 in.), with a corresponding decrease in hydraulic conductivity. The high organic carbon content of the top 30 cm is conducive to high biological activity, which may result in biodegradation of atrazine (dealkylated metabolites); the low pH at just below the top 30 cm is inducive to atrazine hydrolysis (to hydroxyatrazine) catalyzed by the presence of clays of high CEC (chemical degradation). The high soil moisture content (caused by flooding) and the relatively high soil temperatures would also

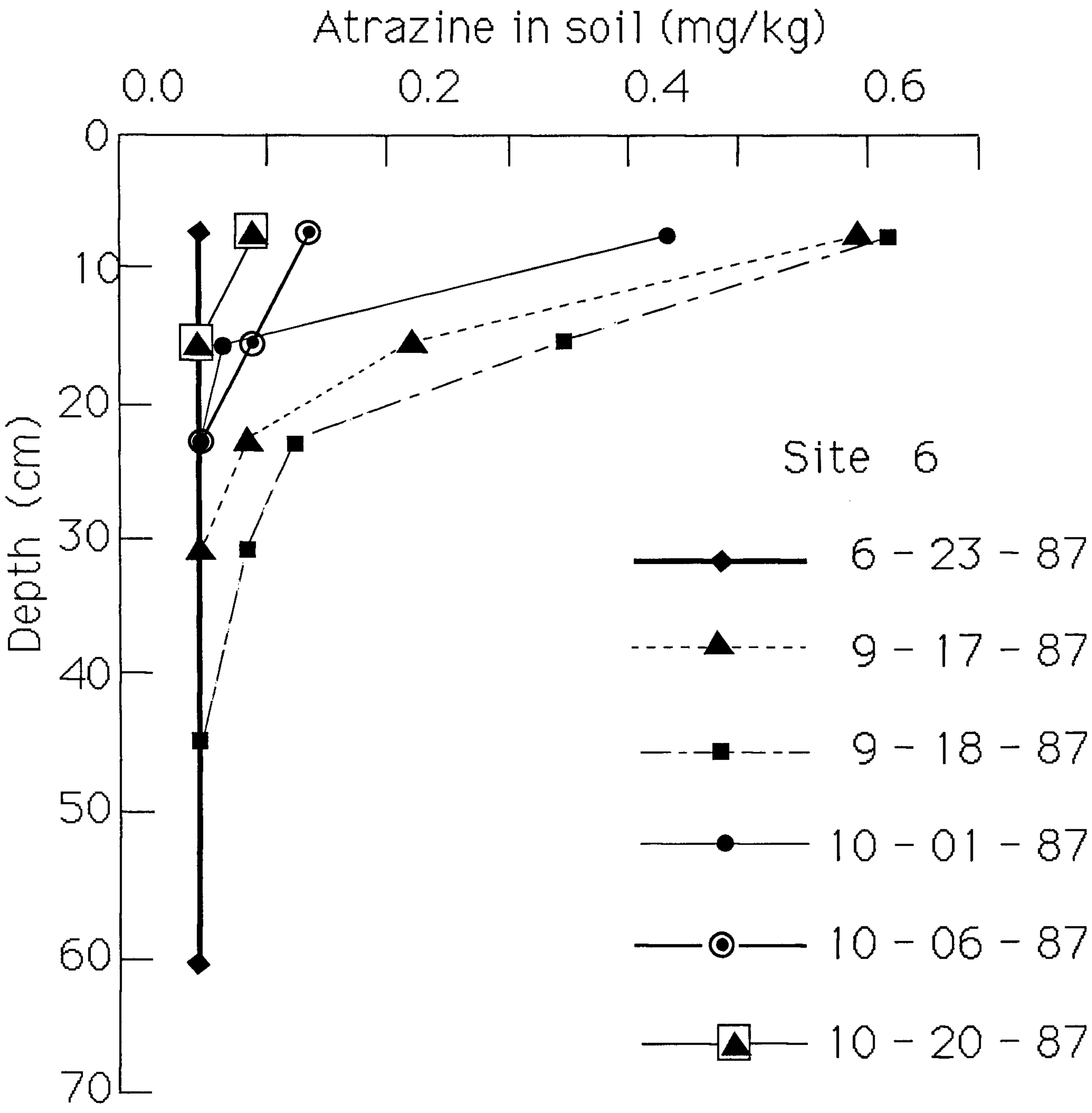

Figure 26. Atrazine profiles at site 6 based on soil cores.

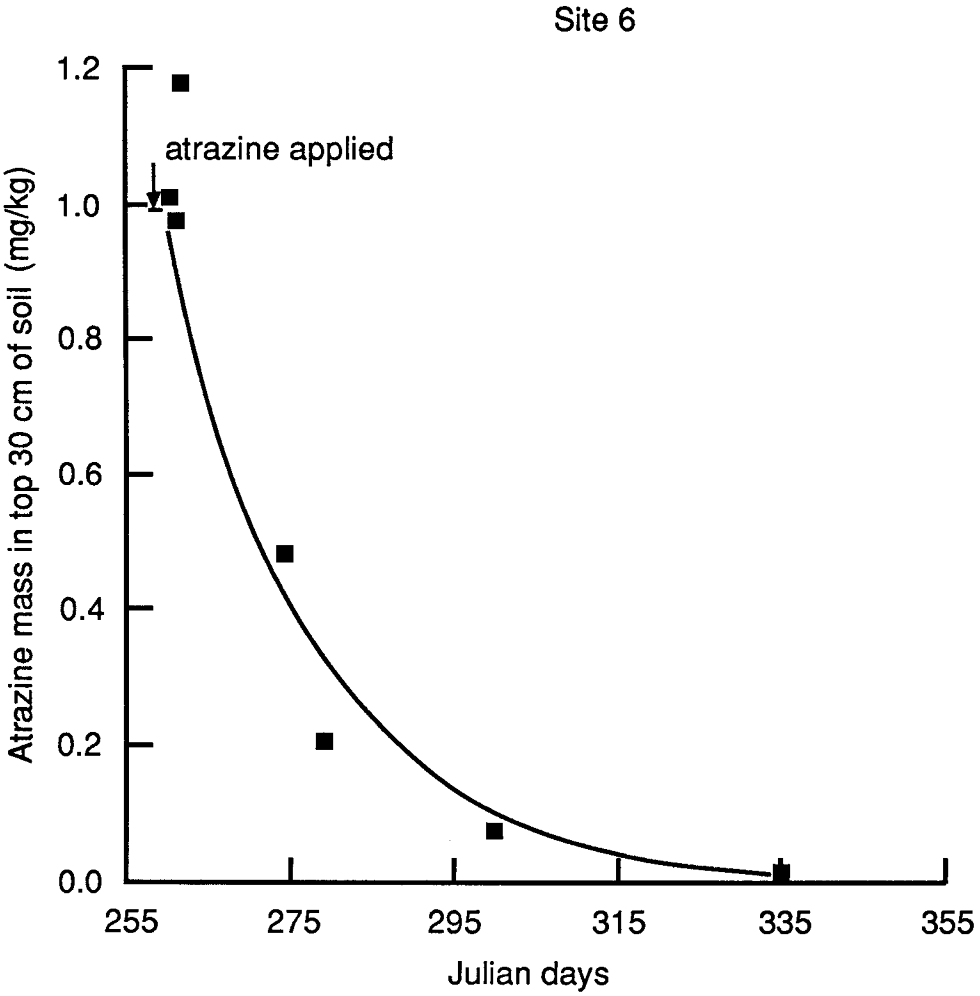

Figure 27. Atrazine mass in the upper 30 cm of soil at site 6, plotted on arithmetic scale.

be expected to stimulate microbial degradation of atrazine in soils. Figure 27 indicates that atrazine degradation may have followed first-order kinetics; that is, the log of the atrazine concentration decreases linearly with time, as shown in Figure 28. The half-life of atrazine (i.e., the time for one-half of the applied atrazine to disappear from the application site) was approximately 13 days at site 6 based on Figure 28. The field-estimated half-life of atrazine is much shorter than the atrazine half-life values reported in other studies [Jury et al.(1987) for example], where the atrazine half-life is more than 2 months. This may be one reason why atrazine was not detected in any of the 1988 surveyed chemigation wells in the Great Bend Prairie by the Kansas State Board of Agriculture (Anderson, 1989).

Core samples of the 0–30 cm and 60–90 cm (0–1 and 2–3 ft) intervals of site 6, collected on February 25, 1988, were analyzed for atrazine and atrazine metabolites, and the results are tabulated in Appendix E. The hydroxyatrazine concentration (0.124 ppm) present in the 0– to 15–cm (6–in) depth interval was 1.6 times the amount of parent atrazine present. For the 15– to 30–cm (6– to 12–in) depth interval the hydroxyatrazine concentration (0.116 ppm) was 0.4 times the amount of parent atrazine present. The hydroxyatrazine concentration for the 60–75–cm (24–30–in) and 75–90–cm (30–36–in) intervals (0.167 ppm and 0.185 ppm, respectively) were 3.1 and more than 4 times the amount of parent atrazine present, respectively, although the parent atrazine was below detection limit (0.05 ppm) for the 75–90–cm (30–36–in) depth. Therefore a significant portion of parent atrazine was degraded into the hydroxy form in the upper 90 cm (3 ft). The dealkylated metabolites of atrazine at the 0–30–cm and 60–90–cm (0–1– and 2–3–ft) depth intervals were below the detection limit (0.05 ppm). Such concentrations seem very low, given the high organic matter content of the upper 30 cm of soil, but cold soil temperatures during the winter sampling period may have limited biological activity. Additional soil samples collected in May and August of 1988 were sent for atrazine metabolite analysis, especially to verify biological activity (Appendix E). The results show significant amounts of both biodegradation by-products (ethylatrazine, G-28279 and isopropylatrazine, G-30033) as well as hydroxyatrazine (G-34048)

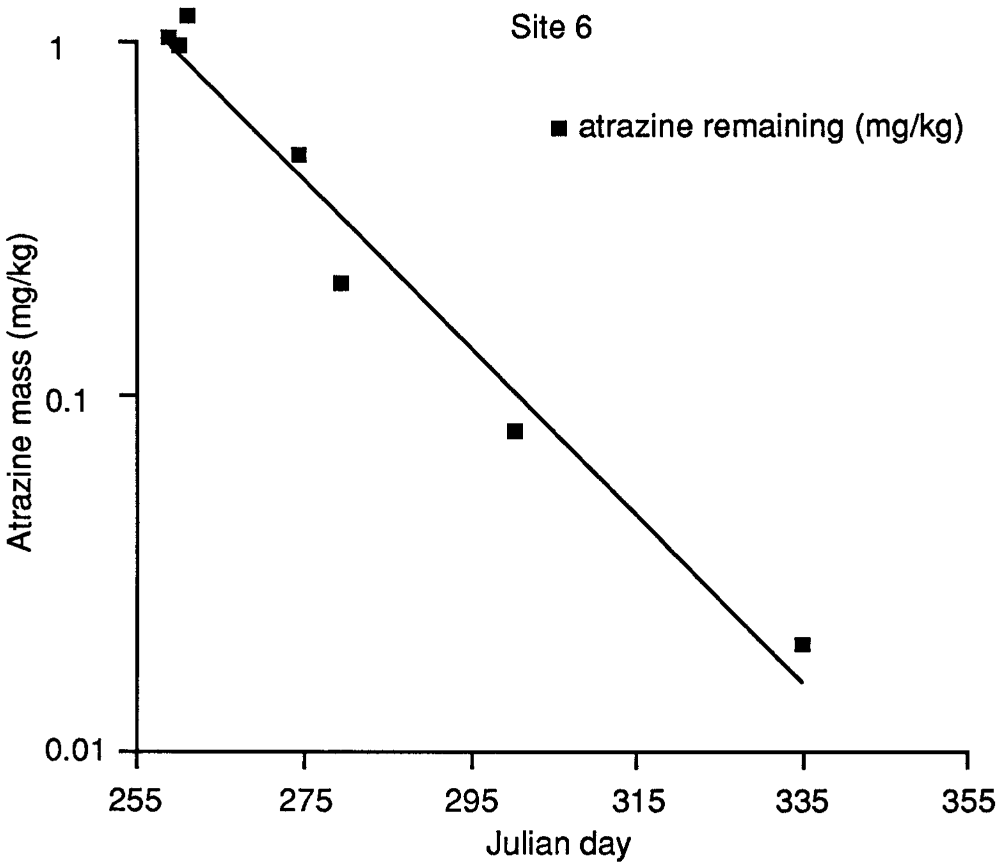

Figure 28. Atrazine mass in upper 30 cm of soil at site 6, plotted on logarithmic scale.

for the 0–15–cm (0–6–in) depth interval on the August 1988 sampling and the 30–45–cm (12–18–in) depth interval on the May 1988 sampling.

No atrazine was observed in any of the observation wells, consistent with the retention and decomposition of atrazine in the upper 75 cm of soil and the observation that no significant concentrations of tracer bromide reached the shallow ground water. All atrazine data are tabulated in Appendix D.

Site 7: The soil profile and its physical and chemical characteristics

The soil profile of this site—designated as Attica soil, a coarse-loamy mixed, thermic Udic Haplustalf—consists of brown to grayish brown loamy fine sand down to 15 cm (5.9 in. or 0.5 ft) comprising the soil Ap horizon which is characterized by a weak granular structure. The Ap horizon is followed by an AB horizon of grayish brown loamy fine sand down to 32 cm (12.6 in.). This horizon is characterized by a weak medium subangular blocky structure and a relatively high bulk density compared with other horizons in the upper part of the profile. Underlying that layer is a brown to yellowish brown fine sandy loam comprising the Bt horizon down to 65 cm (25.6 in. or 2.13 ft). The Bt soil horizon which can be subdivided into two subdivisions [Bt1 (32–50 cm) and Bt2 (50–65 cm)] is slightly hard and friable with moderate medium subangular blocky structure. Yellowish brown loamy fine sand forms the underlying C horizon, down to 157 cm (61.8 in. or 5.15 ft), which can be subdivided into three C subdivisions (C1, C2, and C3). The C horizon is massive and friable with few fine distinct brown to dark brown mottles. Underlying this soil profile is another buried soil consisting of a weak red sandy clay loam comprising another C horizon down to 177 cm (9.7 in. or 5.81 ft). This soil horizon has a massive structure with many reddish brown mottles. Underlying this is a reddish gray B soil horizon, which can be subdivided into a silty clay Bw horizon down to 215 cm (84.6 in. or 7.05 ft), characterized by several wide (approximately 6 cm) vertical cracks filled in with coarser soil, and a silty clay loam Bk horizon down to 240 cm (94.5 in. or 7.87 ft), characterized by strongly effervescent platelike soft masses of lime.

The specific soil horizons and their grain size distributions, as determined by the Soil Conservation Service, are shown in Figure 29. The figure indicates that site 7 has a much sandier soil profile down to 160 cm (5.2 ft) than site 6. X-ray diffraction patterns of the clays of the lower soil horizons (2C4, 2BW, and 2Bk) exhibit "large" montmorillonite peaks and "medium" mica and kaolinite peaks; while patterns for the upper soil horizons (Bt1 and Bt2) exhibit "medium" mica and montmorillonite peaks. The organic carbon content (Fig. 30) of the upper foot of soil is much lower compared with site 6, although the cation exchange capacity of the clay content in site 7 is similar to that of site 6. The bulk density of the soil profile as determined by both the clod and core methods (Fig. 31) shows relatively high compaction at the bottom of the upper 30 cm, decreasing thereafter until it reaches the silty clay soil, where it increases again. The available water capacity of the soil profile is shown in Figure 32. The available water capacity of site 7 is generally lower compared with site 6 (Fig. 8) because of the sandier nature of the soil profile, except where the silty clay soil is encountered at depth [below 180 cm (6 ft)], causing the available water capacity to increase significantly (Fig. 32). The pH distribution in the soil profile (Fig. 33) has a narrower range (6.6 to 7.9 based on a 1:1 soil to water extract) compared with site 6 (5.9 to 9.0 based on a 1:1 soil to water extract). The pH decreases slightly with depth until the silty clayey soil is encountered at depth, where the pH progressively changes from near neutral to slightly alkaline.

The electrical conductivity of water extracted from saturated soil pastes and the exchangeable sodium percentage of the soil profile (Fig. 34) are much less compared with site 6 (Fig. 10), indicating much lower salt content in the soil profile of site 7. The nitrate and chloride depth distributions in the soil profile as sampled in suction lysimeters before chemical flooding of the site, are shown in Figure 35. In general, high nitrate and chloride concentrations in the upper 30 cm (1 ft) of soil are observed, progressively decreasing with depth down to 90–120 cm

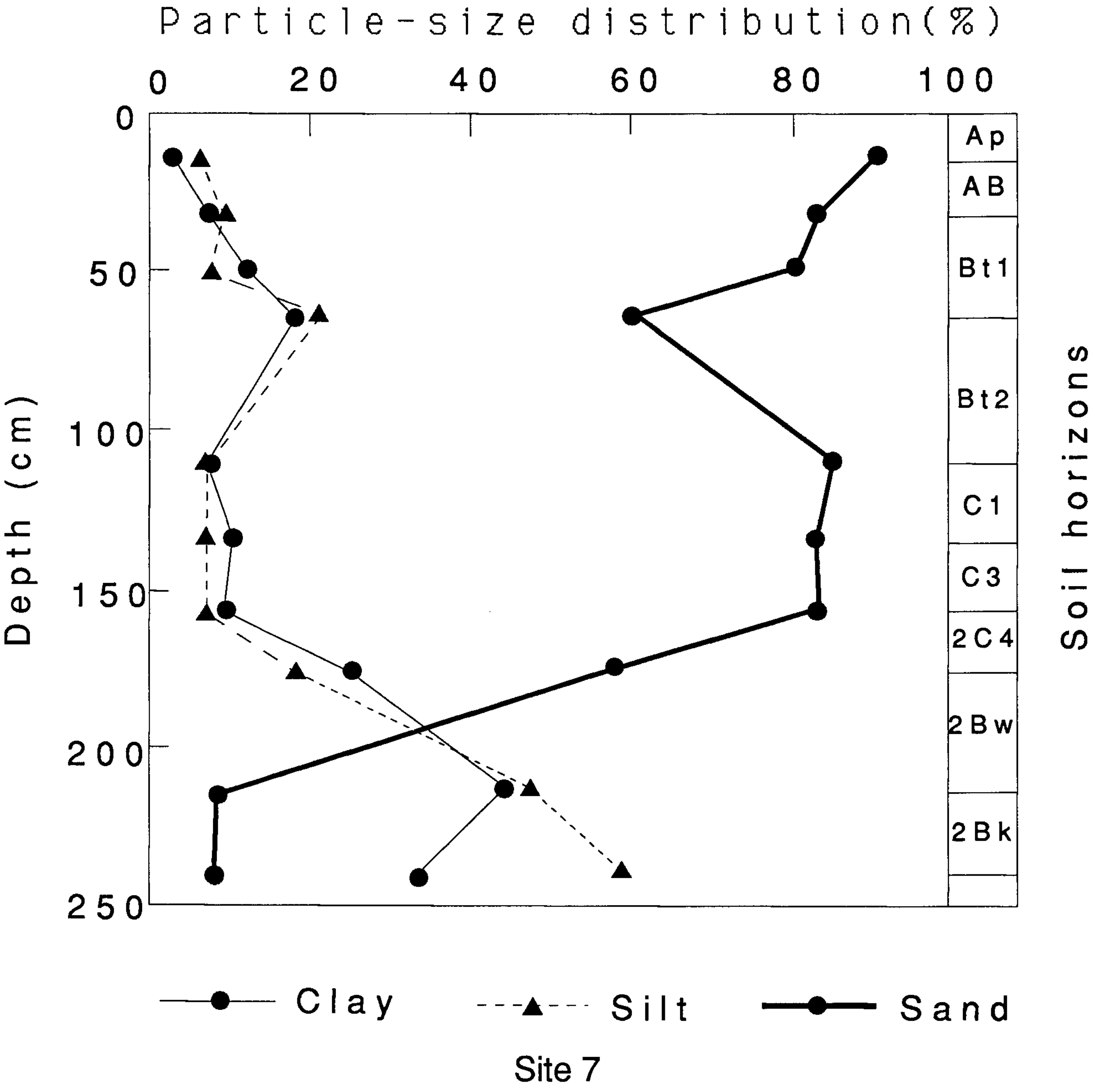

Figure 29. Grain size distribution and soil horizons for site 7.

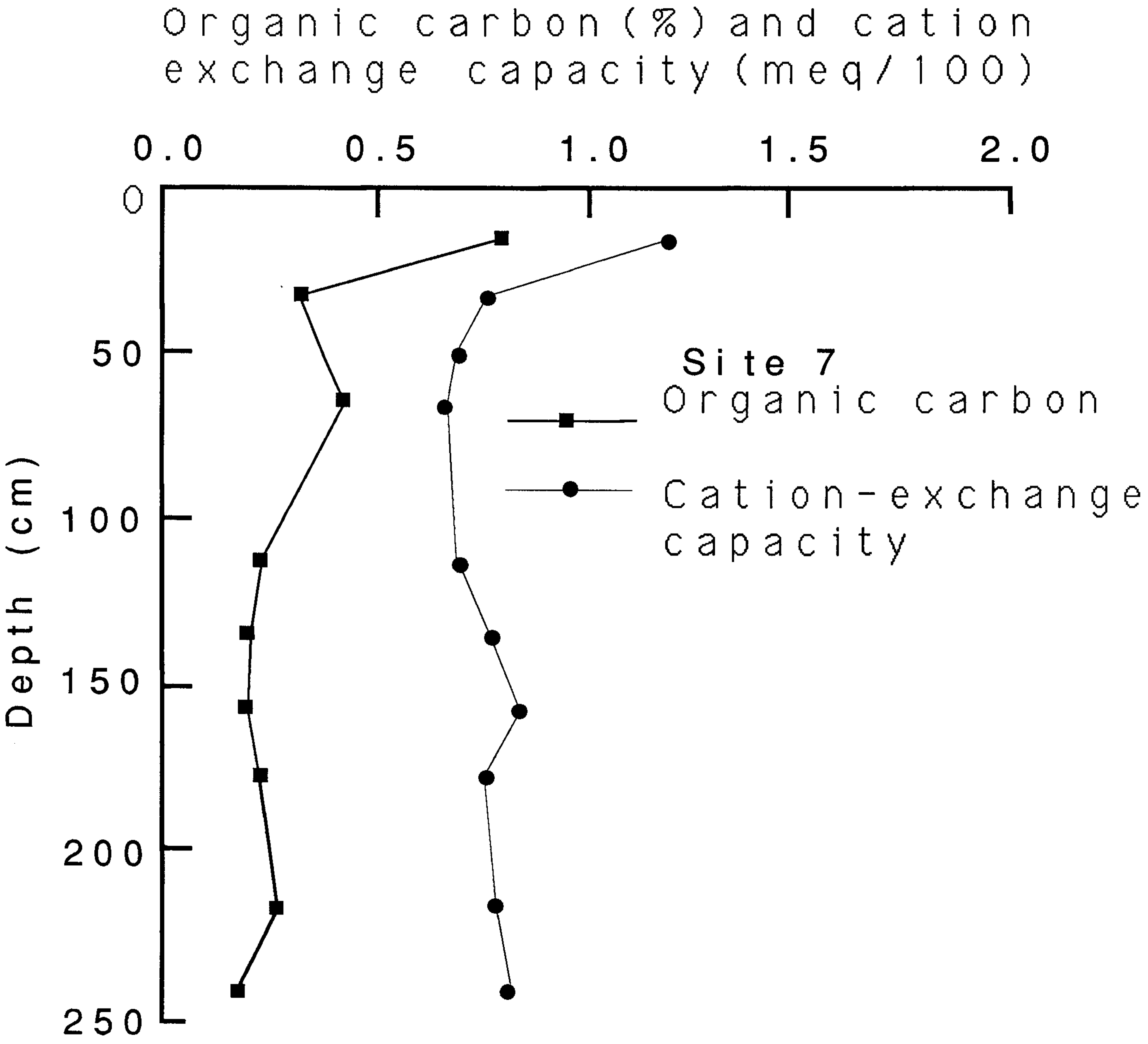

Figure 30. Organic carbon content and cation exchange capacity profiles for site 7.

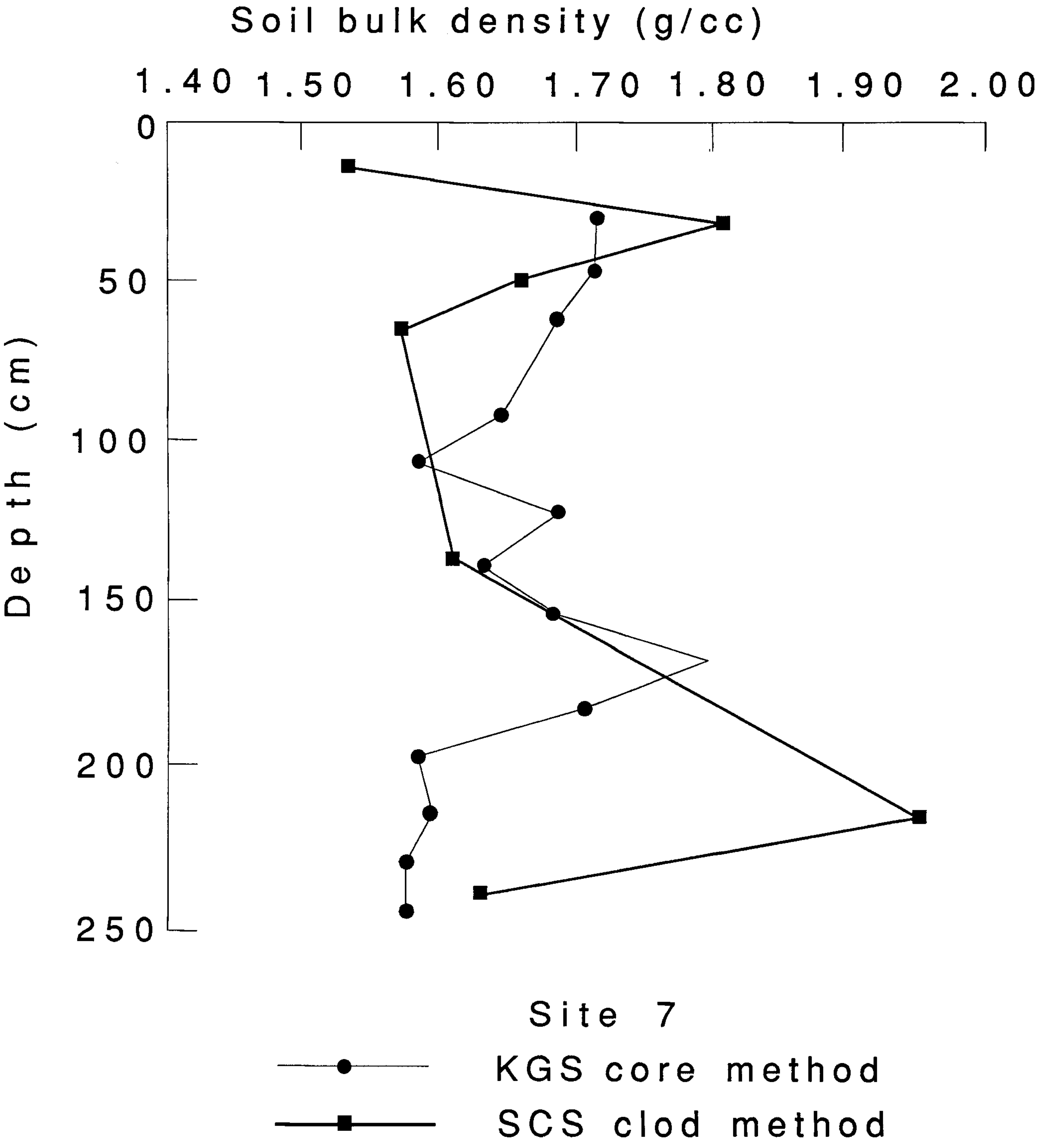

Figure 31. Bulk density distributions determined by the two methods indicated for soil profile at site 7.

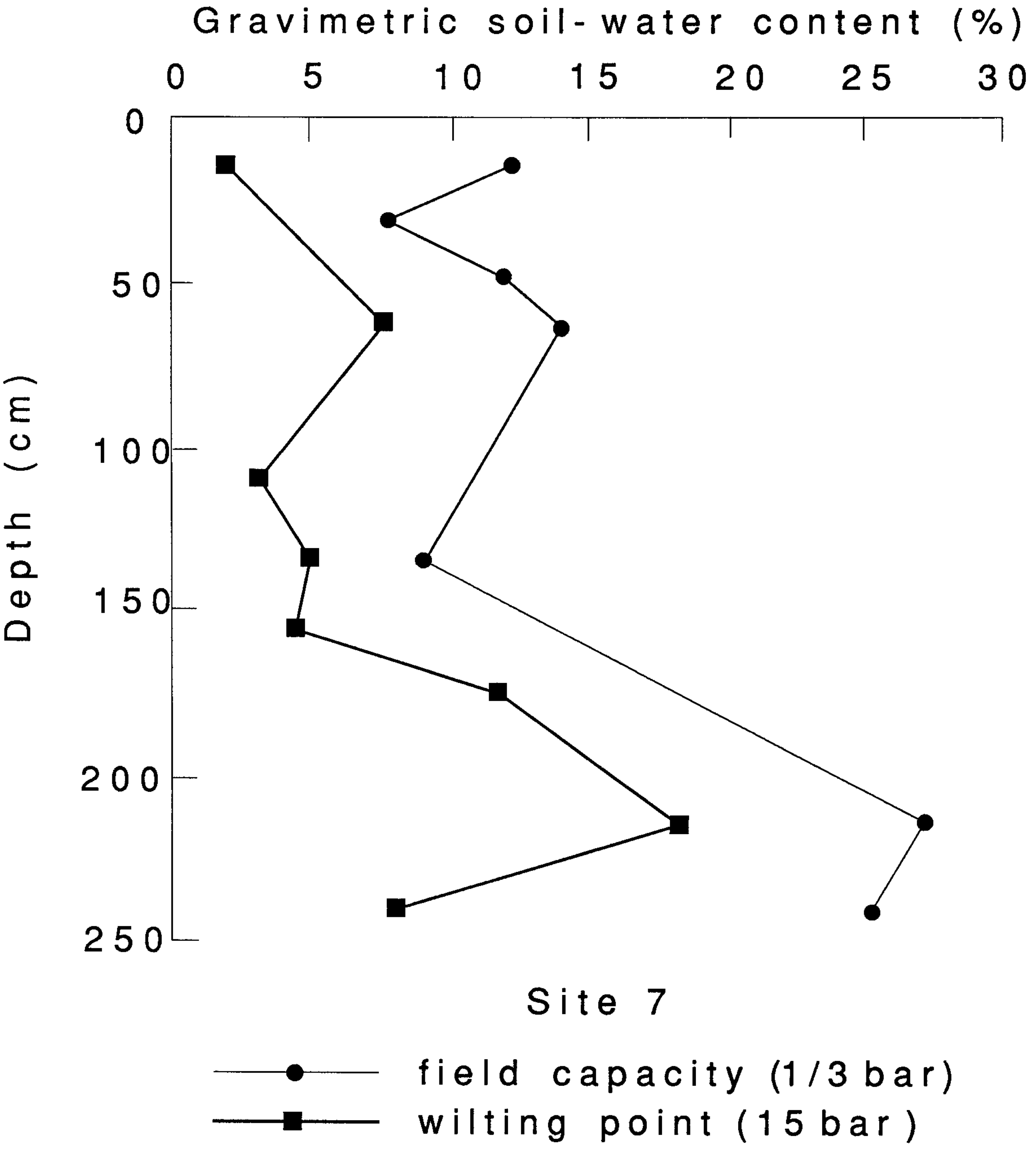

Figure 32. Available water-holding capacity of the soil profile at site 7.

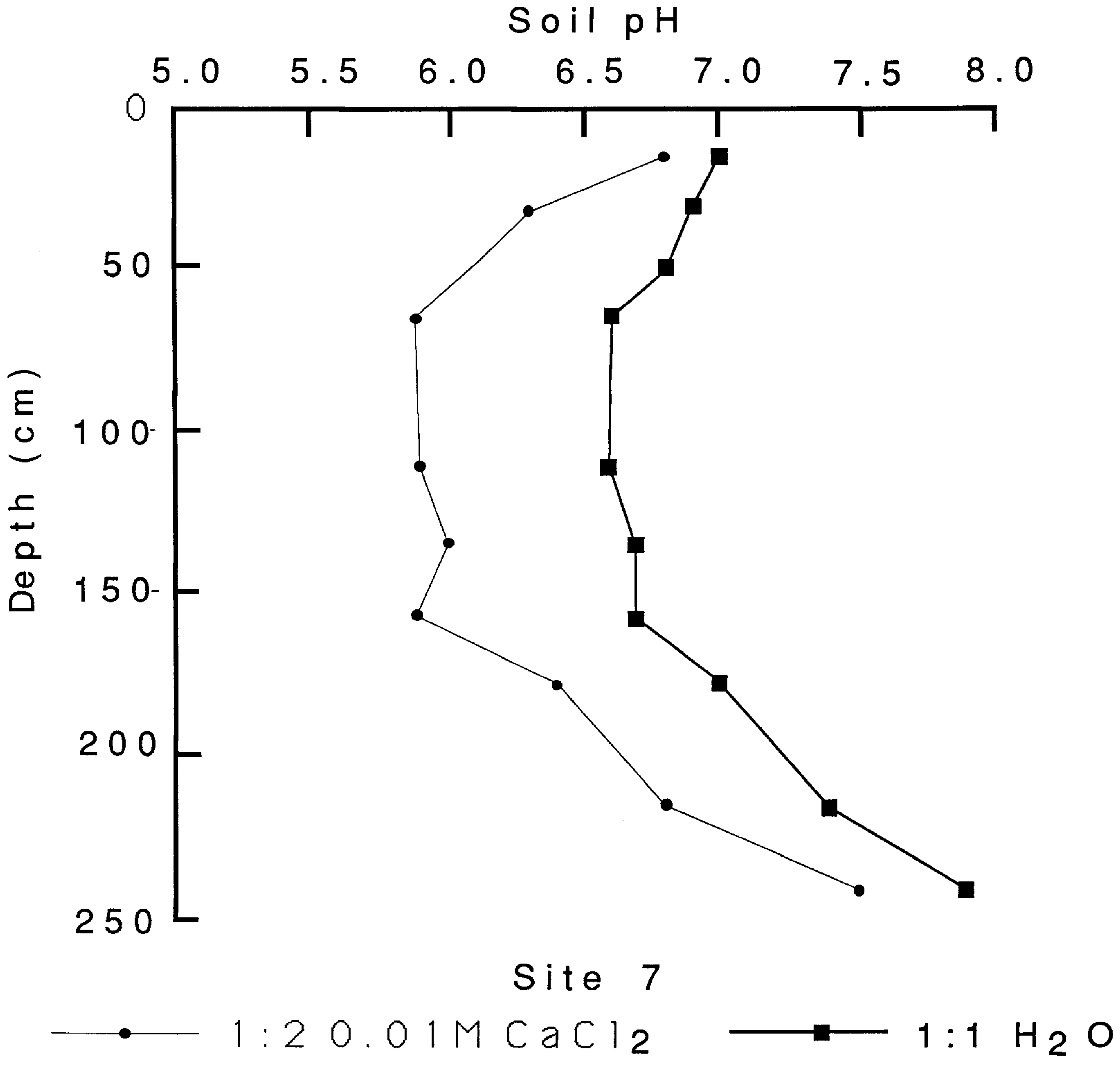

Figure 33. Soil pH profile determined by the methods indicated for site 7.

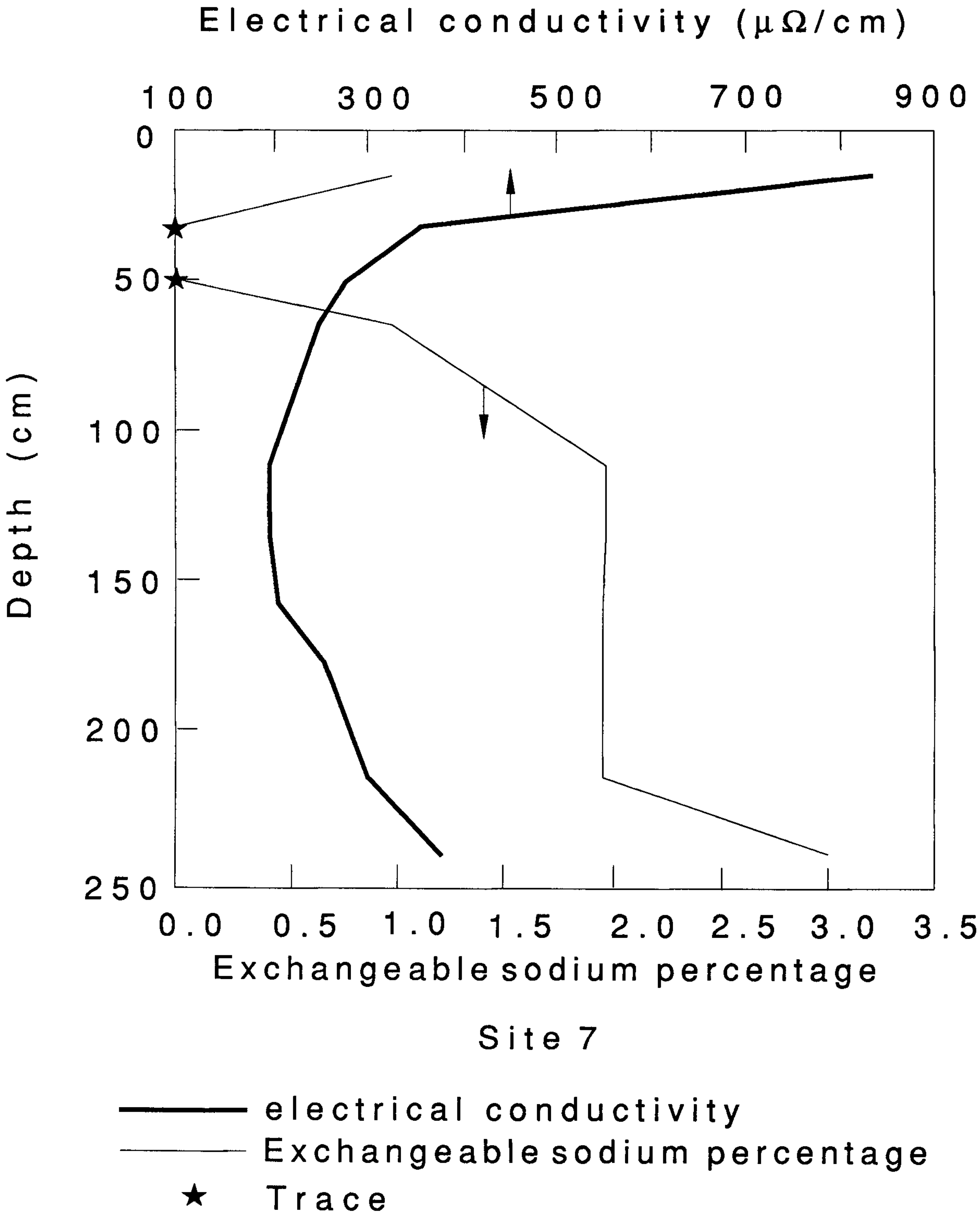

Figure 34. Electrical conductivity and exchangeable sodium percentage for soil profile at site 7.

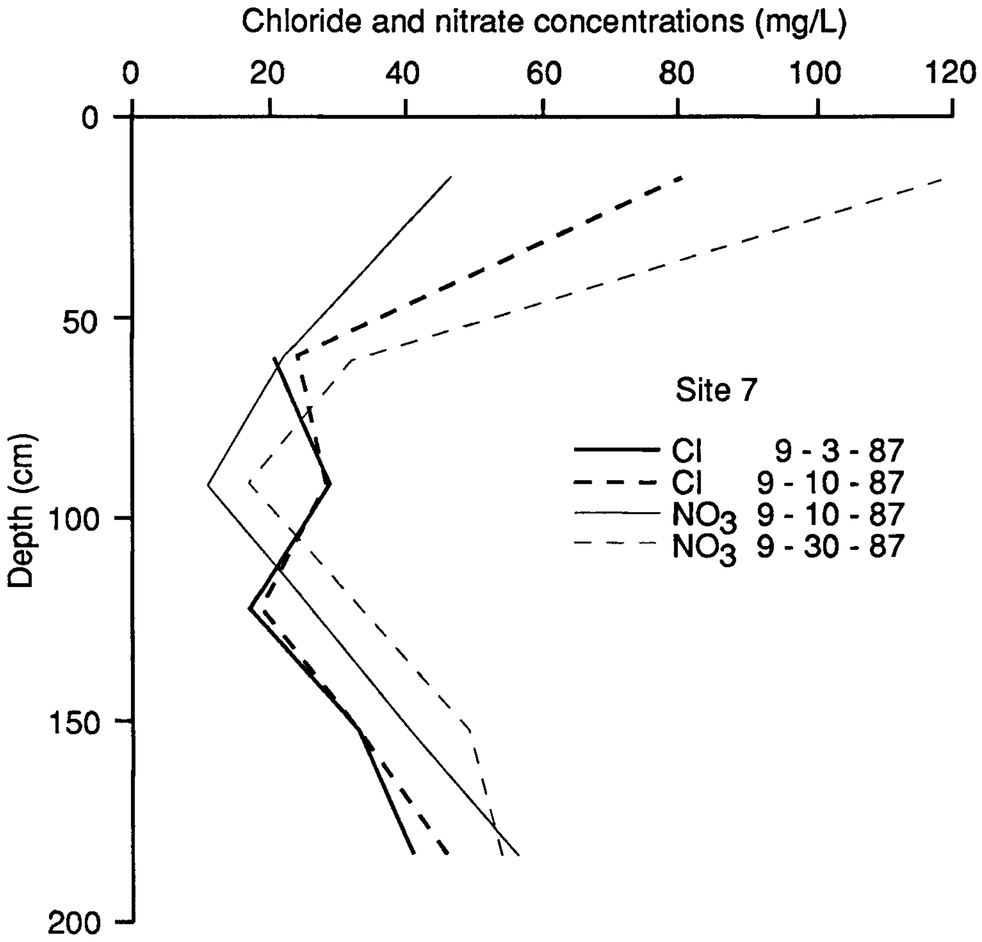

Figure 35. Profiles of chloride and nitrate concentrations from suction lysimeters before flooding at site 7.

(3–4 ft), beyond which they progressively increase with depth. The patterns of electrical conductivity and chloride with depth are similar to each other at this site, in contrast to the corresponding situation at site 6. Both sulfate and chloride concentrations in soil solutions from site 7 are appreciably lower than at site 6. The higher hydraulic conductivity of the soil profile at site 7, as will be shown later, in comparison with that at site 6 apparently does not allow as great a buildup of salts in the soil from evapotranspiration because the salts are more easily flushed by recharge.

Water chemistry of site 7

Site 7 in Pratt county is center-pivot irrigated and was used to grow corn, wheat, and soybeans during this study. At this site the soils are sandy and highly permeable and have low clay and organic carbon contents (see section on soil characteristics). The waters at the site are dominantly Ca-Mg-HCO_3-Cl type (Fig. 36), and the soil zone has less salt present than at site 6.

The specific conductance, chloride, and nitrate graphs show an overall gradual decline during this study (Figs. 37, 38, and 39, respectively). On all three graphs there is a change in concentration approximately at the time of the flood experiment. The declining trend may indicate that the shallow water table was reequilibrating to its background level.

The results of the flooding test indicate that near saturation to a depth of 400 cm (13 ft) occurred within 1 day (see next section). Application of 1000 gal water may have caused a slight piston effect in that lower-conductivity irrigation water (500 µmhos/cm) in the system may have been pushed down to the water table at 470 cm (15.5 ft) depth, causing the deflection seen in the 9.1 m (30 ft) well (Fig. 37). This idea is substantiated by the movement of chloride through the soil zone, as will be seen in the next section. Within five days after flooding there was evidence that some of the higher-chloride-containing water, added during the chemical flood (specific

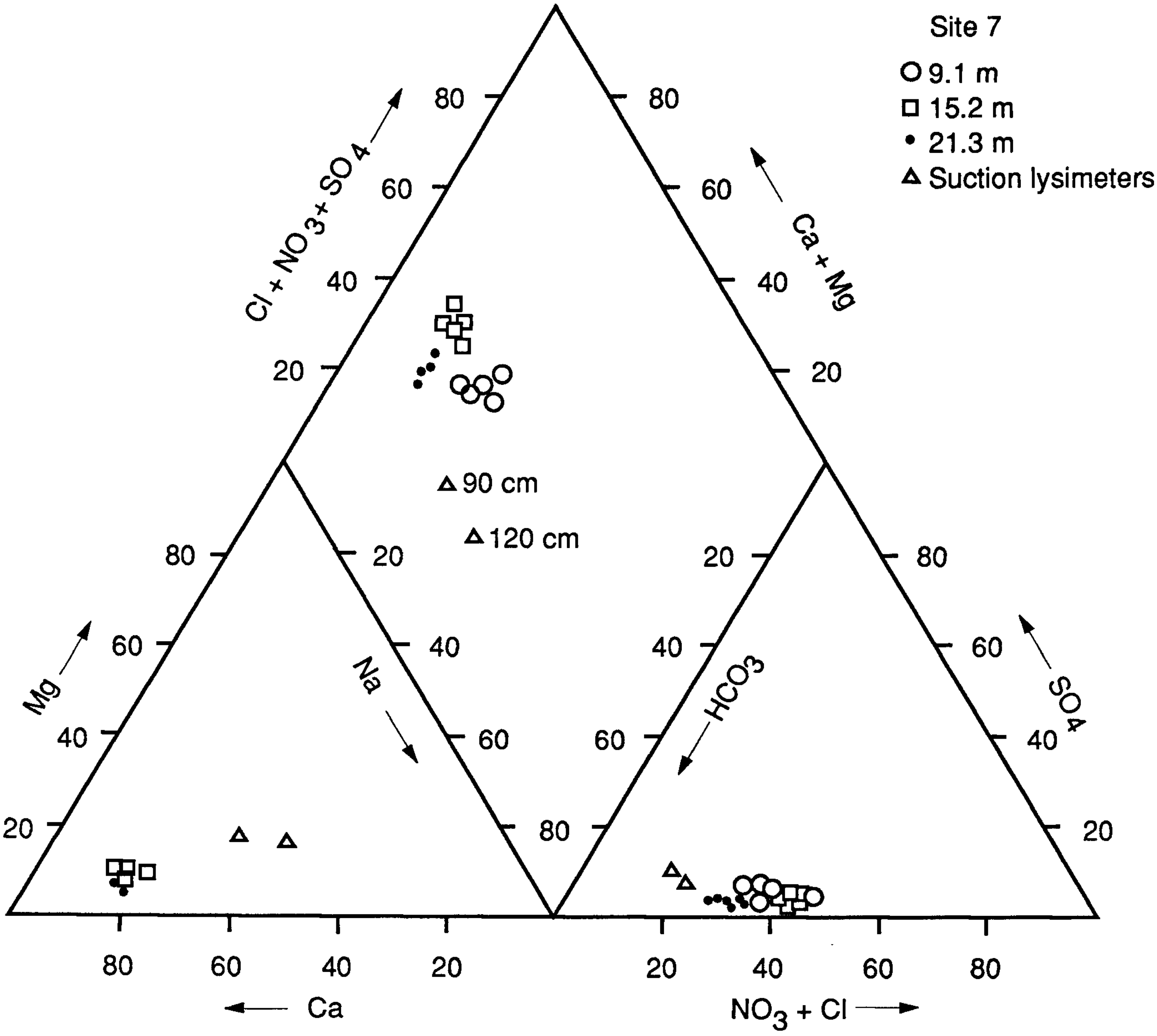

Figure 36. Trilinear diagram showing water chemistry data for three wells and two suction lysimeters at site 7.

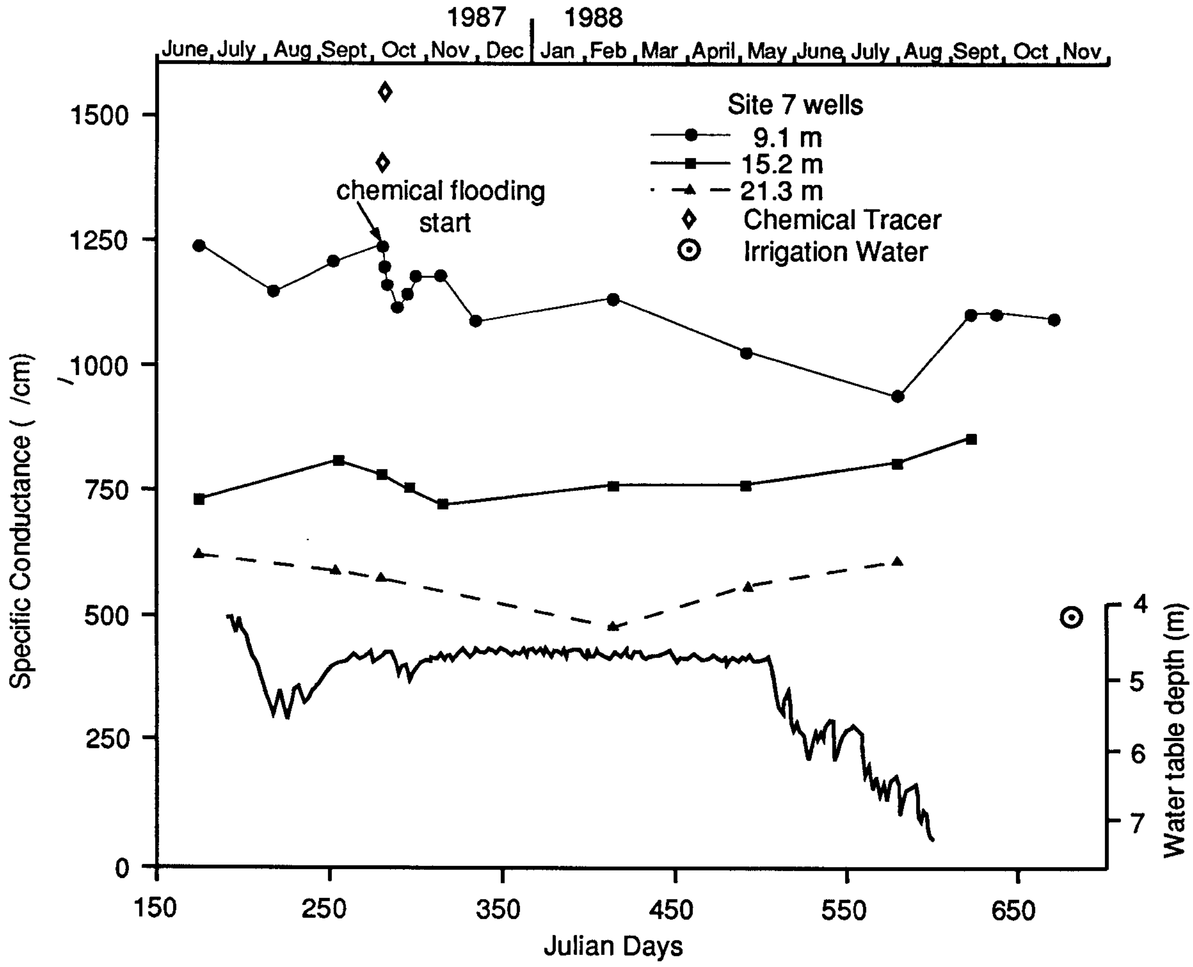

Figure 37. Specific-conductance time-series distribution of observation wells at site 7. Shallow water table is also shown.

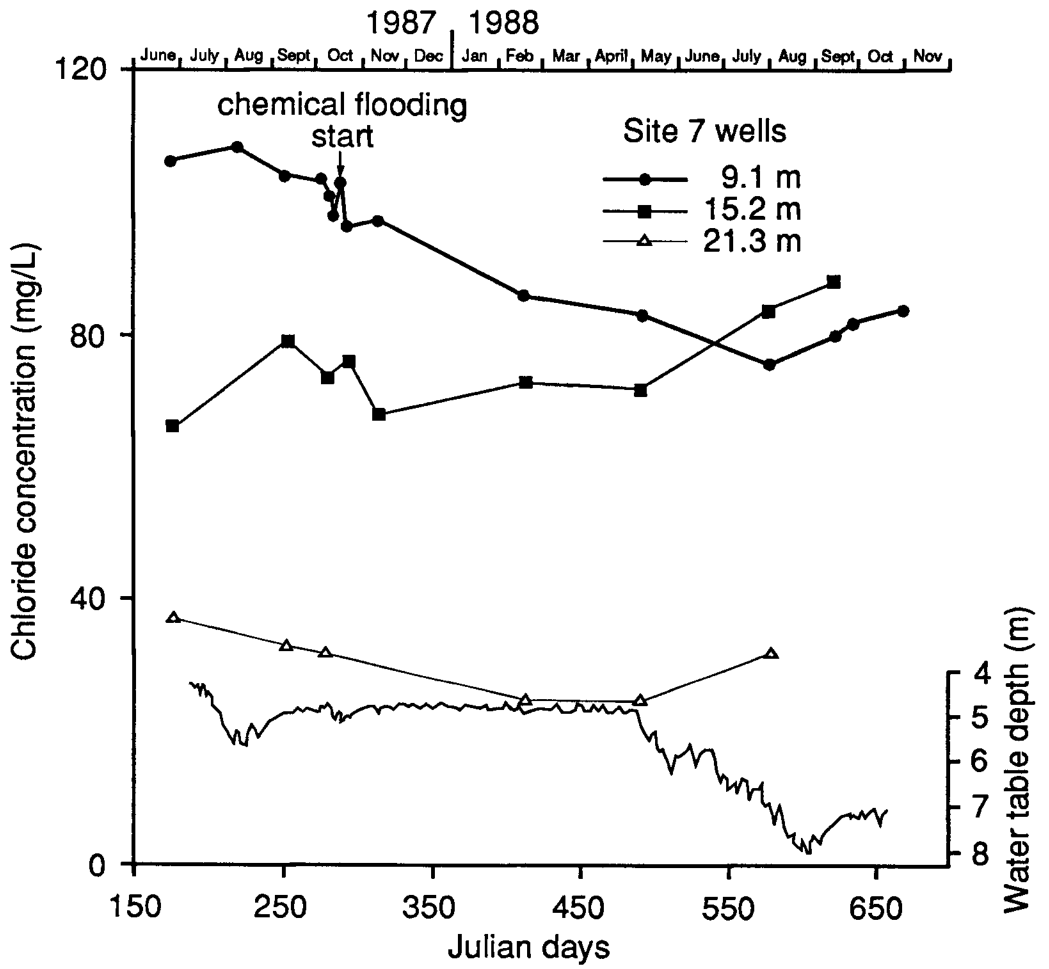

Figure 38. Chloride time-series distribution for observation wells at site 7. Shallow water table is also shown.

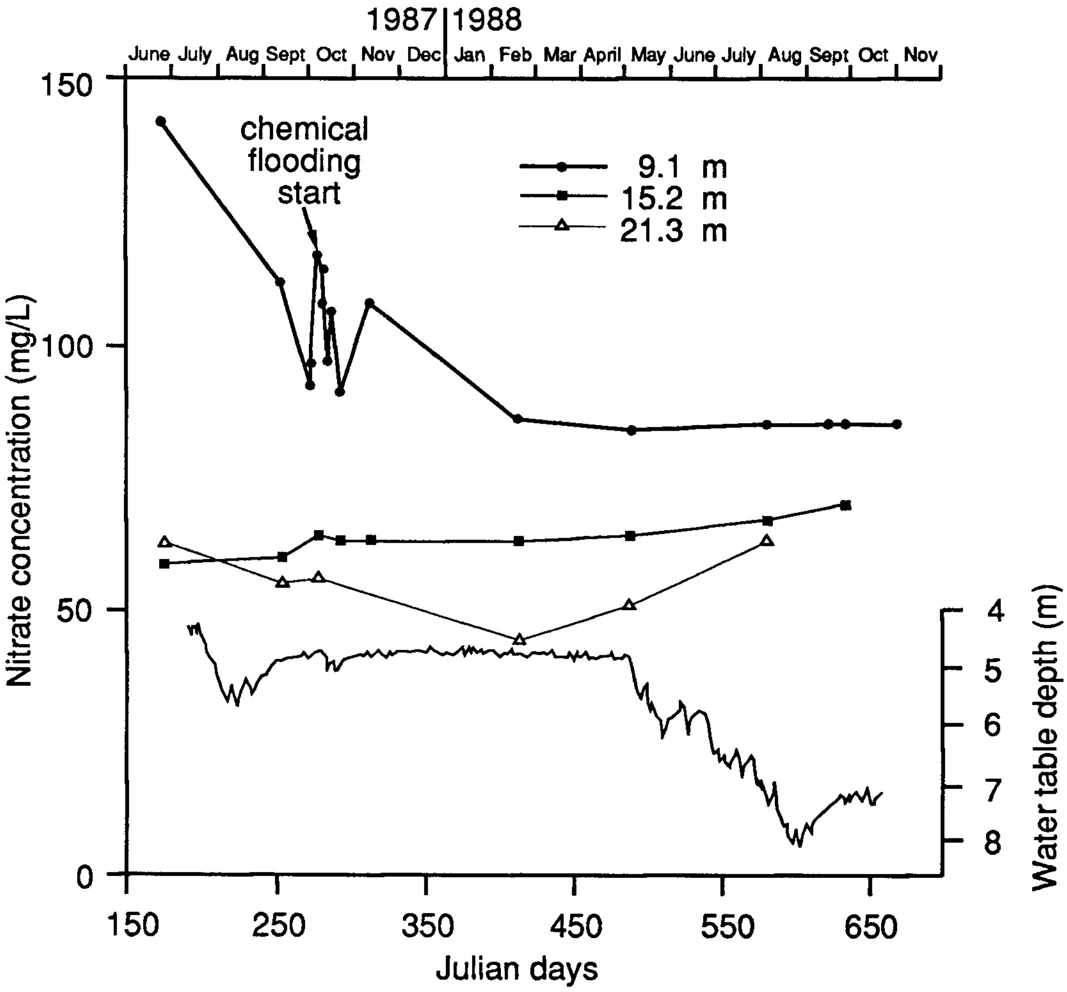

Figure 39. Nitrate time-series distribution for observation wells at site 7. Shallow water table is also shown.

conductance about 900 µmhos/cm) had moved to a depth of 100 cm (40 in.), whereas the chloride content decreased slightly at the 180–cm (6–ft) depth up to 8 days after flooding.

At this site nitrate was the inorganic constituent of most concern. All the wells showed consistently high nitrate values throughout the period of the test (Fig. 39). The concentration of nitrate in the 9.1– m (30–ft) well tends to reflect the timing of irrigation. There appears to be a decrease in nitrate concentration as irrigation continued in June, July, and August 1987, suggesting that dilution of an original quantity of nitrogen may be occurring (Fig. 39). The fluctuation in late September 1987 may reflect application of nitrogen fertilizer in preparation for a new crop (see Table C.5).

The nitrate data for the lysimeters (Table C.2) show a close relationship among fertilizer application, irrigation, and movement of nitrates into the subsurface. There is a noticeable difference in concentrations between times of active irrigation and application of chemicals and times of irrigation with no chemical application (Fig. 40 and Table C.5). The extremely low values of nitrate noted in Table C.2 for the period after September 14, 1988, are difficult to explain at present. Table C.5 shows that no fertilizer was applied after June 1988. Figure 39 shows that irrigation continued into September 1988, during that drought period. The presence of high nitrate at the 120–, 150–, and 180–cm (4–, 5–, and 6–ft) depths during August 1988 (Table C.2) indicates how slowly the nitrate was moving through the soil profile. The low nitrate values in September may indicate utilization of the nitrate by soybeans (the crop planted at the time), utilization of nitrate by bacteria with a release of nitrogen gas, continued movement through the soil profile, or problems with the sampling apparatus. Additional sampling and analyses are required to elucidate these results.

The source for chloride and nitrate-nitrogen in an agricultural setting is usually from the types of fertilizers used on the fields or from concentration of salts in the soil zones resulting from evapotranspiration. Chloride is a conservative tracer because there are not many chemical processes that affect its movement through the vadose zone to the ground water. The Cl/NO_3-N

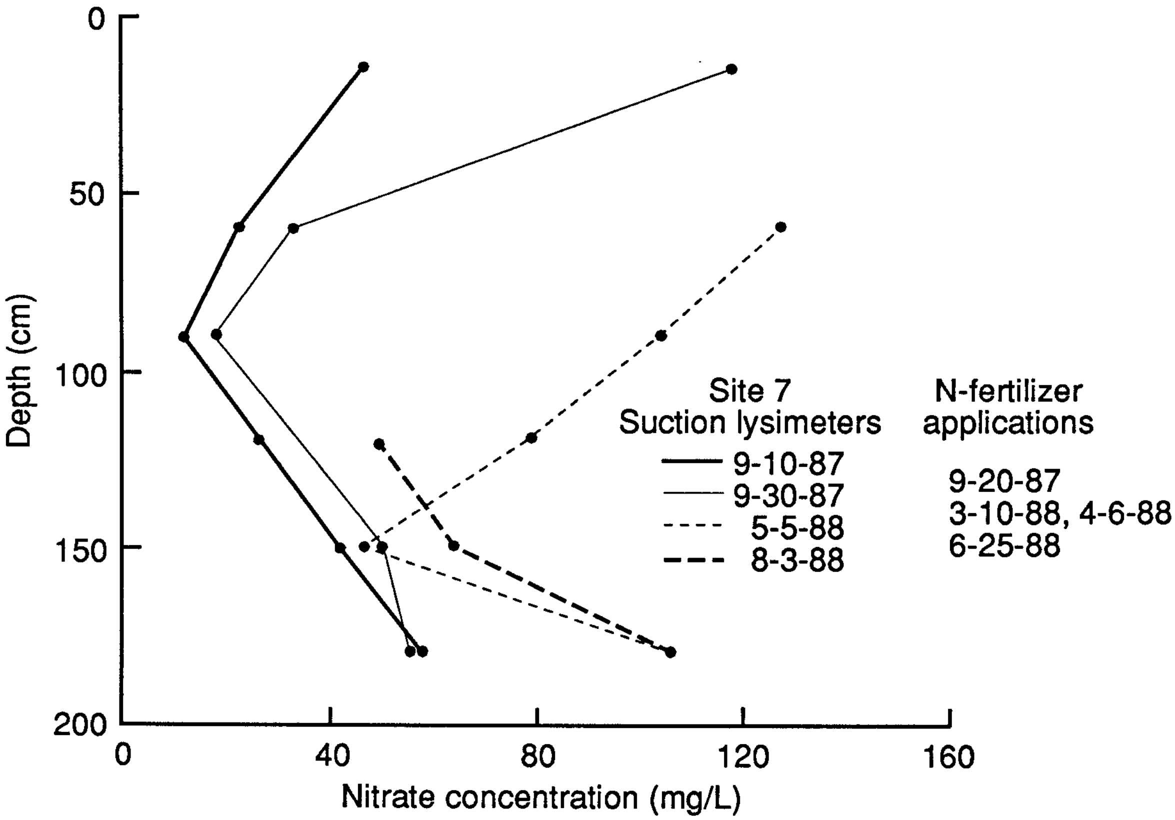

Figure 40. Nitrate concentration profiles from suction lysimeters during 1987 and 1988. Nitrogen fertilizer application dates are also indicated.

weight ratio is often used to evaluate the role of denitrification for elimination of nitrate before the ion moves into the ground water (see literature review on nitrate for references). When the ratio of the two ions becomes large, denitrification or mineralization processes are considered the usual explanation for decrease in nitrate. A low ratio indicates that more nitrate has moved through the vadose zone to the water table, causing an overall increase in nitrate concentration.

Figure 41 shows the Cl/NO_3-N ratio for the wells at site 7. A comparison of the absolute concentrations of chloride and nitrate at the site 7 wells shows a general decrease in concentration with depth (Table C.2). There is a clay zone that occurs between the 9.1– and 15.2–m (30– and 50–ft) wells that may slow the flow of water between these wells. The low Cl/NO_3-N ratio in the 9.1–m (30–ft) well may indicate rapid movement of chloride and nitrate into the subsurface with no possibility of denitrification or mineralization occurring. The Cl/NO_3-N ratio shown in the 15.2–m (50–ft) well (top line on Fig. 41) indicates that nitrate and chloride are not moving into the lower part of the aquifer as quickly and that some of the nitrate is probably removed by denitrification or mineralization processes. The ratio for the 21.3–m (70–ft) well is somewhat anomalous in that it is lower than the ratio for the 9.1 m (30 foot) well. Examination of Table C2 shows that the 21.3 m (70 foot) well generally has lower chloride values than the other two wells and is similar to the irrigation well water at the site. The Cl/NO_3-N ratio for the irrigation well is 5.0 because of the lower chloride and nitrate values (Table C.2). The nitrate values in the 21.3–m (70–ft) well are similar to those of the 15.2–m (50–ft) well. The lower Cl/NO_3-N ratio for the 21.3–m (70–ft) well may be due to the imposition of excess nitrate onto the background water quality at the site.

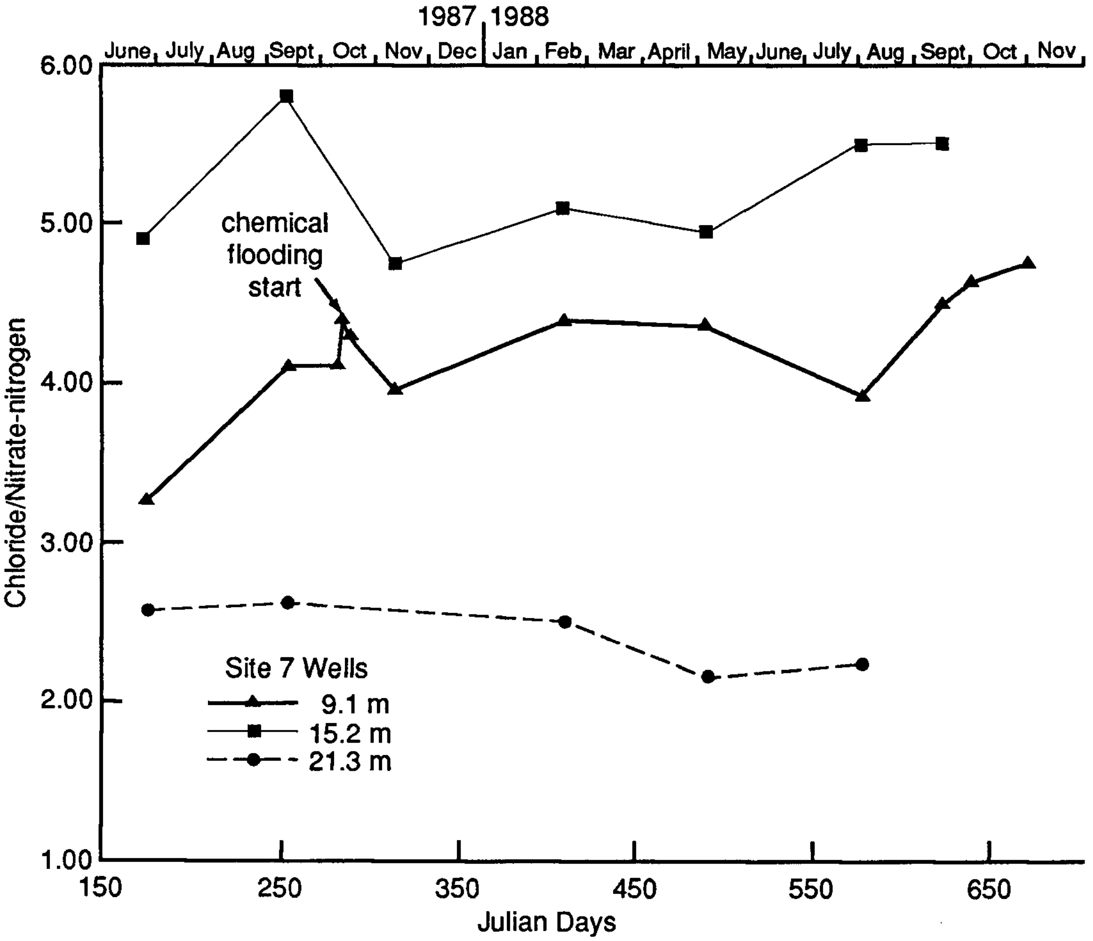

Figure 41. Chloride/nitrate-nitrogen ratio time-series distribution for observation wells at site 7.

Site 7: Chemical flooding

Because of the much sandier nature (and the expected higher hydraulic conductivity under wet conditions) of the soil profile in site 7 as compared with site 6, the site was not flooded with Stafford municipal water before the chemical solution, as was done at site 6. Instead, 3.79 m^3 (1000 gal) of chemical solution of the same composition as used in site 6 was used to flood the site after prewetting the perimeter. The flooded area was nearly rectangular and enclosed approximately 13.5 m^2 (145 ft^2) of surface. The flooding of the site started on October 7, 1987 (10:22 a.m.) and was completed by the next morning. The soil-moisture profile immediately before the flooding started and immediately after the flooding was completed is shown in Figure 42. The flooding caused wetting of the soil profile down to at least 380 cm (12.5 ft). The clayey layer from 165 cm to 240 cm (65 in. to 95 in.) was wet throughout the study period and did not show much change during flooding, while the sandier soil layers both above and below the clayey layer showed large moisture changes during flooding and the subsequent drainage period. Soil moisture drainage curves for 15-cm (6-inch) depth intervals since covering the site with plastic, shown in Figure 43, indicate soil water drainage down to the 380–cm (150–in) plotted depth. The clayey layer from approximately 165 cm to 240 cm (70 in. to 95 in.) did not show any significant drainage.

The instantaneous profile analysis results summarized in Figures 44, 45, and 46 depict the water characteristic curves, the hydraulic conductivity functions, and the Darcy water fluxes for various soil depths, respectively. The sandier nature of site 7 is reflected in the shape of the water characteristic curves (Fig. 44), which show much more decrease in water content with an increase in capillary pressure or suction compared with the more clayey site 6. The sandier texture of site 7 is also reflected in higher saturated hydraulic conductivities as compated with site 6 (Fig. 45).

The chloride contents at all the soil depths sampled were appreciably less than the chloride concentration of the added chemical flood solution. The chemical solution was added in 2 1.89–m^3

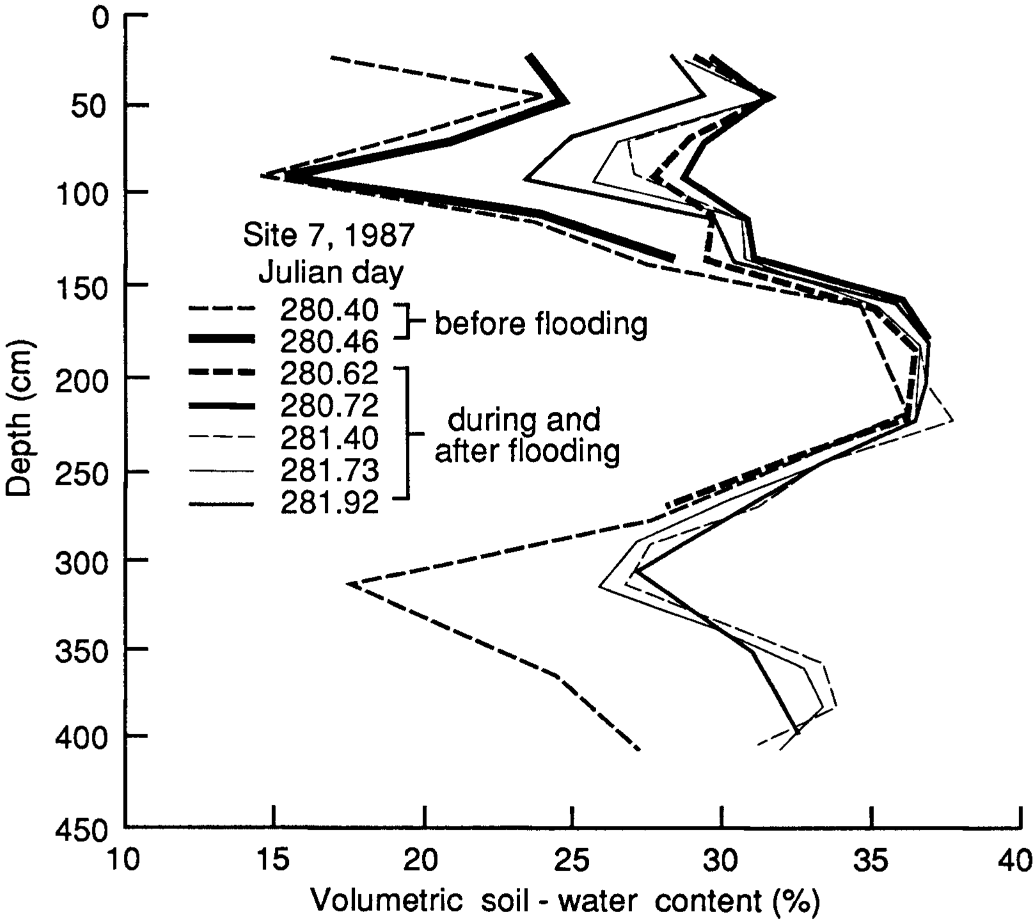

Figure 42. Soil-water profiles before and during flooding at site 7.

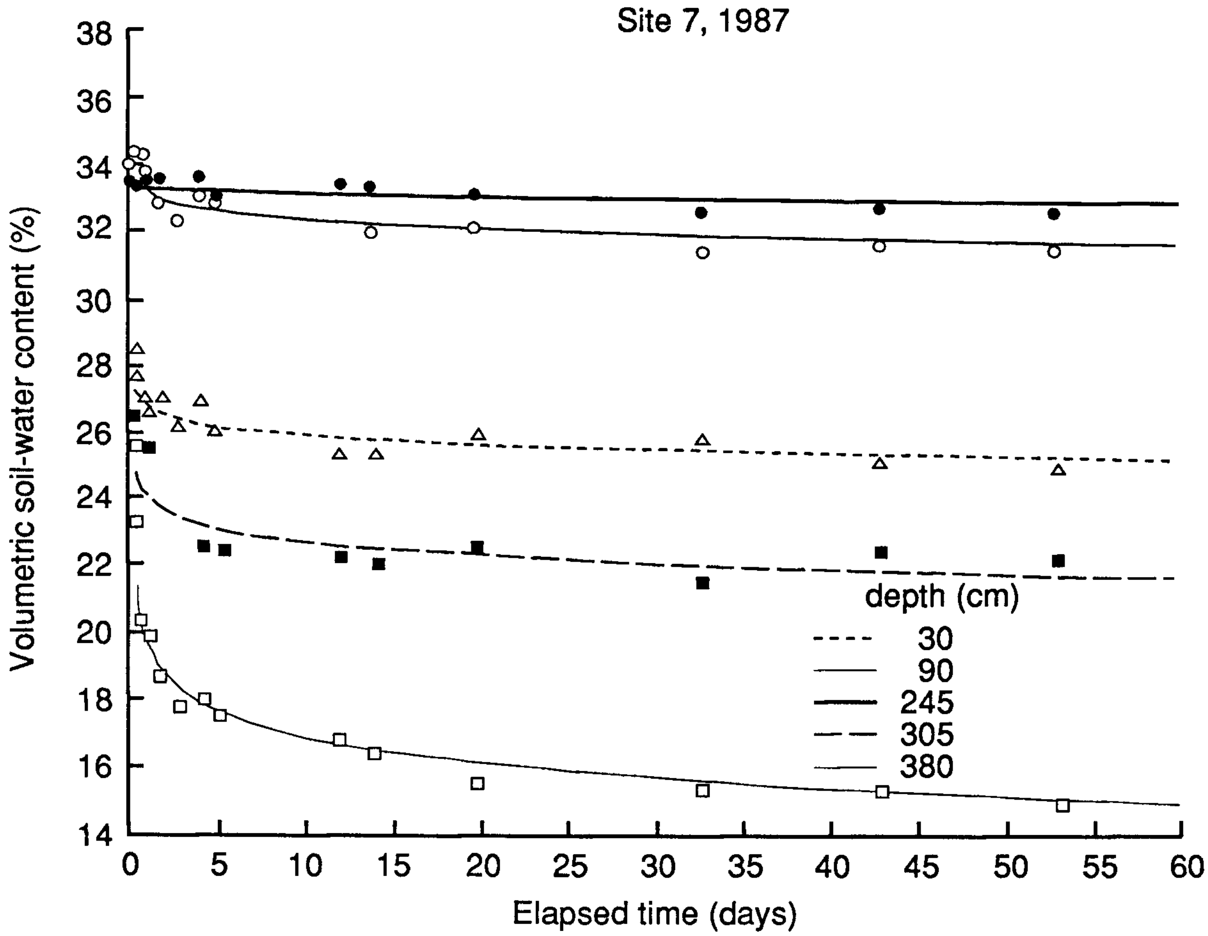

Figure 43. Soil-water content drainage curves for five depths at site 7. Least-squares fit curves using a drying model are also shown.

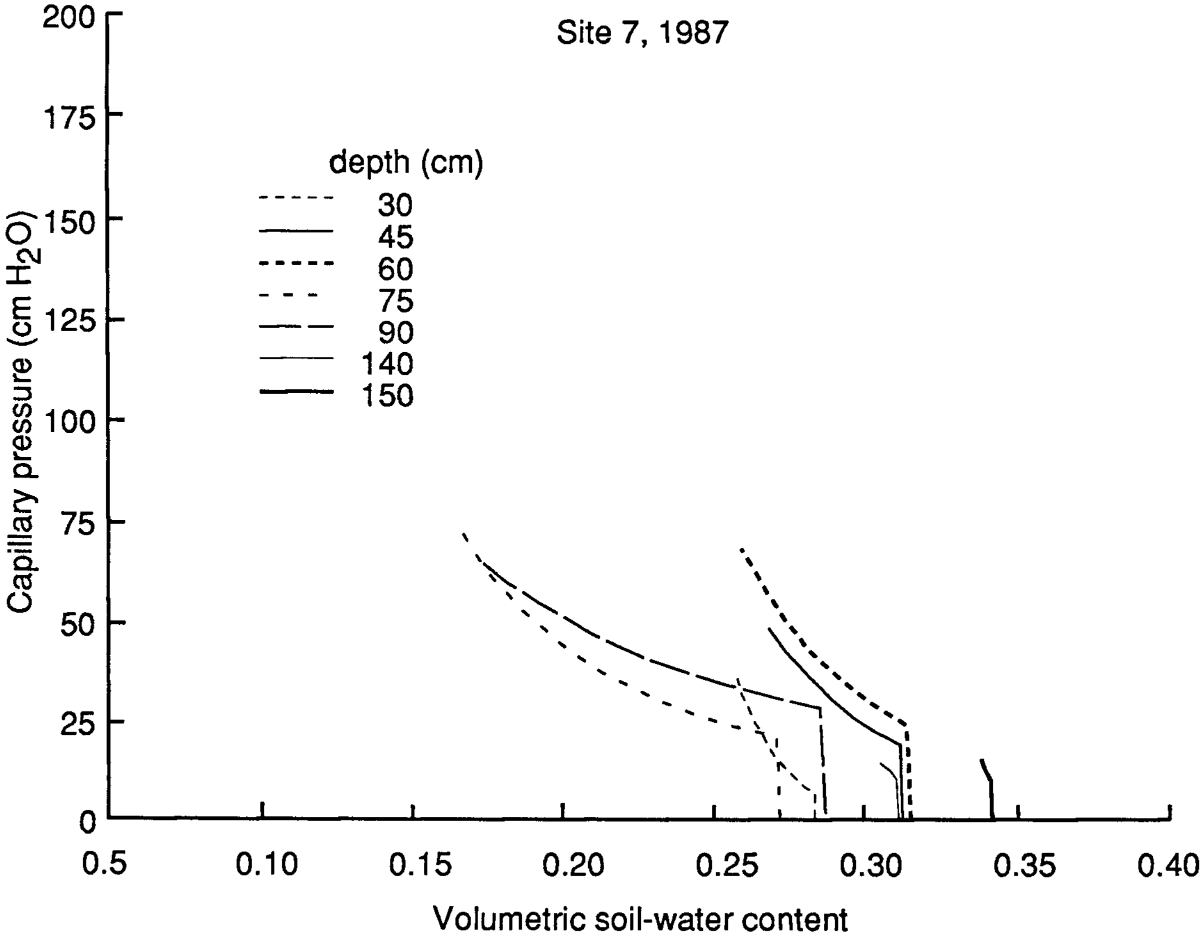

Figure 44. Field-measured water retention curves for site 7.

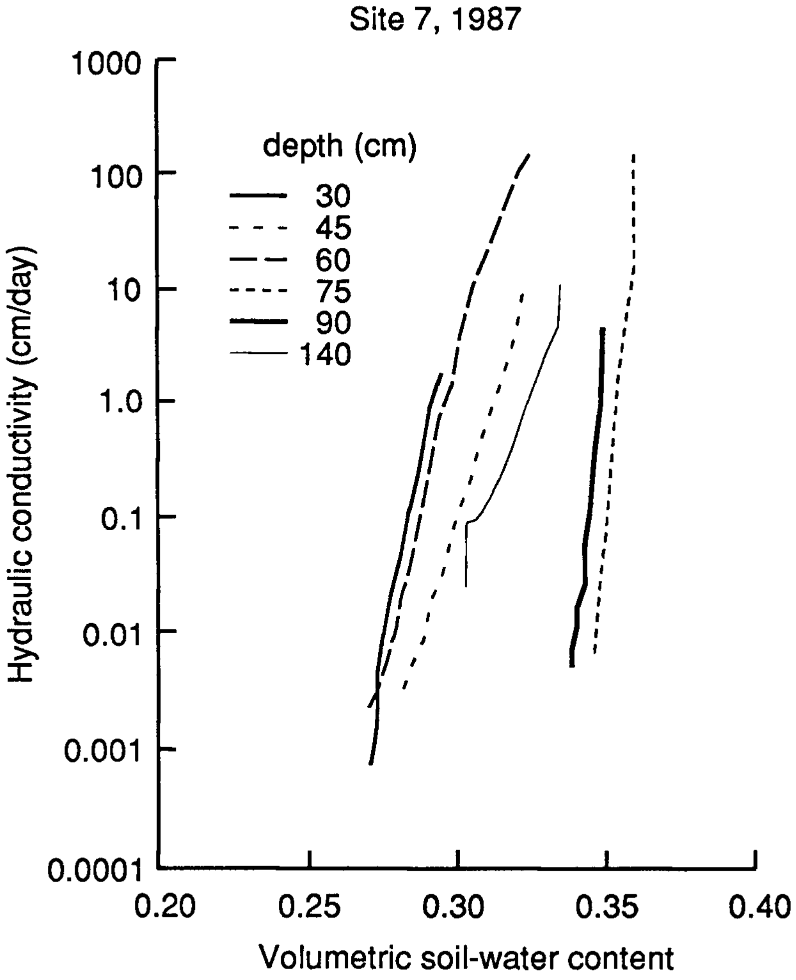

Figure 45. Hydraulic conductivity curves derived from the instantaneous profile technique for site 7.

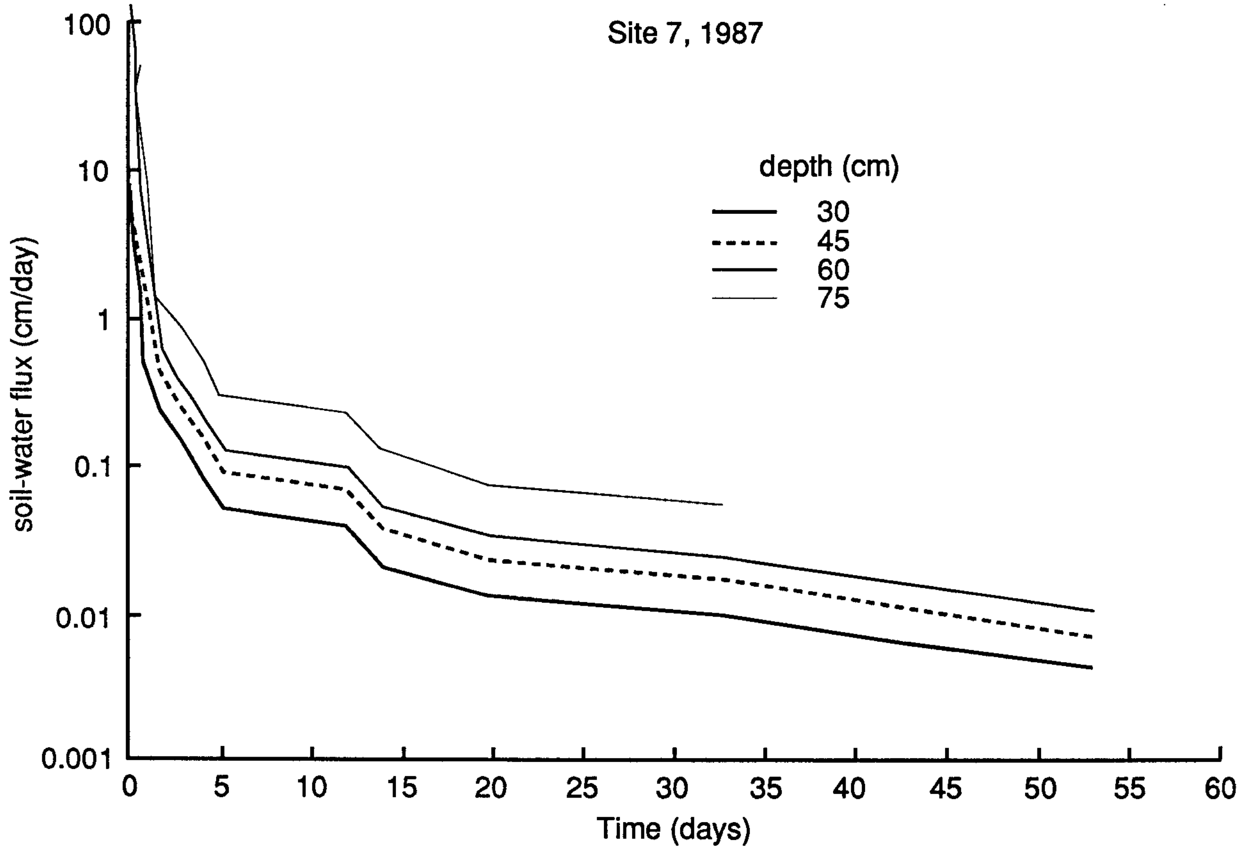

Figure 46. Soil-water flux time distributions derived from the instantaneous profile technique for site 7.

(500–gal) mixes. The first contained 103 mg/L chloride, and the second contained 140 mg/L chloride. The result is that the chloride in the chemical flood waters acted as a minor tracer.

After addition of the chemical flood solution, the chloride concentrations increased when the slug of actual flood water reached the depth sampled (Fig. 47). Chloride concentrations in samples from the shallowest lysimeter rose to above the chloride in the flood water indicating dissolution of near-surface salts in the soil. In general, the deeper the lysimeter, the longer the time before the chloride concentration increased to near that in the flood solution. However, the rates of chloride increases resulting from the movement of flood waters was not uniform with depth and time, suggesting that preferential flow through macropores and fractures in the soil occurred. The chloride concentration then began to decrease in the shallowest lysimeter after several days and in the next shallowest lysimeter after several months. Later increases and decreases in chloride values were probably related to changing conditions because of irrigation and the degree of evapotranspiration at the site. The results indicate that movement of the chemical flood waters and later irrigation waters has a greater control on chloride concentrations than displacement of saline soil solutions in the profile. The distribution of chloride from the suction lysimeters as a function of depth and time (Fig. 48) further supports the lack of significant salt displacement, in contrast to what was observed at site 6.

In addition, we observed no significant change in specific conductance and chloride content matching the chemical flooding in the samples from the wells at site 7 (Figs. 37 and 38). Changes in specific conductance and chloride just after the flooding were of the order of variations observed at other times during the monitoring. The trends in the specific conductance and chloride content of ground water from the 9.14–m (30–ft) well actually decreased during the period from before to about one year after the flooding. Thus no substantial salt displacement occurred at this site in contrast to site 6. Apparently no appreciable concentration of salts had accumulated in the unsaturated zone between the section of soil sampled by the lysimeters and the water table. The

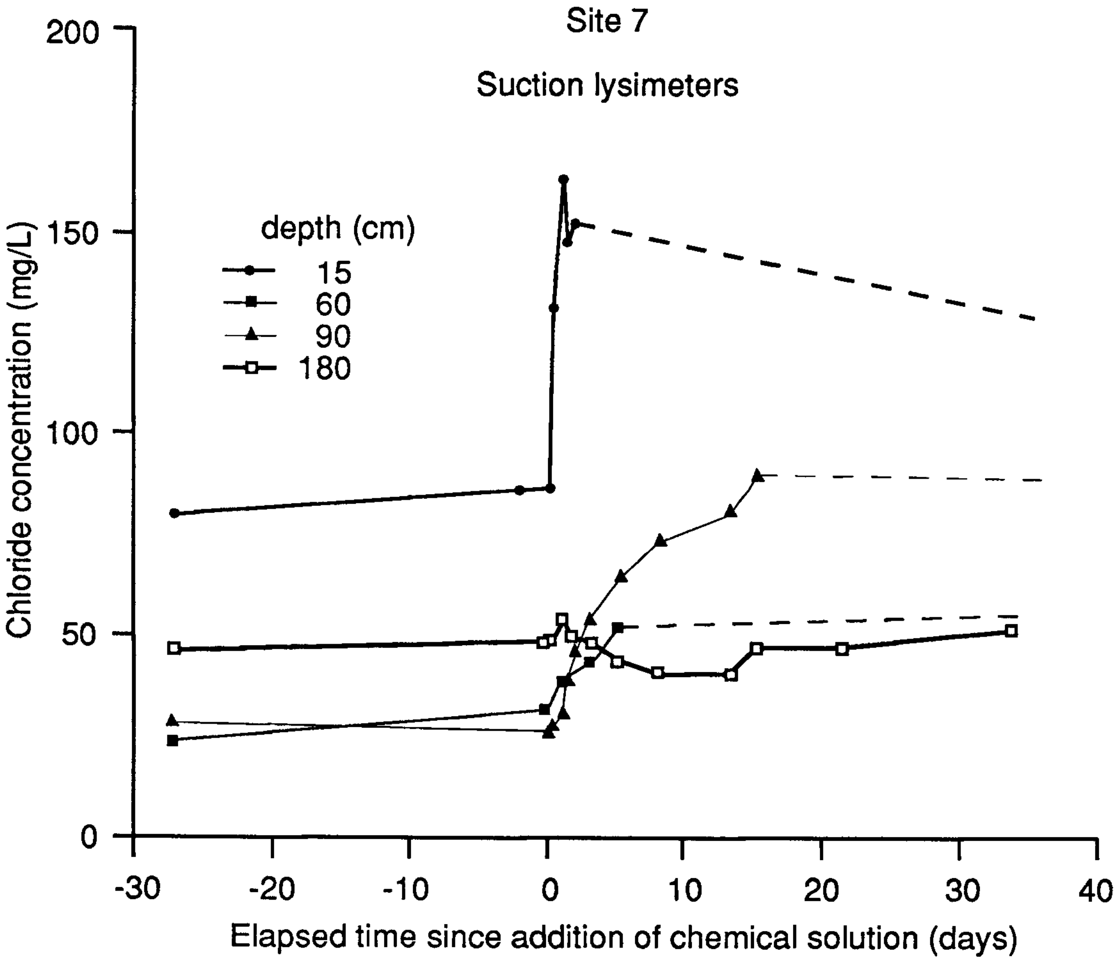

Figure 47. Time-series distribution of chloride from suction lysimeters before, during, and after flooding at site 7.

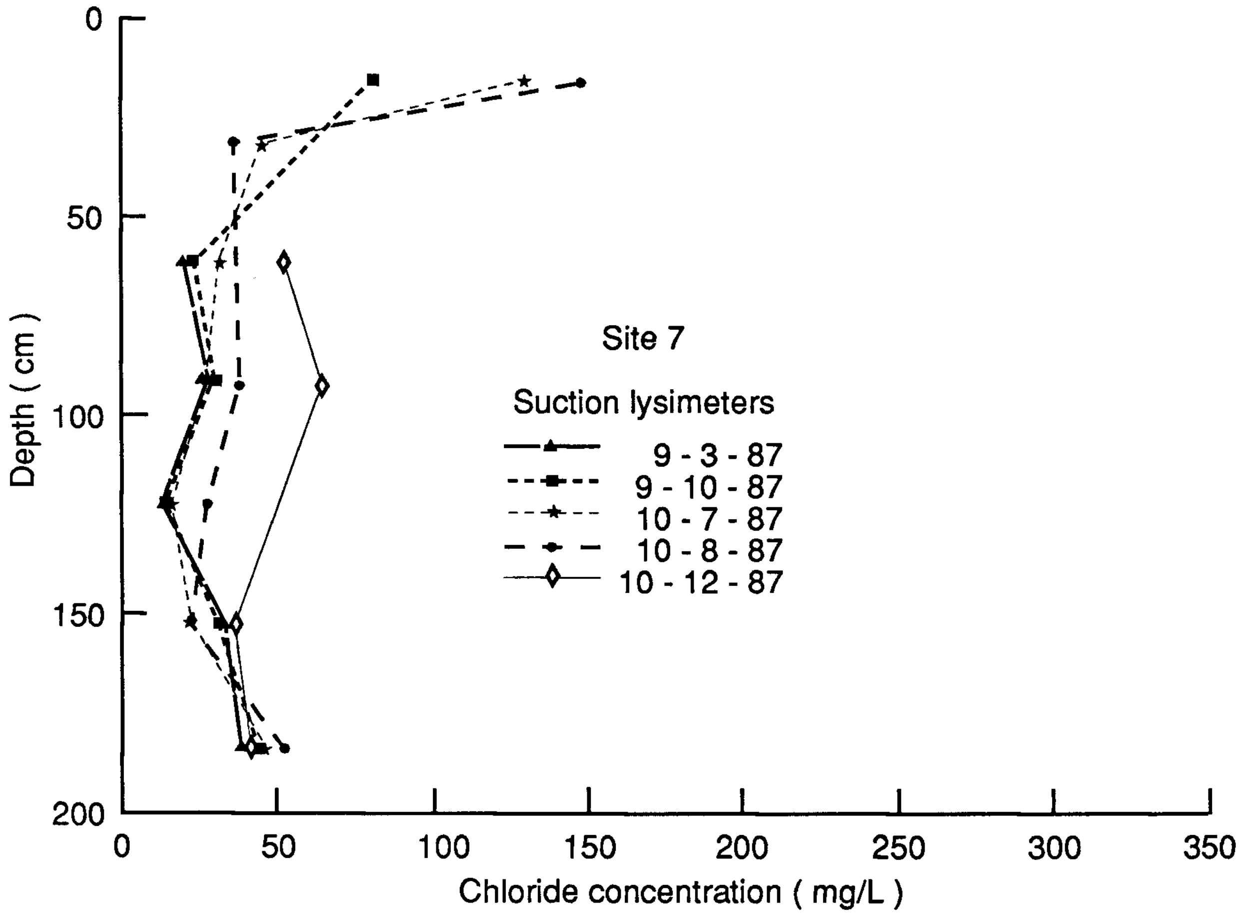

Figure 48. Profiles of dissolved chloride sampled from suction lysimeters before, during, and after flooding at site 7.

greater permeability of the unsaturated zone and the lower dissolved-solids concentration of irrigation waters used are probably the main reasons for the smaller salt accumulation than at site 6.

Bromide. Bromide versus time breakthrough curves through the soil profile are shown in Figure 49. The bromide tracer concentrations for the two 1.89–m^3 (500–gal) portions of the chemical flood waters were 430 mg/L and 457 mg/L, giving an average bromide of 444 mg/L. The added bromide penetrated to all site 7 soil depths sampled by the lysimeter within 1.3 days of initiation of flooding as indicated by bromide concentrations that were at least 50 times background levels. Sampling problems similar to those described earlier for site 6 prevented a detailed set of bromide observations for determining tracer velocity (depth of tracer peak divided by sampling time) and decay.

The bromide-concentration distribution in the soil profile during the first few weeks after flooding (Fig. 50) shows a sigmoid distribution with peaks at the uppermost lysimeter depth [15 cm (0.5 ft)] and the 120–cm (4–ft) depth. Such a distribution could indicate preferential flow, whereby diffuse porous media flow is bypassed by flow through macropores, resulting in higher tracer concentrations at depth than normally expected. A plot of water content with depth (Fig. 51) has several peaks that approximately match the observed bromide peaks in Figure 50. This probably indicates that the increase in water content throughout the soil profile is due mainly to the applied water solution moving through the profile, not to displacement of much of the initial water.

Bromide concentrations in water sampled by the shallowest lysimeter reached a peak 2 days after flooding (Fig. 49), whereas values for all the other depths continued to increase for several months. Maximum bromide contents were measured at 148 days for the 30–cm (1–ft) lysimeter depth and at 252 days for the 60– and 90–cm (2– and 3–ft) lysimeter depths. The time and bromide concentrations for the maximum peaks at these depths were probably not observed because of lysimeter sampling problems. Bromide values for samples from the lysimeters at greater depths were still generally increasing slowly after a year after chemical flooding, indicating the great persistence of soil solutions in the profile. The maximum tracer concentrations observed

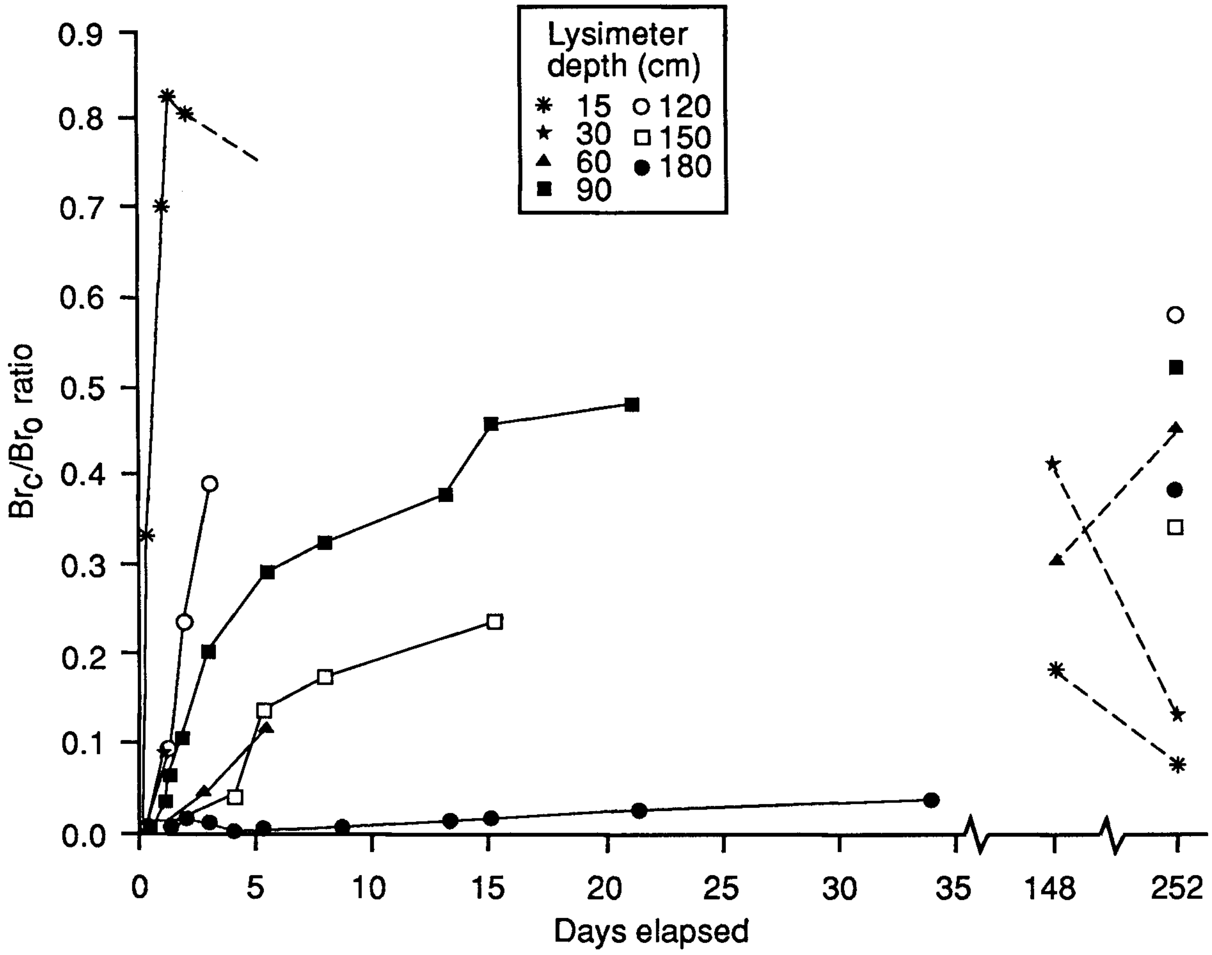

Figure 49. Bromide-concentration breakthrough curves based on suction lysimeter sampling for site 7. Bromide is expressed as a ratio of bromide corrected for background levels (Brc), over bromide tracer concentration in the flooding solution (Br0).

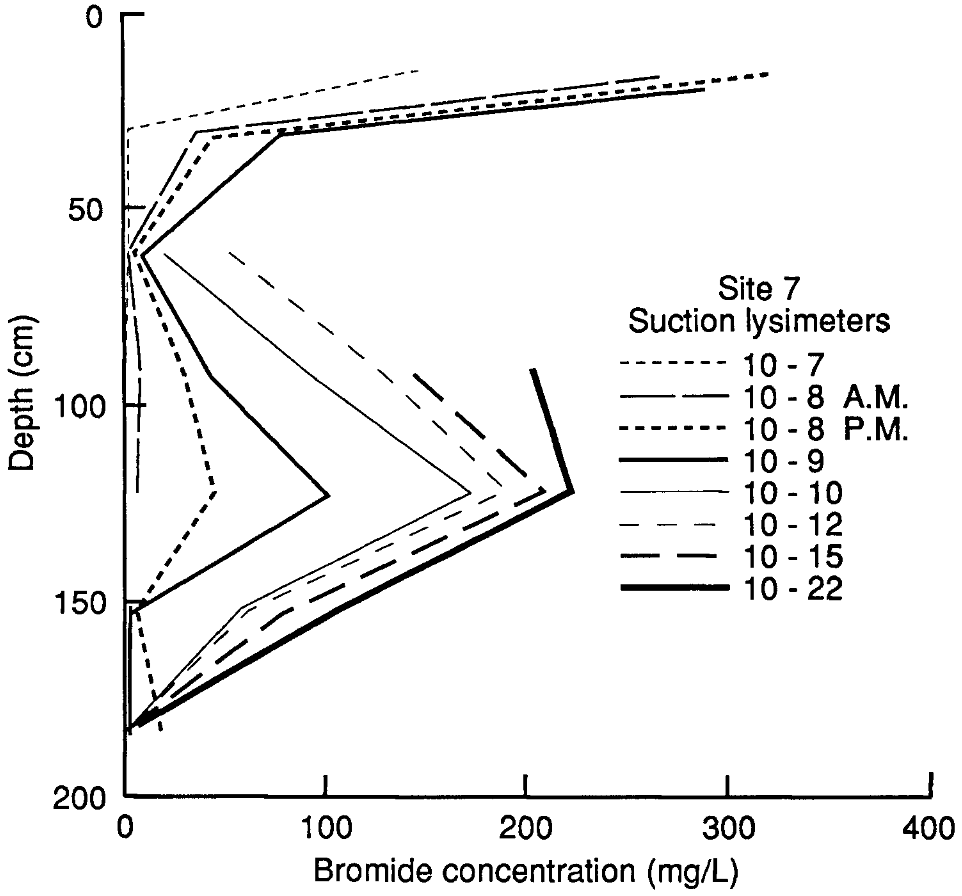

Figure 50. Bromide concentration profiles since chemical flooding was initiated at site 7.

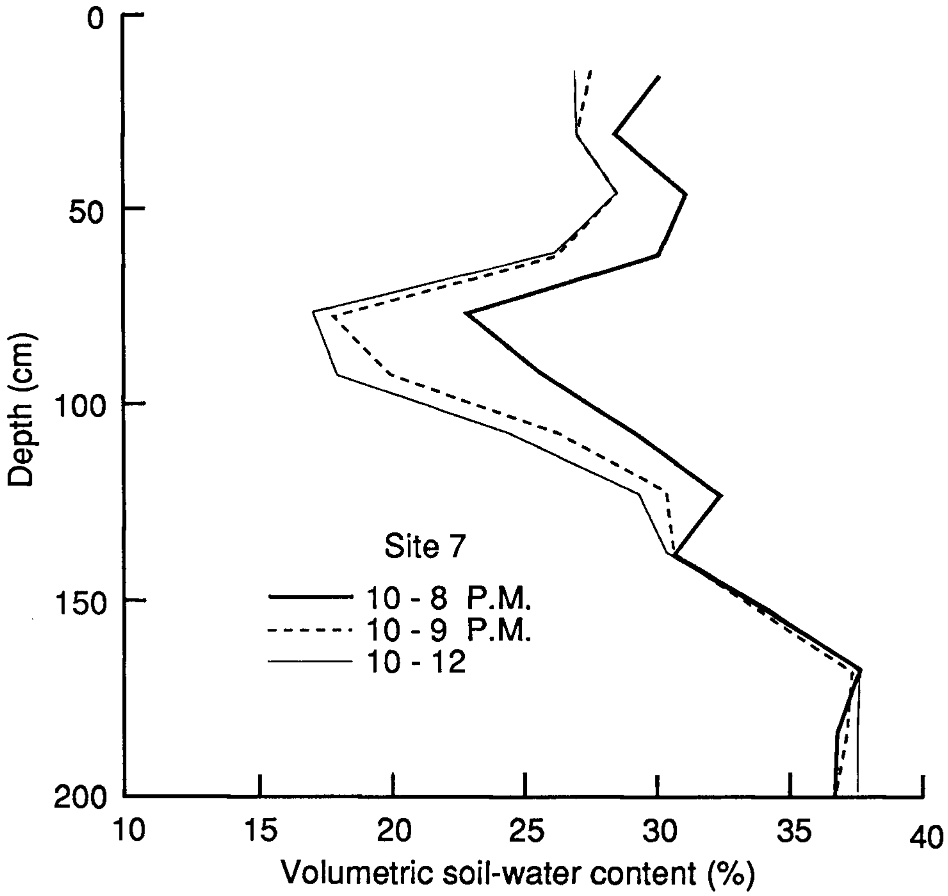

Figure 51. Soil-water content profiles since chemical flooding was initiated at site 7.

to date for all lysimeter depths would show a general persistence in the sigmoid pattern of Figure 50 if plotted as bromide concentration versus depth. For example, the highest bromide concentration measured at the 120–cm (4–ft) depth was higher than that found for any of the other depths except the shallowest.

Although bromide tracer contents in solution extracted from the lysimeter at the 180–cm (6–ft) depth had reached nearly 200 mg/L a year after flooding, no detectable tracer bromide had yet reached the shallowest screened interval [6.1–9.1 m (20–30 ft)] of the aquifer at the site. All bromide data are tabulated in Tables C.2 and C.4.

Atrazine and atrazine metabolites. Many of the suction lysimeters did not work properly at site 7 most of the time. In addition to the reasons given in discussing the results of site 6, vacuum could not be maintained at site 7 because of the porous, sandy nature of the soil. Only the 180–cm (6–ft) deep lysimeter completed in the immediate vicinity of the clayey layer was functional most of the time. Therefore we used soil core data to generate the atrazine breakthrough curves. Although the soil-core data indicate atrazine presence within the soil profile down to the 120–135 cm (48–54 in.) sampled interval within the first 5 days after flooding, suction lysimeter sampling during that same time interval did not detect the presence of atrazine below the upper 15–cm (1/2–ft) depth interval (Fig. 52). This may indicate that much of the atrazine movement bypassed the areas around the lysimeters, probably because of the reduced wetness around the porous cups caused by repeated attempts to induce a high vacuum (60–70 kPa) in the lysimeters or because of preferential flow through macropores, also indicated by the bromide data (Fig. 50). The soil-core data exhibited extreme variability within the flooded area so that reliable breakthrough curves could not be ascertained (Fig. 53). This spatial variability may indicate that the applied water solution was not moving as a front through the soil horizons but was moving according to the spatial variability and soil-water transmission characteristics of the soil pores. However, one definitive observation is that atrazine penetrated to the 120–135–cm (48–54–in.) level within fewer than five days since the flooding started, and no detectable atrazine was found at the 135 to 150 cm

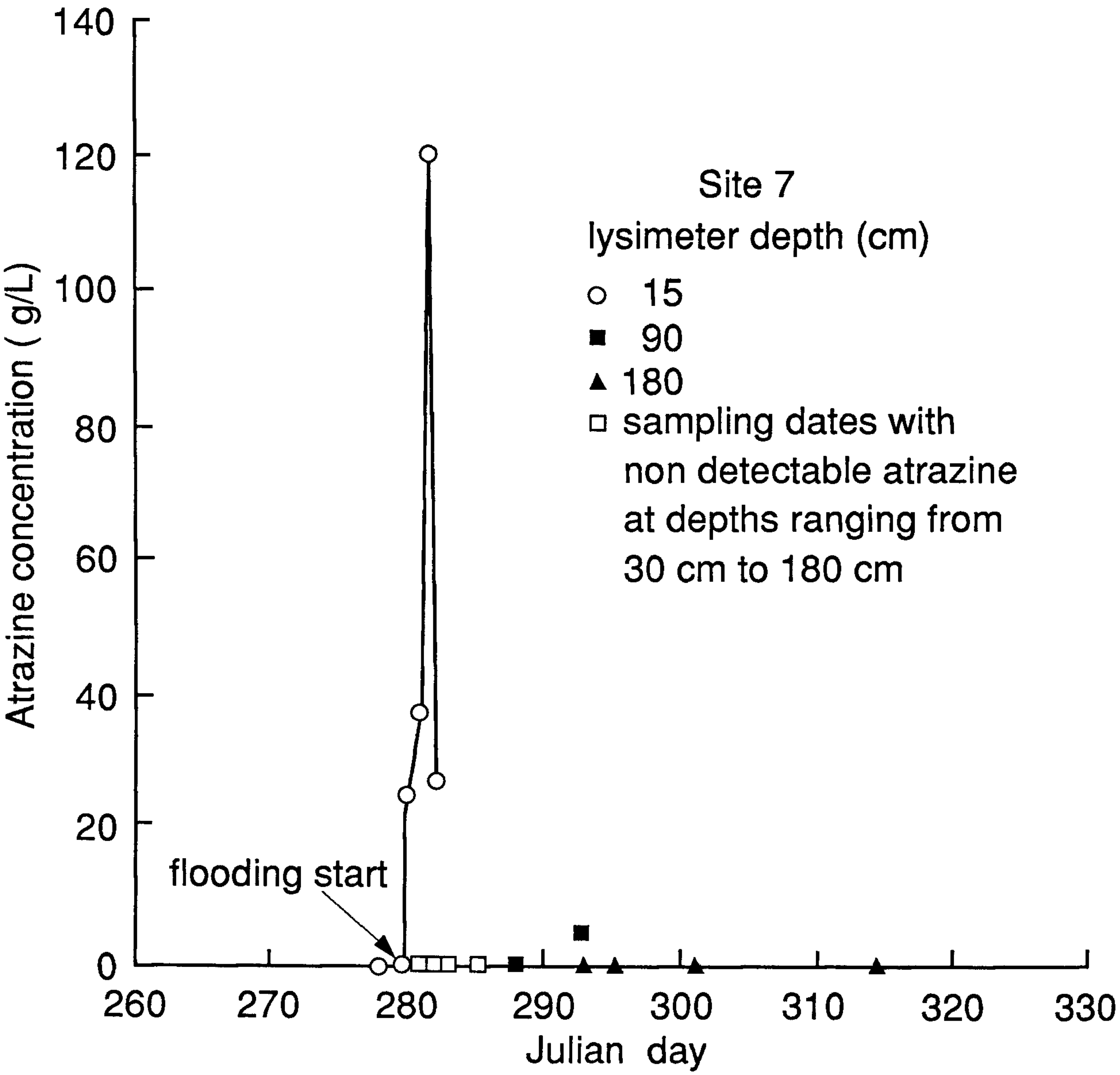

Figure 52. Atrazine breakthrough curves for site 7 based on suction lysimeter sampling.

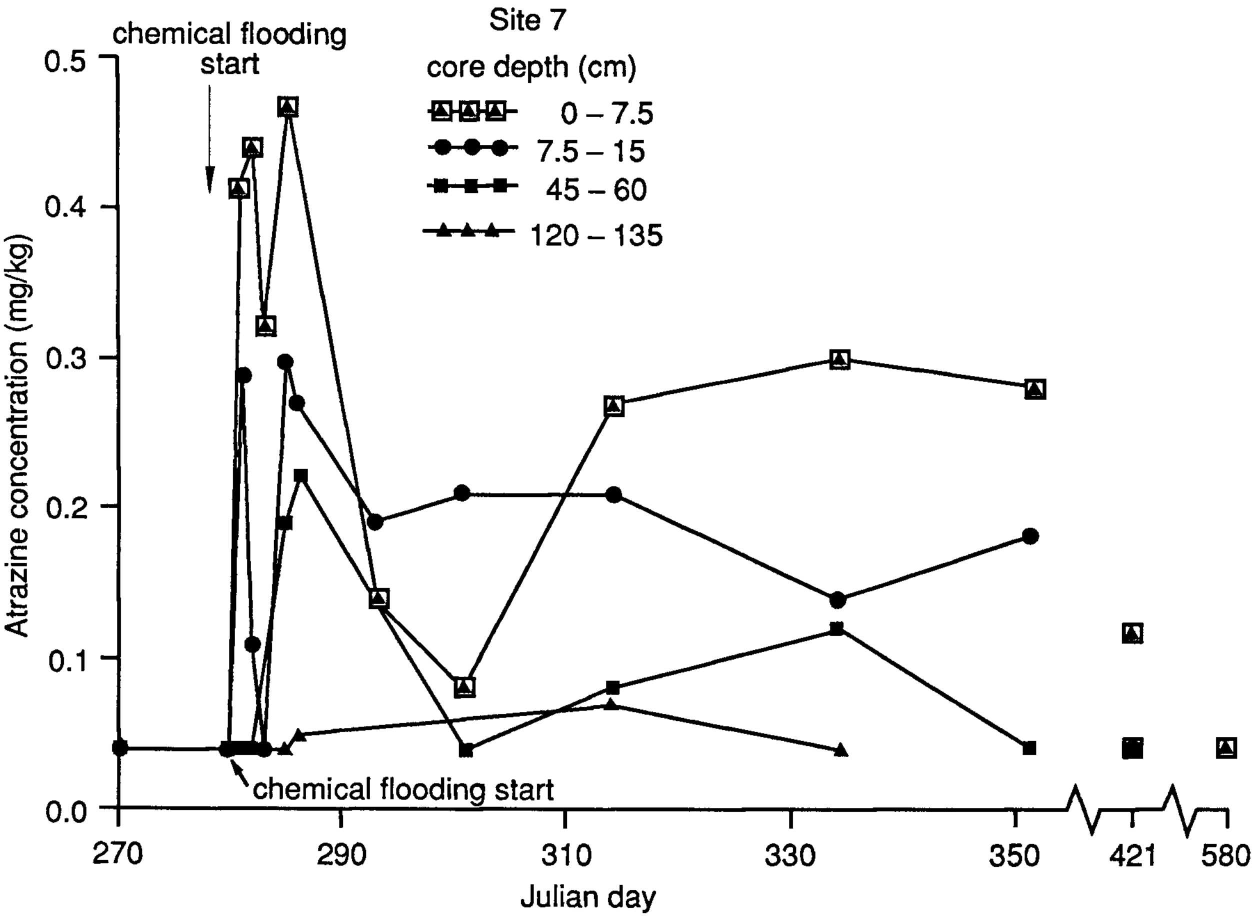

Figure 53. Atrazine breakthrough curves for site 7 based on soil cores. Detection limit is 0.04 mg/kg.

(54–60 inch) depth level. The vertical distribution of atrazine in the soil shows where a sigmoid, bimodal distribution (Fig. 54) with peaks at the 15–cm (0.5–ft) and 45–60–cm (1.5–2–ft) depths. This distribution supports evidence of preferential flow discussed earlier. All atrazine data are tabulated in Appendix D.

To determine the possibility of atrazine hydrolysis at this site, we sent for chemical analysis two 15–cm (6–in.) long soil cores from the 60–75–cm (24–30–in.) and 75–90–cm (30–36–in.) depth intervals, sampled on February 24, 1988. All atrazine degradation by-products are tabulated in Appendix E. Dealkylated by-products, indicative of biodegradation, were found below detection limit (0.05 mg/kg) as was also the case at site 6. The reported hydroxyatrazine concentrations were 0.172 mg/kg and 0.408 mg/kg, respectively, and the reported parent atrazine concentrations were 0.056 mg/kg and <0.05 mg/kg (detection limit), respectively. This may indicate that, even in soils with only slightly acidic conditions (Fig. 33) and low organic matter and cation exchange capacity (Fig. 30), hydrolysis of atrazine still takes place. As was done for site 6, additional soil samples collected in August 1988 were sent for atrazine metabolite analyses, especially to check on biodegradation by-products. The results showed appreciable amounts of both biodegradation products (Appendix E), indicating microbial decomposition of atrazine.

The soil profile temperatures during the flood experiment (October–November 1987) are shown in Figure 55. The soil temperatures increase with depth but decrease with time. However, the temporal temperature decreases at a lower rate when compared with site 6 (Fig. 19).

The sandy nature of the soil profile, the doubling of the amount of chemical flood solution, the much lower organic carbon content (see Fig. 30), and the near neutral pH of the soil profile (Fig. 33), compared with site 6, are the apparent reasons for the deeper penetration of the atrazine to the 120–135–cm (48–54–in.) level, vis-a-vis the much shallower depth penetration at site 6. It should also be noted that, similar to site 6, no atrazine was observed in the shallow or deeper observation wells of site 7.

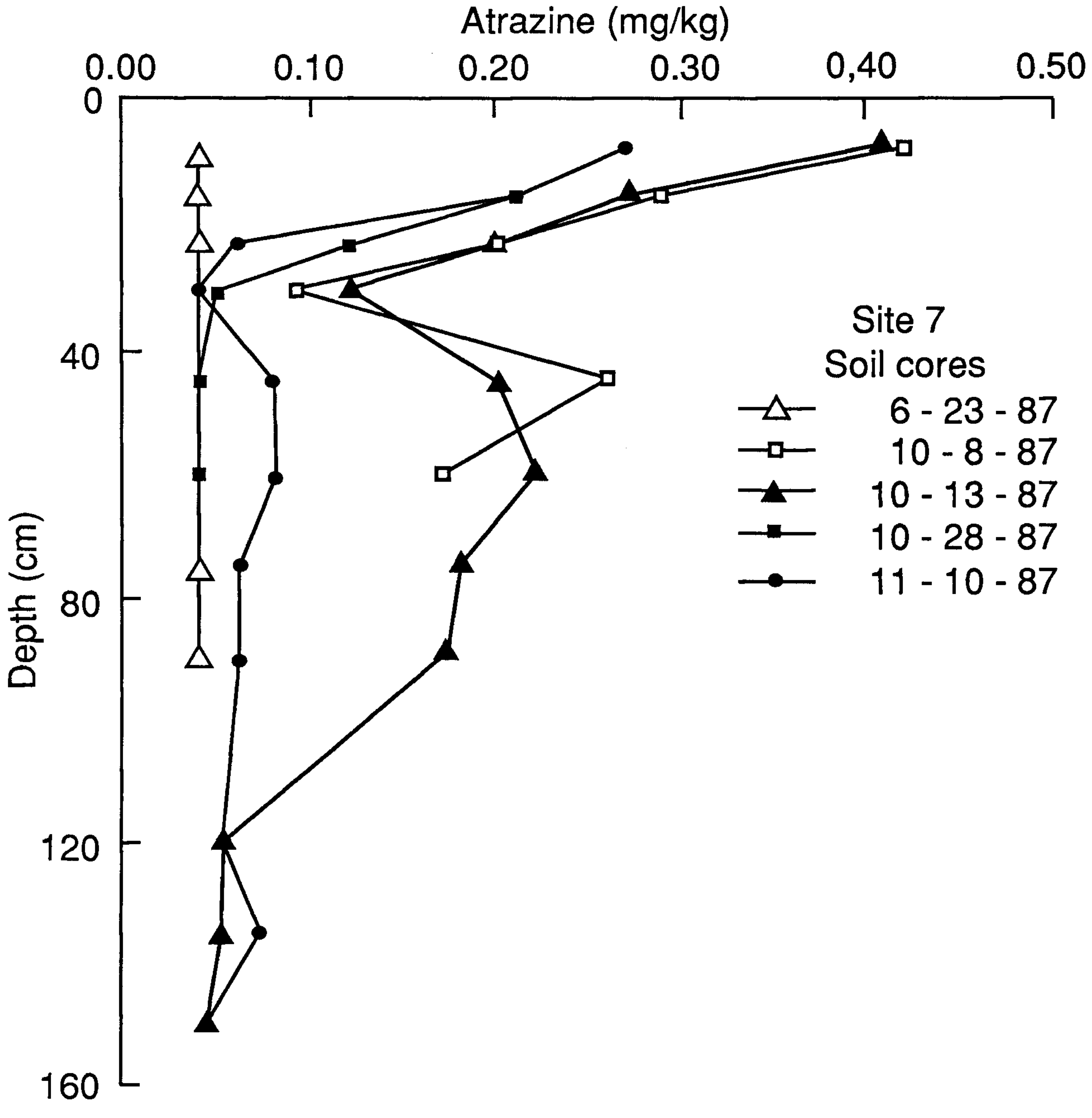

Figure 54. Atrazine profiles at site 7 based on soil cores.

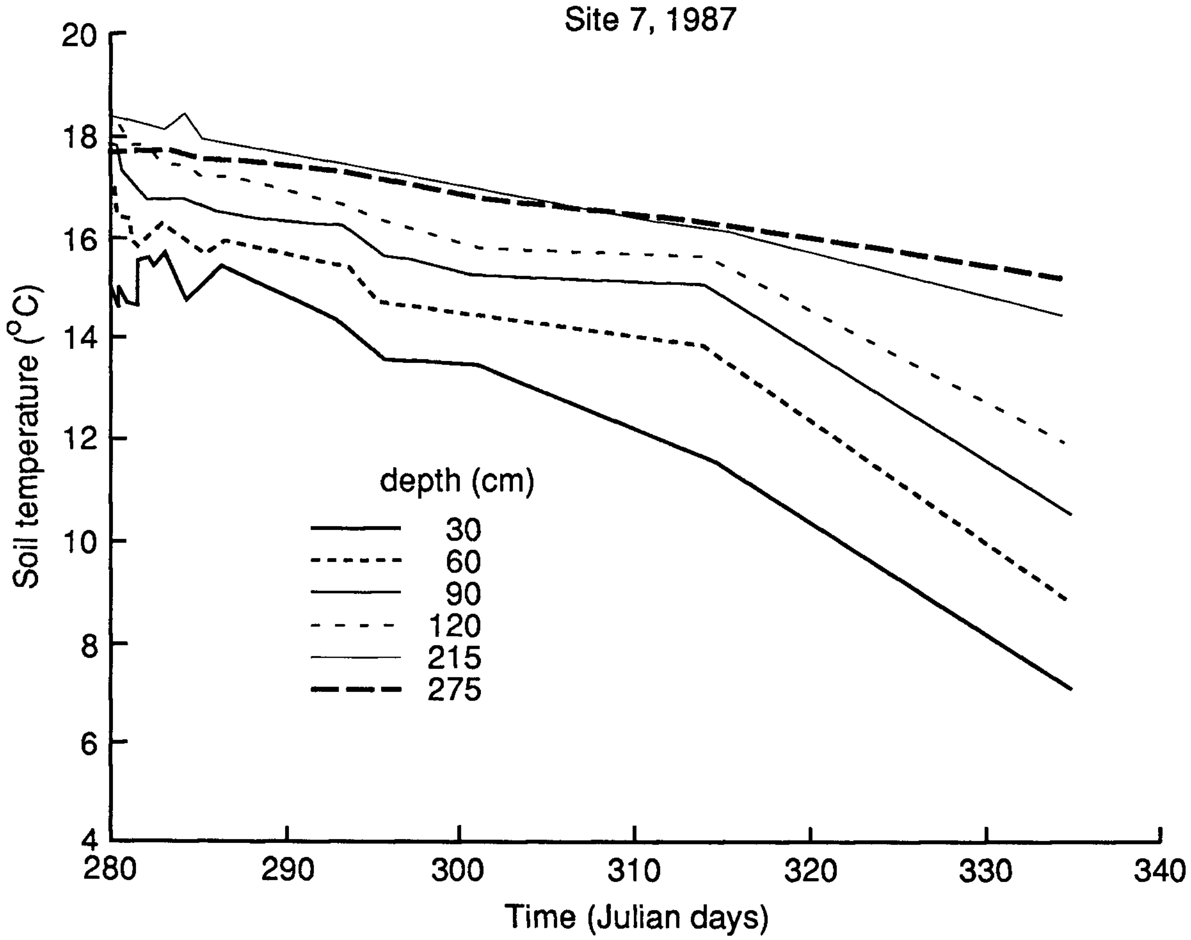

Figure 55. Soil-temperature time-series distribution for six depths at site 7.

Site 10: The soil profile and its physical and chemical characteristics

Site 10 is located in Edwards County on the Great Bend sand plains. Soil at this site is known to be of eolian origin. The soil profile at this site is classified as Pratt soil. The profile consists of brown to pale brown loamy fine sand down to 42 cm (16.5 in.) comprising the soil A horizon. The upper portion of this horizon is characterized by a weak medium-granular structure and a clear wavy boundary, whereas the lower part has a massive structure and a clear wavy boundary. The next horizon is a C zone of light yellowish brown loamy fine sand of massive structure to a depth of 92 cm (36.2 in.) with an abrupt wavy boundary. Below this layer is an AB horizon from 92cm to 105 cm, comprising brown loamy fine sand of massive structure and a clear wavy boundary. The next six zones are subdivisions of the C horizon. Zone C1 [105–117 cm (41.3–46.1 in.)] is a light yellowish brown loamy fine sand with massive structure and a lamellar lens 1 cm thick. Zone C2 [117–145 cm (46.1–57.1 in.)] is a light yellowish brown fine sand of loose, friable structure, with 2 lamellar lenses 1 cm thick. Zone C3 [145–154 cm (57.1–60.6 in.)] is a pale brown sand of loose, friable structure. Zone C4 [154–183 cm (60.6–72.0 in.)] is a light yellowish brown fine sand of massive structure. Zone C5 [183–222 cm (72.0–87.4 in.)] is a yellowish brown loamy fine sand with massive structure that is finely stratified in the upper part and has 1/2–cm (0.2–in.) thick lamellae throughout the horizon, totaling 15 cm (6 in.) thick. Zone C6 [226–263 cm (89.0–103.5 in.)] is a pale brown fine sand of massive structure and with fine stratification.

The specific soil horizons and their grain size distribution (texture), as determined by the Soil Conservation Service, are shown in Figure 56. The sand fraction dominates throughout the profile, and the clay and silt fractions are not a major component in the soil. The organic carbon content and cation-exchange capacity of the soil (Fig. 57) are low, indicating that the soil does not have much potential for retention of chemicals. The electrical conductance for the soil profile is also low indicating that no appreciable concentration of salts has occurred in this profile as it has at sites 6 and 7.

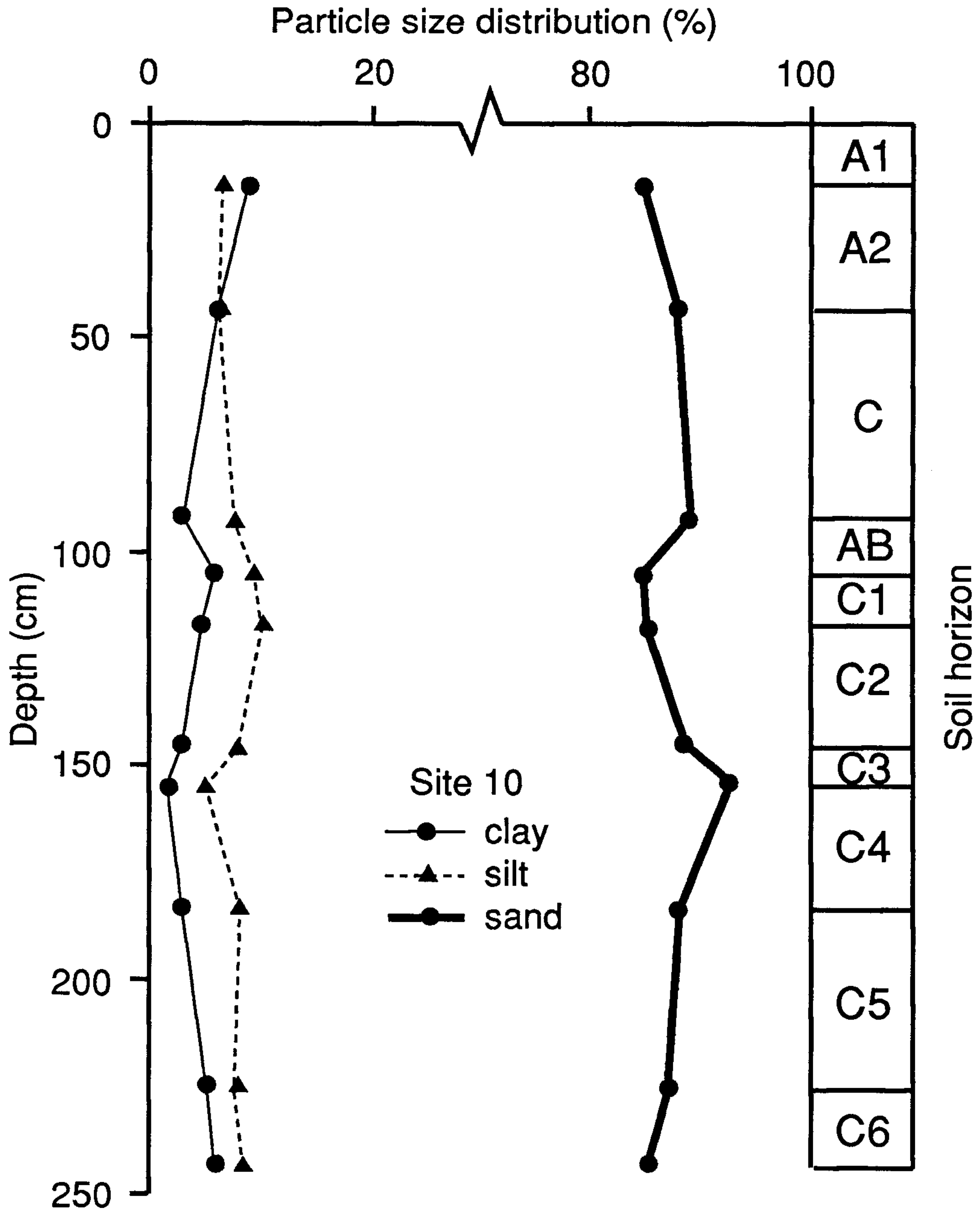

Figure 56. Grain size distribution and soil horizons for site 10.

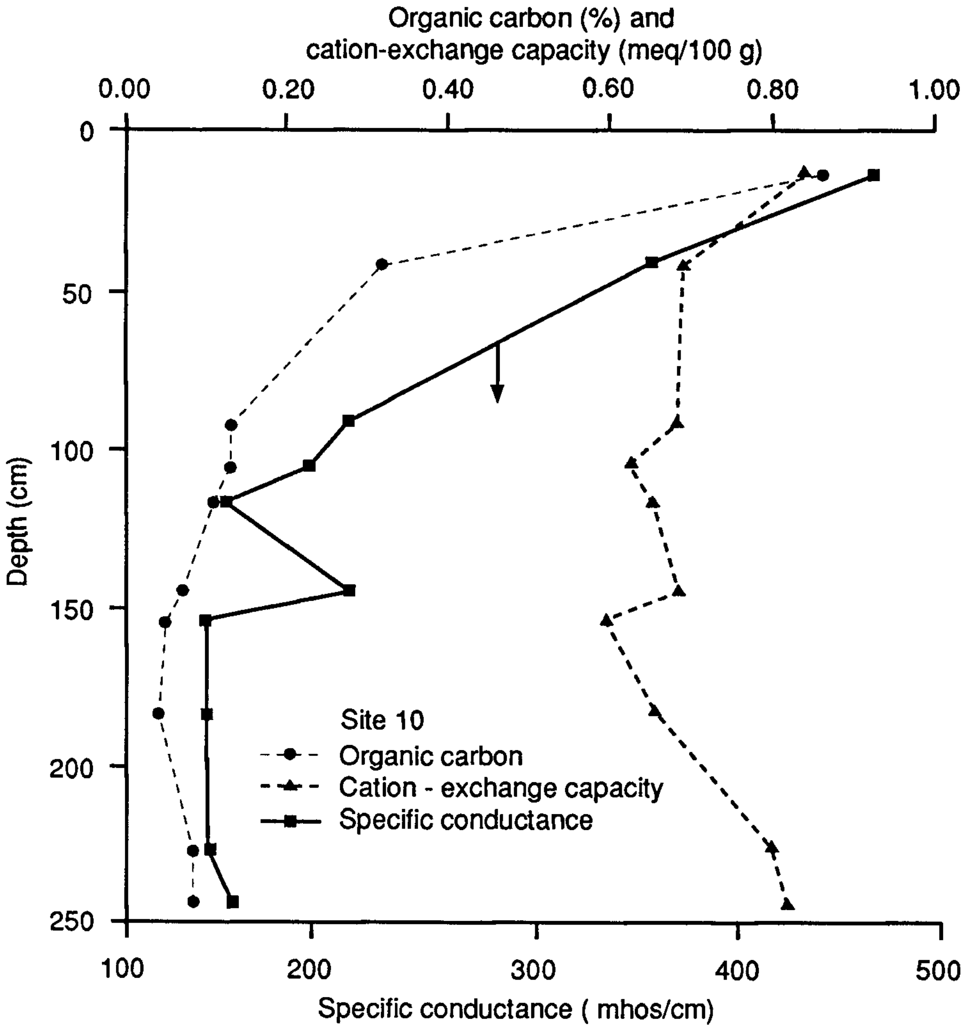

Figure 57. Organic carbon content and cation-exchange capacity profiles for site 10.

Water chemistry of site 10

The water chemistry at site 10 plots on the trilinear diagram as a Ca–HCO_3 water (Fig. 58). This is to be expected because the ions in the water come from the leaching of silts and sands by precipitation water without appreciable evaporative concentration. The specific conductance and total dissolved solids for waters from this site are low in comparison with sites 6 and 7 (Fig. 59). The wells that were measured at site 10 are 18.3 m and 19.8 m (60 ft and 65 ft) deep. Comparison of the total dissolved-solids content of these wells (Fig. 59) with that of both the shallow and deep wells from the other sites shows the impact that continuous irrigation has on the general water quality at sites 6 and 7. All the wells at sites 6 and 7 show much higher total dissolved-solids values throughout the period of study. These higher concentrations illustrate the concentrating effects that evapotranspiration has on causing salt buildup in the upper soil zones. The water chemistry data from this site are tabulated in Table C.3.

Transport modeling

Solute transport during steady-state flow in homogeneous soils is described in this study by the one-dimensional deterministic convection-dispersion equation for a single solute:

$$\frac{\partial C}{\partial t} + \frac{\rho_b}{\theta}\frac{\partial s}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - \mu C\,, \tag{1}$$

where

C is the solute concentration in the liquid phase (M/L^3),

s is the adsorbed concentration per unit mass of the solid phase (M/M),

D is the dispersion coefficient reflecting the combined effects of diffusion and hydrodynamic dispersion on transport (L^2/T),

r_b is the soil bulk density (M/L^3),

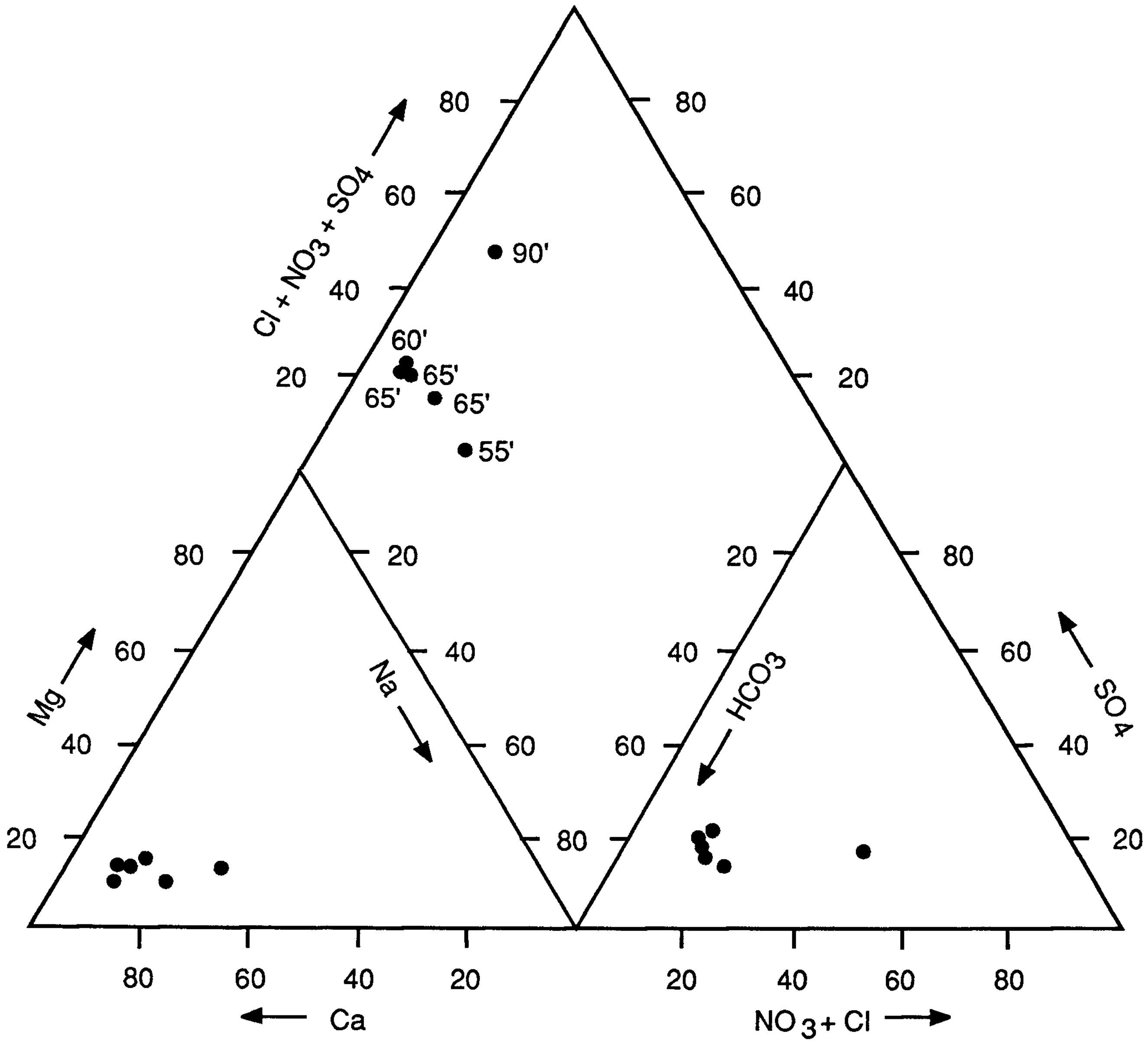

Figure 58. Trilinear diagram showing water chemistry data for three wells at site 10.

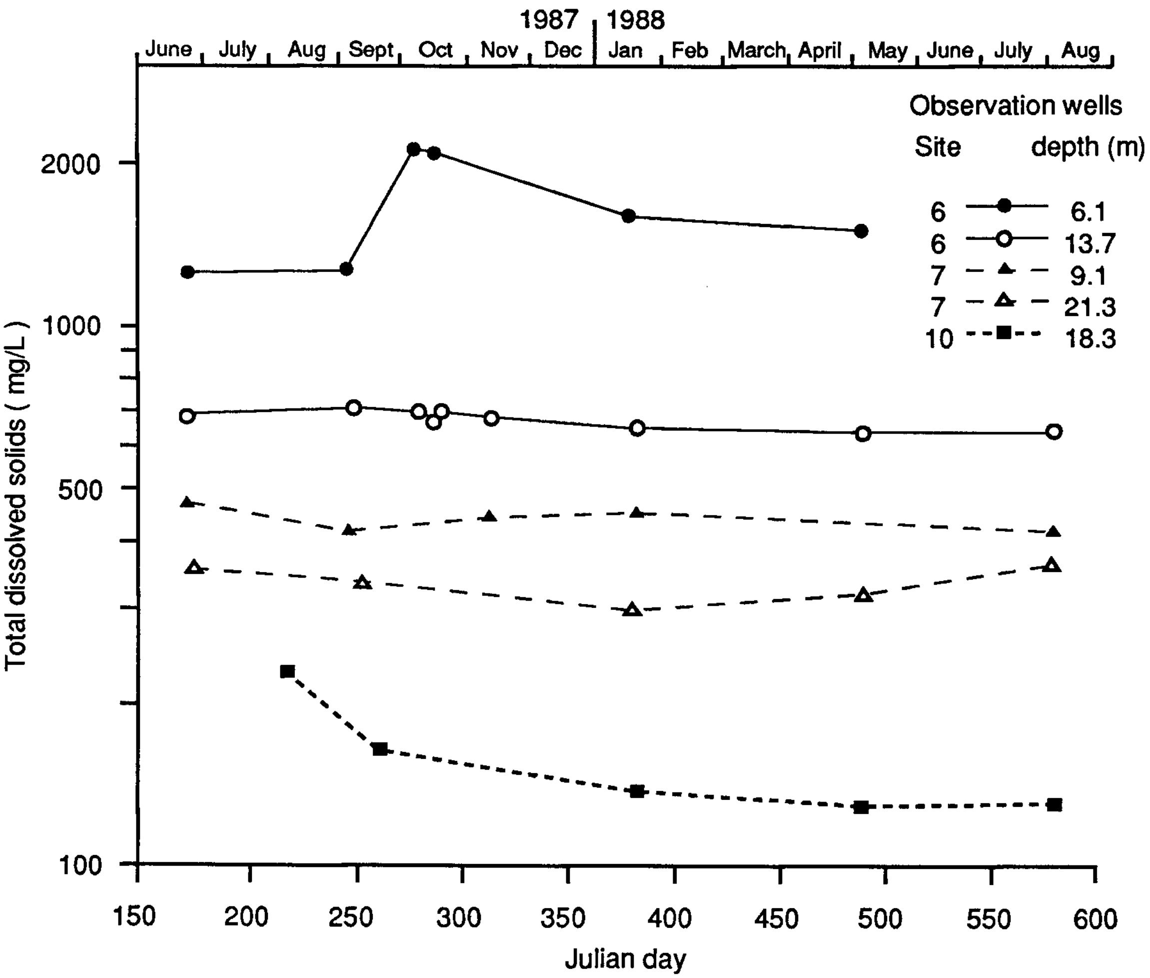

Figure 59. Time-series distribution of total dissolved solids for the shallow and the deepest wells at sites 6 and 7 and for the shallow well at site 10.

θ is the volumetric water content (L^3/L^3),

$v = q/\theta$ is the pore water velocity (L/T), where q is the hydraulic flux density,

x is distance (L),

t is time (T), and

m is the degradation coefficient (T^{-1}), which is assumed to be a rate constant for first-order decay.

Equilibrium adsorbed and solute concentrations are related by an assumed linear or linearized isotherm of the form

$$s = kC \tag{2}$$

where

k is an empirical distribution constant (L^3/M), often referred to as the distribution coefficient K_d.

Assuming local equilibrium conditions exist, substitution of (2) into (1) yields

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - \mu C\,, \tag{3}$$

in which the retardation factor R, which accounts for chemical interaction between the chemical and the porous medium, is given by

$$R = 1 + \frac{\rho_b k}{\theta}. \tag{4}$$

For a mobile, nonreactive chemical, such as bromide, $R = 1$ and $m = 0$, and equation (3) reduces to

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x}. \tag{5}$$

Equations (3) and (5) are solved subject to 1) a uniform initial concentration C_i, 2) a pulse-type boundary condition at the soil surface, and 3) a semi-infinite $(0 \leq x < \infty)$ bottom boundary condition:

$$C(x, 0) = C_i \tag{6a}$$

$$\left(-D\frac{\partial C}{\partial x} + vC\right)\bigg|_{x=0} = \begin{cases} vC_0 & 0 \leq t < t_0 \\ 0 & t \geq t_0 \end{cases} \tag{6b}$$

$$\frac{\partial C}{\partial x}(\infty, t) = 0, \tag{6c}$$

where C_0 is the input concentration and t_0 is the solute pulse duration.

Cassel et al. (1975) and Wierenga (1977) have found that the steady-state solution to the convection-dispersion equation (5), using mean values for Darcian flux and profile water content, gives a good approximation of solute transport data obtained under transient conditions. Thus, even under transient flow conditions, the assumption of an equivalent uniform water flux and water content may be adequate for employing equations (3) and (5).

The analytical solution for this problem is given by van Genuchten and Alves (1982) and by Parker and van Genuchten (1984a) for both volume-averaged resident concentrations of the solute in the liquid phase and flux-averaged concentrations. Volume-averaged concentration refers to the mass of solute per unit volume of fluid contained in an elementary volume of the system at a given instant. Flux-averaged concentration refers to the mass of solute per unit volume of fluid passing through a given cross section at an elementary time interval (Kreft and Zuber, 1978); in other words, it is the ratio of the solute flux to the volumetric fluid flux. A least-squares regression method described by Parker and van Genuchten (1984a) was used to fit the curves of the analytical solution of equations (3), (5), and (6) to the observed data for the suction lysimeters and the 1–in. diameter cores collected at different times during the experiment. The Parker and van Genuchten (1984a) CXTFIT program was used to optimize the unknown (or partially known) parameters v, D, R, m, and t_0 in equations (3) and (6) from observed temporal and spatial concentration data.

One restriction is that v and R cannot be optimized simultaneously because of similar effects on the effective transport rate v/R in the soil profile. For bromide, R was taken to be unity with no adsorption.

Parker and van Genuchten (1984b) showed that a significant difference in calculated parameter values will result depending on whether a volume or a flux-averaged concentration is used. However, for small values of the dimensionless group (vx/D), differences between the two concentration modes should be small. In our case relatively small differences in the bromide-fitted parameters were observed when flux or resident concentrations were employed in the parameter-optimization program.

Although the convective-dispersive transport equation is the foundation on which numerous mathematical analyses of solute transport in porous media have been based, questions have been raised recently regarding the applicability of this model to media exhibiting large variations in pore-water velocities (caused by the presence of continuous large pores) or by field scale variability in hydraulic properties (van Genuchten and Wierenga, 1976; Parker and van Genuchten, 1984b). Nielsen et al. (1986) list other difficulties associated with the use of equation (3) or (5). In using the convective-dispersive model [equation (3) or (5)] one generally assumes that chemical and physical equilibrium exists between the displacing solution and the original soil solution. Unfortunately, it appears that for many soils such an equilibrium does not exist, resulting in partial displacement of the soil solution by the invading solution (Wierenga, 1982, 1987). One partially successful approach to describe solute movement through soils with partial displacement is to divide soil water into mobile and immobile, or stagnant (not in equilibrium with the infiltrating water), zones (van Genuchten and Wierenga, 1976). Solute movement into and out of this immobile water is assumed to be a relatively slow diffusion-controlled process that results in early breakthrough and tailing of solute-distribution curves. Under certain conditions, such as low apparent dispersivity, all solutions of the classical convection-dispersion model yield symmetrical concentration distributions in time and space. Experiments on fractured or aggregate media, however, yield asymmetric spatial and temporal concentration distributions with first moments significantly different from those anticipated for symmetric distributions (e.g., Bouma and Wosten, 1979). Such discrepancies are often regarded as incongruous with the classical convection-dispersion equation (Parker and van Genuchten, 1984b), a view corroborated by our field study results.

As a result of the discrepancies of the convection-dispersion equation vis-a-vis the field results, breakthrough curves for bromide and atrazine could not be successfully simulated with the Parker and van Genuchten (1984a) models, including the two-site–two-region (mobile-immobile zones) nonequilibrium model. The problem was further compounded by the observed large variability of soil-core sampling at random points within the relatively small flooded area of both sites. However, we encountered relatively better results when simulating the vertical profiles of bromide, sampled from suction lysimeters, at different times. The observed exponential decay-type of concentration-depth distributions generally fit the expected classical patterns better than concentration-time breakthrough curves. Table 3 presents two results of bromide-fitted model parameters v, D, and t_0, assuming $R = 1$. Those two sampling dates had the most complete suction lysimeter data. Although the chemical solution at both sites was applied for approximately 1 day at the surface, our shallowest suction lysimeter was at 15 cm (0.5 ft) below the surface. Thus there is some ambiguity as to the exact duration of the applied pulse relative to the sampling port location and the pulse duration was treated as an unknown parameter in this study.

Table 3. Fitted-model parameters for bromide collected from suction lysimeters

Site	Sampling date	v (cm/day) +/- std. error	D(cm^2/day) +/- std. error	t_0 (day +/- std. error	R^2	Number of samples
6	9/18/87	13.52 +/- 0.17	19.20 +/- 1.82	2.43 +/- 0.03	0.9998	6
7	10/8/87	15.65 +/- 1.12	19.76 +/- 8.29	1.61 +/- 0.00	0.9875	7

Although the estimated average pore-water velocity overestimated the average measured pore-water velocity for site 6 and underestimated the one for site 7, as determined from the instantaneous profile method (Figs. 13, 18, 43 and 45), the estimated velocity values are of the correct order of magnitude. Figure 60 depicts the simulated and measured site 6 bromide data for bromide versus depth for September 18, 1987, 3 days after the chemical solution was applied at the site.

Conclusions and recommendations

We find the combined use of flooding experiments for simultaneously studying both the chemical and physical flow characteristics of the study sites a powerful field technique. Although we observed relatively high nitrate concentrations in both the vadose and the aquifer zone in one of our study sites (site 7), atrazine was not detected in either the deeper vadose zone or the underlying aquifer in any of the study sites. We also have no evidence of atrazine accumulation on top of clay layers, despite repeated soil-core sampling before, during, and after the chemical flooding experiments.[2] The evidence, albeit from limited sampling (because of financial constraints), that atrazine readily breaks down to hydroxyatrazine, even if soil pH is not low and even if clay and organic matter content are relatively low, may explain the observed atrazine distribution. Atrazine degradation follows approximately first-order kinetics with a half-life of approximately 2 weeks. We also have evidence of biodegradation by-products, indicating that both biological and chemical degradation occur in the soil profile. Based on the results of this study, the probability that atrazine

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[2] Clay layers sampled during trench excavation August 4–6, 1987, from cropland sites in Pawnee County (T23S, R15W, Sec. 14, Carwile soil; sampled and atrazine-analyzed depths: 38–52 cm; 52–92 cm; 111–123 cm), Edwards County (T24S, R16W, Sec. 5, Naron soil; sampled and atrazine-analyzed depths: 43–68 cm, 68–91 cm, 146–161 cm), Pratt County (site 7; sampled and atrazine-analyzed depths: 32–50 cm, 135–157 cm, 157–167 cm), and Stafford County (site 6; sampled and atrazine-analyzed depths: 48–66 cm, 66–77 cm) revealed no detectable atrazine at a detection limit of 0.04 mg/kg.

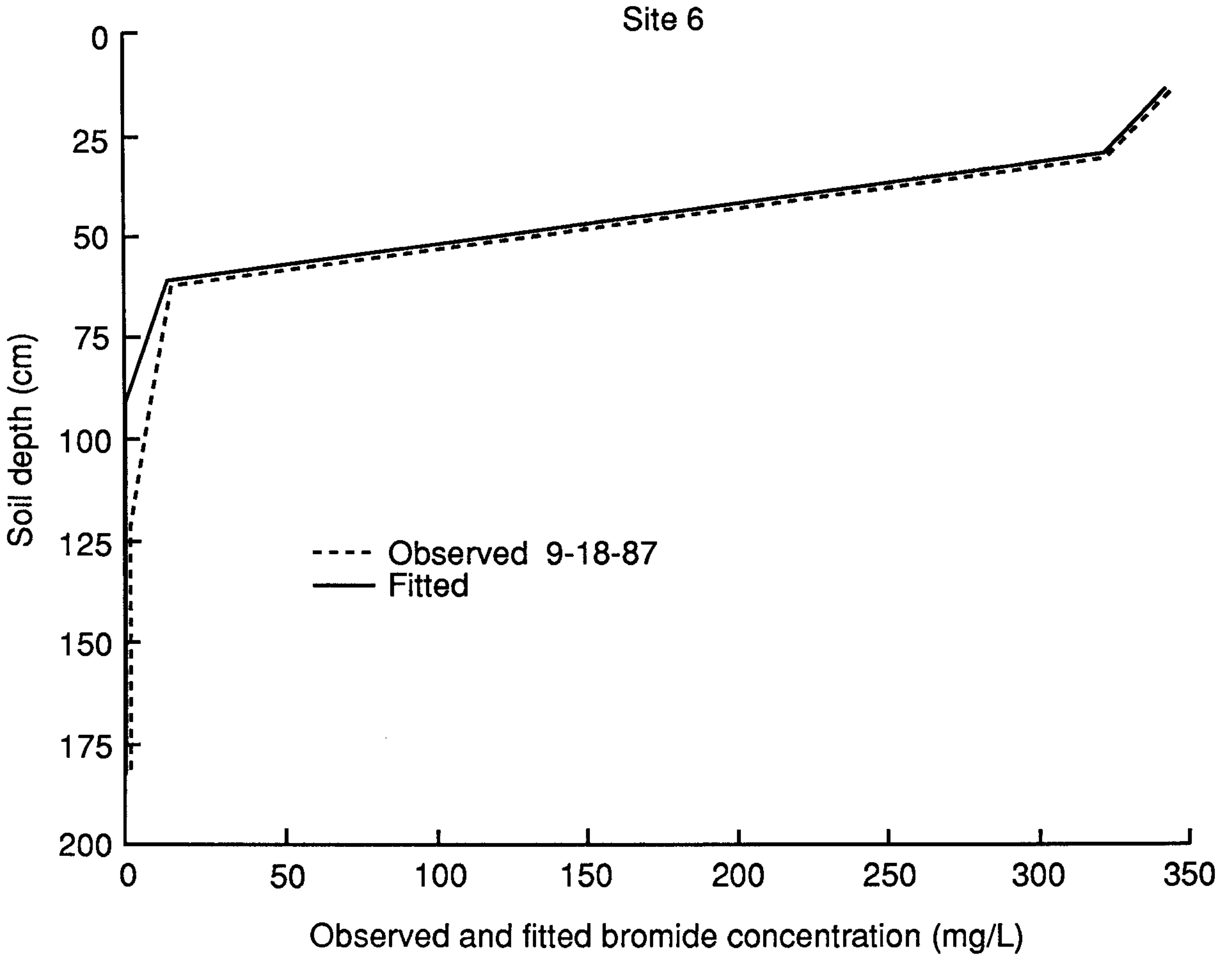

Figure 60. September 18, 1987: observed and fitted flux-averaged bromide concentrations with depth for site 6.

will leach through the soils to the underlying aquifer in the Great Bend Prairie under present conditions does seem remote.

The nitrate data from the suction lysimeters in site 7 indicate a close relationship between irrigation and nitrate movement into the subsurface; that is, nitrate is moving into the deeper soil profile and into the ground water as a consequence of irrigation. However, low nitrate levels in both the soil and the ground water were observed at site 6. Comparison of the total dissolved solids content in the ground water from sites 6, 7, and 10 demonstrates the impact of continuous irrigation on the general ground water quality at sites 6 and 7, which exhibit much higher total dissolved solids than the nonirrigated site 10.

Chemical transport analysis at sites 6 and 7 indicats that the classical processes of chemical movement based on porous media-equilibrium-diffuse flow are not appropriate for either site. The persistence of bromide in the upper soil horizons indicates that the applied solution displaced the existing soil-pore water during percolation at site 6, which was already at or near saturation when the bromide-tagged solution was applied. Thus we have evidence of slug flow or lack of complete mixing between invading and in situ solutions. Some preferential flow was also observed, although to a lesser extent than the slug flow. As a result of such slug movement, piston-type displacement of more saline soil solutions in the soil profile to the water table occurred. The significance of such observations from site 6 to agricultural chemical movement is that, during periods of unusually high rainfall and ponding in the area or during excessive flood irrigation, downward movement of chemicals concentrated in soils could be triggered, affecting the quality of shallow ground water.

In contrast to what was observed at site 6, slug displacement at site 7 was subdued, and channelization or preferential flow of percolating soil water, with little of the initial soil solution being displaced, was dominant. The importance of the results to agricultural chemical movement is that dissolved chemicals can bypass certain soil zones and move to greater depths than expected. When water becomes channelized in field soil, only a small percentage of the total matrix is involved in the flow process. Thus movement of chemicals in field soils occurs through a combination of displacement of native fluids (slug movement) and bypassing of native fluids by preferential flow. Therefore the assumption of diffuse porous media flow under physical and chemical equilibrium between invading and native solutions—a standard assumption in mathematical formulations of contaminant transport—is not supported by our field study. Therefore concentrated efforts to quantify preferential and incompletely mixed flow situations are urgently needed.

As a result of our sampling experience, we offer the following recommendations.

1. Collect multiple samples per depth over a small area of interest, and use the average concentration per depth for analysis.
2. Sample the entire depth of interest in one continuous core. The 30–cm (1–foot) depth intervals we used with a hand core sampler occasionally created cavings at each depth increment, thus altering the soil-profile distribution of the chemical of interest.
3. Do not rely entirely on suction lysimeters because (a) they may fail; (b) one is not certain if leakage along the side walls of the lysimeter occurs; (c) under freezing conditions they do not work; (d) even if they do work, one may not obtain a sample because of soil dryness; and (e) questions on the representativeness of the obtained samples may arise because vacuum application dries up the immediate vicinity of the porous cup and thus soil-water flow may preferentially diverge from the porous cup vicinity. In addition, because of the continuously varying vacuum conditions in the suction lysimeters, different pore fractions are sampled at different times. Therefore, use of both soil cores and suction lysimeters (preferably maintained at constant vacuum) are recommended for chemical sampling.
4. Chemical analyses should be conducted as early as possible after sampling so that problems can be addressed effectively and sampling redone, if necessary. It is essential that sequential or time-series sampling be guided continuously by the chemical

analysis results to provide maximum flexibility. Sending samples to outside labs and waiting for months to receive results defeats the purpose of any serious study.

In addition to these four recommendations, we outline the following research items for further study:

1. A laboratory study of atrazine degradation processes using running pairs of soil columns, one of which is sterilized (either chemically or by autoclaving) so that microbial decomposition of atrazine can be ascertained. These column pairs should be run for different wetness conditions.
2. Monitoring of the present sites and additional sites with regard to additional pesticides and nitrate, with particular emphasis on environmental and land use effects. Given the high nitrate concentrations observed at site 7, a more detailed and regional study of the nitrate problem in the Great Bend Prairie is needed.
3. An evaluation of numerical simulation approaches to agrichemical movement with particular emphasis on preferential flow and incomplete mixing processes.

Appendix A

Literature review on atrazine and nitrate

Agricultural use of pesticides in the United States nearly tripled between 1964 and 1984, with herbicides accounting for 82% of all the pesticides used on major field and forage crops in 1982 (Nielson and Lee, 1987). The finding of agrichemicals in a variety of aquifers indicates a non–point source problem. In Iowa atrazine is detected in shallow wells in Pleistocene and alluvial aquifers (Kelley et al., 1986). In addition, it was found that agrichemical concentrations vary temporally and generally increase in response to increased infiltration (Thompson et al., 1986). The detection of atrazine in ground water and soils in the winter and spring before new application suggests that the chemical is persisting in the subsoil and then leaching through the soil during winter or spring recharge (Hallberg, 1986b).

Numerous studies in Nebraska indicate a slow general increase in atrazine concentrations in areas of sandy soil and irrigation, primarily in the central Platte River basin, where corn is grown. The concentrations are low (200–800 ppt), but the persistence suggests that degradation once the chemical arrives in the aquifer is slow (Wehtje et al., 1981, 1983; Junk et al., 1980). Stratification of atrazine in wells down-gradient from irrigated corn fields in Nebraska reveals that the source is essentially a non–point source distribution.

The United States Department of Agriculture reports that approximately 10.6 million tons of nitrogen fertilizer are used annually in the United States (Hurlburt, 1988). The use of inorganic nitrogen fertilizers, a major source of nitrate contamination in ground water, increased fourfold between 1960 and 1980 (Nielson and Lee, 1987). Studies in Iowa indicate that nitrate concentrations have increased tenfold in direct response to increased fertilization (Thompson et al., 1986). Statistics from the Kansas State Board of Agriculture (1988) indicate that from 1951 to 1987 there has been an eightfold increase in the use of all classes of fertilizers (Kansas State Board of Agriculture, 1988). In Kansas approximately 500,000 tons of nitrogen fertilizer were reported sold for the fall and spring of 1986–1987.

One of the areas of the United States that is most vulnerable to nitrate-nitrogen contamination is the Central Great Plains. The use of the DRASTIC index (Aller et al., 1985) indicates that Kansas falls in a region of high to moderate nitrate levels in ground water in agricultural areas (Nielson and Lee, 1987). Studies in Kansas indicate that low levels of 2,4-D, atrazine, and nitrate are present in ground water in parts of the state (Heiman et al., 1987; Stulken et al., 1987). However, the occurrence of pesticide chemicals has not been shown to be widespread. In a statistically representative study of 103 farmstead wells (used for domestic and farm purposes) throughout the state, Heiman et al. (1987) showed that 3% of the wells had atrazine but that 28% had nitrate levels above the recommended level of 45 ppm as nitrate. Their study suggested that wells in the northeast, north-central, and south-central parts of the state had a higher probability of nitrate contamination than did other sections of the state. No statistical relationship was found between geologic ground-water area and nitrate concentration in ground water. The study showed that the effects of age of the well, location of possible organic contaminant sources, and land use practices were the most useful predictors of contamination for the wells studied. The effects of fertilizer nitrogen as a source of nitrate were not evaluated.

Atrazine

Chemistry of atrazine

The structure of the atrazine molecule is 2-chloro-4-ethylamino,6-isopropylamino,s-triazine. This structure means that a chlorine ion is attached at the number 2 carbon of a triazine ring (composed of three nitrogens and three carbons with double bonds at the 2, 4, and 6 positions of the ring; Figure A.1); the ethylamino group ($-NHC_2H_5$) attached at the number 4 carbon; and the isopropylamino group ($-NH-C_3H_7$) attached at the number 6 carbon (Hassall, 1982; Sheets, 1970;

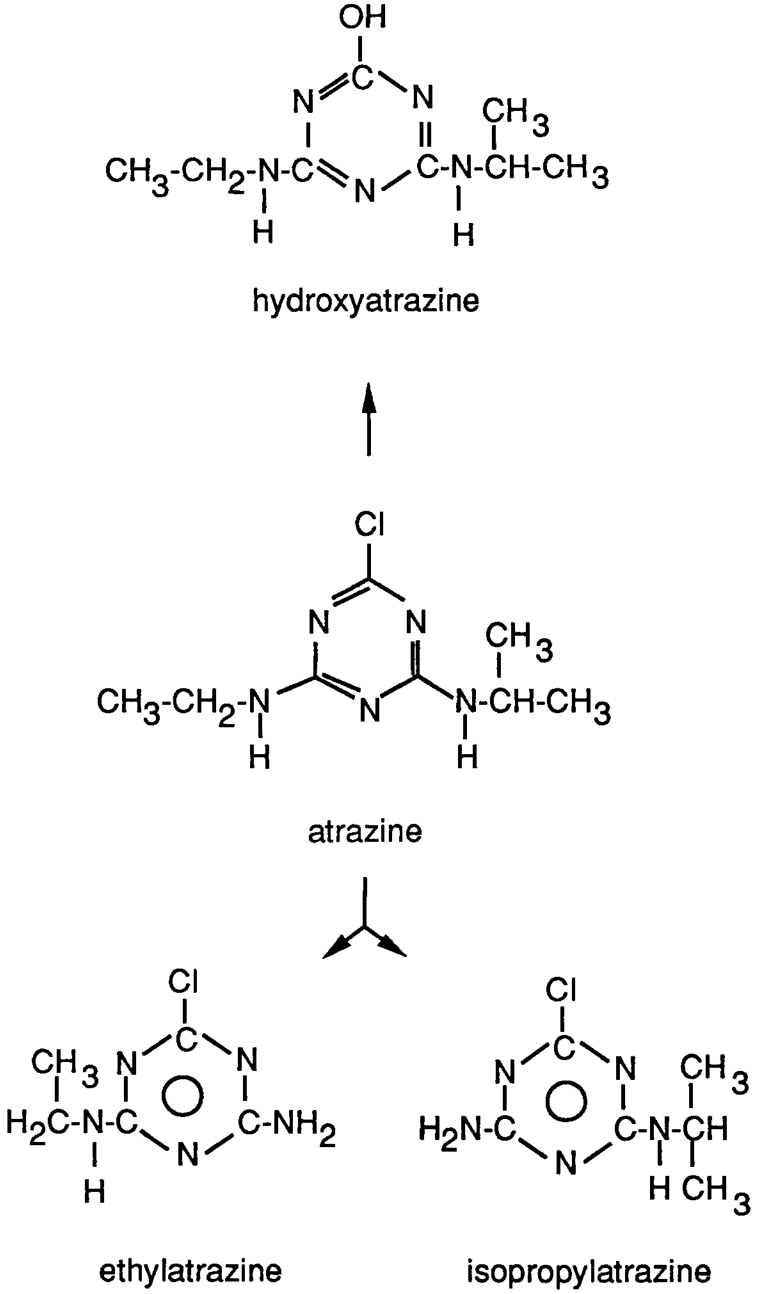

Figure A1. Structure and nomenclature for atrazine and its degradation byproducts.

Harris, 1967). Work by Sheets (1970) indicates that the triazine structure is most responsible for the persistence of these chemicals in soil or water. A methoxy- (OCH_3) group substitution at the number 2 carbon position in the triazine ring is considered more persistent than a Cl- or methylthio (SCH_3) substitution.

Solubility

Properties of a chemical that influence its movement are solubility in water, acidity (pK_a) or basicity (pK_b) of the molecule (the pH of the solution relative to the pK affects the form in which the chemical is dissolved), charge distribution on the organic molecule, and shape and configuration of the molecule (Bailey and White, 1970; Sheets, 1970). Various researchers have come up with conflicting results as to whether or not the solubility of the compound has a primary influence on movement through or adsorption to the soil. Bailey and White (1964), Burnside et al. (1963), and Bailey et al. (1968) indicate that the solubility of the chemical in water has a direct effect on the rate at which the chemical will move through soil. Bailey et al. (1968) found that the magnitude of adsorption of triazines to Na-montmorillonites is directly related to their solubility in water. The most soluble chemicals adsorbed to montmorillonite the tightest. The triazines and their relative solubilities in order of decreasing adsorption capability are: simetone (3200 ppm), atratone (1654 ppm), prometone (750 ppm), atrazine (33 ppm), trietazine (20 ppm),and propazine (8.6 ppm). Work by Rodgers (as summarized by Bailey and White, 1970) found a distinct lack of correlation between solubility and leachability. Rodgers also found that soil type can alter the order of leachability of triazines. In his studies atrazine with solubility of 33 ppm moved farther than simazine (5 ppm), atratone (1654 ppm), or ipatone (100 ppm). Helling (1970) used thin-layer chromatography to demonstrate the relative movement of different families of chemicals in a silty-clay loam soil. In Helling's study, atrazine was in the middle of the group in terms of mobility.

He found in his literature search that there is much debate about the effects of solubility on leachability of various chemicals.

Chemical degradation

The breakdown of atrazine occurs by either microbial degradation or chemical hydrolysis. Whether chemical degradation or microbial degradation is the principal method is still being debated.

Chemical breakdown of atrazine to hydroxyatrazine is facilitated by catalysis resulting from adsorption onto montmorillonite and/or organic matter (Harris, 1967; Armstrong et al., 1967; Russell et al., 1968; Armstrong and Chesters, 1968; Skipper et al., 1978; Li and Felbeck, 1972). Hydroxyatrazine is considered a nonphytotoxic breakdown product. In other words this compound lacks the herbicidal characteristics to affect plants. Work by Russell et al. (1968) and Harris (1967) studied the effects of adsorption of atrazine onto montmorillonite on the rate of degradation of the chemical. The acidity of the clay surface was found to play an important role in the hydrolysis process. No degradation of atrazine was observed in a solution system at pH 3.5 in the absence of clay thus illustrating the catalytic function of the clay. Bailey et al. (1968) also found that adsorption of basic organic compounds by montmorillonite-type clays depends on the surface acidity on the clay and not on the pH of the suspension.

Work by Armstrong and Chesters (1968) and Harris (1967) also supports the role of catalysis resulting from adsorption on soil colloidal surfaces. The adsorption results from hydrogen bonding between the adsorbent carboxyl group and the atrazine ring nitrogen atom. Hydrolysis occurs because of the electron deficiency of the ring carbon attached to the electronegative chlorine and positive nitroge ions. This deficiency causes susceptibility to displacement by strong nucleophilic (positive-charge-loving) agents such as hydroxyl ions (Armstrong et al., 1967). In a neutral pH region (pH $\approx$7) weak nucleophilic agents such as H_2O

are unable to replace the chlorine on the molecule. However, hydrogen bonding to the ring nitrogen atom causes further electron withdrawal from the electron-deficient carbon atom, enabling the weak nucleophile H_2O to replace the chlroine.

Studies by Skipper et al. (1978) indicate that under acidic field conditions smectite-type clays are expected to enhance the chemical hydrolysis of atrazine. Work by Russell et al. (1968) indicates that chemical hydrolysis occurs as a result of protonation (presence of hydrogen ions) at the colloidal surface. This was not found by Armstrong and Chesters (1968).

Soil pH and organic matter content largely control the rate of atrazine hydrolysis; for soils of similar pH atrazine degradation rates increase with increased atrazine adsorption (Armstrong et al., 1967). The interaction of *s*-triazines (atrazine in particular) with humic acid compounds was studied by Sullivan and Felbeck (1968) and by Li and Felbeck (1972). They suggested that hydrogen bonding of atrazine onto humic acid decreased the energy of activation (amount of energy needed to cause the reaction to proceed) and consequently increased the rate of hydrolysis. Tests showed that atrazine mixed with 0.2 g humic acid decomposed much faster than in solutions without the humic acid. These studies suggest that alignment of the atrazine molecule on humic acid may play an important role in the humic acid–catalyzed hydrolysis of atrazine.

Work by Obien and Green (1969) on four Hawaiian soils indicates that atrazine degradation is more closely related to pH (faster on low pH soils) than to organic matter content or adsorption. Degradation increased when temperature was increased from 30° C to 50° C indicating a chemical rather than biological process.

Biological degradation

Biological degradation of atrazine results in two daughter products : deethylated atrazine (2-chloro-4-amino-6-isopropyl-amino-*s*-triazine) and deisopropylamino atrazine (2-chloro-4-amino-6-ethylamino-s-triazine). Deethylated atrazine is a potential herbicide that might explain the phytotoxicity of soils where analytical data indicate low levels of atrazine (Sirons et al., 1973). Sirons et al. used a soil with pH = 7 composed of 32% clay and 4.8% organic matter, with a cation-exchange capacity of 22.8 meq/100 g. The pH is much higher than in the studies of chemical hydrolysis in which pH was in the 3.5–4.5 range. These workers failed to detect hydroxyatrazine in their products, leading them to believe that microbial degradation was the primary pathway. Most of the studies involving microbial degradation of atrazine used soils in the neutral to alkaline pH range (Kaiser et al., 1970).

The effects of temperature are also important. Work by Harris and Warren (1964) indicates that adsorption of atrazine increases with decreasing temperature, the availability of atrazine being greater at higher temperatures. More rapid decomposition of chloro-s-triazines in warm soils may be the result of a combination of conditions: increased microbial activity and increased availability and solubility of the chemical (Kaiser et al., 1970). Work by Roeth et al. (1969) indicates that chemical hydrolysis may occur first with a subsequent microbial attack on the hydroxyatrazine form. Skipper and Volk (1972) provide additional evidence that microbes attack the hydroxyatrazine ring rather than the parent molecule.

Kaiser et al. (1970) summarize the debate on chemical and biological degradation the best. The primary control is the soil environment. Hydrolysis of atrazine to hydroxyatrazine probably dominates at high temperature (>30°C) and low pH (<5.5). Neutral pH favors bacterial degradation. At basic pH (>8.5) hydrolysis again dominates. Low temperature and moisture levels are unfavorable for both routes of breakdown. Physical characteristics of the soil, aeration, inorganic and organic nutrients, and quantity of clay and organic matter also play a major role in determination of whether one or both processes will occur.

Factors affecting movement of herbicides

Many factors influence the movement of herbicides from the surface to the ground water. Some of these are land use, such agricultural practices as type of tillage used, climate, hydrogeology, soil characteristics, net aquifer recharge rates, depth to water, and characteristics of the unsaturated zone and aquifer (Nielson and Lee, 1987).

The dominant controls on the movement of pesticides through soils are the pH of the soil, the quantity of organic matter and clay (particularly montmorillonite and vermiculite types), hydraulic conductivity, and soil-moisture content (Helling and Gish, 1986; Bailey and White, 1964, 1970; Helling, 1970; Yaron et al., 1985). Use of models, field experiments, and laboratory studies indicates that the movement of herbicides, particularly atrazine, is influenced most by hydraulic conductivity, pH, soil moisture, and amount of organic matter.

Soil pH and organic matter content

Soil pH and the percent of organic matter in the soil are two primary controls in the breakdown process of herbicides. Armstrong et al. (1967) indicate that hydrolysis of atrazine (replacement of the chlorine attached to the number 2 carbon in the triazine ring with a hydroxyl group) into the hydroxyatrazine daughter product is controlled by pH and the percent of organic matter in the soil. Hydrolysis is catalyzed by adsorption onto soil and by an increased concentration of H^+;that is, increased acidity (lower pH) increases the hydrolysis process (see section on chemistry of atrazine).

Hiltbold and Buchanan (1977) found that with each unit increase in soil pH atrazine persisted from 9 to 29 days longer, depending on soil type. Bailey and White (1964) found that adsorption of herbicides with widely differing molecular structures increases as pH decreases. In addition, the bioactivity of the herbicides (ability of the herbicide to be utilized by plants) is lowest in soils that are high in organic matter and clay content and highest in light-textured soils.

Burnside et al. (1963) found that atrazine leaches most in a sandy soil with a low organic matter content and a pH of 6.8 and least in a soil with a high content of clay and organic matter and a low pH. Soils with low pH tend to cause increased adsorption onto clays or organic matter and thus permit chemical hydrolysis to occur (Frissel and Bolt, 1962; Weber et al., 1969; McGlamery and Slife, 1966).

Many studies have indicated that increased organic matter content and cation exchange capacity (CEC), in addition to an acidic environment, enhance the adsorption of herbicides onto soils (Armstrong et al., 1967; Bailey and White, 1964,1970; Hayes, 1970; Helling and Gish, 1986; McGlamery and Slife, 1966; Talbert and Fletchall, 1965). The studies indicate that statistically and experimentally the adsorption of herbicides is best predicted by the amount of organic matter in the soil.

Soil moisture content

Soil moisture is another property that may affect the breakdown potential of an herbicide. Several studies indicate that decreased soil moisture results in increased adsorption of herbicides to the soil (Bailey and White, 1964; Dao and Lavy, 1978). Lower soil moisture may result in the adsorption of the chemical onto the soil or the precipitation of the chemical if the ratio of water to chemical is below the substance's equilibrium solubility. An increase in the concentration of salts in the solution causes a decrease in the solubility of the herbicide and a resulting increase in adsorption of the chemical onto the soil (Hurle and Freed, 1972; Swanson and Dutt, 1973; Dao and Lavy, 1978).

Temperature

Studies of the effects of temperature on the adsorption of herbicides onto soil have yielded mixed results. Bailey and White (1964) found increased adsorption of herbicides to soil with increased temperature. They believe that seasonal variation in temperature acts as a brake for the release of the chemical over time. Later, Bailey and White (1970) suggested that increased temperature causes a decrease in adsorption of herbicides because of effects on the solubility of the chemical and vapor pressure effects. Harris and Warren (1964) and McGlamery and Slife (1966) found more atrazine desorbed at temperatures of 50°C or 70°C than at 0°C for a soil with 30% vermiculite clay and 6.8% organic matter. These workers also concluded that the effect of temperature is less than the effect of pH on the adsorption process.

The results are quite different for humic acid. Adsorption increases at 40°C to nearly twice the amount at 0.5°C. This is the opposite of what occurrs with the mineral system. The percentage of recovery of atrazine from humic acid increases when pH is raised to 7 but is small when pH is low.

Dao and Lavy (1978) found that increased temperature resultes in increased adsorption of the chemical as a result of temperature effects on solubility and vapor pressure. Low temperatures yield a higher concentration of chemical in the soil water. This is contrary to what other workers have found. Hayes (1970) found that more atrazine is adsorbed at lower temperature (20°C) than at higher temperature (70°C). Harris and Warren (1964) found that adsorption of atrazine onto organic soils is the same at 50°C and 0°C. Talbert and Fletchall (1965) found that, as temperature increases, adsorption of atrazine decreases.

Hydraulic conductivity

A model developed by Helling and Gish (1986) indicates that hydraulic conductivity is the most important factor affecting the movement of atrazine through a soil, with organic matter content and bulk density the next important factors. Plots of available data indicate that movement of atrazine increases with increases in hydraulic conductivity. A survey of the literature by Helling and Gish showed the occurrence of atrazine in ground water in areas with sandy alluvial soils, in karst regions, and in permeable soils in general (Nebraska and Iowa for example). Schneider et al.

(1977) showed that atrazine accidentally introduced into a fine sandy aquifer will move but can be recovered by pumping within 10 days of the last injection. Wehtje et al. (1981, 1983) showed the presence of small quantities of atrazine downdip from heavily irrigated corn-producing areas with sandy soils in Nebraska. Downward leaching through sandy soils with little clay or silt is considered the primary route of entry into the aquifer. Approximately 0.07% of the chemical applied reaches the aquifer. The researchers postulate that the rest is removed by chemical hydrolysis.

Nitrate

Chemical processes concerning nitrate

There have been many articles written about the occurrence of nitrate and other nitrogen compounds in ground water. The major forms of dissolved nitrogen are NO_3 (nitrate), NO_2- (nitrite), NH_4^+ (ammonium ion), NH_3 (ammonia), N_2 (nitrogen), N_2O (nitrous oxide), and organic nitrogen. Organic nitrogen is nitrogen that is incorporated in organic substances (Freeze and Cherry, 1979).

Nitrate can either enter the ground-water system directly as nitrate from wastes or fertilizers or be converted by oxidation of ammonium ion from organic matter or from fertilizers. The process of oxidation of ammonium ion to nitrite is called nitrification:

$$NH_4^+ + \frac{3}{2}O_2 \rightarrow NO^{2-} + 2H^+ + H_2O. \qquad (A.1)$$

This process usually occurs in the unsaturated zone and is frequently aided by bacterial action. Nitrite is rather unstable and will be either reduced or oxidized. In the presence of oxygen nitrobacteria aid in the oxidation of nitrite to nitrate:

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \qquad (A.2)$$

Under oxidizing conditions in ground water, nitrate is the dominant form of nitrogen. Nitrate is highly mobile in ground water with no transformation and little or no retardation as a result of its anionic state (Freeze and Cherry, 1979). With a decline in oxygen content of the water denitrification of nitrate to nitrite can occur. If the dissolved oxygen content of the ground water remains low, the nitrite may be reduced to nitrous oxide or to nitrogen gas. Denitrification most frequently occurs in the unsaturated zone, where high organic matter content, abundant nitrate, and appropriate bacteria are available. There has been little work done on denitrification processes in ground water itself.

Nitrate and nitrite anions are not absorbed by clay soils because both the soil particles and the anions have a negative charge. The ammonium ion has a positive charge and so can bind to negatively charged clay particles. The ammonium ion can be oxidized at a later time by microorganisms to nitrate or nitrite and thus move through the soil-water system. The nitrification process of binding nitrate by means of transformation to ammonium ion or the attachment of ammonium ion from fertilizer to organic matter or clays results in the mineralization of nitrogen in the soil. The mineralization process acts as a potential future source of nitrate nitrogen if conditions change and the nitrogen is mobilized by oxidation of the ammonium ion to nitrate.

Exner and Spalding (1979) showed that in sandy loam soils in Holt County, Nebraska, there is a measurable difference between irrigated areas with non–point sources of contamination, areas with point source contamination (such as septic systems or feedlots), and pristine ground water areas. Evaluation of excess hardness ($Ca^{2+} + Mg^{2+}$) in relation to bicarbonate (HCO_3-) and nitrate (NO_3-) suggests that the formation of nitric acid by denitrification of nitrate may contribute to the formation of excess hardness resulting from dissolution of soil carbonates or the oxidation of soil carbon. Additional evaluation of the water chemistry from non-point-source contamination areas indicates that higher concentrations of nitrate correspond to increases in sulfate and chloride. All these ions are added to cultivated fields mainly as anhydrous ammonia, liquid nitrogen, potash

(KCl and K_2SO_4), and sulfamag ($MgSO_4$-K_2SO_4). The positive correlation of sulfate:nitrate, and chloride:nitrate implies that the dissolution of concentrated anionic sources, such as commercial fertilizers, is a major source of nitrate in this area.

Sources of nitrate in soils and ground water

Hurlbut, in a feature article in a recent issue of *Water Well Journal* (Hurlburt, 1988) used interviews with various investigators to discuss the problem of nitrate contamination in ground water. Workers in Canada, Arizona, and Nebraska all indicate that agricultural use of nitrogen fertilizers may be a major source of non-point-source nitrate contamination in ground water. The mechanics of how the contamination occurs varies from region to region. In Canada and Nebraska there is evidence that nitrate contamination occurs in sandy, well-drained soils (Hill, 1982; Spalding et al., 1980). Work in Iowa indicates a major problem with leaching of nitrates and pesticides in areas of thin soil cover and karst subsurface systems. There is a direct correlation among rate of application, precipitation events, and quantity of contaminants found in the ground-water system (Hallberg, 1986a).

Spalding (1984) showed that movement of nitrate in sandy soils in Nebraska is strongly influenced by precipitation and irrigation return flows. There is a decrease in nitrate with depth in the aquifer. The upper part of the shallow aquifer is the most affected by contamination. The lower values in the deeper part of the aquifer are due to slow vertical movement.

High nitrate concentrations are also found in ground water beneath fine-grained sediments. Spalding and Kitchen (1988) showed that fine-grained soils are not enough to prevent leaching when excess nitrogen is applied to soil. In theory, the vertical movement of water through fine-textured clayey silts should be relatively slow, as should the transport of applied nitrate that has leached through the crop rooting zone. Spalding and Kitchen demonstrated that over a 15-year period nitrate had moved at least 60 ft through fine-grained sediments and that up to 1200 lb N per acre had accumulated in the vadose zone beneath a test site treated with 400 lb N per acre per year. The storage of this amount of nitrate in fine-grained sediments indicates a probable future non–point source for nitrate in underlying ground water.

Stratification of nitrate in ground water is seen in alluvial wells in Iowa and Nebraska (Thompson et al., 1986; Spalding, 1984). In addition, temporal and spacial variations are prominent in both these areas. The soils and aquifer materials tend to be sands and gravels with occasional clay and silt lenses. Stratification of higher nitrate concentration in the shallow ground water with decreasing concentration with depth may be due to lack of vertical flow or the possibility of denitrification processes.

A survey of nitrate nitrogen in ground water in Merrick County, Nebraska by Spalding et al. (1978) indicated good correlation between coarse-textured soils and high nitrate nitrogen levels. The primary suspected source for the nitrate nitrogen is commercial nitrogen fertilizer on irrigated corn. Spalding et al. also found that high nitrate nitrogen was correlated with water use but not with well construction. The areas of low–, medium–, and high–nitrate nitrogen concentration were related to intensity of irrigation.

In Nebraska a survey of soil cores under native rangeland and irrigated corn in sandy soils showed a magnitude higher concentration of nitrate in the soil beneath the irrigated site than at the native rangeland site (Hergert, 1982). Another study by Hergert (1978) in Nebraska on management of nitrogen in sandy soils showed that normal precipitation will move any residual nitrate deeper into the soil during the winter and early spring. This nitrogen is essentially lost for crop production. One cannot rely on residual nitrate nitrogen in sandy soils to fertilize the next crop because it is too susceptible to leaching (nitrate movement). Two keys for nitrogen management in sandy soils were offered: The quantity of nitrogen must be tuned to the amount that plants will take up during different periods of their development; and the timing and amount of irrigation water must be regulated. Hergert (1978) showed that the use of nitrogen fertilizer in the irrigation system enabled the quantity of nitrogen applied to be keyed more tightly to the needs of the crop being grown.

Geologic nitrogen

The occurrence of geologic nitrogen (nitrogen associated with certain geologic formations of sedimentary origin) in the deep loess deposits of southwestern and central Nebraska is another possible source for nitrate formation and migration to ground water (Boyce et al., 1976). A study in Nebraska found NO_3- at depths of about 7 m to approximately 30 m. Nitrate nitrogen values ranged from 25 ppm to 45 ppm but have been reported up to 87 ppm. The leaching of the nitrate has been related to increased irrigation in this region. Other possible sources for nitrate are nitrification of organic nitrogen in paleosols within the soil zone, nitrate leached from surface soils following periods of drought during which nitrification would be greater than plant uptake and after which nitrate would move through the system, and fixed NH_4^+ released and nitrified over the recent geologic past.

Strathouse et al. (1980) showed the association of different chemical forms of nitrogen with different sedimentary facies. One basin had fine-grained sediments with a high organic matter content and therefore more organically bound nitrogen as a primary source for nitrogen. Total nitrogen and nitrate concentrations increased from older to younger geologic sediments. The other basin consisted of coarse clastics with a high total nitrogen concentration that occurred in the fixed ammonium phase bound to smectite clays. The source of nitrogen from that basin was fixed ammonium bound to layer silicates. Strathouse et al. concluded that sediment type (lithology) and Eh conditions were the major controls on the formation and movement of nitrate nitrogen in different sedimentary rocks and soils.

Keeney (1986) summarized other studies of sources of geologic nitrogen. Shales are a source of nitrogen in South Dakota, Montana, and California. Natural soil nitrate has been identified as a source of nitrate contamination in Runnels County, Texas. The increased use of irrigation has caused increased movement of nitrate in dryland farming areas of Texas, Nebraska, and California.

Nitrate and chloride profiles as indicators of movement

Various studies use the Cl/NO_3-N ratio or the inverse ratio as an indicator of the movement of the two ions through the unsaturated zone to ground water and as an indicator of the occurrence of denitrification in the soil profile. Other studies use separate profiles of the two ions to compare movement to ground water. There does not seem to be a standard method to evaluate collected data. A summary of each type of study is given in the following sections. The studies that use the ratio method for determination of denitrification processes usually deal either with coarse sediments or clay and organic matter rich sediments.

Endelman et al. (1974) showed that loamy sand is highly susceptible to leaching by rainfall or irrigation with a resultant loss of nitrate and chloride from fertilizers used at the site. The nitrate nitrogen and chloride moved 15–20 cm/day under a 2.5–cm daily water application. The similarity of the profiles of these two ions in the soil indicates that chloride is a possible tracer for the movement of nitrate nitrogen and also a good indicator of the loss of nitrate through denitrification.

Lund (1982) studied the variation in concentration of nitrate nitrogen and chloride in ground water below four agricultural fields with sandy loam soils to evaluate the spatial and temporal variations of these ions in the unsaturated zone. At all sites spacial variation was found. Spatial variation in leaching rates of soil solutions results in nonuniform movement of nitrate and chloride pulses below the root zone.

In Nebraska the overall rate of increase of nitrate nitrogen in ground water beneath fine-grained sediments thicker than 100 ft is 0.1–0.2 mg/L/yr. This is a small increase when compared with the rate in sandy soils with shallow ground water (0.4–1.0 mg/L/yr; Spalding, 1984), but it does indicate that fine-grained and vadose sediments are not adequate protection to prevent contamination of ground water. Spalding and Kitchen (1988) showed that in 15 years nitrate moved vertically at least 60 ft through fine-textured unsaturated sediments in Nebraska.

Smith and Davis (1974) showed that bromide and nitrate move at similar rates unless some denitrification of the nitrate occurs. They suggested using bromide instead of chloride as a tracer because of the common occurrence of chloride in soils, rocks, fertilizers, precipitation, etc. Work with soil columns shows that movement of the two anions in surface soils due to either mineralization of the nitrogen or denitrification is not similar. In the subsoils the breakthrough curves for both anions are similar. Autoclaving the surface soils results in breakthrough curves similar to the subsoils, thus indicating the role of microbial action on the movement of nitrate through the soils.

Use of Cl/NO_3-N (or NO_3-N/Cl) Ratios

Kimble et al. (1972) indicate that the NO_3-N/Cl ratio decreases at all depths from fall to spring, suggesting that denitrification rather than leaching is responsible for a significant portion of the nitrate loss. Because both nitrate and chloride are negative ions, neither would be held by negatively charged soil particles and both should move through the soil at a similar rate. Kimble et al. showed a significant decrease in nitrate nitrogen with depth, whereas the chloride content stayed constant or increased because of previous applications of fertilizers. A comparison of applications of NH_4NO_3 fertilizer with dairy manure indicates that more nitrate is lost by leaching when nitrogen is applied as inorganic fertilizer than as dairy manure because of the greater potential for denitrification in the manure.

Gambrell et al. (1975) studied denitrification processes in well-drained and poorly drained soils in North Carolina. In the well-drained soil the carbon content was 2–5 mg/L, Eh was in the well-oxidized range (500–700 mV), and the lack of saturated conditions for extended periods of time resulted in movement of much of the nitrogen into the shallow ground water. The poorly drained soil had an Eh <300 mV and a carbon content of 10–15 mg/L. These conditions are sufficient to cause denitrification of the residual nitrate nitrogen from fertilizer. Little nitrate moved from this soil into shallow ground water. The NO_3-N/Cl ratios also indicate a marked decrease in nitrate concentration with depth.

In California Devitt et al. (1976) chose six sites with different soil characteristics to evaluate the effect of soil profile characteristics on the movement of nitrate nitrogen to ground water. There were three sites each of either coarse-textured soils of sandy content or fine clayey soils. Soil moisture samplers were used to collect the water. The coarse-textured soils had high redox potentials throughout with low denitrification potential. Nitrate moved downward in these profiles as a result of irrigation. The Cl/NO_3-N ratio for the coarse-textured soils was fairly constant with depth, indicating that the primary source of the nitrate was fertilizer and that the nitrate was moving through the system and not being denitrified. In the clayey soils the ratio increased with depth, indicating that denitrification was occurring. The redox potential near the clay zones was well within the range necessary for denitrification to occur.

Cameron et al. (1979) showed that in a well-drained sandy soil Cl/NO_3-N ratios indicate predominant loss by leaching rather than denitrification of the nitrate. Occasionally the nitrate nitrogen loss is less than the chloride loss during a particular time period, indicating that nitrate is produced by nitrification of fertilizer ammonium nitrogen and from mineralization. Nitrogen and chloride losses were associated with irregular diffuse bulges rather than with distinct peaks of solute moving steadily downward. The bulges appeared to be directly related to rainfall events.

Saffigna and Keeney (1977) studied the distribution of nitrate and chloride in ground water under irrigated farms in the sand plains of Wisconsin. The soils used in this study were classified as sandy loam. The study showed that both chloride and nitrate were significantly higher than background water quality. There was a wide variation in nitrate and chloride values between wells in any given area, but the Cl/NO_3-N ratio was much less variable. In most areas where sandy soil is farmed potassium chloride and nitrogen fertilizers are applied in roughly equal proportions. In Saffigna and Keeney's study it was assumed that more of the nitrogen than chloride was removed with the harvested crop and therefore a Cl/NO_3-N ratio greater than 1 was acceptable.

Both Hill (1982) and Egboka (1984) did regional surveys of nitrate and chloride in areas of Canada. Hill found that the ratio of Cl/NO_3-N was fairly constant under potato fields in sandy soils. The nitrate content of ground water under poorly drained soils (pastureland and woodlands) was low, indicating that denitrification had occurred. Regression analysis revealed a significant positive correlation between the nitrate nitrogen concentration in ground water and the average rate of fertilizer application in the area. A positive association between the ground-water chloride concentration and the rate of potassium chloride fertilizer application together with consistent Cl/NO_3-N ratios in ground water under potato farms suggests that fertilizer is the major source of nitrate in the aquifer. Egboka (1984) surveyed several watersheds and potential point sources for nitrate concentration with depth. He found that an increase of the Cl/NO_3-N ratio indicates that denitrification has occurred at depth. The rate of application of potassium chloride and nitrogen fertilizers was approximately the same. He also found that areas with a deep water table and sandy soils would have no change in the ratio and the movement of nitrate into the aquifer.

Appendix B

Chemical analysis methodology

Determination of atrazine in soil

Reference Method: Method 3550. "Sonication Extraction," in Test Methods for Evaluating Solid Waste. Vol. 1B. Laboratory Manual Physical/Chemical Methods, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C. 20460. November 1986. SW-846 Third Edition.

Summary of Method: 50.0 g of sample is sonicated with 200 mL of 1:1 hexane:acetone. The extract is decanted, concentrated to dryness, and the residue taken up in 10.0 mL of hexane. The extract is scanned and quantitated using a Hewlett Packard (HP) 5890A Gas Chromatograph with an HP 5970 Mass Selective Detector in the "single ion monitoring mode" specifically for atrazine.

Determination of atrazine in water

Reference Method: Method 507. "Determination of Nitrogen- and Phosphorus-containing Pesticides in Ground Water by Gas Chromatography with a Nitrogen-Phosphorus Detector," September 1986 supplement to Methods for the Determination of Organic Compounds in Finished Drinking Water and Raw Source Water, Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

Summary of Method: A 1–L volume of sample (or volume available diluted to 1 L) is extracted with methylene chloride; the extract is dried through anhydrous sodium sulfate, concentrated to dryness, and the residue taken up in 5.0 mL hexane. The extract is scanned for atrazine using a Hewlett Packard 5710 Gas Chromatograph with a Nitrogen/Phosphorus Detector.

Any sample extracts positive for atrazine are confirmed and secondarily quantitated using a Hewlett Packard (HP) 5890A Gas Chromatograph with an HP 5970 Mass Selective Detector in the "single ion monitoring mode" specifically for atrazine.

Determination of atrazine and its two dealkylated metabolites (G-30033 and G-28279) in soil

Reference Method: Method CHR-2.1: "Determination of atrazine, G-30033, and G-28279 residues in soil using gas chromatography." Minnesota Valley Testing Laboratories. Internal Mimeo.

Summary of Method: Atrazine and its dealkylated metabolites are extracted from soil by refluxing with acetonitrile:water (90:10). The extract is evaporated and the residues dissolved in acetone. Atrazine and metabolite concentrations are determined by capillary column gas chromatography with flame thermionic detection and external standard quantitation. The method is sensitive to 0.05 ppm.

Determination of hydroxyatrazine (G-34048) in soil

Reference Method: Method CHR-3: "Determination of G-34048 residues in soil using high performance liquid chromatography." Minnesota Valley Testing Laboratories. Internal Mimeo.

Summary of Method: Hydroxyatrazine is extracted from soil by Soxhlet extraction using methanol:water (80:20). The extract is cleaned by solvent partitions and column chromatography to remove nonpolar triazines and interferences. The final aqueous solution containing the hydroxyatrazine is chromatographed by using paired-ion-reversed phase HPLC. Residues are quantitated by UV absorption at 240 nm. The method is sensitive to 0.05 ppm.

Bromide determination

We used an automated colorimetric method to measure bromide concentration in water. We followed the automated phenol red method involving segmented-flow analysis, as described by Basel et al. (1982) and further modified by Whittemore (personal communication, 1987), in earlier determinations in our study. For later measurements, we used the automated fluorescein method of the US Geological Survey (Fishman and Friedman, 1985) because it is more accurate near the detection limit for natural waters. To automate both methods, we used a Technicon AutoAnalyzer II, consisting of an autosampler, proportioning pump, appropriate analytical cartridge, spectrophotometer, and strip chart recorder. We corrected chloride concentrations for the bromide in the sample because of bromide interferences in chloride determinations. The detection limit for both methods is 10 mg/L.

Inorganic analyses

We obtained initial nitrate concentrations using ultraviolet absorption spectroscopy with an analytical error of ±5 ppm. Once the initial level was established, we used standard colormetric autoanalyzer techniques to determine nitrate (±0.5 ppm), sulfate (±4 ppm), and chloride (±2 ppm) and sometimes phosphate and ammonia. We did not determine the error for phosphate because of problems with sediment interference before use of filtration in the field. We also did not determine the error for ammonia because of its small concentration in the samples. We measured the cations Ca^{2+} (±1.7 ppm), Mg^{2+} (±0.3 ppm), Na^{+} (±0.8 ppm), and K^{+} (±0.08 ppm) with a Jarrel-Ash inductivity-coupled plasma (ICP) unit and measured bicarbonate (+0.9 ppm) by potentiometric titration using an autotitrimeter. pH was measured at the same time. We measured specific conductance (±2%) in the laboratory with a Labline meter at 25°C.

Sample collection

We collected samples for major ion analysis in a 500 mL unacidified bottle (Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, Br^-, SO_4^{2-}, PO_4^{2-}, and NH_4^+) and an acidified 200 mL bottle (trace elements and NO_3-). We collected atrazine samples from the wells in 1–gal acid-washed bottles supplied by the Kansas State Board of Agriculture and samples from the lysimeters in 1–L or smaller acid-washed and acetone-rinsed brown bottles with teflon seals.

We measured specific conductance, pH, and temperature in the field whenever possible. The wells were either bailed dry and allowed to recover or were bailed sufficiently to remove several casing volumes of water. We used a Teflon bailer for sampling; it was rinsed with acetone and deionized water between uses.

Appendix C

Water chemistry analyses

Table C.1. Site 6 Water Chemistry.

Date	Site depth (ft)	Lab or Field SPCD	Field pH	Lab pH	TDS calc mg/L	Water Temp. °C	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	Sr mg/L	HCO_3 mg/L	SO_4 mg/L	Cl mg/L	NO_3 mg/L	PO_4 mg/L	NH_4 mg/L	Br mg/L
Wells																		
6-22-87	20	2450		8.0	1258		211	31	218	5.8	1.4	275	33	594	29	1.9	0.2	
	34	1060		8.2	569		68	12	134	5.0	0.5	319	39	147	6.6	0.2	0.3	
	45	870		8.3	471		67	7.1	113	3.6	0.4	291	26	110	0.8	0.1	<0.1	
	54	960		7.9	522		70	7.1	128	3.7	0.4	281	27	145	2.4	0.2	<0.1	
8-6-87	20	2450												619				0.60
	34	1030												133				0.19
9-3-87	20	2500																
	34	1150																
	45	760																
9-9-87	20	2475	7.15	7.5	1280	17.5	211	29	240	5.1	1.3	305	41	582	21	2.0	0.1	0.57
	34	1075	7.65	8.0	544	19.0	76	13	115	5.5	0.6	351	38	120	3.0	0.75	0.2	0.29
	45	765	7.65	7.8	419	17.0	66	6.8	91	3.8	0.4	286	23	80	7.3	0.27	0.2	0.30
9-16-87	20	4250																
9-18-87	20	4020	7.10			16.0								1076				1.37
	34	1000	7.55			16.0								116				0.22
	45	760	7.75			16.0								80				0.15
9-22-87	20	4100																
9-25-87	20	3800																
10-1-87	20	4100																
	34	1000																
	45	780																
10-6-87	20	3890	7.25	7.6	2113	17.0	346	49	397	7.0	2.1	300	94	1050	19	0.24	0.1	1.17
	34	970																
	45	770																
10-9-87	20	3880																
10-14-87	20	3800		7.4	2085	15.5	342	49	387	6.5	2.1	298	83	1050	19	0.87	0.1	1.18
	34	980																
	45	780																
10-20-87	20	3800		7.9		18.0	342	48	376	6.9	2.1	296	77	1037	19			
	45	780		8.1		18.0	67	7.2	95	4.5	0.4	289	25	89	0.4			
10-27-87	20	3750																
	45	780																
11-10-87	20	3400		7.7	1922	13.0	319	45	355	7.5	2.0	300	70	957	19			
	45	790		8.0	439	13.0	66	7.2	99	4.4	0.4	291	25	94	0.2			0.22
11-30-87	20	2890																
12-17-87	20	3120																
2-16-88	20	3000		7.6	1595	10.0	269	37	294	5.6	1.6	296	50	771	21	0.23	1.1	0.91
	34	1015		7.8	547	11.0	100	14	94	6.1	0.7	362	37	109	8.6	<0.1	0.2	0.15
	45	830		8.0	448	10.0	62	6.9	108	3.7	0.4	285	24	102	1.1	0.1	0.3	0.12

Table C.1. Site 6 Water Chemistry (continued)

Wells (continued)

Date	Site depth (ft)	Lab or Field SPCD	Field pH	Lab pH	TDS calc mg/L	Water Temp. °C	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	Sr mg/L	HCO_3 mg/L	SO_4 mg/L	Cl mg/L	NO_3 mg/L	PO_4 mg/L	NH_4 mg/L	Br mg/L
5-4-88	20	2845	7.15	7.8	1499	15.0	257	35	275	5.7	1.6	292	46	713	22			0.62
	34	945	7.45	7.9	525	18.0	96	13	90	5.8	0.6	353	35	97	14			0.20
	45	860	7.40	7.9	453	17.5	60	7.0	110	3.8	0.4	282	25	108	0.5			0.16
8-3-88	34	950	7.50	8.0	524	20.0	98	13	91	6.0	0.6	346	34	97	14	<0.1	0.2	0.10
	45	710	7.20	7.7	410	21.5	71	6.9	79	3.6	0.4	272	21	81	13	<0.1	<0.1	0.07
9-13-88	20	3000	7.60			20.0								816	21			0.88
	34	980	7.35			22.0								108	14			0.10
11-2-88	20	2950	6.60			20.0								758	21			
6-23-87	Stafford	660		8.2	359		72	5.3	61	4.1	0.3	224	18	77	11	0.1	<0.1	
8-6-87	Stafford	975												157				0.14
9-3-87	Stafford	1010		7.4	542		83	9.5	114	3.1	0.5	250	43	157	8.7	0.13	<0.1	0.16
1-30-89	SW Well	1220		7.9			72	7.9	177	3.4	0.4	258	34	223	0.4			
	West Well	1050		7.7			71	7.0	141	3.5	0.4	241	30	187	0.1			
	Albert	990		7.9			63	6.1	137	3.1	0.4	265	28	162	<0.1			

Table C.1. Site 6 Water Chemistry (continued)

Date	Site depth (ft)	Lab or Field SPCD	Field pH	Lab pH	TDS calc mg/L	Water Temp. °C	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	Sr mg/L	HCO_3 mg/L	SO_4 mg/L	Cl mg/L	NO_3 mg/L	PO_4 mg/L	NH_4 mg/L	Br mg/L
Lysimeters																		
9-9-87	1													173				
	2													327				
	4													329				0.16
	5													311				
9-10-87	0.5	835	7.95			22.0								123				
	1	1000	7.55			22.0								163				
	2	1550	8.15			23.0								286	8.3			
	3	2440	8.15			23.0								288				0.20
	4	3850	8.15			24.0								454				0.38
	5	2350	8.15			21.5								322				
	6	2080	8.05			21.0								294				
9-15-87	1	985	7.95			21.0								149				
	2	1530	8.15	8.00	877	22.0	44	16	293	3.3	0.4	381	73	258	1.7	0.35	<0.1	0.07
	3	3200	8.15	7.80	2049	22.0	60	24	745	5.2	0.5	1087	317	363	<0.1	0.24	<0.1	0.22
	4	4300	8.15			22.5								526	1.0			0.67
	5	2300	8.15			23.0								297	5.8			
	6	1520	8.35			23.0								216				0.03
9-15-87	BrSol	1450	7.45			23.5								381				376
9-16-87	CrA	615	8.65	8.15	334	21.0	48	5.5	69	14	0.3	149	22	102	0.1	0.67	0.1	
	CrB	515	8.15	8.30	279	25.0	47	5.2	49	14	0.2	154	18	69	1.1	0.94	0.1	
9-18-87	1	1500	7.6			18.5								149				325
	2	1440				18.5								205				13.4
	3	2630	8.05			17.5								280				6.3
	5	1900	8.40			16.5								227				5.0
	6	1860	8.30			16.5								190				6.9
8-3-88	6	3850	7.90			26.5							178	388				13.8

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*A, Peace Creek upstream; B, Peace Creek downstream

Table C.2. Site 7 Water Chemistry.

Wells

Date	Site depth (ft)	Lab or Field SPCD	Field pH	Lab pH	TDS calc mg/L	Water Temp. °C	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	Sr mg/L	HCO_3 mg/L	SO_4 mg/L	Cl mg/L	NO_3 mg/L	PO_4 mg/L	NH_4 mg/L	Br mg/L
6-23-87	30	1240		8.10	689		127	19	81	2.6	0.6	370	29	106	142	0.4	0.2	
	50	730		8.00	397		94	8.4	31	4.6	0.3	237	17	66	59	0.2	0.1	
	70	620		8.20	359		97	6.5	23	4.2	0.3	229	15	37	63	0.2	0.1	
8-6-87	30	1175				15.0								108				0.17
9-10-87	30	1225	7.15	7.80	701	16.0	156	18	75	2.4	0.6	404	34	104	112	0.17	0.1	0.13
	50	810	7.25	7.70	437	15.0	115	9.4	29	4.7	0.3	248	18	79	60	0.23	<0.1	0.15
	70	590	7.55	7.60	336	16.0	91	6.1	22	4.2	0.3	222	15	33	55	0.17	0.1	0.04
9-30-87	30														93			
10-1-87	30														96			
10-6-87	30	1220	7.45	7.90	711	19.0	159	18	78	2.4	0.6	404	34	103	117	0.21	0.1	0.16
10-7-87	50	770	7.65	7.80	434	17.0	117	9.2	29	4.5	0.3	243	17	74	64	0.22	<0.1	0.15
	70	580	7.55	7.80	337	17.0	92	6.2	22	3.5	0.3	223	15	32	56	0.17	<0.1	0.11
10-8-87	30	1190				16									115			.17
10-9-87	30	1165				13												.21
10-10-87	30	1160		8.00	695	13.2	157	18	74	2.7	0.6	402	36	101	108	0.31	<0.1	0.12
10-12-87	30	1140		7.70	676		158	18	70	2.3	0.6	401	36	97	97	<0.1	<0.1	
10-15-87	30	1140		8.00	692	13.0	158	18	73	2.7	0.6	399	36	103	105	0.95	0.1	
10-20-87	30	1140		8.0	666		154	18	71	3.1	0.6	401	35	96	91			
	50	760		8.0	432		115	9.1	28	4.4	0.3	242	17	76	63			
11-10-87	30	1150		8.00	678	14.0	141	17	76	2.7	0.5	408	35	97	108			0.11
	50	750		8.00	418	13.0	111	8.7	28	5.0	0.3	239	16	68	63			0.13
2-17-88	30	1120		7.70	646	11.0	150	17	69	1.9	0.5	401	38	86	86	<0.1	<0.1	0.10
	50	740		7.80	418	11.0	112	8.7	27	3.7	0.3	233	16	73	63	0.13	0.1	0.14
	70	490		7.70	301	10.0	82	5.5	20	3.5	0.3	217	14	25	44	0.22	0.1	0.05
5-4-88	30	1060		7.70	634	15.5	148	16	69	1.9	0.5	395	37	83	84			0.09
	50	760	7.05	7.80	424	16.0	118	8.4	26	2.7	0.3	238	16	72	64			0.13
	70	560	7.40	7.70	316	16.5	87	5.9	19	3.4	0.3	224	14	25	51			0.06
8-2-88	30	1000	7.10	7.60	636	21.0	143	16	75	2.5	0.5	404	39	76	85	<0.1	0.2	0.28
	50	810	7.05	7.80	459	20.0	124	10	29	4.0	0.4	249	18	84	67	<0.1	<0.1	0.15
	70	600	7.10	7.80	362	20.0	96	6.6	21	3.9	0.3	223	15	32	63	0.16	0.1	0.07
9-14-88	30	1100				22.0								80	85			0.21
	50	860	7.25			23.0								88	70			0.17
9-27-88	30	1100	7.55			21.0							38	82	85			0.16
11-2-88	30	1100	7.20			20.0								84	85			
11-3-88	Irrig W.	500		7.7	277		69	5.4	26	3.1	0.3	200	13	33	29			<0.05

Table C.2. Site 7 Water Chemistry (continued)

Lysimeters

Date	Site depth (ft)	Lab or Field SPCD	Field pH	Lab pH	TDS calc mg/L	Water Temp. °C	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	Sr mg/L	HCO_3 mg/L	SO_4 mg/L	Cl mg/L	NO_3 mg/L	PO_4 mg/L	NH_4 mg/L	Br mg/L
9-3-87	2	448	7.45			26.0								21				<0.05
	3	448	6.45			24.0								29				<0.05
	4	538	6.7			24.5								17				0.07
	5	620	6.85			24.0								33				0.06
	6	568	7.65			28.0								41				<0.05
9-10-87	0.5													80	46			
	2	463	7.95			24.0								24	22			
	3	490	7.75	7.00	266	24.0	49	11	38	4.9	0.3	215	18	28	11	0.1	0.1	
	4	525	7.15	6.80	309	25.0	47	11	58	1.9	0.3	246	25	19	26	0.05	0.1	
	5	640	7.75			23.0								33	41			
	6	714	7.85			25.0								46	56			
9-30-87	0.5														118			
	2														32			
	3														17			
	5														49			
	6														54			
5-4-88	2	1210	6.65			15.0									127			
	3	1220	6.85			16.0									103			
	4	1300	6.85			15.5									77			
	5	950	7.35			16.0									45			
	6	990	6.8			16.0								135	106			84
6-15-88	3													116	113			239
	6	1800		7.90	1082		78	21	298	0.3	0.6	496	75	81	110	0.05	<0.1	170
8-2-88	4	1125	6.55			27.0							45	82	48	0.3	<0.1	246
	5	1200	6.85			26.5							26	93	63	<0.1	0.1	176
	6	980	6.95	7.50	577	30.0	99	23	61	1.7	0.7	136	27	90	105	<0.1	0.2	184
9-12-88	0.5													56				15.6
	2													118				75
	3	1310												174				139
	4	1150												111				275
	5													81				198
	6	950												73				172
9-14-88	1	850	7.10			25.0								67				15.5
	3	1020	7.30			23.5								119	0.3			69

Table C.2. Site 7 Water Chemistry (continued)

Lysimeters con't.

Date	Site depth (ft)	Lab or Field SPCD	Field pH	Lab pH	TDS calc mg/L	Water Temp. °C	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	Sr mg/L	HCO_3 mg/L	SO_4 mg/L	Cl mg/L	NO_3 mg/L	PO_4 mg/L	NH_4 mg/L	Br mg/L
9-16-88	0.5													61				13.8
	1													67				15.7
	2													84	0.3			36
	3													125				70
	4													118				283
	5													95				196
	6													81				183
9-27-88	1	770				25.5									0.5			
	2	900				23.0									0.4			
	3	1080	6.55			22.0							60.0	139	<0.1			83
	4	1200	6.45			22.0							50.0	131	<0.1			281
	5	1150				21.0							21.0	106	0.5			225
	6	975	6.65			20.0									1.2			
11-1-88	0.5	735				21.0								54				11.8
	4	1225				22.0								142	1.1			269
	5	1105				23.5								104	0.3			203
11-3-88	0.5													56				13.2
	1													75				19.0
	3													77				30
	6													89				189

Table C.3. Site 10 Water Chemistry.

Wells

Date	Site depth (ft)	Lab or Field SPCD	Field pH	Lab pH	TDS calc mg/L	Water Temp. °C	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	Sr mg/L	HCO_3 mg/L	SO_4 mg/L	Cl mg/L	NO_3 mg/L	PO_4 mg/L	NH_4 mg/L	Br mg/L
6-24-87	90	360		8.20	287		55	7.1	11	2.0	0.4	144	41	8.2	12	0.1	<0.1	
8-6-87	60	240												4.6				
	90	240												3.7				
9-17-87	55	400	7.65	7.90	228	16.5	48	6.5	28	6.5	0.3	165	23	24	11	1.1	<0.1	
	60	240	7.5	7.65	136	17.0	39	4.2	5.1	1.4	0.2	100	18	5.7	13	9.1	0.1	
	65	300	7.65	7.90	166	16.5	42	5.0	12	2.2	0.2	118	25	9.2	12	1.8	0.1	
2-17-88	60	260		7.80	142	12.0	41	4.2	5.0	1.4	0.2	105	20	4.1	14	0.56	0.1	
	65	250		7.80	138	12.0	38	4.2	5.9	1.7	0.2	101	18	5.0	15	0.6	0.1	
5-3-88	65	230	7.25	7.70	130	16.0	36	4.0	5.1	1.2	0.2	97	17	3.7	15			
8-2-88	65	235	7.1	7.80	131	22.0	36	4.1	5.5	1.5	0.2	96	17	3.5	16	0.56	0.2	

Table C.4. Additional Chloride and Bromide Data for Site 6

Date	Well depth (ft)	Cl mg/L	Br mg/L
9-16-87	20	1137	2.35
9-21-87	20	1074	1.31
9-22-87	20	1105	1.24
9-25-87	20	1022	1.23
9-29-87	20	1063	1.17
9-29-87	34	113	0.29
9-29-87	45	84	0.17
10-1-87	20	1060	1.21
10-1-87	34	108	0.27
10-1-87	45	84	0.20
10-6-87	34	107	0.30
10-6-87	45	85	0.18
10-9-87	20	1045	1.19
10-14-87	34	109	0.24
10-14-87	45	87	0.18
10-20-87	20	1040	1.14
10-20-87	45	89	0.21
10-27-87	20	1017	1.16
10-27-87	45	89	0.22
11-10-87	20	957	1.07
12-1-87	20	859	1.07
12-17-87	20	815	1.04
1-20-88	20	839	1.06

Date	Lysimeter depth (ft)	Cl mg/L	Br mg/L
9-15-87(a)	0.5	121	
9-15-87(b)	0.5		2.3
9-15-87(b)	1	150	
9-15-87(b)	2	218	0.03
9-15-87(b)	3	296	0.09
9-15-87(b)	4		0.70
9-16-87(a)	0.5	146	250
9-16-87(a)	1	155	120
9-16-87(a)	2	177	0.60
9-16-87(a)	3	280	0.18
9-16-87(a)	4	527	0.74
9-16-87(a)	5	259	
9-16-87(a)	6	215	0.03
9-16-87(b)	1	156	231
9-16-87(b)	2	174	6.8
9-16-87(b)	3		1.07
9-16-87(b)	4		0.79
9-16-87(b)	5		1.00
9-16-87(b)	6		0.12
9-17-87	1	163	308
9-17-87	3	277	2.9
9-17-87	4		0.82
9-17-87	5	237	1.97
9-18-87	0.5		346
9-18-87	1	149	325
9-18-87	4	529	0.83
9-21-87	3	259	13.6
9-21-87	4	537	0.82
9-21-87	5	254	3.4
9-21-87	6		0.70
9-23-87	1	165	316
9-23-87	2	179	32.8
9-23-87	4		0.73
9-23-87	6	200	0.64
9-25-87	1	153	312
9-25-87	2	167	72
9-25-87	6		0.73
9-29-87	4	553	1.03
9-29-87	5	266	3.1
9-29-87	6	229	1.16
10-1-87	4	539	0.84
10-1-87	5	264	3.0
10-1-87	6	239	1.10
10-6-87	4	547	0.91
10-6-87	6	254	1.15
6-16-88	1	117	197
6-16-88	4	484	3.8

Table C.5. Additional Chloride and Bromide Data for Site 7

Date	Well depth (ft)	Cl mg/L	Br mg/L
10-7-87	30		0.20
10-13-87	50		0.15
10-13-87	70		0.07
10-20-87	30	96	0.10
10-20-87	50	76	0.14
10-28-87	30		0.13
10-28-87	50		0.17

Date	Lysimeter depth (ft)	Cl mg/L	Br mg/L
10-5-87	0.5	87	0.05
10-7-87(a)	3	27	0.08
10-7-87(a)	4	20	0.11
10-7-87(a)	5	28	0.11
10-7-87(a)	6	49	0.13
10-7-87(a)	1E		0.11
10-7-87(a)	2E		0.22
10-7-87(b)	0.5	131	147
10-7-87(b)	1	45	2.0
10-7-87(b)	2	32	3.2
10-7-87(b)	3	28	0.10
10-7-87(b)	4	19	0.11
10-7-87(b)	5	25	0.11
10-7-87(b)	6	49	0.13
10-7-87(b)	1E		0.32
10-7-87(b)	2E		0.22
10-8-87(a)	0.5	162	313
10-8-87(a)	2	40	5.7
10-8-87(a)	3	31	7.6
10-8-87(a)	4	18	4.6
10-8-87(a)	1E		0.3
10-8-87(a)	2E		0.12
10-8-87(b)	0.5	148	365
10-8-87(b)	1	36	44
10-8-87(b)	2		5.8
10-8-87(b)	3	39	29
10-8-87(b)	4	29	43
10-8-87(b)	5	24	7.0
10-8-87(b)	6	54	16
10-8-87(b)	2E		0.12
10-9-87	0.5	152	357
10-9-87	3	46	48
10-9-87	4	45	106
10-9-87	5	28	8.2
10-9-87	6	50	6.4
10-9-87	1E		0.06
10-10-87	2	44	21
10-10-87	3	54	90
10-10-87	4	61	173
10-10-87	6	49	3.9
10-10-87	1E		0.11
10-11-87	5	31	20
10-11-87	6		2.0
10-12-87	2	53	52
10-12-87	3	65	129
10-12-87	5	38	62
10-12-87	6	44	0.84

Table C.5. Additional Chloride and Bromide Data for Site 7 (continued)

Date	Well depth (ft)	Cl mg/L	Br mg/L	Date	Lysimeter depth (ft)	Cl mg/L	Br mg/L
				10-13-87	1E		0.16
				10-15-87	3	73	144
				10-15-87	5	42	78
				10-15-87	6	41	2.5
				10-15-87	1E		0.06
				10-15-87	2E		0.11
				10-20-87	3	81	168
				10-20-87	6	41	5.6
				10-20-87	1E		0.07
				10-22-87	3	90	204
				10-22-87	5	52	105
				10-22-87	6	48	6.4
				10-28-87	3		214
				10-28-87	6	48	10.6
				10-28-87	1E		0.04
				11-10-87	6	52	17
				11-10-87	1E		0.04
				2-17-88	6	51	82
				3-3-88	0.5	66	80
				3-3-88	1	112	182
				3-3-88	2	88	128
				6-15-88	0.5	27	32.7
				6-15-88	1	39	61
				6-15-88	2	129	205
				6-15-88	4	102	267
				6-15-88	5	74	155
				10-7-87	Br Sol'n 1	103	430
				10-7-87	Stafford water	132	0.07
				10-7-87	Br Sol'n 2	140	457

E: outside flooded perimeter

Table C.6. Application Schedule for Chemicals at Site 7, Pratt County (Information from Servi-tech, Inc., Dodge City, Kansas)

Chemical Type	Chemical Name	Quantity Applied	Date
Herbicide	2,4-D LV Ester	0.75 pt /acre	4-19-87
Fertilizer	28-0-0	10 lb. /acre	4-19-87
Fertilizer	28-0-0	50 lb. /acre	4-23-87
Fertilizer	10-34-0	50 lb. /acre	4-23-87
Fertilizer	Thio-sul	30 lb. /acre	4-23-87
Herbicide	Lass EC	2.5 pt /acre	4-24-87
Herbicide	Atrazine 4L	1.5 pt /acre	4-24-87
Fertilizer	28-0-0	107 lb. /acre	5-87/6-87
Fertilizer	82-0-0	98 lb. /acre	5-20-87
Bacteriacide	N-Serve	1 pt /acre	5-20-87
Fertilizer	82-0-0	98 lb. /acre	6-03-87
Insecticide	Lorsban	1.5 pt /acre	7-23-87
Insecticide	Lorsban	1.5 pt /acre	7-30-87
Fertilizer	46-0-0	87 lb. /acre	9-20-87
Fertilizer	18-46-0	50 lb. /acre	9-20-87
Fertilizer	0-0-60	100 lb. /acre	9-20-87
Fertilizer	46-0-0	130 lb. /acre	3-10-88
Fertilizer	28-0-0	55 lb. /acre	4-06-88
Fertilizer	Thio-sul	35 lb. /acre	4-06-88
Fungicide	Tilt	4 oz /acre	4-27-88
Fertilizer	28-0-0	50 lb. /acre	6-25-88
Fertilizer	10-34-0	50 lb. /acre	6-25-88
Fertilizer	Thio-sul	30 lb. /acre	6-25-88
Herbicide	Lasso EC	2 qt /acre	6-27-88
Herbicide	Treflan EC	1.5 pt /acre	6-27-88
Herbicide	Cobra	12.5 oz /acre	7-13-88

No chemicals were added after July, 1988.

Appendix D

Atrazine analyses in soil and water

Table D.1. Atrazine in Water Samples, Site 6 , Stafford County

	Well depth (ft)						Lysimeter depth (ft)													
	20.0		34.0		45.0		0.5		1.0		2.0		3.0		4.0		5.0		6.0	
Sample Date	µg/L	limit µg/L	µg/L	limit µg/L	µg/L	limit µg/L	µg/L	limit µg/L	µg/L	limit µg/L	µg/L	limit µg/L	µg/L	limit µg/L	µg/L	limit µg/L	µg/L	limit µg/L	µg/L	limit µg/L
6-23-87	ND	0.5	ND	0.5	ND	0.5														
9-09-87	ND	0.5	ND	0.5	ND	0.5			ND	3.8	ND	3.8	ND	6.3	ND	3.8				
9-09-87/A																	ND	7.1		
9-09-87/C							ND	5.6												
9-10-87																			ND	3.8
9-14-87/1A									ND	5.0										
9-15-87							ND	16.7	ND	3.8					ND	3.8				
9-15-87/1A							ND	5.3												
9-15-87/1B							11.6	5.9												
9-16-87	ND	0.5																		
9-16-87/2A							160	5.7	35.4	2.3	ND	2.5	ND	4.5						
9-16-87/2B							202.0	5.6	97.2	2.5	ND	6.3	ND	7.7						
9-17-87/3A							235	26.3	135	3.8			ND	7.1						
9-18-87	ND	0.5																		
9-18-87/4A									156	2.5	ND	3.8	ND	3.3	ND	8.3				
9-21-87/5A													ND	2.0						
9-22-87	ND	0.5																		
9-23-87/6A									137	5.9	ND	6.7							ND	6.2
9-25-87	ND	0.5																		
9-25-87/7A									110	5.6	ND	5.6	ND	16.7					ND	8.3
9-29-87	ND	0.5	ND	0.5	ND	0.5														
9-29-87/8A									107	6.3			ND	8.3					ND	3.8
10-1-87	ND	0.5	ND	0.5	ND	0.5														
10-1-87/9A									97.0	6.3	ND	4.2	ND	16.7						
10-6-87			ND	0.5																
10-6-87/13A															ND	3.8			ND	10.0
10-6-87/14A	ND	0.5	ND	0.5	ND	0.5														
10-9-87/17A	ND	0.5																		
10-14-87	ND	0.5	ND	0.5	ND	0.5														
10-20-87	ND	0.5			ND	0.5														
10-27-87	ND	0.5			ND	0.5														
11-10-87	ND	0.5			ND	0.5														
1-20-88	ND	0.5																		
2-16-88	ND	1.0	ND	1.0	ND	1.0														
5-4-88	ND	0.4																		
5-19-88+											61.9	3.1	6.2	1.5			ND	0.8	ND	4.4
8-3-88/B			0.9	0.4	ND	0.4													2.4	1.7
9-13-88	ND	0.4	ND	0.4																
11-1-88	ND	0.4																		

+ After this date, suction lysimeters moved inside the fence (inside the field proper but still within the flooded area).

Table D.2. Atrazine in Soils, Site 6, Stafford County

	6-23-87		7-16-87		8-6-87A		8-6-87B		9-10-87/A		9-10-87/B		9-16-87		9-16-87/RE*		9-17-87		9-18-87	
Depth (in)	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg
0–3	ND	0.04	0.04	0.04	ND	0.04	0.13	0.04	0.06	0.04	0.04	0.04	0.54	0.04			0.62	0.04	0.63	0.04
3–6	ND	0.04	ND	0.04	ND	0.03	ND	0.04	ND	0.04	0.06	0.04					0.23	0.04	0.35	0.03
6–9	ND	0.04	ND	0.04	ND	0.04	ND	0.04	ND	0.03	ND	0.03	0.21	0.04			0.09	0.03	0.12	0.03
9–12	ND	0.04	ND	0.04	ND	0.03	ND	0.03	ND	0.03	ND	0.03	0.26	0.03			0.03	0.03	0.08	0.03
12–18	ND	0.04	ND	0.04					ND	0.04	ND	0.04	0.30+	0.04	0.21+	0.04	ND	0.04	ND	0.04
18–24	ND	0.04											0.04	0.04	0.12+	0.03	ND	0.04	ND	0.04
24–30	ND	0.04											ND	0.04			ND	0.04	ND	0.04
30–36	ND	0.04											ND	0.04			ND	0.04	ND	0.04

	9-22-87		9-25-87		10-1-87		10-6-87		10-9-87		10-14-87		10-20-87		10-27-87		11-10-87		12-1-87++	
Depth (in)	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg
0–3	0.18	0.04	0.14	0.04	0.43	0.04	0.13	0.03	0.36	0.04	0.18	0.04	0.06	0.04	0.08	0.03	0.14	0.04	ND	0.03
3–6	ND	0.03	ND	0.03	0.05	0.04	0.08	0.03	0.05	0.04	0.07	0.04	ND	0.03	ND	0.04	0.08	0.03	ND	0.03
6–9	0.05	0.04	ND	0.04	ND	0.03	ND	0.04	ND	0.04	ND	0.03	ND	0.05	ND	0.04	ND	0.04	ND	0.04
9–12	ND	0.03	ND	0.03	ND	0.03	ND	0.03	ND	0.03	ND	0.03	ND	0.04	ND	0.03	ND	0.03	ND	0.03
12–18																				
18–24																				
24–30																				
30–36																				

	12-17-87		2-25-88		5-4-88A[1]		5-4-88D[2]		8-3-88B		9-13-88		11-2-88	
Depth (in)	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg
0-3"	0.27	0.05	0.10	0.03	ND	0.03	0.24	0.03	0.17	0.03	0.07	0.04	ND	0.05
3-6"	0.36	0.04	ND	0.04	ND	0.03	0.05	0.03	0.06	0.03	0.07	0.03	ND	0.04
6-9"	0.29	0.04	ND	0.04	ND	0.04	ND	0.03	0.07	0.05	0.03	0.03	ND	0.05
9-12"	0.20	0.03	ND	0.04	ND	0.03	ND	0.03	0.04	0.03	ND	0.04	ND	0.05
12-18"	0.19	0.04	ND	0.04	ND	0.04	0.24	0.04	0.1+	0.04	ND	0.04	ND	0.04
18-24"	0.09	0.04	ND	0.04	ND	0.04	ND	0.04	ND	0.04	ND	0.04	ND	0.04
24-30"	ND	0.04	ND	0.04	ND	0.04	0.28	0.04			ND	0.04	ND	0.04
30-36"	0.09	0.04	ND	0.04	ND	0.04	ND	0.04			ND	0.03	ND	0.04

*Repeat analysis.

+Sample probably contaminated.

++ Field (and plot) plowed <u>after</u> this date.

1Outside cornfield but within flooded site.

2 Inside corn field and within flooded site.

Table D.3. Atrazine in Water Samples, Site 7, Pratt County

Sample	Well depth (ft)						Lysimeter depth (ft)														Lysimeter					
	30.0		50.0		70.0		0.5		1.0		2.0		3.0		4.0		5.0		6.0		1E*		2E*		1S*	
Date	µg/L	limit µg/L	µg/L	limit µg/L	µg/L	limit µg/L	µg/L	limit µg/L	µg/L	limit µg/L	µg/L	limit µg/L	µg/L	limit µg/L	µg/L	limit µg/L	µg/L	limit µg/L	µg/L	limit µg/L	µg/L	limit µg/L	µg/L	limit µg/L	µg/L	limit µg/L
6-23-87	ND	0.5	ND	0.5	ND	0.5																				
9-3-87							ND	5.9			ND	3.8	ND	3.8	ND	3.8	ND	3.8	ND	3.8						
10-5-87	ND	0.5					ND	7.7									ND	5.0								
10-7-87/1A	ND	1.0	ND	0.5	ND	0.5	22.2	7.7																		
10-8-87/2A	ND	1.0					38.0	5.9	ND	16.7			ND	3.3	ND	5.6	ND	12.5	ND	20.0	ND	12.5	ND	8.3		
10-8-87/2B							121	6.3					ND	12.5							ND	16.7	ND	10.0		
10-9-87/3A	ND	1.0					24.9	5.6					ND	10.0	ND	16.7									ND	12.5
10-10-87/4A	ND	1.0							ND	50.0	ND	16.7	ND	11.1	ND	20.0										
10-12-87/6A	ND	0.5									ND	7.1	ND	8.3			ND	10.0	ND	16.7						
10-13-87	ND	0.5	ND	0.5	ND	0.5															ND	10.0				
10-15-87	ND	0.5									ND	33.3	ND	6.7					ND	9.1	ND	5.0	ND	10.0		
10-20-87	ND	0.5	ND	0.5									4.9	4.5					ND	11.1	ND	2.3				
10-22-87													ND	10.0												
10-28-87	ND	0.5	ND	0.5															ND	16.7	ND	2.5				
11-10-87	ND	0.5	ND	0.5															ND	11.1	ND	3.8				
1-20-88	ND	0.5																								
2-17-88	ND	1.0	ND	1.0	ND	1.0													ND	7.7						
3-3-88							53	4.5	28	2.9	20	6.7														
5-4-88	ND	0.4									36.3	0.8	48.7	0.4	48.0	0.4	57.8	0.8	1.0	0.8						
8-3-88	ND	0.4	ND	0.4	ND	0.4									28.1	1.1	21.1	0.8	2.9	1.7						
9-12-88							8.8	2.3			3.4	0.9	7.9	1.6	9.2	1.9	6.0	2.9	ND	1.7						
9-14-88	ND	0.4	ND	0.4					3.9	2.2			6.3	1.6												
9-16-88							5.3	2.2	3.4	1.6	ND	2.4	6.1	1.8	13.7	1.8	4.9	3.2	ND	4.7						
11-1-88	ND	0.4					ND	4.5							18.7	0.4	3.4	0.8								
11-3-88							ND	2.7	ND	3.6			ND	4.4					ND	3.5						

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*Outside the perimeter of the flooded area.

Table D.4. Atrazine in Soils, Site 7, Pratt County

Depth	6-23-87		8-6-87		9-10-87		10-6-87		10-8-87[1]		10-8-87[2]		10-9-87		10-10-87		10-12-87		10-13-87	
(in)	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg
0–3	ND	0.04	ND	0.04	ND	0.04	ND	0.03	0.25	0.04	0.42	0.04	0.44	0.04	0.32	0.04	0.47	0.08	0.41	0.06
3–6	ND	0.04	ND	0.03	ND	0.04	ND	0.04	0.28	0.03	0.29	0.03	0.11	0.03	ND	0.03	0.30	0.03	0.27	0.03
6–9	ND	0.04	ND	0.03	ND	0.04	ND	0.03	0.13	0.03	0.20	0.03	ND	0.03	ND	0.04	0.21	0.05	0.20	0.03
9–12	ND	0.04	ND	0.03	ND	0.04	ND	0.03	0.04	0.03	0.09	0.03	ND	0.03	ND	0.03	0.15	0.03	0.12	0.03
12–18	ND	0.04							0.12	0.04	0.26	0.04			ND	0.04	0.16	0.04	0.20	0.04
18–24	ND	0.04							ND	0.04	0.17	0.04			ND	0.04	0.19	0.04	0.22	0.04
24–30	ND	0.04							0.19	0.04					ND	0.04	0.06	0.04	0.18	0.04
30–36	ND	0.04							0.06	0.04					ND	0.04	ND	0.04	0.17	0.04
36–42																	0.19	0.04	0.16	0.04
42–48																	0.12	0.04	0.05	0.04
48–54																	0.04	0.04	0.05	0.04
54–60																	ND	0.04	ND	0.04

Depth	10-20-87		10-28-87		11-10-87		11-30-87		12-17-87		2-24-88		5-4-88		8-2-88		9-14-88		11-2-88	
(in)	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg	mg/kg	limit mg/kg
0–3	0.14	0.03	0.08	0.05	0.27	0.04	0.30	0.04	0.28	0.04	0.12	0.03	0.11	0.03	0.03	0.03	ND	0.03	ND	0.04
3–6	0.19	0.03	0.21	0.04	0.21	0.03	0.14	0.04	0.18	0.03	ND	0.04	0.11	0.04	ND	0.03	ND	0.03	ND	0.04
6–9	ND	0.03	0.12	0.03	0.06	0.03	ND	0.03	ND	0.03	ND	0.03	0.21	0.04	ND	0.03	ND	0.03	ND	0.04
9–12	ND	0.03	0.05	0.03	0.04	0.03	0.05	0.03	ND	0.03	ND	0.03	0.09	0.03	ND	0.03	ND	0.04	ND	0.04
12–18			ND	0.04	0.08	0.04	0.15	0.04	ND	0.04	ND	0.04	0.09	0.04	ND	0.03	ND	0.04	ND	0.04
18–24			ND	0.04	0.08	0.04	0.12	0.04	0.04	0.04	ND	0.04	ND	0.04	ND	0.04	ND	0.04	ND	0.04
24–30					0.06	0.04	0.13	0.04			ND	0.04	0.10	0.04	ND	0.04	ND	0.04	ND	0.04
30–36					0.06	0.04	0.13	0.04			ND	0.04	0.05	0.04	ND	0.04	ND	0.04	ND	0.04
36–42					0.11	0.04	0.12	0.04					ND	0.04	ND	0.04	ND	0.04	ND	0.04
42–48					0.05	0.04	0.12	0.04					ND	0.04	ND	0.04	ND	0.04	ND	0.04
48–54					0.07	0.04	0.04	0.04					ND	0.04	ND	0.04			ND	0.04
54–60					ND	0.04	ND	0.04					ND	0.04	ND	0.04			ND	0.04

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1 Sample drawn at 10:30 a.m.

2 Sample drawn at 5:00 p.m.

Appendix E

Table E.1. Atrazine degradation by-products analyses for sites 6 and 7

			Biodegradation byproducts		
Sampling Date	Depth (in.)	Parent atrazine (ppm)	G-34048 hydroxyatrazine	G-28279 ethylatrazine	G-30033 isopropylatrazine
Site 6					
2-25-88	0–6	0.078	0.124	<0.05	<0.05
	6–12	0.299	0.116	<0.05	<0.05
	12–18	0.175		<0.05	<0.05
	18–24	0.077		<0.05	<0.05
	24–30	0.054	0.167	<0.05	<0.05
	30–36	<0.05	0.185	<0.05	<0.05
5-4-88	12–18	<0.05	0.163	0.631	0.090
	18–24	<0.05	<0.05	<0.05	0.082
8-3-88	0–6	0.085	0.177	0.351	0.202
	6–12	<0.05	<0.05	<0.05	<0.05
Site 7					
2-24-88	0–6	0.062		<0.05	<0.05
	6–12	0.050		<0.05	<0.05
	12–18	0.056		<0.05	<0.05
	18–24	<0.05		<0.05	<0.05
	24–30	0.056	0.172	<0.05	<0.05
	30–36	<0.05	0.408	<0.05	<0.05
8-2-88	0–6	<0.05	<0.05	0.073	<0.05
	6–12	<0.05	<0.05	0.124	0.061
	12–18	<0.05	<0.05	0.089	0.063
	18–24	<0.05	<0.05	<0.05	0.081
	24–30	<0.05	<0.05	0.105	0.120
	30–36	<0.05	0.134	0.067	0.189

* Moisture-corrected residues. Detection limit 0.05 ppm. Analyses by Minnesota Valley Testing Laboratories, Inc.

References

Aller, L., Bennet, T., Lehr, J. H., and Petty, R. J.(National Water Well Association), 1985. DRASTIC—a standardized system for evaluating ground water pollution potential using hydrogeologic settings: Ada, OK, Robert S. Kerr Environmental Research Laboratory, US Environmental Protection Agency (EPA/600/2-85/018), May 1985.

Alexander, M., 1977. Introduction to Soil Microbiology. 2nd ed., John Wiley and Sons, New York.

Anderson, M. P., 1979. Using models to simulate the movement of contaminants through ground water flow systems: Chemical Rubber Company Critical Reviews in Environmental Control, v. 19, p. 97–156.

Anderson, M. P., 1989. Chemigation well water quality study. Mimeograph report, Division of Plant Health, Kansas State Board of Agriculture, Topeka, KS.

Armstrong, D. E., and Chesters, G., 1968. Adsorption catalyzed chemical hydrolysis of atrazine: Environmental Science and Technology, v. 2, no. 9, p. 683–689.

Armstrong, D. E., Chesters, G., and Harris, R.F., 1967. Atrazine hydrolysis in soil: Soil Science Society of America Proceedings, v. 31, p. 61–66.

Bailey, G. W., and White, J. L., 1964. Review of adsorption and desorption of organic pesticides by soil colloids, with implications concerning pesticide bioactivity: Agriculture and Food Chemistry, v. 12, no. 4, p. 324–332.

Bailey, G. W., and White, J. L., 1970. Factors influencing the adsorption, desorption, and movement of pesticides in soil; *in*, Residue reviews. V. 32, the triazine herbicides, F.A. Gunther and J.D. Gunther, eds.: New York, Springer-Verlag, p. 29–92.

Bailey, G. W., White, J. L., and Rothberg, T., 1968. Adsorption of organic herbicides by montmorillonite: role of pH and chemical character of adsorbate: Soil Science Society of America Proceedings, v. 32, p. 222–234.

Baker, D. B., Krieger, K. A., Tichards, P. R., and Kramer, J. W., 1985. Effects of intensive agricultural land use on regional water quality in northwestern Ohio: Perspectives on Nonpoint Source Pollution, US Environmental Protection Agency, EPA 440/5-85-001, Washington, D.C., p. 201–208.

Basel, C. L., Defreese, J. D., and Whittemore, D. O., 1982. Interferences in automated phenol red method for determination of bromide in water: Analytical Chemistry V. 54, 2090–2094.

Biggar, J. W., and Nielson, D. R., 1967. Miscible displacement and leaching phenomenon: Agronomy Monograph, v. 11, p. 254–274.

Birkeland, P. W., 1984. Soils and Geomorphology. Oxford Univ. Press, New York.

Boast, C. W., 1973. Modeling the movement of chemicals in soil by water: Soil Science, v. 115, p. 224–230.

Bouma, J., and Wosten, J. H. M., 1979. Flow patterns during extended saturated flow in two undisturbed swelling clay soils with different macrostructures. Soil Science Society of America Journal, v. 43, p. 43:16–22.

Bower, H., 1978. Groundwater hydrology: New York, McGraw-Hill Book Co., p. 424–432.

Boyce, J. S., Muir, J., Edwards, A., Seim, E.C., and Olson, R.A., 1976. Geologic nitrogen in Pleistocene loess of Nebraska: Journal of Environmental Quality, v. 5, no. 1, p.93–96.

Burnside, O. C., Fenster, C. R., and Wicks, G. A., 1963. Dissipation and leaching of monuron, simazine, and atrazine in Nebraska soils: Weeds, v. 11, no. 3, p. 209–213.

Cameron, D. R., Kowalenko, C. G., and Campbell, C. A., 1979. Factors affecting nitrate nitrogen and chloride leaching variability in a field plot: Soil Science Society of America Journal, v. 43, p. 455–460.

Cassel, K. K., van Genuchten, M. Th., and Wierenga, P. J., 1975. Predicting anion movement in disturbed and undisturbed soils. Soil Science Society of America Proceedings, v. 39 p. 1015–1019.

Council for Agricultural Science and Technology (CAST), 1985. Agriculture and groundwater quality: Ames, Iowa, Iowa State University, 62 p.

Dao, T. H., and Lavy, T. L., 1978. Atrazine adsorption on soil as influenced by temperature, moisture content and electrolyte concentration: Weed Science, v. 26, no. 3, p. 303–308.

Devitt, D., Letey, J., Lund, L. J., and Blair, J. W., 1976. Nitrate-nitrogen movement through soil as affected by soil profile characteristics: Journal of Environmental Quality, v.5, no. 3, p. 282–288.

Egboka, B. C. E., 1984. Nitrate contamination of shallow groundwaters in Ontario, Canada: The Science of the Total Environment, v. 35, p. 53–70.

Endelman, F. J., Keeney, D. R., Gilmour, J. T., and Saffigna, P. G., 1974. Nitrate and chloride movement in the Planfield loamy sand under intensive irrigation: Journal of Environmental Quality, v. 3, no. 3, p. 295–298.

Exner, M. E., and Spalding, R. F., 1979. Evolution of contaminated groundwater in Holt county, Nebraska: Water Resources Research, v. 15, no. 1, p. 139–147.

Fishman, M. J., and Friedman, L. C. (eds.), 1985. Methods for determination of inorganic substances in water and fluvial sediments; *in* Techniques of water-resources investigations of the United States Geological Survey, bk. 5, ch. A1: US Geological Survey, Open-File Report 85-495, p. 178–181.

Freeze, R. A., and Cherry, J. A., 1979. Groundwater, Englewood Cliffs, N.J., Prentice-Hall, Inc., p. 413–416.

Frissel, M. J., and Bolt, G. H., 1962. Interaction between certain ionizable organic compounds (herbicides) and clay minerals: Soil Science, v. 5, p. 284–291.

Gambrell, R. P., Gilliam, J. W., and Weed, S. B., 1975. Denitrification in subsoils of the North Carolina coastal plain as affected by soil drainage: Journal of Environmental Quality, v. 4, no. 3, p.311–316.

Gianessi, L. P., 1986. A national pesticide usage data base—resources for the future: Washington, D.C., 13 p.

Gilliom, R. J., Alexander, R. B., and Smith, R. A., 1985. Pesticides in the nation's rivers, 1975–1980, and implications for future monitoring: US Geological Survey, Water-Supply Paper 2271, 26 p.

Hallberg, G. R., 1985. Groundwater quality and agricultural chemicals: a perspective from Iowa: Proceedings of the North Central Weed Control Conference, v. 40, p. 130-147.

Hallberg, G. R., 1986a. From hoes to herbicides—agriculture and groundwater quality. Journal of Soil and Water Conservation, v. 41, no. 6 p. 357–364.

Hallberg, G. R., 1986b. Overview of agricultural chemicals in ground water; *in*, Proceedings of agricultural impacts on ground water—a Conference, Dublin, Ohio, National Water Well Association, p.1–66.

Harris, C. I., 1967. Fate of 2-chloro-*s*-triazine herbicides in soil: Journal of Agriculture and Food Chemistry, v. 15, no. 1, p. 157–162.

Harris, C. J., and Warren, G. F., 1964. Adsorption and desorption of herbicides by soil: Weeds, v. 12, p. 120–126.

Hassall, A. K., 1982. Herbicides that act through soils; *in*, The chemistry of pesticides: London, Macmillan Press, p.302-309.

Hayes, M. H. B., 1970. Adsorption of triazine herbicides on soil organic matter, including a short review on soil organic matter chemistry; *in*, Residue reviews, vol. 32, the triazine herbicides, F. A. Gunther and J. D. Gunther, eds.: New York, Springer-Verlag, p. 131–174.

Heiman, A., Steichen, J., Koellicker, J., Grosh, D., and Yearout, R., 1987. Results of Kansas farmstead well water quality study; *in*, Proceedings of the conference on hazardous waste research, L. E. Erickson, ed.: Manhattan, KS, Kansas State University, p. 38–51.

Helling, C. S., 1970. Movement of *s*-triazine herbicides in soil; *in*, Residue reviews, v. 32, The triazine herbicides, F. A. Gunther and J. D. Gunther, eds.: New York, Springer-Verlag, p. 175–210.

Helling, C. S., and Gish, T. J., 1986. Soil characteristics affecting pesticide movement into groundwater; *in*, Evaluation of pesticides in ground water, American Chemical Society Symposium Series 315, W. Y. Garner, R. C. Honeycutt, and H. N. Nigg, eds.: Washington, D.C., American Chemical Society, p. 14–38.

Hergert, G. W., 1978. Nitrogen losses from sprinkler-applied nitrogen fertilizer: Nebraska Water Resources Research Institute, A-045-NEB, Lincoln, NE, 47 p.

Hergert, G. W., 1982. Distribution of mineral nitrogen under native range and cultivated fields in the Nebraska sandhills: National Technical Information Service, PB83-150367, Springfield, VA, 84 p.

Hill, A. R., 1982. Nitrate distribution in the ground water of the Alliston region of Ontario, Canada: Ground Water, v. 20, no. 6, p. 696–702.

Hillel, D., Krentos, V. D., and Stylianou, Y., 1972. Procedure and test of an internal drainage method for measuring soil hydraulic characteristics in situ. Soil Science, v. 114, p. 395–400.

Hiltbold, A. E., and Buchanan, G. A., 1977. Influence of soil pH on persistance of atrazine in the field: Weed Science, v. 25, no. 6, p. 515–520.

Hoar, S. K., Blair, A., Holmes, F. F., Boysen, C. D., Robel, R. J., Hoover, R., and Fraumeni, J. F., 1986. Agricultural herbicide use and risk of lymphoma and soft-tissue sarcoma. Journal of the American Medical Association, v. 256, no. 9, p. 1141–1147.

Hurlburt, S., 1988. The problem with nitrates: Water Well Journal, v. 42, no. 8, p.37–42.

Hurle, K. B., and Freed, V. H., 1972. Effect of electrolytes on the solubility of some 1,3,5-triazines and substitutes ureas and their adsorption on soil: Weed Research, v. 12, p. 1–10.

Jester, W. A., and Uhler, K. A., 1974. Identification and evaluation of water tracers amenable to post-sampling neutron activation analysis: Pennsylvania State University Institute for Research on Land and Water Resources, Research Publication no. 85, 92 p.

Junk, G. A., Spalding, R. F., and Richard, J. J., 1980. Areal, vertical, and temporal differences in ground water chemistry; II, Organic constituents: Journal of Environmental Quality, v. 9, no. 3, p. 479–483.

Jury, W. A., Foght, D. D., and Farmer, W.J., 1987. Evaluation of pesticide groundwater pollution potential from standard indices of soil-chemical adsorption and biodegradation. Journal of Environmental Quality, vol. 16 no. 4, p. 422–428.

Kaiser, P., Pochon, J., and Cassini, R., 1970. Effect of triazine herbicides on soil microorganisms; *in*, Residue reviews, v. 32, The triazine herbicides, F. A. Gunther and J. D. Gunther, eds.: New York, Springer-Verlag, p. 211–234.

Kansas State Board of Agriculture, 1988. Tables of fertilizer use from 1986–1987, Topeka, Ks.

Kelley, R., and Wnuk, M., 1986. Little Sioux River synthetic organic compound municipal well sampling survey: Iowa Department of Water, Air, and Management, 24 p.

Kelley, R., Hallberg, G. R., Johnson, L. G., Libra, R. D., Thompson, C. A., Splinter, R. C., and DeTroy, M. G., 1986. Pesticides in ground water in Iowa; *in*, Proceedings of agricultural impacts on ground water, Dublin, Ohio, National Water Well Association, p. 622–647.

Keeney, D., 1986. Sources of nitrate to ground water: Chemical Rubber Company. Critical Reviews in Environmental Control, vol.16, no. 3, p. 257–304.

Kimble, J. M., Barlett, R. J., McIntosh, J. L., and Varney, K. E., 1972. Fate of nitrate from manure and inorganic nitrogen in a clay soil cropped to continuous corn: Journal of Environmental Quality, v.1,no. 4, p. 413–415.

Kreft, A., and Zuber, A., 1978. On the physical meaning of the dispersion equation and its solutions for different initial and boundary conditions: Chemical Engineering Sciences, v. 33, p. 1471–1480.

Li, G. C., and Felbeck, G. T., Jr., 1972. Atrazine hydrolysis as catalyzed by humic acids: Soil Science, v. 14, no. 3, p. 201–209.

Lund, L. J., 1982. Variations in nitrate and chloride concentrations below selected agricultural fields: Soil Science Society of America Journal, v. 46, p.1062–1066.

McGlamery, M .D., and Slife, F. W., 1966. The adsorption and desorption of atrazine as affected by pH, temperature, and concentration: Weeds, v. 14, no. 3, p. 237–239.

Nielsen, D. R.,van Genuchten, M. Th., and Biggar, J.W., 1986. Water flow and solute transport processes in the unsaturated zone: Water Resources Research, v. 22 no. 9, p. 895–1085.

Nielsen, E. G., and Lee, K. L., 1987. The magnitude and costs of groundwater contamination from agricultural chemicals: US Department of Agriculture, National Resource Economic Division.

Obien, S. R., and Green, R. E., 1969. Degradation of atrazine in four Hawaiian soils: Weed Science, v. 17, no. 4, p. 509–514.

Parker, J. C., and van Genuchten, M.Th., 1984a. Determining transport parameters from laboratory and field tracer experiments: Virginia Agricultural Experimental Station Bulletin, 84-3, 96 p.

Parker, J. C. and van Genuchten, M. Th., 1984b. Flux-averaged and volume-averaged concentrations in continuum approaches to solute transport. Water Resources Research, v. 20, p. 866–872.

Richards, L. A. (ed.), 1969. Diagnosis and improvement of saline and alkali soils. Agriculture Handbook no. 60, US Salinity Laboratory, US Department of Agriculture, Agricultural Research Service, 160 p.

Roeth, F. W., Lavy, T. L., and Burnside, O. C., 1969. Atrazine degradation: Weed Science, v. 17, no. 2, p. 202–205.

Rose, C. W., Stern, W. R., and Drummond, J. E., 1965. Determination of hydraulic conductivity as a function of depth and water content for soil in situ. Australian Journal of Soil Research, v. 3, p. 1–9.

Russell, J. D., Cruz, M., and White, J. L., 1968. Mode of chemical degradation of *s*-triazines by montmorillonite: Science, v. 160, p. 1340–1342.

Saffigna, P. G., and Keeney, D. R., 1977. Nitrate and chloride in ground water under irrigated agriculture in central Wisconsin: Ground Water, v. 15, no. 2, p. 170–177.

Sandyland Agricultural Experiment Station, 1983. Precipitation: Manhattan, KS., Kansas State University, p.3.

Schneider, A. D., Wiese, A. F., and Jones, O. R., 1977. Movement of three herbicides in a fine sand aquifer: Agronomy Journal, v. 69, p. 432–436.

Sheets, T. J., 1970. Persistence of triazine herbicides in soils; *in*, Residue reviews, v. 32, The triazine herbicides, F. A. Gunther, and J. D. Gunther eds.: New York, Springer-Verlag, p. 287–310.

Sirons, G. J., Frank, R., and Sawyer, T., 1973. Residues of atrazine, cyanazine, and their phytotoxic metabolites in a clay loam: Journal of Agricultural Food Chemistry, v. 21, no. 6, p. 1016–1020.

Skipper, H. D., and Volk, V. V., 1972. Biological and chemical degradation of atrazine in three Oregon soils: Weed Science, v. 20, no. 4, p. 344–347.

Skipper, H. D., Volk, V. V., Mortland, M. M., and Raman, K. V., 1978. Hydrolysis of atrazine on soil colloids: Weed Science, v.26, no.1, p. 46-51.

Smith, S. J., and Davis, R. J., 1974. Relative movement of bromide and nitrate through soils: Journal of Environmental Quality, v. 3, no. 2, p.152–155.

Spalding, M. E., 1984. Implication of temporal variations and vertical stratification of groundwater nitrate-nitrogen in the Hall county special use area: Nebraska Water Resources Research Institute, report no. 372906, Lincoln, University of Nebraska, 30 p.

Spalding, R. F., and Kitchen, L. A., 1988. Nitrate in the intermediate vadose zone beneath irrigated cropland: Ground Water Monitoring Review, v. 8, no. 2, p.89–95.

Spalding, R. F., Junk, G. A., and Richard, J. J., 1980. Pesticides in groundwater beneath irrigated farmland in Nebraska, August 1978: Pesticides Monitoring Journal, v.14, no.2, p.70–73.

Spalding, R. F., Gormly, J. R., Curtiss, B. H., and Exner, M. E., 1978. Nonpoint nitrate contamination of ground water in Merrick county, Nebraska: Ground Water, v. 16, no. 2, p.86–95.

Steichen, J., Koelliker, J., Grosh, D., Herman, A., Yearout, R., and Robbins, V., 1988. Contamination of farmstead wells by pesticides, volatile organics, and inorganic chemicals in Kansas. Ground Water Monitoring Review, v. 8 no. 3, p. 153–160.

Strathouse, S. M., Sposito, G., Sullivan, P. J., and Lund, L. J., 1980. Geologic nitrogen: a potential geochemical hazard in the San Joaquin Valley, California: Journal of Environmental Quality, v.9, no. 1, p. 54–60.

Stullken, L. E., Stamer, J. K., and Carr, J. E., 1987. Reconnaissance of water quality in the High Plains aquifer beneath agricultural lands, south-central Kansas: US Geological Survey Water Resources Investigations Report 87-4003, 25 p.

Sullivan, J. D., and Felbeck, G. D., Jr., 1968. A study of the interaction of *s*-triazine herbicides with humic acids from three different soils: Soil Science, v. 106, no. 1, p. 42–52.

Swanson, R. A., and Dutt, G. R., 1973. Chemical and physical processes that affect atrazine and distribution in soil systems: Soil Science Society of America Proceedings, v. 37, p. 872–876.

Talbert, R. E., and Fletchall, O. H., 1965. The adsorption of some *s*-triazines in soils: Weeds, v. 13, no. 1, p. 46–52.

Tennyson, L. C., and Settergren, C. D., 1980. Percolate water and bromide movement in the root zone of effluent irrigation sites: Water Resources Bulletin, v. 16, no. 3, p. 433–437.

Thompson, C. A., Libra, R. D., and Hallberg, G. R., 1986. Water quality related to ag-chemicals in alluvial aquifers in Iowa; *in*, Proceedings of the agricultural impacts on ground water—a conference, National Water Well Association, Dublin,Ohio, p. 224–242.

US Environmental Protection Agency, 1986. Method 506—determination of nitrogen- and phosphorus-containing pesticides in ground water by gas chromatography with a nitrogen-phosphorus detector, supplement to "Methods for the determination of organic compounds in finished drinking water and raw source water": Cincinnati, Ohio, US Environmental Protection Agency, Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory.

US Environmental Protection Agency, 1986. Method 3550—sonication extraction; *in*, Test methods for evaluating soild waste, v. 1B; Laboratory Manual physical/chemical methods: Washington, D.C., US Environmental Protection Agency Office of Solid Waste and Emergency Response, SW-846, third edition.

van Genuchten, M. T., and Wierenga, P. J., 1976. Mass transfer studies in sorbing porous media, I. Analytical solutions: Soil Science Society of America Journal, v. 40, p. 473–480.

van Genuchten, M. T., and Alves, W. J., 1982. Analytical solutions of the one-dimensional convective-dispersive solute transport equation: Technical Bulletin 1661, US Department of Agriculture, 151 p.

Watson, K. K., 1966. An instantaneous profile method for determining the hydraulic conductivity of unsaturated porous materials: Water Resources Research, v. 2, p. 709–715.

Weber, J. B., Weed, S. B., and Ward, T. M., 1969. Adsorption of *s*-triazines by soil organic matter: Weed Science, v. 17, no. 4, p. 417–421.

Wehtje G., Leavitt J. R. C., Spalding R. F., Mielke L. N., and Schepers, J. S., 1981. Atrazine contamination of groundwater in the Platte valley of Nebraska from non-point sources: The Science of the Total Environment, v. 21, p. 47–51.

Wehtje, G. R., Spalding, R. F., Burnside, O. C., Lowry, S. R., and Leavitt, J. R. C., 1983. Biological significance and fate of atrazine under aquifer conditions: Weed Science, v. 31, p. 610–618.

Whittemore, D. O., 1984. Geochemical identification of salinity sources; *in*, Salinity in watercourses and reservoirs (Proceedings of the International Conference on State-of-the-Art Control of Salinity), R. H. French, ed.: Stoneham, Massachusetts, Butterworth Publishers, p. 505–514.

Whittemore, D. O., 1988. Bromide as a tracer in ground-water studies—geochemistry and analytical determination: Proceedings Ground Water Geochemistry Conference, Dublin, Ohio, National Water Well Association, p. 339–360.

Wierenga, P. J., 1977. Solute distribution profiles computed with steady-state and transient water movement models: Soil Science Society of America Journal, v. 41, p. 1050–1055.

Wierenga, P. J., 1982. Solute transport through soils—mobile-immobile water concepts; *in*, Symposium on unsaturated flow and transport modeling, Proceedings,E. M. Arnold, G. W. Gee and R.W. Nelson, eds.: Battelle Pacific Northwest Laboratory, p. 211–226. PNL-SA-10325, US Nuclear Regulatory Commission NUREG/CP-0030.

Wierenga, P. J., 1987. Solute transport: *in*, Future developments in soil science research, Madison, Wisconsin, Soil Science Society of America, p. 23–34.

Yaron, B., Gerstl, Z., and Spencer, W. F., 1985. Behavior of herbicides in irrigated soils; *in*, Advances in soil science, B. A. Stewart, ed.: New York, Springer-Verlag, v. 3, p. 121–212.