Kansas Geological Survey Ground Water Series 12

Movement and aquifer contamination potential of atrazine and inorganic chemicals in central Kansas croplands

Marios Sophocleous, M. A. Townsend,
Costas Orountiotis, R. A. Evenson,
D. O. Whittemore, C. E. Watts,
and E. T. Marks

Executive summary

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. The Great Bend Prairie is a prime agricultural area in Kansas where agrichemicals have been used for decades. However, until recently, no study had been conducted in that area to assess the impact of these practices on the Great Bend aquifer, which yields water for irrigation, industrial, municipal, and domestic uses. Our initial conception was that the shallow aquifer of the region would either contain appreciable amounts of various agrichemicals, such as nitrogen fertilizer derivatives and atrazine, or the agrichemicals would be held "in transit" in the unsaturated zone on top of the shallow clay layers in the region if they were not present in the aquifer. Therefore the purpose of this project was 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. We outfitted three sites in the Great Bend Prairie with instruments to monitor the processes involved in the movement and concentration of agrichemicals in soils and the underlying aquifers. Two sites (site 6, in Stafford County, and site 7, in Pratt County), characterized by different soil types but used for growing the same crop (irrigated corn), were examined in detail. A third site (site 10, in Edwards County), which is not cultivated (pastureland) and on which agrichemicals have never been used, was selected as the control site. We studied experimentally the simultaneous movement of both atrazine and bromide by flooding the study sites. Other inorganic chemicals, such as nitrates and chlorides, were also studied. The purpose of the flooding experiments was not necessarily to simulate actual field conditions but to evaluate the potential of atrazine to be leached into 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 horizons was conducted before the flooding experiments. Although we observed relatively high nitrate concentrations in both the unsaturated zone and the aquifer zone in one of our study sites, atrazine was not detected in either the deeper unsaturated zone or the underlying aquifer in any of the study sites. We also have no evidence of atrazine accumulation on top of clay layers. We found that atrazine readily breaks down to other often nontoxic by-products, thus explaining why atrazine was not detected deeper in the soil profile and in the underlying shallow aquifer. Based on the limited results of this study, the probability that atrazine will leach through the soils to the underlying aquifer in the Great Bend Prairie under present conditions seems remote. The nitrate data from 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. The total dissolved solids content (the amount of dissolved material in a sample of water) in the ground water from sites 6 and 7 was much higher than that from the nonirrigated site 10, again demonstrating the impact of continuous irrigation on ground-water quality. The classical processes of chemical movement did not fit the data well at the studied sites. The significance of such observations to agricultural chemical movement is that, during periods of unusually high rainfall and ponding or during excessive flood irrigation, downward movement of chemicals concentrated in soils might be triggered and dissolved chemicals might bypass certain soil zones and move to greater depths than expected.

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Abstract

We conducted flooding experiments 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. To characterize in situ the hydraulic and chemical properties of the appropriately instrumented field sites, we used the instantaneous profile method supplemented by means of an organic (atrazine) and an inorganic (bromide) tracer chemical. Atrazine readily hydrolyzed into hydroxyatrazine and biodegraded to ethylatrazine and isopropylatrazine, thus explaining why atrazine was not detected deeper in the soil profile and in the underlying shallow aquifer. The classical processes of chemical movement based on equilibrium conditions and diffuse flow through porous media did not fit the data well at either site. Incompletely mixed slug flow predominates at one of the sites, and preferential flow predominates at the other. 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 in both the vadose and the saturated zone were observed in one of the sites, which is characterized by sandy soil. The nitrate data indicate a close relationship between nitrogen fertilizer application, irrigation, and nitrate movement into the subsurface.

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 in regard to the high toxicity and health implications of such agrichemicals on humans and animals. A recent epidemiologic study of occurrences of non-Hodgkins lymphoma (NHL) in Kansas found farm herbicide use to be highly correlated 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 29 of 103 statistically representative samples collected statewide had nitrate levels above the maximum contaminant level for drinking water and 8 had detectable pesticides, with 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 statewide average nitrate concentration from 3 mg/L to 10.3 mg/L nitrate-nitrogen from the 1950's to 1983 (Hallberg, 1986b). Also, pesticides and elevated nitrate concentrations were present in all types of aquifer statewide in Iowa—glacial, alluvial, carbonate, and bedrock—indicating a non-point-source problem (Hallberg, 1985). Atrazine persisted in ground water year-round in both Iowa and Nebraska (Hallberg, 1985; Wehtje et al., 1983). Pesticides also were detected in public water supplies, particularly those in shallow alluvial systems and surface waters in Iowa and Ohio (Kelley and Wnuk, 1986; Baker et al., 1985).

Recently discovered incidences of ground-water pollution from agrichemicals throughout the United States and the resulting series of environmental laws regulating the use and disposal of chemicals on land surfaces have created a new surge of interest in field-scale solute transport studies. Table 1, adapted from the Council for Agricultural Science and Technology (CAST) (1985) report, summarizes some facts about the constituents of principal concern in croplands overlying significant ground-water aquifers. The transport of dissolved chemicals with percolating water has been studied for many years under controlled laboratory conditions but has received relatively little experimental study under field conditions until recently (Biggar and Nielsen, 1967; Boast, 1973). As a result, most chemical transport models developed over the last decade for use in field-scale transport simulations use laboratory results to formulate the 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 the mechanisms for moving to ground water is mostly qualitative. The retardation processes and factors are poorly understood. We designed the present study to address some of these problems.

The Great Bend Prairie is a prime agricultural area in Kansas where agrichemicals have been used for decades. However, until recently, no study had been conducted in that area to assess the impact of these practices on the Great Bend aquifer, which yields water for irrigation, industrial, municipal, and domestic uses. [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 (GMD5), 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.] Water resources for most of the Great Bend Prairie are locally managed by the GMD5, whose goal is to maintain an adequate amount of good quality water for present and future needs (fig. 1). Recent studies that indicate aquifer pollution

TABLE 1—SUMMARY OF PROMINENT FACTS ABOUT THE PRINCIPAL CONSTITUENTS OF GROUND WATER UNDERLYING CROPLANDS.

Constituent	Sources	Soil processes affecting the amount lost to ground water	Tendency to move downward through soils in percolating water	Comments
Soluble salts	Irrigation water Organic materials Fertilizers Weathering of minerals Rainfall Absorption and cation exchange	Precipitation and dissolution of carbonates and sulfates Weathering of soil minerals	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 ground water is incidental to water movement and is a loss to crop production potential
Pesticides	Commercial products Decomposition Volatilization	Retention by soil 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

Adapted from CAST (1985).

from agrichemicals in neighboring states with similar agricultural practices raised considerable concern in Kansas. Our initial conception was that the shallow aquifer of the region would either contain appreciable amounts of various agrichemicals, such as nitrogen fertilizer derivatives and atrazine, or the agrichemicals would be held "in transit" in the unsaturated zone on top of the shallow clay layers in the region if they were not present in the aquifer. 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 improved nutrient, pesticide, and water management, can be encouraged.

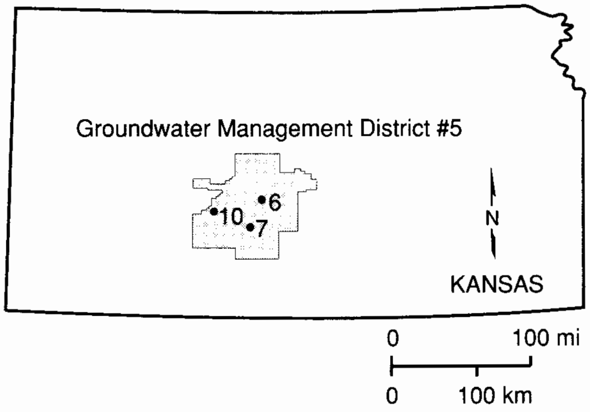

FIGURE 1—LOCATION OF FIELD SITES.

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*, 36 million kilograms (79 million pounds) of atrazine active ingredient are used annually for weed control on corn and sorghum crops and for nonselective weed control on grain and pasturelands. In Kansas atrazine is the most commonly used herbicide; nearly 2.5 million kilograms (5.5 million pounds) of atrazine or combinations including atrazine were applied to Kansas farmlands in 1978 (Nilson and Johnson, 1980). During the last decade, atrazine has been 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 the obvious choice for further study.

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 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, groundwater 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 of atrazine and nitrate is presented here.

Atrazine

The movement of atrazine and other herbicides depends 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. Past studies have generally been conducted under laboratory conditions using repacked soil columns or small soil samples as medium. These studies are useful for demonstrating basic chemical processes that affect the movement of herbicide chemicals; however, they are not a substitute for the field situation. In a farm field other factors come into play, such as the presence or absence of routes of preferential flow (macropores caused by worms, plant roots, desiccation cracks, or small fractures), incompletely mixed parcels of water and chemical solutions, and slug and blob flow.

Degradation of atrazine strongly depends on the soil environment (Sheets, 1970). The physical characteristics of the soil (aeration, exposure to light, inorganic and organic nutrients, soil pH, quantity of clay and organic matter) play a major role in the chemical and biologic degradation of atrazine. Microbial degradation results in nitrogen dealkylation of atrazine side chains (see fig. A.1) to produce deethylated atrazine and/or deisopropylated atrazine (Kaufman and Kearney, 1970). Microbial degradation is temperature and moisture dependent and increases with the amount of soil organic carbon and associated nutrients (Skipper and Volk, 1972), which are the major constituents of microbial food. Microbial community size in mineral soils has been directly related to organic matter content (Alexander, 1977). Chemical degradation occurs as a hydrolysis reaction at the number 2 carbon of the atrazine ring, producing hydroxyatrazine. Adsorption onto soil colloids is a prerequisite for hydrolysis (Armstrong et al., 1967). Atrazine adsorption 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 over the movement of herbicides through the soil to ground water. Many states (e.g., Nebraska and Iowa) are finding the chemicals in their alluvial aquifers but are only beginning to evaluate the factors responsible for preventing or permitting the movement. Studies in Kansas indicate that atrazine enters surface waters through attachment to soil particles, which are carried by runoff water from fields (Gilliom et al., 1985). The occurrence of atrazine in ground water is limited, and the chemical is usually not detected unless there is 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 on the occurrence and migration of nitrates through soil to ground water indicates that nitrate contamination in many areas is a non-point-source problem. Much of the work cited in appendix A suggests that fertilizer use in conjunction with excess precipitation and/or irrigation practices is a primary source of the nitrate. In several states, such as Nebraska and Iowa, the combination of well-drained sandy to silty soil conditions, fertilizer use, and irrigation has caused a widespread problem. Work in Kansas indicates that there is a trend toward increased nitrate concentrations in ground water.

Studies in Nebraska and California indicate that contamination from oxidation of nitrogen bound up in sediments also is probable. 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.

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

Site selection and instrumentation

We instrumented three field sites in the Great Bend Prairie to monitor the in situ processes involved in the movement and concentration of agrichemicals in soils and the underlying aquifers (see fig. 1). Two sites [site 6 (NESWSENW sec. 36, T. 23 S., R. 12 W.) and site 7 (NWNESENE sec. 11, T. 26 S., R. 14 W.); 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 (SESWSESE sec. 1, T. 25 S., R. 19 S.); fig. 1], which is not cultivated (pastureland) and on which agrichemicals have never been used, was selected as the control (pristine) site.

All three sites were outfitted with a number of observation wells screened at different depth intervals, a neutron-probe access tube for monitoring soil moisture, tensiometers at various depths, and a recording rain gauge. This instrumentation was the minimum necessary for characterizing soil-water movement (the agrichemical transporting vehicle) through the soil to the underlying aquifer. The two sites located in cornfields had additional instrumentation: a weather station, suction lysimeters installed at depths of 15, 30, 60, 90, 120, 150, and 180 cm (0.5, 1, 2, 3, 4, 5, and 6 ft), and 11 thermistors to measure soil temperatures from the near-surface to 275 cm (9.0 ft) below ground surface. Figure 2 illustrates the instrumentation at each site.

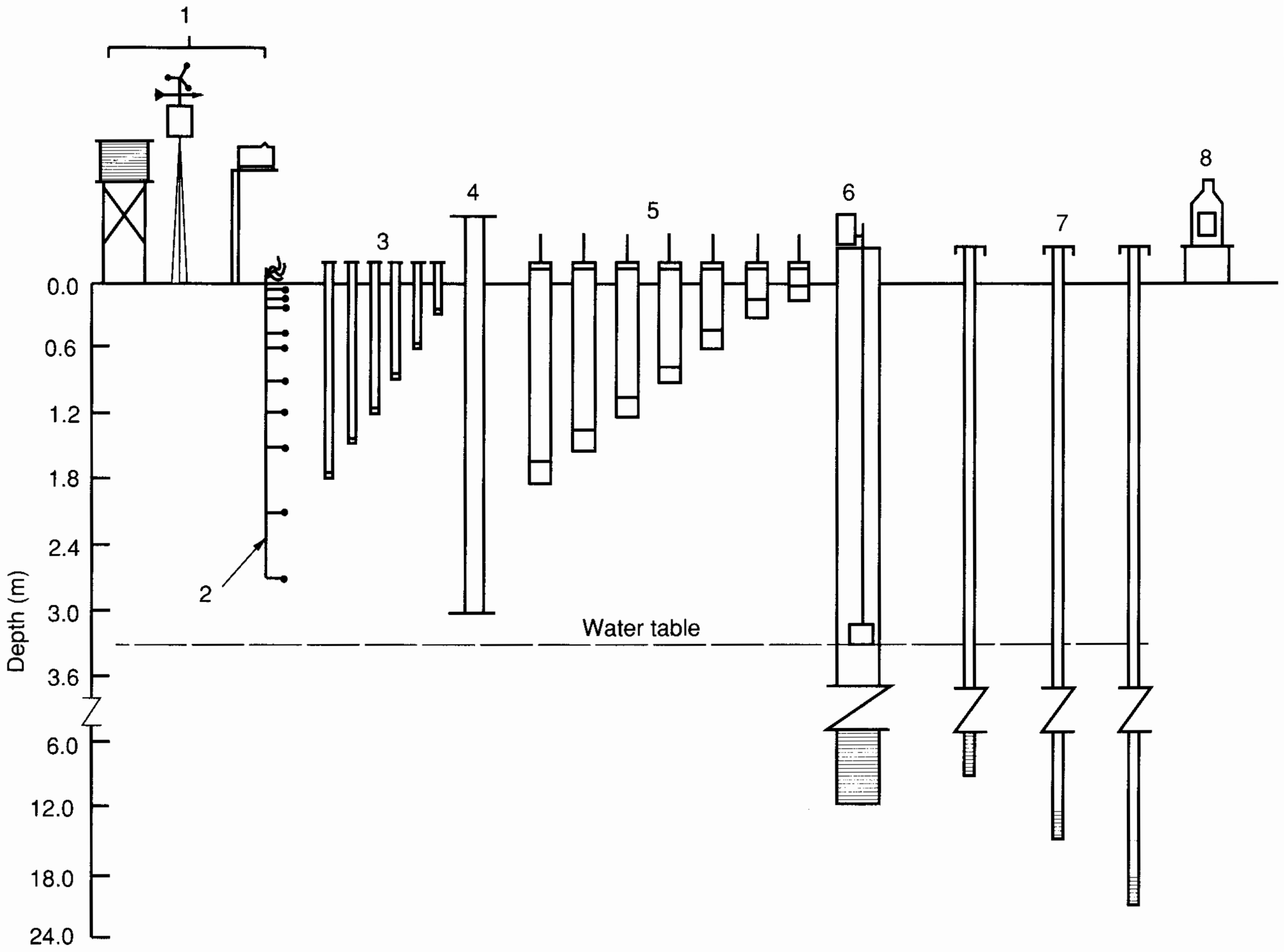

FIGURE 2—Schematic layout of site instrumentation. 1, Weather station; 2, thermistors; 3, tensiometers; 4, neutron-probe access tube; 5, suction lysimeters; 6, observation well; 7, piezometers; 8, recording rain gauge.

Methodology

Because of their chemical nature, organic and other chemicals interact with soil, water, and biota when applied to farmland. It is generally useful to study 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 level in the environment and its low toxicity to plants and animals. Therefore we studied the simultaneous movement of both an organic chemical (atrazine) and a conservative inorganic tracer (bromide) by running flooding experiments at sites 6 and 7. 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 to be leached into 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 a 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 content, cation-exchange capacity (CEC), bulk density, water content at various applied pressures, extractable ions, soil pH, electrical conductivity, clay mineralogy, and various other physical and chemical soil characteristics.

The flooding experiments had a dual purpose: (1) to contrast 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-probe access tube was mowed as close to the ground as possible. Planks [244 × 40 cm (8 × 1.3 ft)] were connected with door hinges to form a hexagon (site 6) or a rectangle (site 7) around the site. The structure was secured with a 5–8-cm (2–3-in) groove dug around the inner perimeter and wooden stakes placed outside the planks at the mowed site, forming a diked enclosure of 14–15 m^2 (150–160 ft^2) around the instrumentation and the shallowest observation well. The planks were covered with 3–5-mil-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)] indicated near steady-state conditions, addition of the chemical solution to the diked area was stopped. At that time the chemical solution ponded to 5–10 cm (2–4 in). This ponding head differential was due to the uneven or nonlevel surface of the flooded sites. 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, as can be inferred from the various time-series plots and from appendixes C and D. Soil cores [2.5 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 logistic reasons, the flooding experiments were initiated on September 9, 1987, for site 6 and on October 7, 1987, for site 7 after the corn had been harvested. The plastic cover was removed from both sites in December 1987, after snow had 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. The augered hole diameter was 17.2 cm (6.75 in). Clean rubber gloves were used to handle PVC casing and auger flights. Each auger flight section was washed with potable water and 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 the PVC well screen and the 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 filled with potable water to prevent sand from lodging between the casing and the stem when 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 gravel-packed using coarse-grained 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 sealed 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 the annular space was filled to the ground surface. After letting the grout settle for a few days, the well was completely developed by bailing, pumping water out of the well, or 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.

Neutron-probe access tubes

A 5-cm (2-in) galvanized steel pipe was used as an access tube for the neutron probe at each site. Its bottom was sealed with a rubber stopper using adhesive sealant to prevent water from entering the pipe. 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 inserted into the sampler slots, thus isolating a known volume of soil [60 cm^3 (3.7 in^3)]. Excess soil from both ends of the sampler were discarded, the putty knives were pulled out, and the 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 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 (15.0 ft). The access tube was then inserted into the 5-cm (2-in) hole and pushed down with a twisting motion, creating a snug fit. The neutron probe was inserted into the access tube, and three 30-s field neutron readings were taken at depth intervals of 15 cm (6 in). A set of 10 standard count neutron readings were taken before inserting the probe in the access tube.

The soil samples were subsequently oven-dried, and the bulk density and moisture content on a dry weight basis were

TABLE 2—SUMMARY DATA ON OBSERVATION WELLS AT THE THREE STUDY SITES.

	Observation well diameter		**Total depth**		**Screen interval**		
Site	**cm**	**in**	**m**	**ft**	**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

calculated, from which the volumetric water content was determined. The ratios (R's) of field to standard neutron counts for all 15-cm (6-in) depth intervals were regressed against the corresponding measured volumetric moisture content values. A regression equation was derived to convert neutron count readings to soil-moisture content ($\theta = -0.0672 + 0.2695R$). A common calibration curve was developed by combining the calibration results from each site, as shown in fig. 3, to increase significantly the number of data points in the regression analysis. A linear least-squares curve, with a correlation coefficient of 0.9507, was fitted through the data.

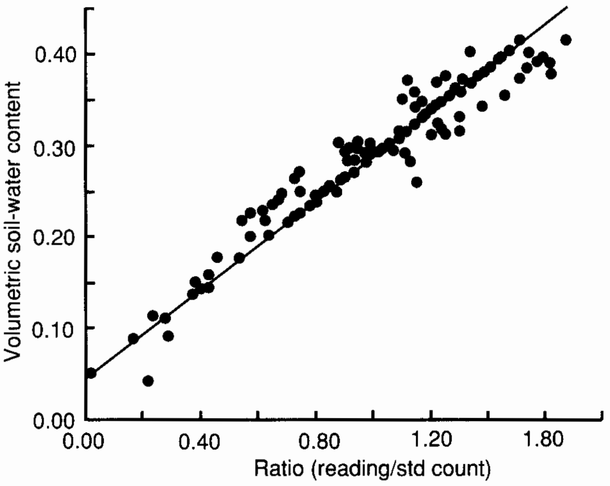

FIGURE 3—Field calibration curve for neutron probe for sites 6, 7, and 10.

Tensiometers

Tensiometers were constructed in-house from 100-kPa (1-bar) ceramic cups (Soil Moisture Corporation, part 655X1–B1M1) epoxied to 1.9-cm (0.75-in) PVC pipe. A 15-cm (6-in) clear acrylic tube snugly fitting inside the pipe was also epoxied on top, with a rubber septum providing a sealing cap. A pressure transducer needle probe (tensimeter) inserted into the tensiometer rubber septum was used to read the capillary pressure. Before being inserted into the soil, all tensiometers were checked for leaks by filling them with water and letting them stand for 24 hr in plastic buckets with water covering the ceramic cups. After these checks the tensiometers were filled with deaired, deionized water and installed near the neutron-probe 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 inserted in the hole to a snug fit. The rest of the hole was then backfilled with the augered soil while water was sprayed into it. The septum was protected from exposure to weather 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 [15–180 cm (0.5–6 ft)]. A silica flour slurry was mixed with water, the hole wetted, and the slurry 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. A vacuum was then applied to the lysimeter.

Soil temperature thermistors

A hole was hand augered with the 5-cm (2-in) auger to 275 cm (108 in) below ground surface. Thermistors (YSI series 400 general-purpose probes) were taped to a 3-m (10-ft) wooden dowel at the following places: 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 with a plastic bag and further protected by covering the protruding dowel with a 15-cm (5-in) long 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/ha atrazine, or 0.22 g/m^2 (2 lb/acre atrazine 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 × 10^6 lb soil, or 1.0 mg/kg atrazine. We increased the quantity of atrazine in the flooding experiment solution to 1.5 mg/L (which amounted to 0.45 g/m^2 for site 6 and to 1.0 g/m^2 for site 7) to ensure that enough atrazine was available for possible downward leaching during one field application. Liquid Atrazine 4L herbicide (Platte Chemical Co., Inc.), which contains 4 lb (1.814 kg) active ingredient per gallon (3.785 L) (or 40.8% active ingredient; that is, 479 g/L atrazine active ingredient) was used to prepare the chemical solutions. A concentration of 1.5 mg/L of atrazine equals 5.68 × 10^{-3} g/gal atrazine, and because the active ingredient in Atrazine 4L is 40.8%,

$$\frac{5.68\times10^{-3}}{0.408}=1.39\times10^{-2}\ \mathrm{g/gal}$$

Atrazine 4L was required. Because a 500-gal (1.89-m^3) tank was available for mixing the chemical solution, 6.96 g Atrazine 4L was mixed in the tank filled with municipal water from Stafford (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 a hundredfold dilution by soil solutions. The tracer solution was prepared with sodium bromide (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 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 were analyzed to determine the exact concentrations of both bromide and atrazine.

At site 6, 1.89 m^3 (500 gal) chemical solution containing atrazine and bromide was applied after the soil profile was nearly saturated with municipal water from Stafford. At site 7, 3.79 m^3 (1000 gal) chemical solution of the same concentration as that at 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%. Bromide was determined at the Kansas Geological Survey (KGS) 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 profiles

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. A generally fining-upward sedimentary sequence can be recognized.

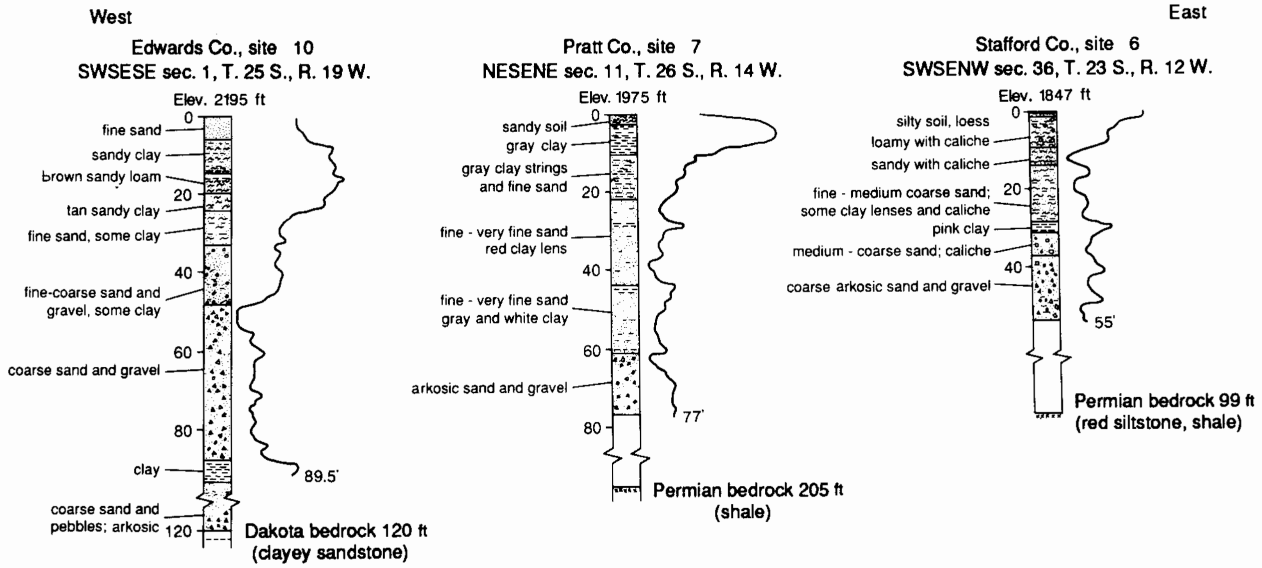

FIGURE 4—Geologic logs for each site based on drill cuttings and gamma-ray geophysical logs.

Site 6

Soil profile and physical and chemical characteristics

The soil profile at site 6—an Ost soil, a fine-grained loamy, mixed, thermic Typic Argiustoll—consists of grayish-brown silt loam down to 40 cm (16 in or 1.3 ft) (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 (3-in) thick grayish-brown E horizon with a silt loam texture and a weak medium-platy structure. A relatively hard brown to yellowish-brown silty clay loam layer underlies the E horizon down to 77 cm (30 in or 2.5 ft), making up the Bt horizon, which is characterized by a moderate, medium prismatic and subangular, blocky structure with many fine platelike soft masses of lime and common fine irregular salt masses; this Bt horizon is strongly effervescent. 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). This second soil has a clay loam texture and is characterized by many rounded carbonate nodules that are strongly effervescent. A third light-brown buried soil is also present, consisting of a Bt horizon of subangular blocky structure and a transitional BC layer down to the maximum analyzed depth of 230 cm (90.5 in or 7.5 ft). This third soil also has a clay loam texture and is characterized by many rounded carbonate nodules that are strongly effervescent.

The soil horizons and their grain-size distribution (texture), as determined by the Soil Conservation Service (SCS), are shown in fig. 5. It can be seen from the figure that the clay fraction increases significantly in the 45–90-cm (1.5–3.0-ft) 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 they relate to organic chemical movement through the soil will be shown later.

According to the SCS, the clay fractions of all analyzed soil horizons (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 (1.3 ft) than in the rest of the soil profile. Organic carbon makes up over one-half of the organic matter, and therefore the 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 1.72 times the percentage of organic carbon (Birkeland, 1984). Soil organic matter considerably

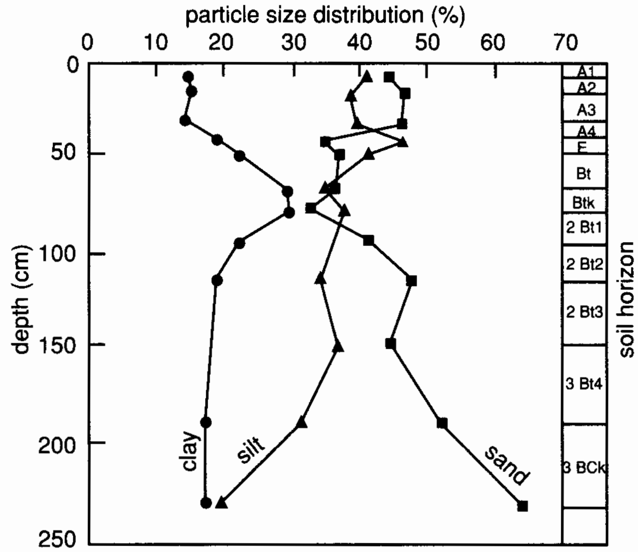

FIGURE 5—Grain-size distribution and soil horizons for site 6.

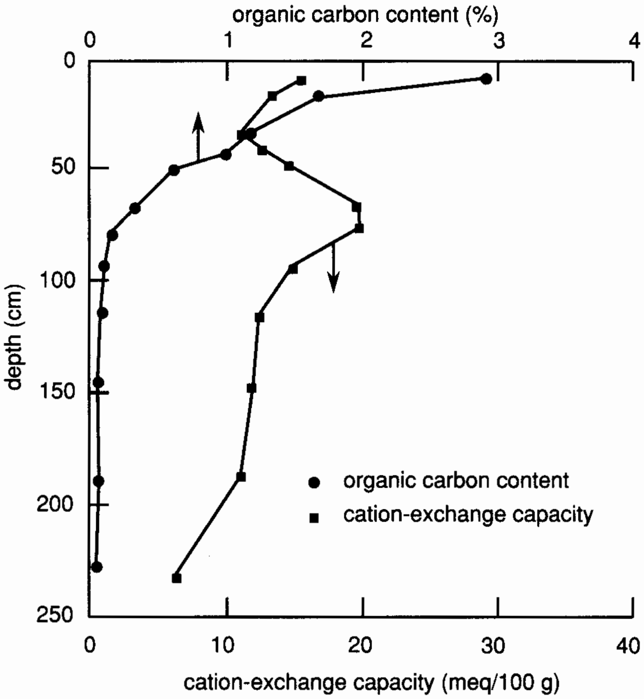

FIGURE 6—Organic carbon content and cation-exchange capacity profiles for site 6.

increases both the water-holding capacity and the CEC of soils. The organic acids produced from organic matter form chelating compounds that increase the solubility of some ions in the soil environment. The carbon dioxide gas that is evolved during humus formation (the bulk of the soil organic matter) reaches concentrations higher than those in the atmosphere and ultimately forms carbonic acid, which lowers the soil pH.

The CEC of the soil profile is also shown in fig. 6. In addition to a relatively high proportion of organic matter, this figure shows that the near-surface soil has a relatively high CEC, which gradually decreases toward the bottom of the upper 30 cm (1 ft) of soil. In general, the CEC profile follows the clay content profile (fig. 5). Most soil colloids (inorganic and organic) have a net negative surface charge and thus attract cations. The strength of cation attraction varies with the colloid and the particular cation, and some cations may exchange with others. The total negative charge on the surface is the CEC. It is expressed in milliequivalents per 100 g oven-dried material.

The soil bulk density, determined by the core method using a Madeira sampler and by the clod method (analyzed by the SCS), is shown in fig. 7. An increase in bulk density with depth is evident and apparently results from the 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 the field capacity (specific retention) and the permanent wilting point (the point at which the moisture is so tightly held by the soil particles that the roots can no longer extract it). Water and chemical retention and movement in soil 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 solution 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 fig. 9. The soil approaches definitely acidic conditions just below the upper 30 cm (1 ft), whereas below the 60-cm (2-ft) depth it approaches moderately alkaline conditions. Soil pH is often related to dissociation, adsorption, and chemical alteration of organic chemicals, 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 content and the type and amount of carbonate minerals and dissolved carbonate anions. A large amount of organic matter induces acidity, except when counterbalanced by a high concentration of soluble carbonates.

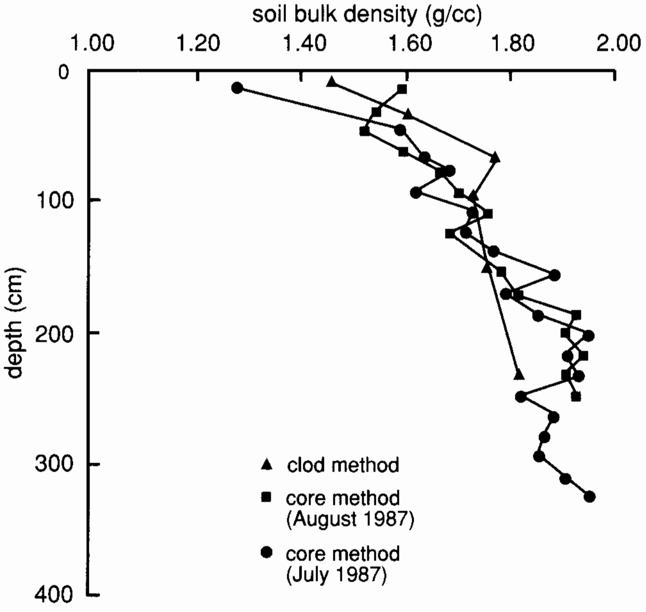

FIGURE 7—BULK DENSITY DISTRIBUTIONS determined by the two methods indicated for the soil profile at site 6.

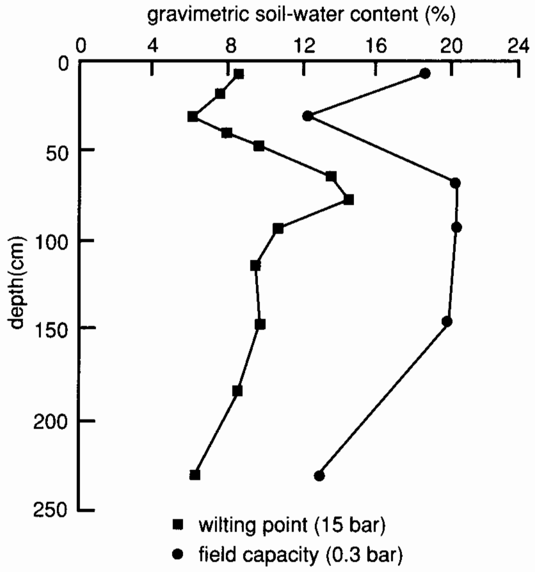

FIGURE 8—AVAILABLE WATER-HOLDING CAPACITY OF THE SOIL profile at site 6.

The soil profile contains an appreciable amount of salts, especially in the lower horizons below 120 cm (4.0 ft) and in the upper 30 cm (1.0 ft), as shown by the electrical conductivity of the 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 fig. 10. The lower part of the soil profile below 120 cm (4.0 ft) contains a significant amount of sodium, enough to influence hydraulic conductivity. However, in the 2Bt1 horizon [77–93 cm (2.5–3.1 ft)] and the 2Bt2 horizon [93–113 cm (3.1–4.82 ft)] the salt content is low enough to keep the clay in a dispersed state, given the relatively high sodium content of these horizons (fig. 10).

Water chemistry

Site 6 is located in Stafford County at the edge of a flood-irrigation field used for growing corn during the period of study. The average precipitation in the area is 61 cm/yr (24 in/yr) (Sandyland Agricultural Experiment Station, 1983). The site has a zone of concentrated salts in the upper 6.1 m (20 ft) of the soil, as shown by the background specific conductance measurements collected from the 6.1-m, 10.1-m, and 13.7-m (20-ft, 33-ft, 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 (see 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 indicate clay layers between the 6.1-m and 10.1-m (20-ft and 33-ft) wells (see fig. 4). These layers may prevent movement of salts to the lower aquifer zones.

A definite source of the salts in the sampled soil solutions and ground water is the paleosols at depth. 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 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 Ca–Na–HCO$_3$–Cl water (fig. 11). As stated previously, this composition 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 (20 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 (6.1-m and 10.1-m) wells are similar to the levels recorded for the 38-ft (11.5-ft) GMD5 ground-water quality network well (26 mg/L nitrate in the quarter section east of our test site) (table C.1). This implies that the water in the monitoring wells reflects the overall ground-water flow from the farm.

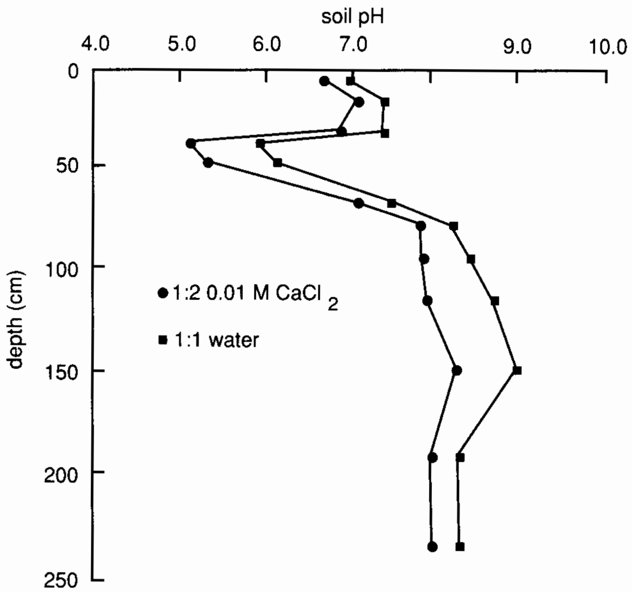

FIGURE 9—Soil solution pH at site 6.

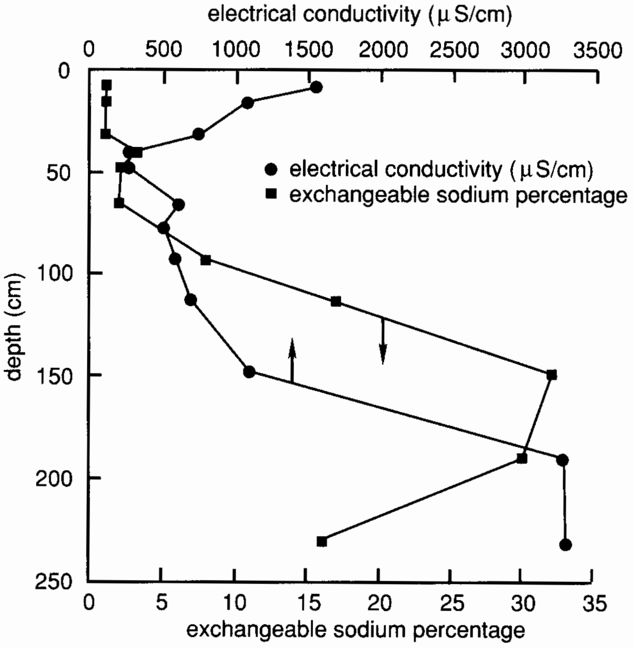

FIGURE 10—Electrical conductivity and exchangeable sodium percentage for the soil profile at site 6.

Water and chemical flooding

The soil-moisture profile at site 6 just before flooding indicated dry conditions throughout most of the soil profile (fig. 12). To reduce lateral water movement from the area to be flooded to the surrounding area and to increase the soil water content, we flooded the perimeter strip of the area with 3.79 m^3 (1000 gal) of Stafford municipal water on September 9, 1987. We covered the wetted perimeter area with plastic immediately and then flooded 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 1.89 m^3 (500 gal) of chemical solution (atrazine and sodium bromide) for 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 and enclosed 15.4 m^2 (166 ft^2) of soil. As soon as the chemical slug seeped into the soil (September 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 flooding show that the soil became nearly saturated down to approximately 270 cm (8.9 ft) (fig. 12). Soil-moisture drainage curves for 15-cm (6-in) depth intervals after covering the site with plastic are shown in fig. 13, where soil-water drainage down to the 230-cm (7.5-ft) 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 sometimes other dissolved inorganic constituents. The distribution of dissolved chloride with depth, plotted in fig. 14, suggests that the flooding freshwater (with 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 fig. 10). However, there also is evidence of some preferential movement of floodwaters through the profile. Flood solutions appeared to dissolve salts at the 120-cm (3.9-ft) depth, but the high chloride contents were not displaced to soil horizons immediately below 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 60 cm (2 ft) appears to substantiate the idea of concentration and precipitation of constituents from the soil solution. The salts would then be available for dissolution and deeper penetration during prolonged wet periods or excessive irrigation, as simulated by the flood experiment.

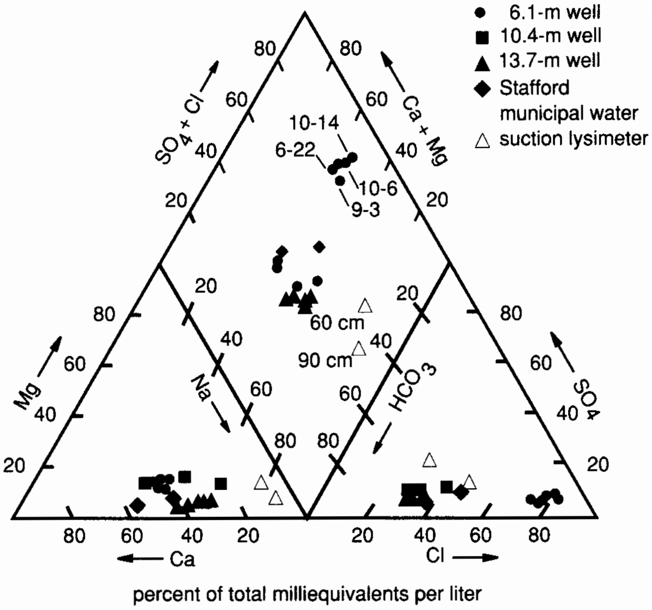

FIGURE 11—Trilinear diagram showing water chemistry data for three wells, two suction lysimeters, and Stafford municipal water (used for flooding) at site 6.

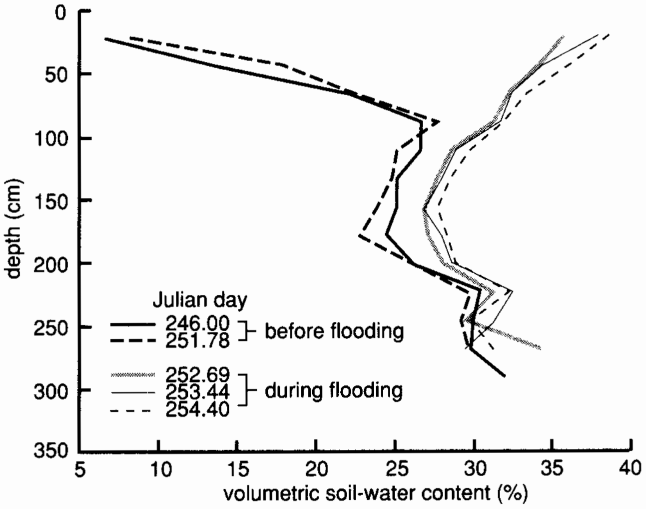

FIGURE 12—Soil-water content profiles before and during flooding in 1987 at site 6.

The source of the high-conductivity water is probably the abundant irregular salt masses and rounded carbonate nodules, which increase with depth throughout the soil profile below the A and E soil horizons (see fig. 5). The measured electrical conductivity of water extracted from saturated soil pastes before the flooding experiments generally increased with depth and ranged from 2000 µS/cm to >3000 µS/cm below the 120-cm (3.9-ft) depth; the specific conductance of suction lysimeter samples ranged from 2300 µS/cm to 4300 µS/cm over the sampled depth intervals of 90–150 cm (3.0–4.9 ft) during flooding (table C.1). Data from drillers' logs indicate increasing caliche amounts from the near-surface down to almost 9 m (30 ft), whereas the unconsolidated sediments become sandier with depth below 1.5 m (4.9 ft). Although the upper 75 cm (2.5 ft) of the soil profile was dry before the flooding experiment, the profile below 2 m (7 ft) was relatively wet (see fig. 12). The sandier and wetter nature of the deeper sediments would facilitate transmission of saline solutions to the shallow water table [3.4 m (11-ft) deep]. To saturate the unsaturated soil profile within the diked area at site 6, 3.83 m^3 (1010 gal) of water would be required, assuming no displacement of native pore water and no lateral flow. Thus the remaining 6.58 m^3 (1740 gal) 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 (8.9-ft) water column [based on the 6.1-m (20-ft) well and a 3.4-m (11-ft) depth to water], the concentration of the leaching solution needed to raise the ground-water conductance from 2500 µS/cm to 4200 µS/cm (see fig. 8) would be 5800 µS/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. Many lysimeters, 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 fig. 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 (20 ft)] 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 piston-like 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.

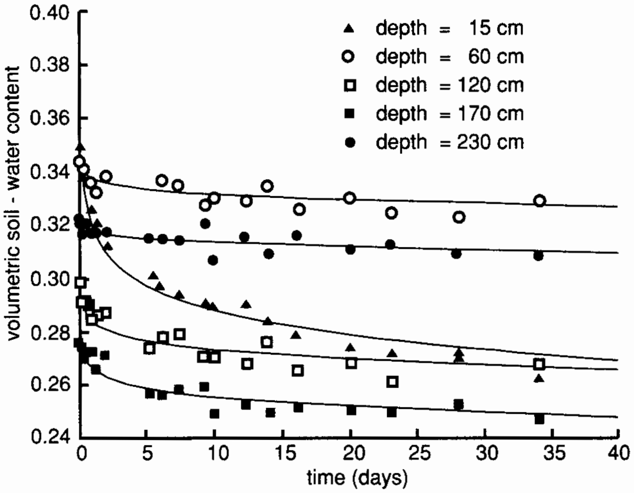

FIGURE 13—SOIL-WATER DRAINAGE CURVES in 1987 for five depths at site 6. The curves were derived by means of a least-squares fit using a drying model.

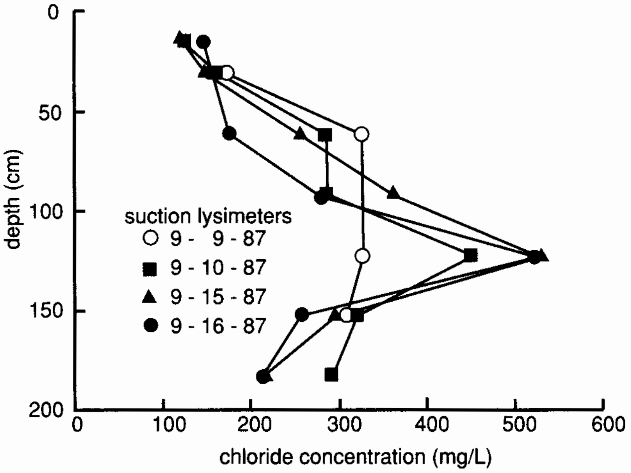

FIGURE 14—PROFILES OF DISSOLVED CHLORIDE sampled from suction lysimeters during flooding at site 6.

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 figs. 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 show only a minor 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 decrease with time can be readily recognized.

The soil profile temperatures during the flooding experiment (September to November 1987) are shown in fig. 19. A progressive soil temperature decrease with time at all measured depths is evident. The figure also shows that during September there was 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, biologic, and chemical processes occurring in that soil. In low-temperature (cold) soils chemical and biologic rates are slow, with absorption and transport of water and chemical species adversely affected.

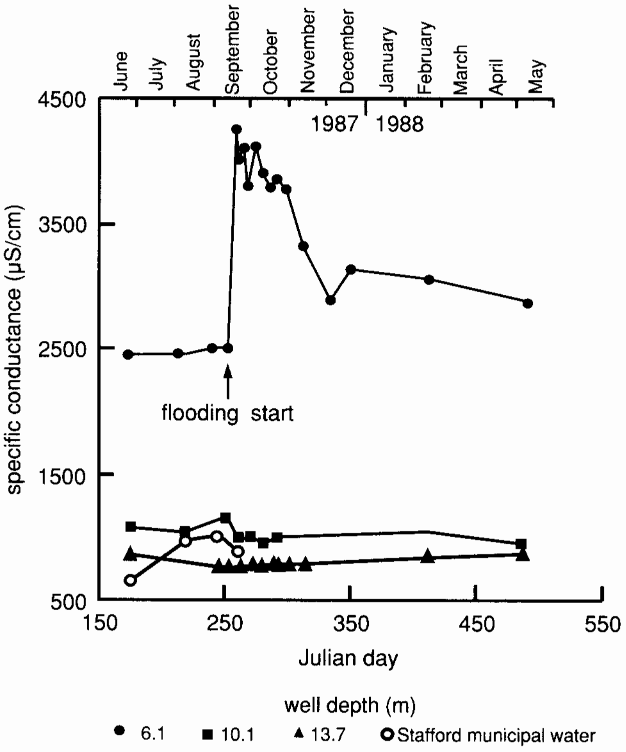

FIGURE 15—SPECIFIC-CONDUCTANCE TIME-SERIES DISTRIBUTION of observation wells and of Stafford municipal water used for flooding at site 6.

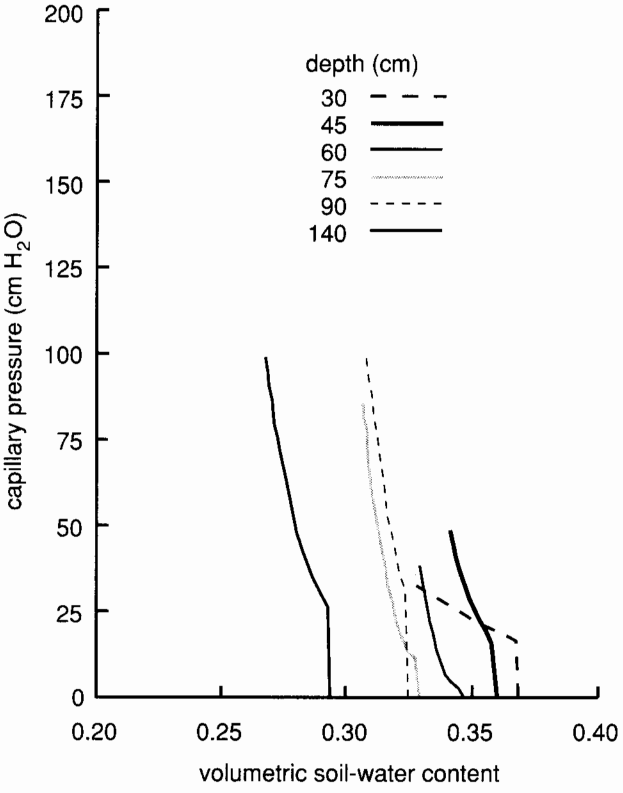

FIGURE 16—FIELD-MEASURED WATER-RETENTION CURVES FOR site 6.

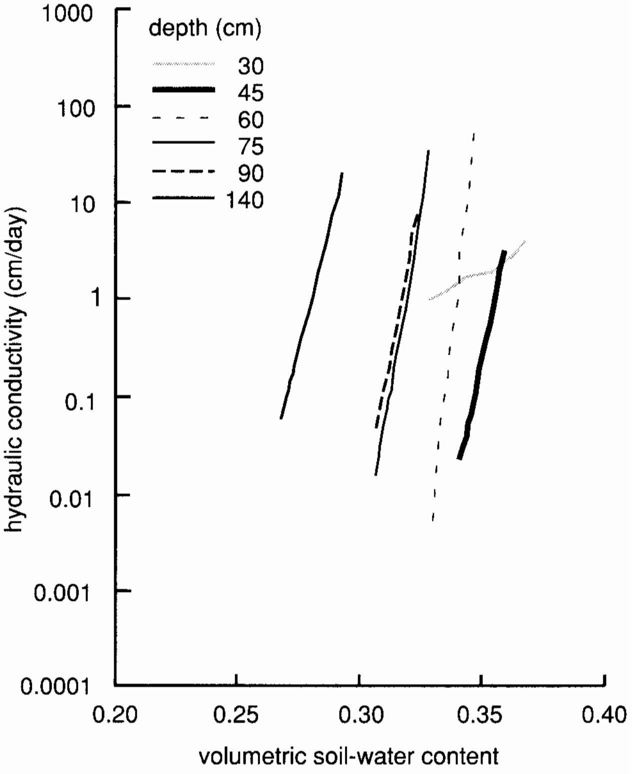

FIGURE 17—HYDRAULIC CONDUCTIVITY CURVES derived from the instantaneous profile technique for site 6.

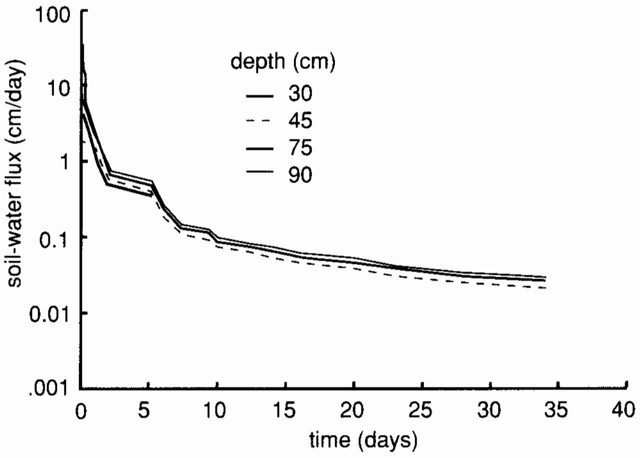

FIGURE 18—SOIL-WATER FLUX TIME DISTRIBUTIONS derived from the instantaneous profile technique for site 6.

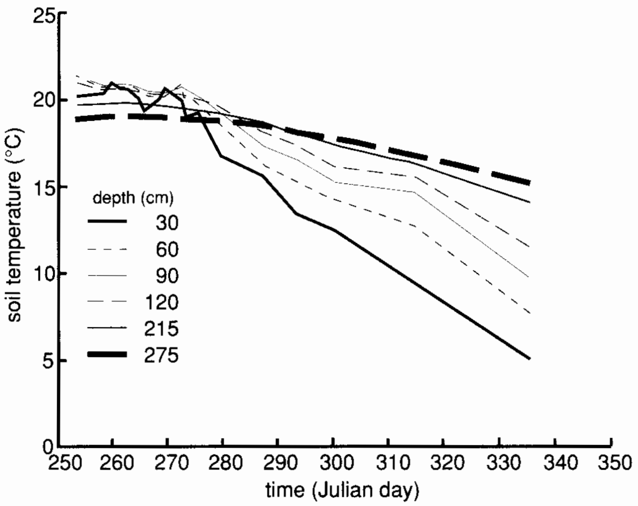

FIGURE 19—Soil-temperature time-series distribution for six depths at site 6.

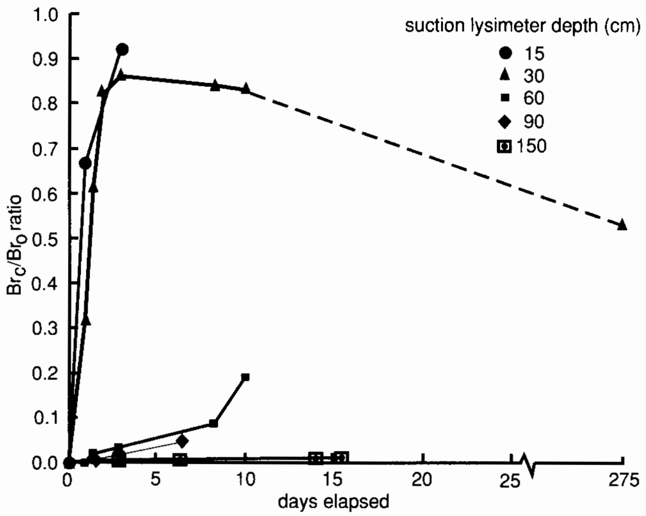

FIGURE 20—Bromide concentration breakthrough curves based on suction lysimeter sampling for site 6. Bromide is expressed as the ratio of bromide corrected for background levels (Br_c) to bromide tracer concentration in the flooding solution (Br_0).

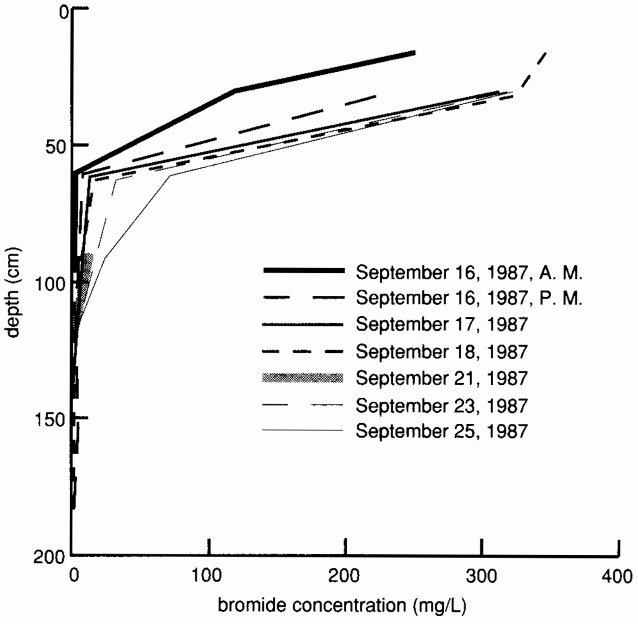

FIGURE 21—Bromide concentration profiles after chemical flooding was initiated at site 6.

Bromide

Bromide concentrations versus time after the start of chemical flooding are shown by the tracer breakthrough curves through the soil profile based on suction lysimeter sampling (fig. 20). Bromide concentrations were corrected by subtracting the small background values at each depth (mostly in the range of 0.1–0.2 mg/L). The actual bromide content of the chemical solution applied was 376 mg/L. The added bromide penetrated to the 150-cm (5-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 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 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 fig. 21; 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 fig. 21. Lack of complete data at later times prevented 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 flooding (see figs. 17 and 18) and the existence of a clayey underlying soil zone (see fig. 5). The greater apparent penetration of the applied water is due to the infiltration of floodwater without tracer before initiation of the chemical flood.

The bromide time-series distribution from the shallow 6.1-m (20-ft) observation well has a pattern similar to the specific conductance and chloride time-series distributions for the same well (see 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 to exist naturally in the deep soil because the accompanying rise in chloride in the well water kept the bromide/chloride 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 fig. 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 indicate that the relative distribution of the bromide tracer with depth does not correspond to the water content distribution in the soil profile (fig. 23). This observation supports the deduction from figs. 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 is minor. As a consequence of this displacement, the bromide tracer remains near the soil surface, thus explaining its persistence in the upper foot of soil.

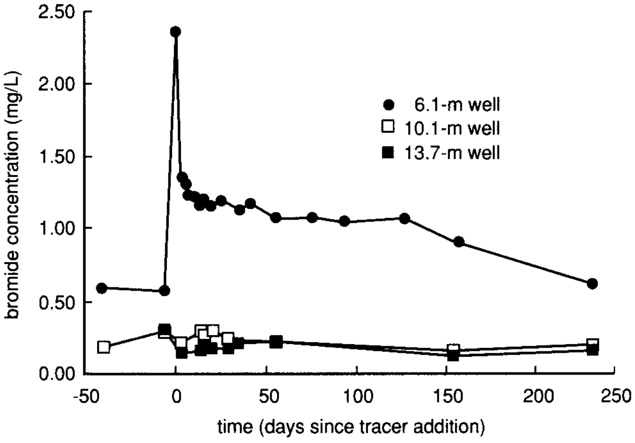

FIGURE 22—Bromide concentration time-series distribution from site 6 observation wells.

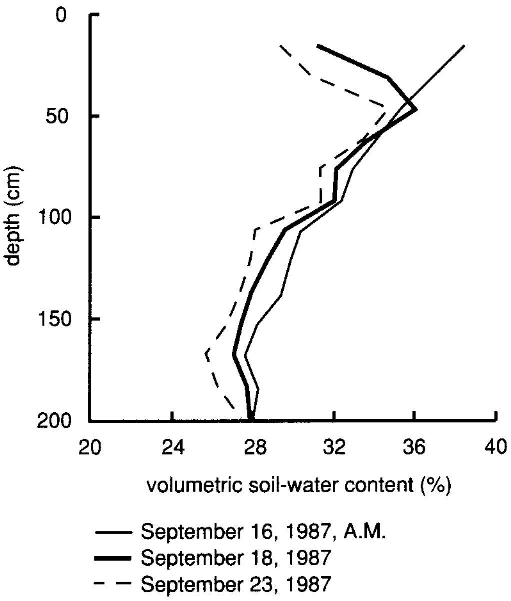

FIGURE 23—Soil-water content profiles since chemical flooding was initiated at site 6.

Atrazine and atrazine metabolites

The atrazine versus time breakthrough curve based on suction lysimeter sampling is shown in fig. 24. The atrazine breakthrough curve based on soil core extraction is shown in fig. 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, which result from random noise. Otherwise the breakthrough curves are similar to the ones based on suction lysimeters. The vertical distribution of atrazine in the soil decays exponentially 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 given that the calculated soil-water fluxes decreased drastically to a fraction of 1 cm/d within a few days of covering the site with plastic (see 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 3 days after chemical flooding, the mass balance accounted for 97–100% of the applied atrazine. However, after 3 days, only 10–50% of the atrazine mass could be accounted for (fig. 27).

Physical and chemical properties of the soil profile essential for biologic 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 CEC of the soil in the top 30 cm (1 ft) 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 biologic activity, which may result in biodegradation of atrazine (dealkylated metabolites). The low pH at just below the top 30 cm induces atrazine hydrolysis (to hydroxyatrazine), which is 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 stimulate microbial degradation of atrazine in soils. Figure 27 indicates that atrazine degradation at site 6 may have followed first-order kinetics; that is, the logarithm of the atrazine concentration decreases linearly with time, as shown in fig. 28. The half-life of atrazine (i.e., the time for one-half

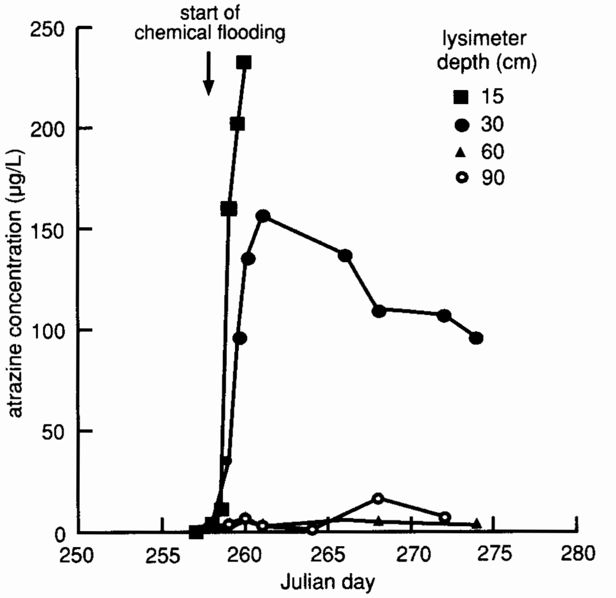

FIGURE 24—Atrazine breakthrough curves for site 6 based on suction lysimeter sampling.

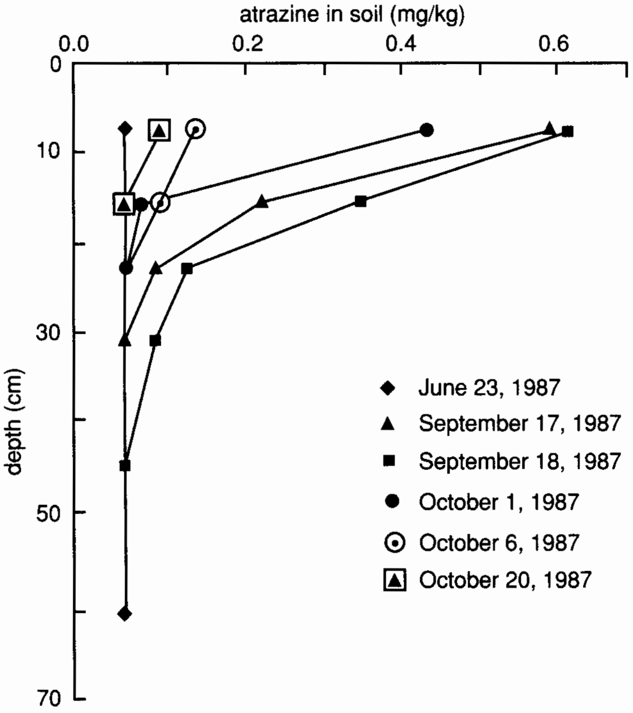

FIGURE 26—Atrazine profiles at site 6 based on soil cores.

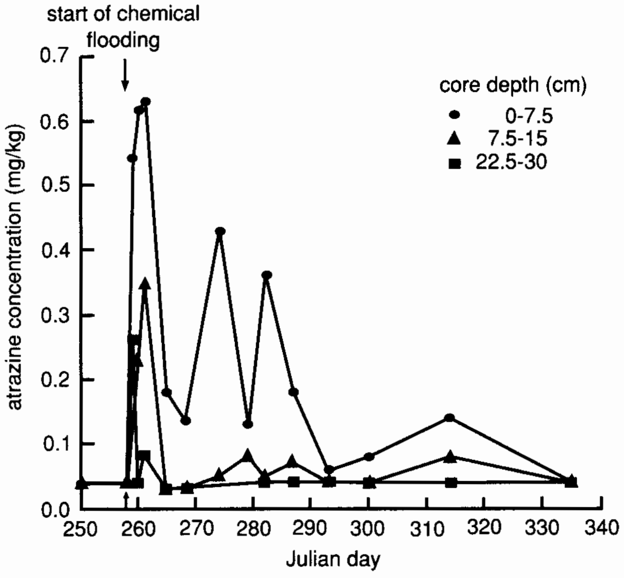

FIGURE 25—Atrazine breakthrough curves for site 6 based on soil cores. Detection limit is 0.04 mg/kg.

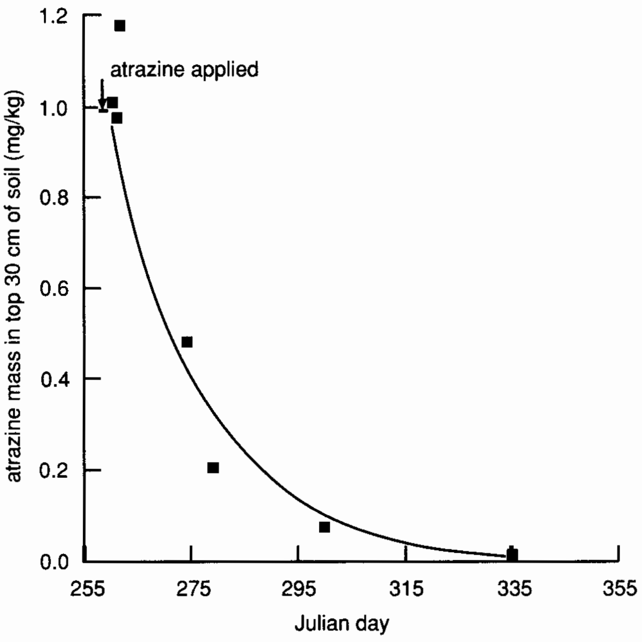

FIGURE 27—Atrazine mass in the upper 30 cm of soil at site 6, plotted on an arithmetic scale.

of the applied atrazine to disappear from the application site) was approximately 13 days at site 6 (based on fig. 28). The field-estimated half-life of atrazine is much shorter than the half-life of more than two months reported in other studies [e.g., Jury et al. (1987)]. 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 (0–1-ft) and 60–90 cm (2–3-ft) intervals of site 6, collected on February 25, 1988, were analyzed for atrazine and atrazine metabolites; the results are tabulated in appendix E. The hydroxyatrazine concentration (0.124 mg/kg) present in the 0–15-cm (0–6-in) depth interval was 1.6 times the amount of parent atrazine present. For the 15–30-cm (6–12-in) depth interval, the hydroxyatrazine concentration (0.116 mg/kg) 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 mg/kg and 0.185 mg/kg, respectively) were 3.1 and >4 times the amount of parent atrazine present, respectively, although the parent atrazine was below the detection limit (0.05 mg/kg) for the 75–90-cm (30–36-in) depth. Therefore an appreciable portion of parent atrazine degraded into hydroxyatrazine in the upper 90 cm (3 ft). The dealkylated metabolites of atrazine at the 0–30-cm (0–1-ft) and 60–90-cm (2–3-ft) depth intervals were below the detection limit (0.05 mg/kg). Such concentrations seem low, given the high organic matter content of the upper 30 cm (1 ft) of soil, but cold soil temperatures during the winter sampling period may have limited biologic activity. Additional soil samples collected in May and August 1988 were sent for atrazine metabolite analysis, especially to verify biologic activity (appendix E). The results show significant amounts of biodegradation by-products [ethylatrazine (G–28279) and isopropylatrazine (G–30033)] and hydroxyatrazine (G–34048) for the 0–15-cm (0–6-in) depth interval from the August 1988 sampling and the 30–45-cm (12–18-in) depth interval from the May 1988 sampling.

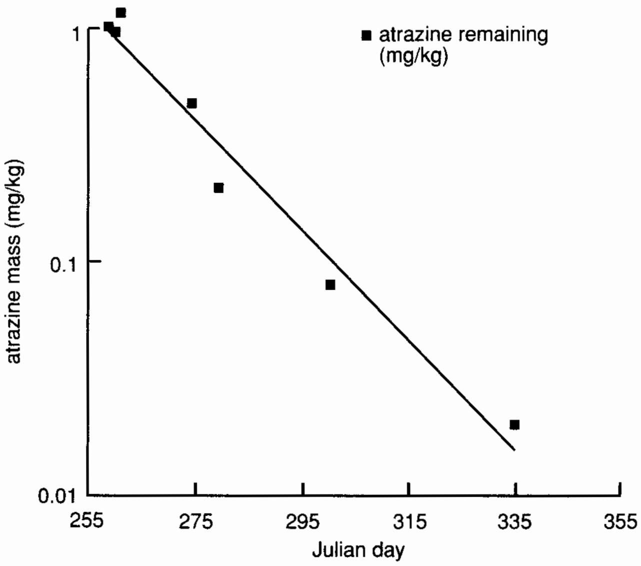

FIGURE 28—ATRAZINE MASS IN THE UPPER 30 cm (1 ft) OF SOIL AT site 6, plotted on a logarithmic scale. The data points (filled squares) indicate the amount of atrazine remaining (mg/kg).

No atrazine was observed in any of the observation wells, an observation that is consistent with the retention and decomposition of atrazine in the upper 75 cm (2.5 ft) of soil and the lack of significant concentrations of tracer bromide in the shallow ground water. All atrazine data are tabulated in appendix D.

Site 7

Soil profile and physical and chemical characteristics

The soil profile of site 7—an Attica soil, a coarse-grained, loamy, mixed, thermic Udic Haplustalf—consists of brown to grayish-brown loamy fine-grained sand down to 15 cm (5.9 in). This sand forms 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-grained sand down to 32 cm (12.6 in). This horizon is characterized by a weak, medium subangular, blocky structure with a relatively high bulk density compared with other horizons in the upper part of the profile. Underlying the AB horizon is a brown to yellowish-brown fine-grained sandy loam down to 65 cm (26 in) (the Bt horizon). The Bt soil horizon, which can be subdivided into two units [Bt1, at 32–50 cm (1.0–1.6 ft) and Bt2, at 50–65 cm (1.6–2.1 ft)], is slightly hard and friable with a moderate, medium subangular, blocky structure. Yellowish-brown loamy fine-grained sand forms the underlying C horizon, down to 157 cm (5.15 ft), which can be subdivided into three subhorizons (C1, C2, and C3). The C horizon is massive and friable with a few fine, distinct brown to dark-brown mottles. Underlying this soil horizon is another buried soil consisting of a weak red sandy clay loam forming another C horizon down to 177 cm (5.81 ft). This soil horizon has a massive structure with many reddish-brown mottles. Underlying this is a reddish-gray B horizon, which can be subdivided into a silty clay Bw horizon [down to 215 cm (7.05 ft)] characterized by several wide [6 cm (2 in)] vertical cracks filled with coarser soil and a silty clay loam Bk horizon [down to 240 cm (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 SCS, are shown in fig. 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; 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 than that at site 6, and the CEC of the clay content at site 7 is also much lower than that at site 6, except at depths below 160 cm (6 ft), where the silty clay to clay loam layers are encountered (fig. 29).

The bulk density of the soil profile, determined by the clod and core methods, shows relatively high compaction at the bottom of the upper 30 cm (1 ft) (fig. 31). The soil becomes less compact below this level until the silty clay soil is reached, at which point compaction increases again. The available water capacity of the soil profile at site 7 is shown in fig. 32; it is generally lower than that at site 6 (see 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)]. The nature of the silty clay soil causes the available water capacity to increase significantly (fig. 32).

The pH distribution in the soil profile (fig. 33) has a narrower range (6.6–7.9 based on a 1:1 soil to water extract) compared with site 6 (5.9–9.0 based on a 1:1 soil to water extract). The pH decreases slightly with depth until the silty clay soil is encountered at depth, at which point the pH progressively changes from nearly 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 (see fig. 10), indicating a much lower salt content in the soil profile of site 7. The nitrate and chloride depth distributions in the soil profile, as sampled from suction lysimeters before chemical flooding of the site, are shown in fig. 35. In general, there are high nitrate and chloride concentrations in the upper 30 cm (1 ft) of soil that progressively decrease with depth down to 90–120 cm (3–4 ft), beyond which they progressively increase with depth. The patterns of electrical conductivity and chloride concentration with depth are similar to each other at site 7, 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. As will be shown later, the higher hydraulic conductivity of the soil profile at site 7 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 water recharge.

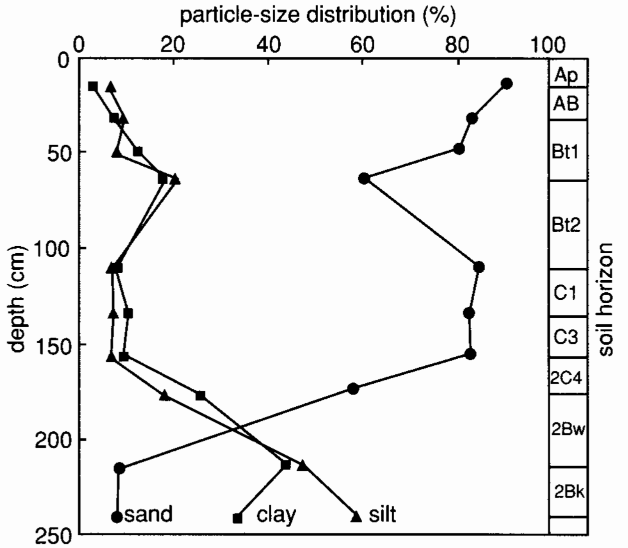

FIGURE 29—Grain-size distribution and soil horizons at site 7.

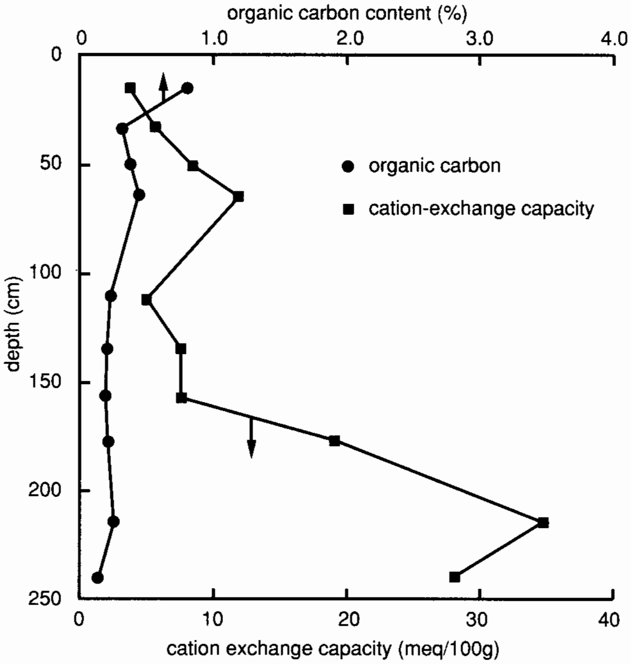

FIGURE 30—Organic carbon content and cation-exchange capacity profiles for site 7.

Water chemistry

Site 7 in Pratt County is center-pivot irrigated and was used to grow corn, wheat, and soybeans during this study. The soils are sandy and highly permeable and have low clay and organic carbon contents, as mentioned previously. The waters at the site are predominantly 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 time-series distributions showed an overall gradual decline during this study (figs. 37, 38, and 39). In all three figures there is a change in concentration approximately at the time of the flooding 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

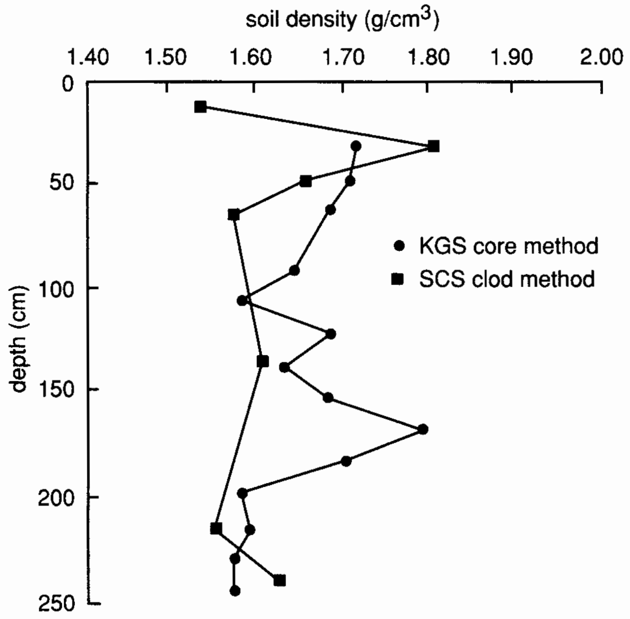

FIGURE 31—SOIL BULK DENSITY DISTRIBUTIONS determined by the core and clod methods for site 7.

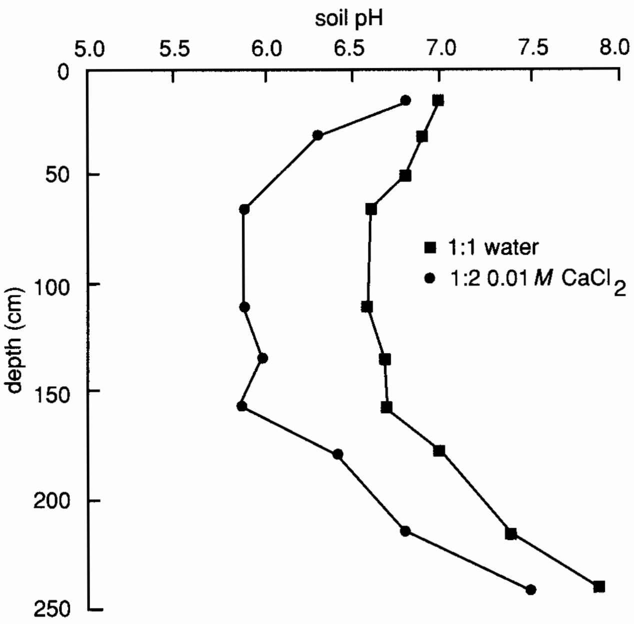

FIGURE 33—SOIL SOLUTION pH PROFILE for site 7.

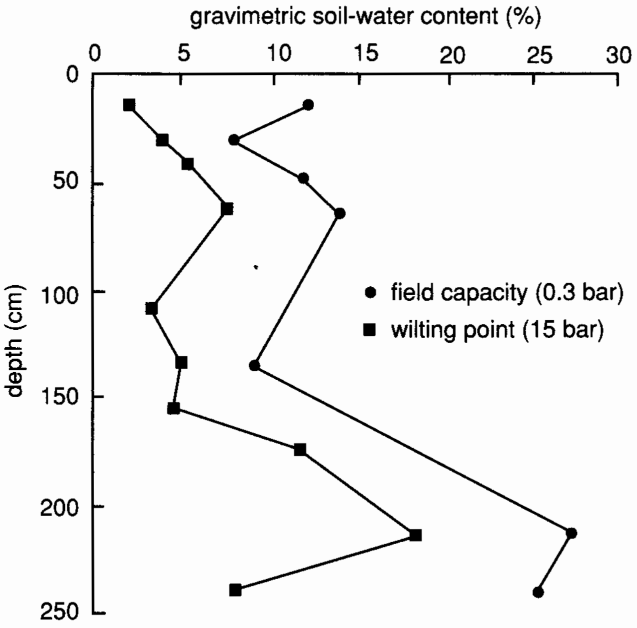

FIGURE 32—AVAILABLE WATER-HOLDING CAPACITY of the soil profile at site 7.

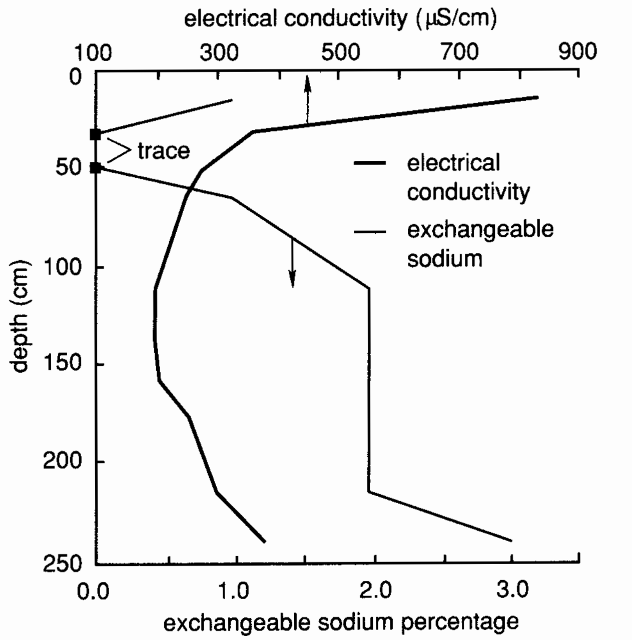

FIGURE 34—ELECTRICAL CONDUCTIVITY AND EXCHANGEABLE sodium percentage for the soil profile at site 7.

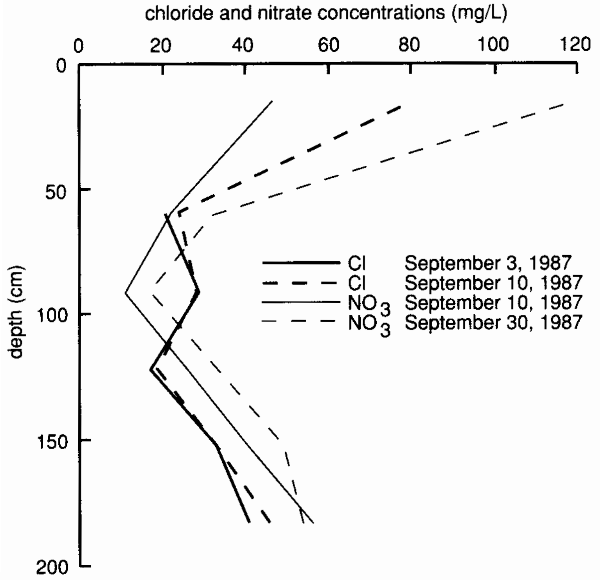

FIGURE 35—PROFILES OF CHLORIDE AND NITRATE CONCENTRATIONS from suction lysimeters before flooding at site 7.

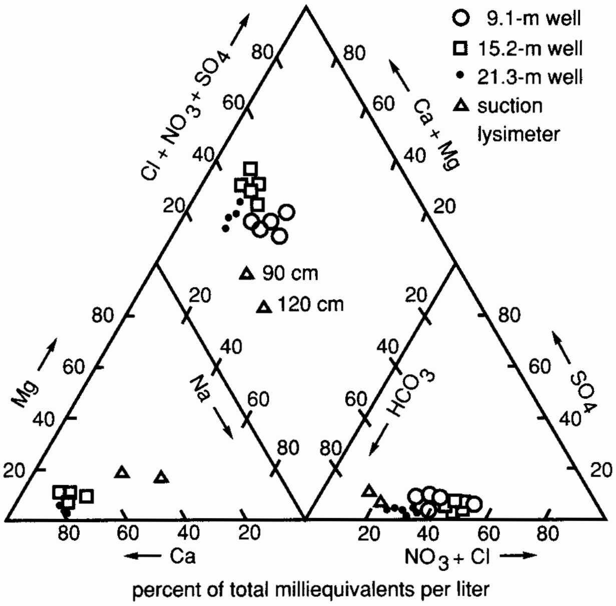

FIGURE 36—TRILINEAR DIAGRAM SHOWING WATER CHEMISTRY data for three wells and two suction lysimeters at site 7.

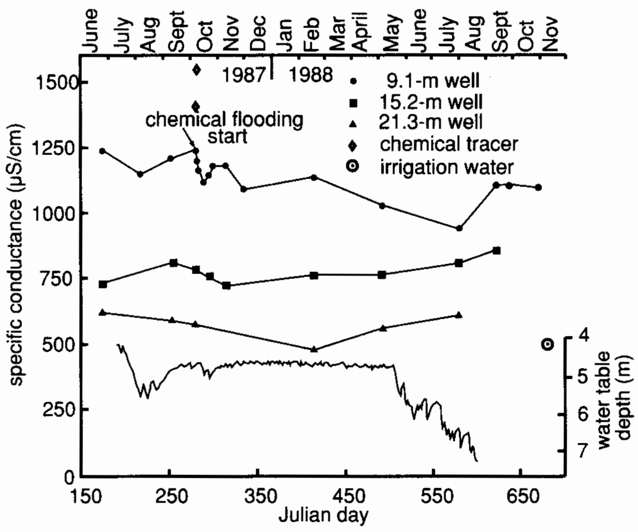

FIGURE 37—SPECIFIC CONDUCTANCE TIME-SERIES DISTRIBUTION of observation wells at site 7. Shallow water table is also shown.

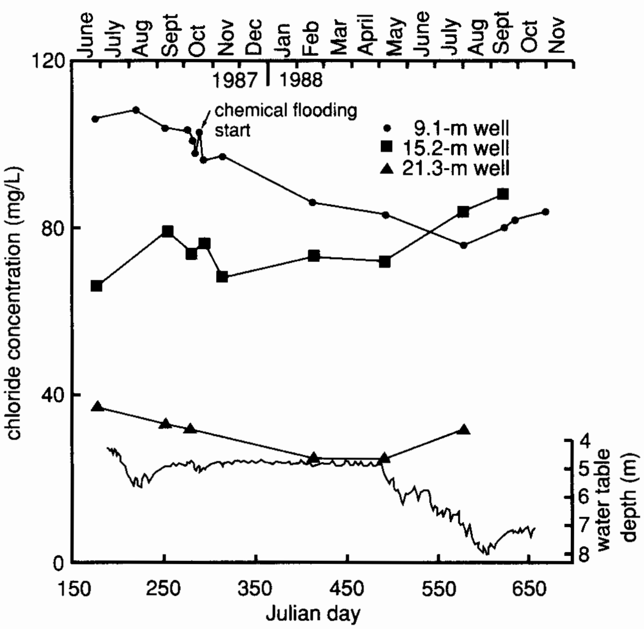

FIGURE 38—CHLORIDE TIME-SERIES DISTRIBUTION for observation wells at site 7. Shallow water table is also shown.

next section). Application of 1000 gal (3.79 m^3) of water may have caused a slight piston effect in that lower conductivity irrigation water (500 µS/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 5 days of flooding there was evidence that some of the higher-chloride-containing water, added during the chemical flood (specific conductance of 900 µS/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 site 7 nitrate was the inorganic constituent of most concern. The concentration of nitrate in all the observation wells reflects previous farming practices at the site and in the general vicinity of the site. There is little correlation between the irrigation at the site and the concentration found in the ground water. The increased nitrate concentration in the 9.1-m (30-ft) well at the time of the flooding experiment is probably related to a combination of macropore flow and piston-type flushing of preexisting nitrate in the deeper vadose zone. The fluctuation in the fall of 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 a drought period. High nitrate concentrations at the 120-, 150-, and 180-cm (4-, 5-, and 6-ft) depths in August 1988 (table C.2) indicate how slowly nitrate moves through the soil profile. The low nitrate values in September 1988 may indicate utilization of the nitrate by soybeans (the crop planted at the time) or 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 of most chloride and nitrate-nitrogen in an agricultural setting is usually from the concentration of salts in the soil zones resulting from evapotranspiration and from the fertilizers used on the field, respectively. 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 weight ratio is often used to estimate the role of denitrification for elimination of nitrate before the ion moves into the ground water (for references see the literature review on nitrate in appendix A). When the Cl/NO$_3$-N ratio becomes large, denitrification processes usually explain the decrease in nitrate. A low ratio indicates that

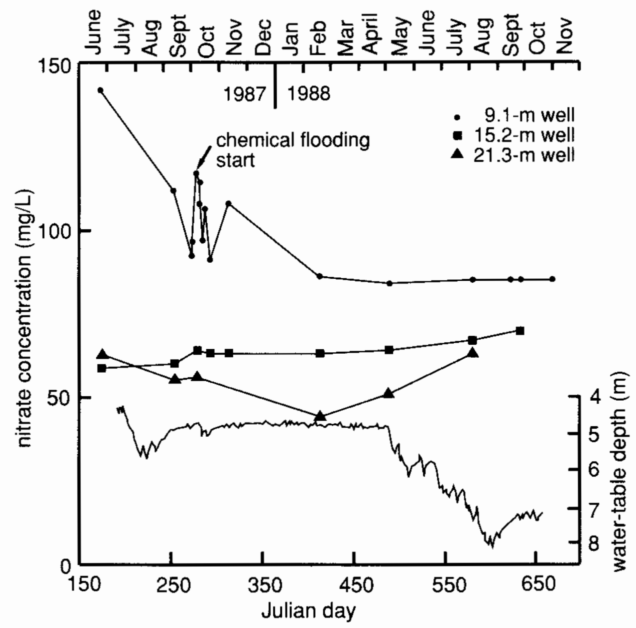

FIGURE 39—Nitrate time-series distribution for observation wells at site 7. Shallow water table also is shown.

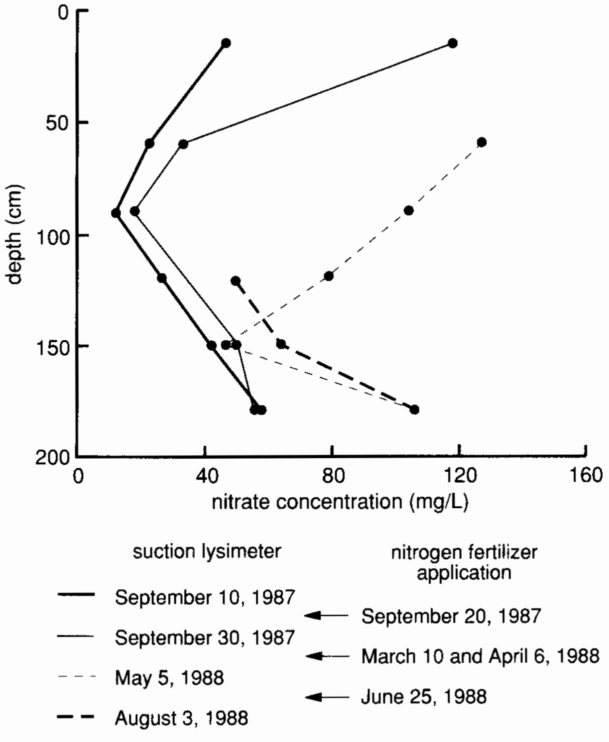

FIGURE 40—Nitrate concentration profiles from suction lysimeters during 1987 and 1988. Nitrogen fertilizer application dates are also indicated.

more nitrate than chloride is present and that more nitrate has moved through the vadose zone to the water table, causing an overall increase in ground-water nitrate concentration. During the study period, potassium chloride was added once (see table C.5). Other than dissolved salts in the soil zone, there was no additional source of chloride at this site.

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 and hence promote stratification between these wells. The Cl/NO_3-N ratio of 4.0–4.43 in the 9.1-m (30-ft) well may indicate rapid movement of chloride and nitrate into the subsurface with no possibility of denitrification occurring. The Cl/NO_3-N ratio of 5.0 or greater, shown in the 15.2-m (50-ft) well (top line in 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 through denitrification. The ratio for the 21.3-m (70-ft) well is somewhat anomalous; it is lower than the ratio for the 9.1-m (30-ft) well. Examination of table C.2 shows that the 21.3-m (70-ft) well generally has lower chloride values than the other two wells and is similar to the irrigation well water [at 33.5 m (110 ft)] at the site. The Cl/NO_3-N ratio for the irrigation well is 5.0 because of slightly higher chloride than nitrate concentrations (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.

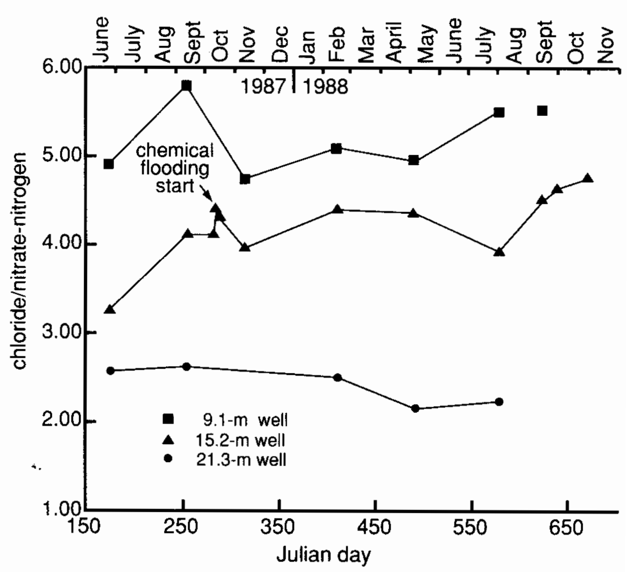

FIGURE 41—Chloride/nitrate-nitrogen ratio time-series distribution for observation wells at site 7.

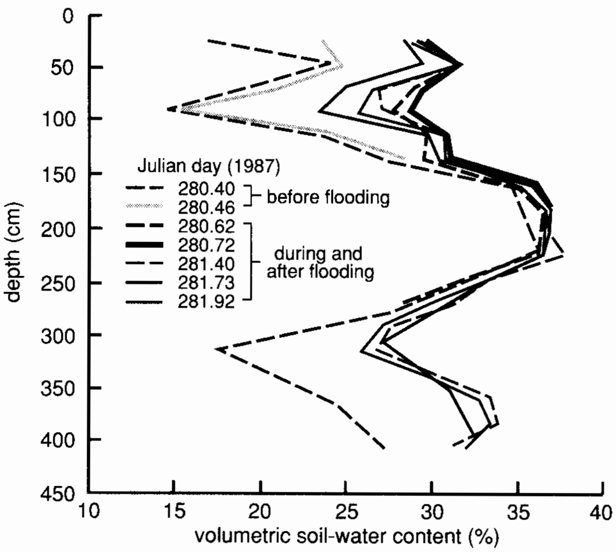

FIGURE 42—Soil-water profiles before and during flooding at site 7.

Chemical flooding

Because of the much sandier nature (and the expected higher hydraulic conductivity under wet conditions) of the soil profile at site 7 compared with site 6, the site was not flooded with Stafford municipal water before applying the chemical solution, as was done at site 6. Instead, 3.79 m^3 (1000 gal) of chemical solution of the same composition as that used at site 6 was used to flood the site after prewetting the perimeter. The flooded area was nearly rectangular and enclosed 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 flooding and immediately after flooding is shown in fig. 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 (65–95 in) was wet throughout the study period and did not show much change during flooding; 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-in) depth intervals since covering the site with plastic, shown in fig. 43, indicate soil-water drainage down to the 380-cm (150-in) plotted depth. The clayey layer from 165 cm to 240 cm (70–95 in) did not show any significant drainage.

Figures 44, 45, and 46 show the instantaneous profile analysis results for 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 that the water content decreases much more with an increase in capillary pressure or suction than the more clayey site 6. The sandier texture of site 7 is also reflected in higher saturated hydraulic conductivities compared with site 6 (fig. 45).

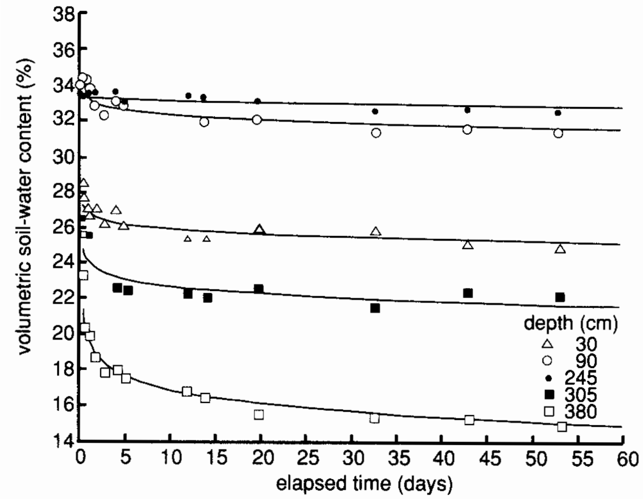

FIGURE 43—Soil-water content drainage curves for five depths at site 7. The curves were derived by means of a least-squares fit using a drying model.

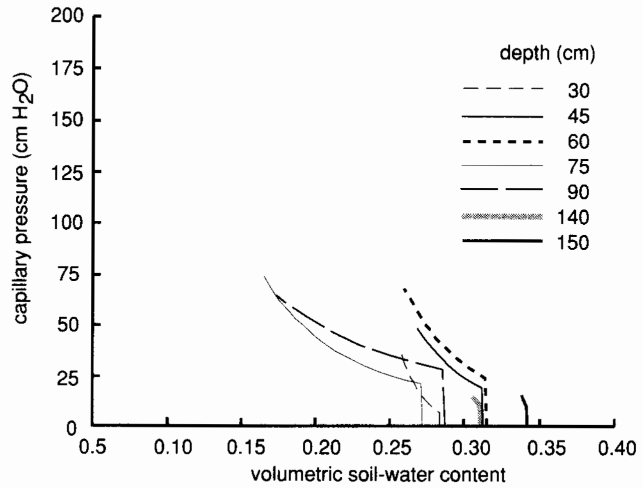

FIGURE 44—Field-measured water-retention curves for site 7.

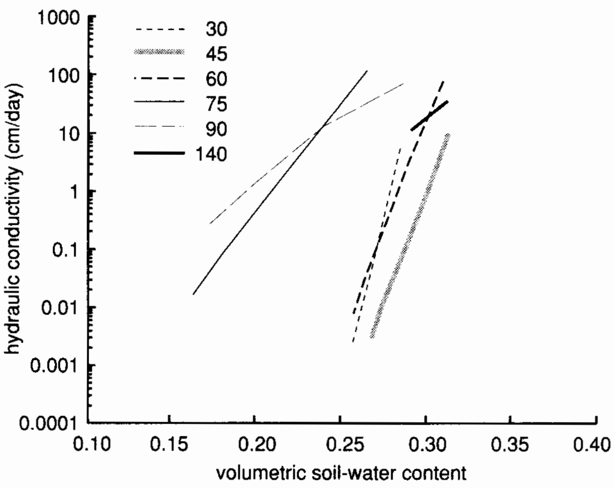

FIGURE 45—Hydraulic conductivity curves derived by means of the instantaneous profile technique for site 7.

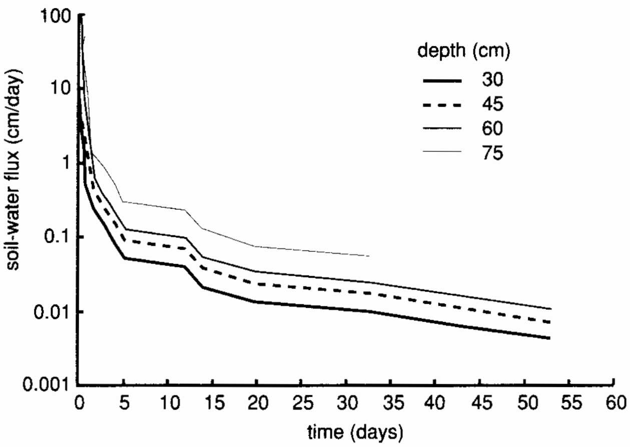

FIGURE 46—Soil-water flux time distributions (for 1987) derived by means of the instantaneous profile technique for site 7.

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 two 1.89-m^3 (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 floodwaters acts as a minor tracer.

After the chemical flood solution was added, the chloride concentrations increased when the slug of actual floodwater reached the sampled depth (fig. 47). Chloride concentrations in samples from the shallowest lysimeter were above the chloride concentration in the floodwater, 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 a value near that in the flood solution. However, the rate of chloride increase resulting from the movement of floodwaters was not uniform with depth and time, suggesting that preferential flow through macropores and fractures in the soil occurred. The chloride concentration 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 concentrations were probably related to changing conditions resulting from irrigation and evapotranspiration at the site. The results indicate that movement of the chemical floodwaters and later irrigation waters exerts more control over chloride concentration 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 (see figs. 37 and 38). Changes in specific conductance and chloride just after 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 flooding to about 1 year after flooding. Thus no substantial salt displacement occurred at this site in contrast to site 6. Apparently there was no appreciable accumulation of salts in the unsaturated zone between the section of soil sampled by the lysimeters and the water table. The greater permeability of the unsaturated zone and the lower dissolved solids concentration of the irrigation waters are probably the main reasons for the smaller salt accumulation at site 7 than at site 6.

Bromide

Bromide versus time breakthrough curves through the soil profile are shown in fig. 49. The bromide tracer concentrations for the two 1.89-m^3 (500-gal) portions of the chemical floodwaters were 430 mg/L and 457 mg/L, giving an average bromide concentration of 444 mg/L. The added bromide penetrated to all site 7 soil depths sampled by the lysimeter within 1.3 days after flooding began, as indicated by bromide concentrations that were at least 50 times the background level. Sampling problems similar to those described 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 shows a sigmoidal distribution with peaks at the uppermost lysimeter depth [15 cm (0.5 ft)] and at the 120-cm (4-ft) depth (fig. 50). Such a distribution indicates preferential flow, whereby diffuse flow through porous media is bypassed by flow through macropores, resulting in higher tracer concentrations at depth than normally expected. A plot of water content versus depth (fig. 51) has several peaks that approximately match the observed bromide peaks in fig. 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.

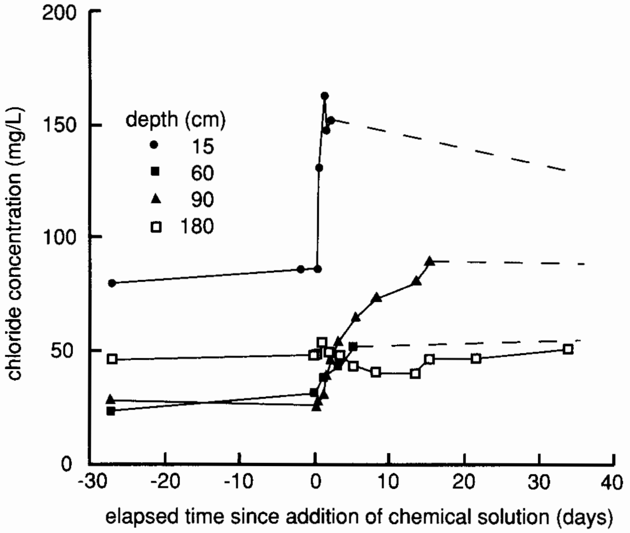

FIGURE 47—Chloride time-series distribution from suction lysimeters before, during, and after flooding at site 7.

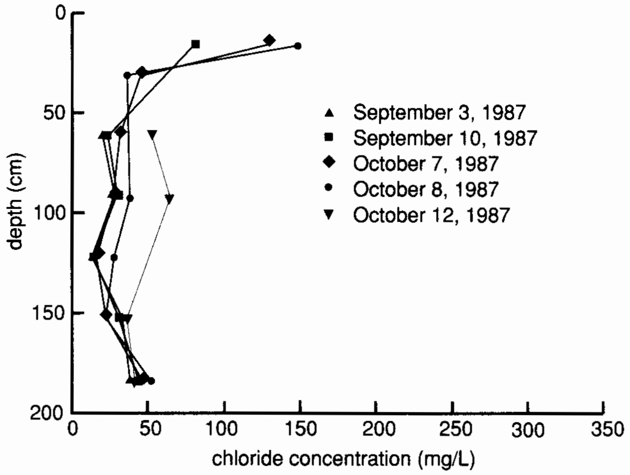

FIGURE 48—Profiles of dissolved chloride sampled from suction lysimeters before, during, and after flooding at site 7.

Bromide concentrations in water sampled by the shallowest lysimeter reached a peak two days after flooding (see 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-cm and 90-cm (2-ft 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 generally were still increasing slowly after a year after chemical flooding, indicating the great persistence of soil solutions in the profile. The maximum tracer concentrations observed to date for all lysimeter depths would show a general persistence in the sigmoidal pattern of fig. 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 solutions 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.

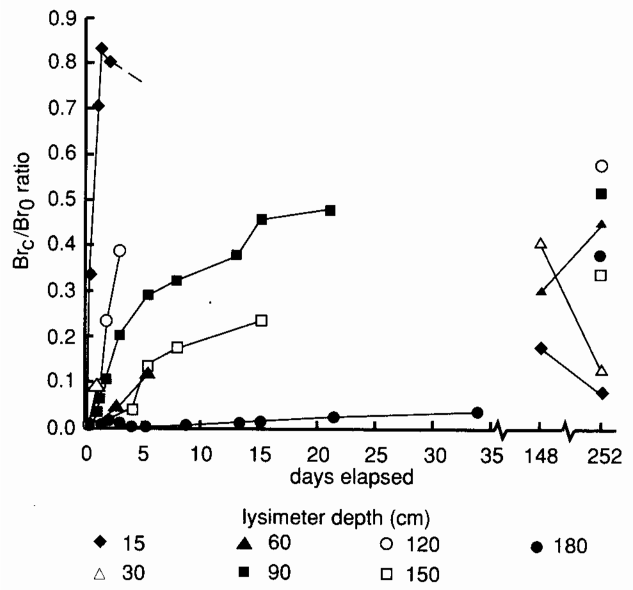

FIGURE 49—BROMIDE CONCENTRATION BREAKTHROUGH CURVES based on suction lysimeter sampling for site 7. Bromide is expressed as a ratio of bromide corrected for background levels (Br_c), over bromide tracer concentration in the flooding solution (Br_0).

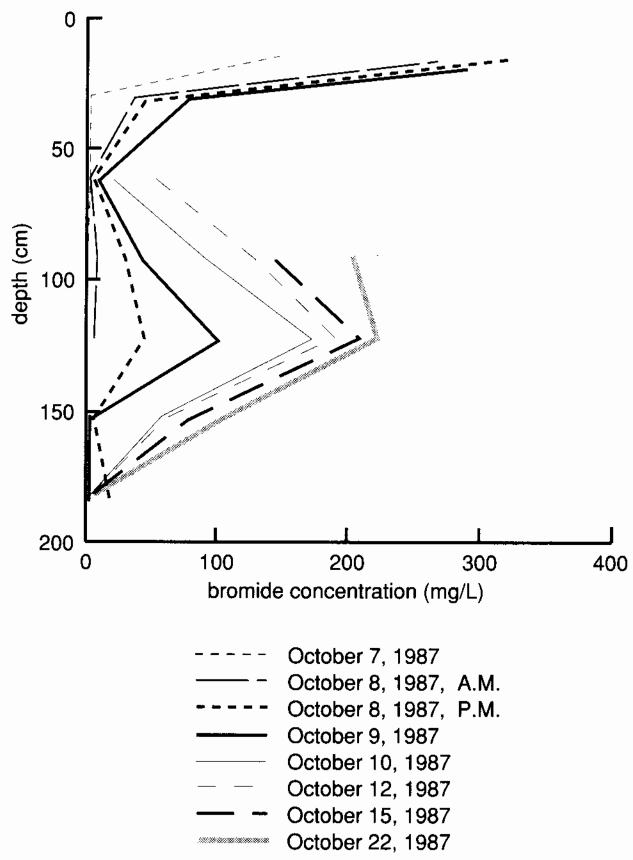

FIGURE 50—BROMIDE CONCENTRATION PROFILES SINCE CHEMICAL flooding was initiated at site 7.

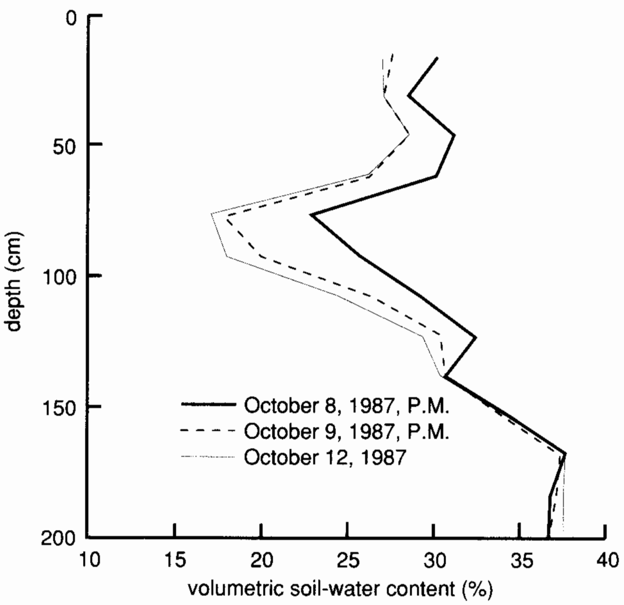

FIGURE 51—SOIL-WATER CONTENT PROFILES SINCE CHEMICAL flooding was initiated at site 7.

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, a 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 the presence of atrazine 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 atrazine below the upper 15-cm (0.5-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 (see fig. 50).

The soil core data exhibit extreme variability within the flooded area, and reliable breakthrough curves could not be ascertained (fig. 53). This spatial variability probably indicates 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 5 days after flooding and no detectable atrazine was found at the 135–150-cm (54–60-in) depth level. The vertical distribution of atrazine in the soil shows a sigmoidal bimodal distribution (fig. 54), with peaks at the 15-cm (0.5-ft) and

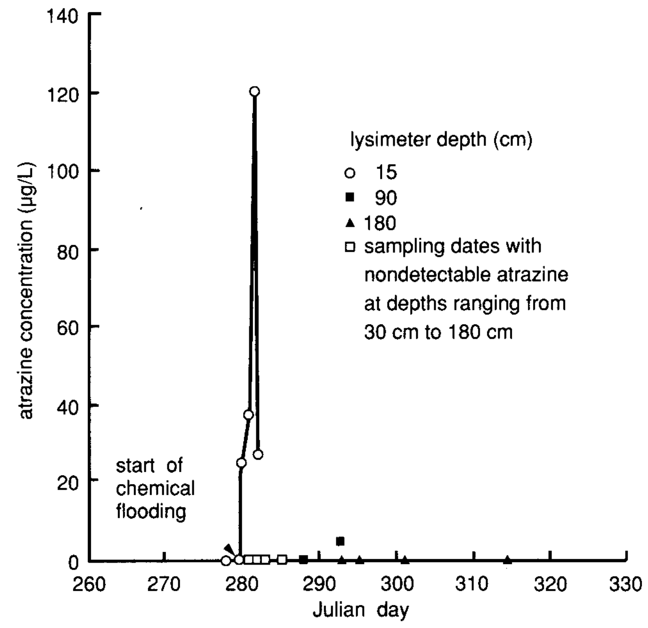

FIGURE 52—ATRAZINE BREAKTHROUGH CURVES FOR SITE 7 based on suction lysimeter sampling.

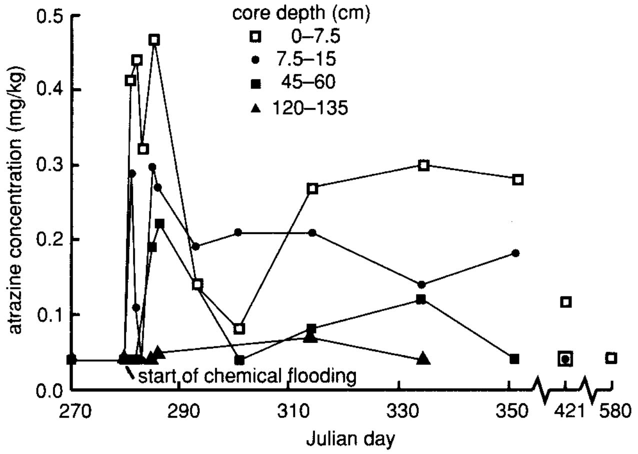

FIGURE 53—ATRAZINE BREAKTHROUGH CURVES FOR SITE 7 based on soil cores. Detection limit is 0.04 mg/kg.

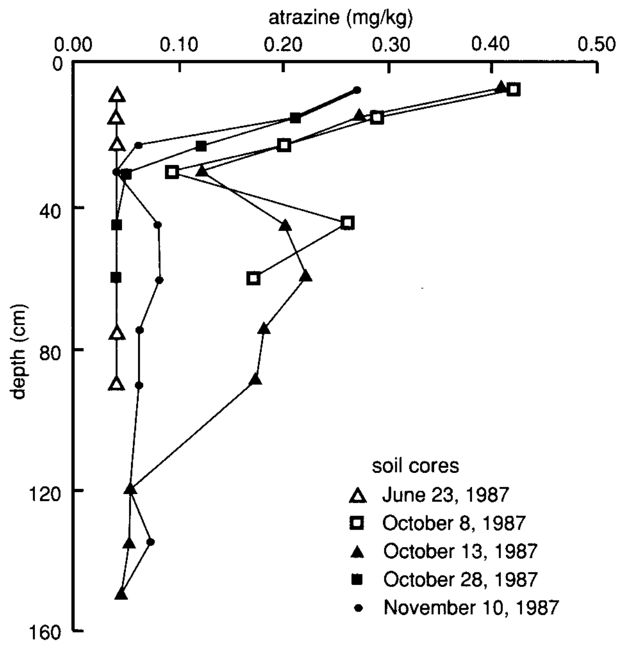

FIGURE 54—ATRAZINE PROFILES AT SITE 7 based on soil cores.

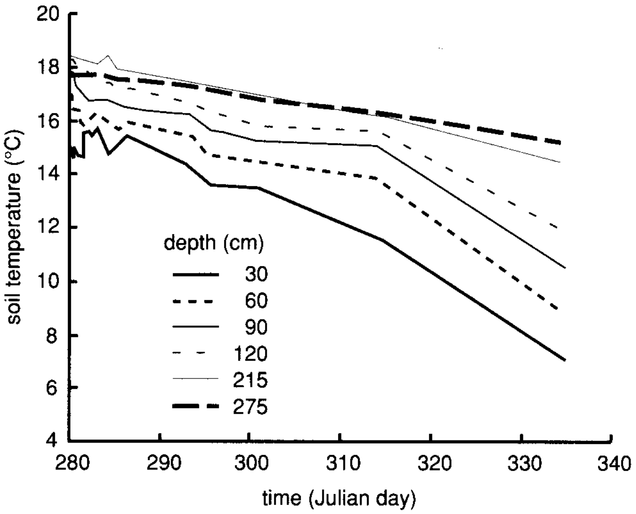

FIGURE 55—SOIL-TEMPERATURE TIME-SERIES DISTRIBUTION for six depths at site 7.

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 chemically analyzed 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. The results of all atrazine degradation by-product analyses are tabulated in appendix E. Dealkylated by-products, indicative of biodegradation, were found below the detection limit (0.05 mg/kg), as was 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 hydrolysis of atrazine still takes place, even in soils with only slightly acidic conditions (see fig. 33), low organic matter contents, and low CEC (see fig. 30). As was done at site 6, additional soil samples collected in August 1988 were sent for atrazine metabolite analyses, especially to check for biodegradation by-products. The results showed appreciable amounts of both ethylatrazine and isopropylatrazine (appendix E), indicating microbial decomposition of atrazine.

The soil profile temperatures during the flooding experiment (October–November 1987) are shown in fig. 55. The soil temperature increases with depth but decreases with time. However, the temporal temperature decreases at a lower rate compared to site 6 (see 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 (see fig. 33), compared to site 6, are the apparent reasons for the deeper penetration of atrazine to the 120–135-cm (48–54-in) level. It should also be noted that, similar to site 6, no atrazine was observed in the shallow or deeper observation wells of site 7.

Site 10

Soil profile and physical and chemical characteristics

Site 10 is located in Edwards County on the Great Bend sand plains. The soil at this site is known to be of eolian origin and was sampled as Pratt soil. The classification of this soil based on SCS laboratory data is Alfic Ustipsamments. The profile consists of brown to pale-brown loamy fine-grained sand down to 42 cm (17 in), making up the A horizon. The upper portion of this horizon is characterized by a weak medium granular structure, whereas the lower part has a massive structure; the upper and lower parts are separated by a clear wavy boundary. The next horizon is a C zone of light yellowish-brown loamy, fine-grained sand of massive structure to a depth of 92 cm (36 in) with an abrupt wavy boundary. Below this layer is an AB horizon from 92 cm to 105 cm (36–41 in) composed of brown loamy, fine-grained sand of massive structure with 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-grained sand with massive structure and a lamellar lens 1 cm (0.4 in) thick. Zone C2 [117–145 cm (46.1–57.1 in)] is a light yellowish-brown fine-grained sand of loose, friable structure with 2 lamellar lenses 1 cm (0.4 in) 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-grained sand of massive structure. Zone C5 [183–222 cm (72.0–87.4 in)] is a yellowish-brown loamy, fine-grained sand with massive structure that is finely stratified in the upper part and has 0.5-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-grained sand of massive structure with fine stratification.

The specific soil horizons and their grain-size distribution (texture), as determined by the SCS, are shown in fig. 56. The sand fraction dominates throughout the profile, and the clay and silt fractions are only minor components of the soil. The organic carbon content of the soil is low, indicating that the soil does not have much potential for retention of chemicals (fig. 57). The electrical conductance for the soil profile is also low, indicating that no appreciable concentration of salts has occurred.

Water chemistry

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 content 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 showed much higher total dissolved solids values throughout the period of study. These higher concentrations illustrate the concentrating effects that evapotranspiration has on salt 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:

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

where C is the solute concentration in the liquid phase [M/L^3], s is the adsorbed mass 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], ρ_b is the soil bulk density [M/L^3], 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 and θ is the volumetric water content), x is the distance [L], t is time [T], and μ 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

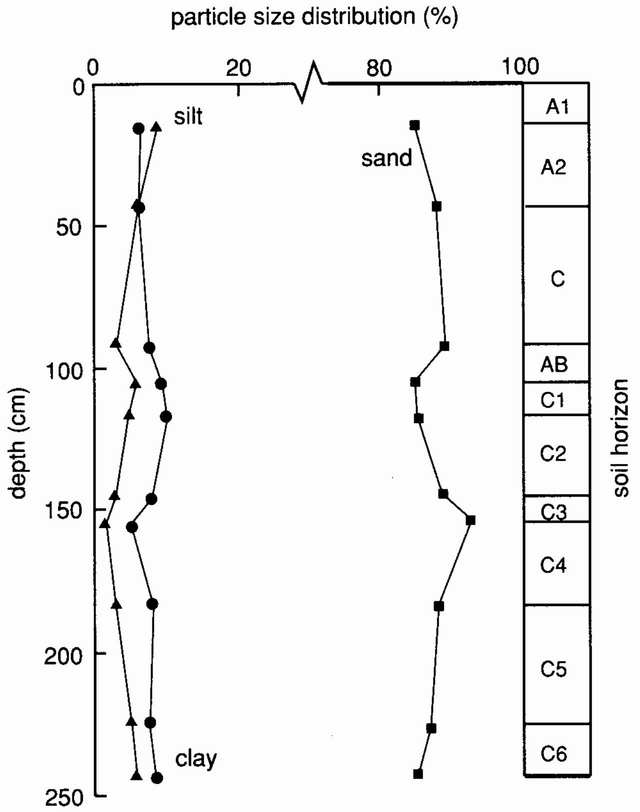

FIGURE 56—GRAIN-SIZE DISTRIBUTION AND SOIL HORIZONS FOR site 10.

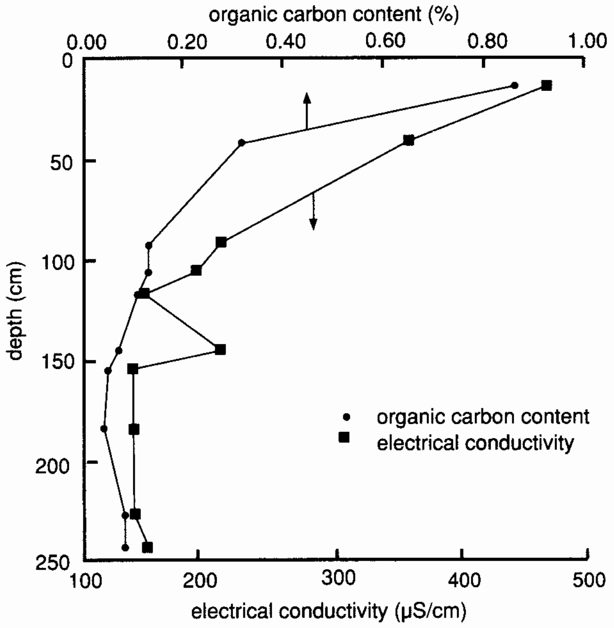

FIGURE 57—ORGANIC CARBON CONTENT AND ELECTRICAL conductivity for site 10.

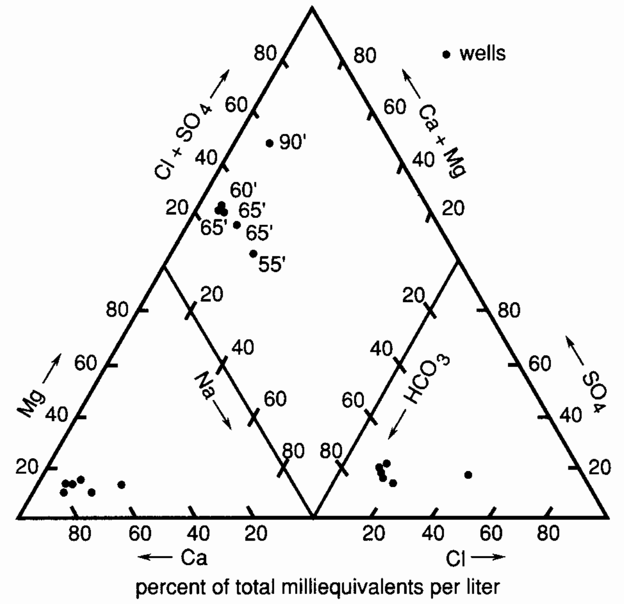

FIGURE 58—TRILINEAR DIAGRAM SHOWING WATER CHEMISTRY data for three wells at site 10. Numbers next to points indicate depths (in feet).

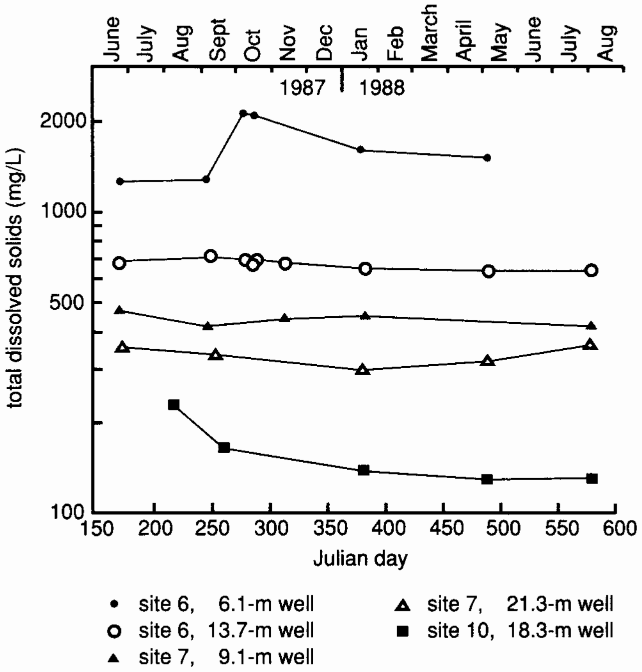

FIGURE 59—TIME-SERIES DISTRIBUTION OF TOTAL DISSOLVED solids for the shallowest and the deepest observation wells at sites 6 and 7 and for the shallow observation well at site 10.

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

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

Assuming that local equilibrium conditions exist, substitution of Eq. (2) into Eq. (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

$$R = 1 + (\rho_b k/\theta). \tag{4}$$

For a mobile, nonreactive chemical, such as bromide, $R = 1$ and $\mu = 0$, and Eq. (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 a uniform initial concentration C_i, a pulse-type boundary condition at the soil surface, and a semi-infinite ($0 \le x < \infty$) bottom boundary condition:

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

$$\left(-D\frac{\partial C}{\partial x} + vC\right)\Bigg|_{x=0} = \begin{cases} vC & 0 \le t < t_0 \\ 0 & t \ge t_0 \end{cases}, \tag{6b}$$

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

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, by using mean values for Darcian flux and profile water content, the steady-state solution to the convection-dispersion Eq. (5) 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 Eqs. (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), that is, the ratio of the solute flux to the volumetric fluid flux. We used the least-squares regression method described by Parker and van Genuchten (1984a) to fit the curves of the analytical solution of Eqs. (3), (5), and (6) to the observed data for the suction lysimeters and the 1-in (2.5-cm) diameter cores collected at different times during the experiment. To optimize the unknown (or partially known) parameters v, D, R, m, and t_0 in Eqs. (3) and (6) from observed temporal and spatial concentration data, we used the Parker and van Genuchten (1984a) CXTFIT program. 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 there is a significant difference in calculated parameter values that depends 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 convection-dispersion 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 Eq. (3) or (5). In using the convection-dispersion model [Eq. (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 partly successful approach to describing 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). Convection-dispersion transport is confined to the mobile water phase, and solute movement into and out of the immobile water is assumed to be a relatively slow diffusion-controlled process; these combined processes result 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 symmetric 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 Wösten (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 results.

TABLE 3—Fitted model parameters for bromide collected from suction lysimeters.

Site	Sampling date	v (cm/d) ± std. error	D (cm^2/d) ± std. error	t_0 (day) ± std. error	R^2	Number of samples
6	Sept. 18, 1987	13.52 ± 0.17	19.20 ± 1.82	2.43 ± 0.03	0.9998	6
7	Oct. 8, 1987	15.65 ± 1.12	19.76 ± 8.29	1.61 ± 0.00	0.9875	7

As a result of the discrepancies of the convection-dispersion equation vis-à-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 of concentration-depth distributions generally fits 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 $R = 1$. The two sampling dates used in the table had the most complete suction lysimeter data. Although the chemical solution at both sites was applied for approximately one day at the surface, our shallowest suction lysimeter was at a depth of 15 cm (0.5 ft). Thus the exact duration of the applied pulse relative to the sampling port location is somewhat ambiguous, and the pulse duration was treated as an unknown parameter in this study.

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 (see 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, three days after the chemical solution was applied at the site.

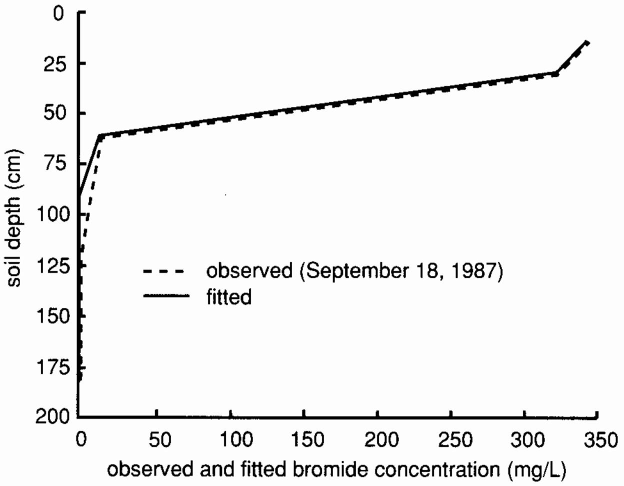

FIGURE 60—Observed (dashed line) and fitted (solid line) flux-averaged bromide concentrations with depth for site 6. The observed data were taken on September 18, 1987.

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. [Clay layers sampled during trench excavation on August 4–6, 1987, from cropland sites in Pawnee County (sec. 14, T. 23 S., R. 15 W., Carwile soil; samples for atrazine analysis taken from 38–52 cm, 52–92 cm, and 111–123 cm [1.2–1.7 ft, 1.7–3.0 ft, and 3.6–4.0 ft]), Edwards County (sec. 5, T. 24 S., R. 16 W., Naron soil; samples for atrazine analysis taken from 43–68 cm, 68–91 cm, and 146–161 cm [1.4–2.2 ft, 2.2–3.0 ft, and 4.8–5.3 ft]), Pratt County (site 7; samples for atrazine analysis taken from 32–50 cm, 135–157 cm, and 157–167 cm [1.0–1.6 ft, 4.4–5.2 ft, and 5.2–5.5 ft]), and Stafford County (site 6; samples for atrazine analysis taken from 48–66 cm and 66–77 cm [1.6–2.2 ft and 2.2–2.5 ft]) revealed no detectable atrazine at a detection limit of 0.04 mg/kg.] 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 two weeks. We also have evidence of biodegradation by-products, indicating that both biologic and chemical degradation occur in the soil profile. Based on the results of this study, the probability that atrazine will leach through the soils to the underlying aquifer in the Great Bend Prairie under present conditions seems remote.

The nitrate data from the suction lysimeters at 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 contents than the nonirrigated site 10.

Chemical transport analysis at sites 6 and 7 indicates that the classical processes of chemical movement based on equilibrium conditions and diffuse flow through porous media 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 slug flow. As a result of 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 might 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, predominated. 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 flow through porous media 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-ft) 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) leakage along the side walls of the lysimeter cannot be verified and quantified; (c) they do not work under freezing conditions; (d) even if they do work, one may not obtain a sample because of soil dryness; and (e) the obtained samples may not represent true soil conditions because vacuum application dries up the area in 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 we recommend using both soil cores and suction lysimeters (preferably maintained at constant vacuum) 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 laboratories 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 under 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 persists in the subsoil and then leaches 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 (0.2–0.8 µg/L), but the persistence suggests that degradation is slow once the chemical arrives in the aquifer (Wehtje et al., 1981, 1983; Junk et al., 1980). Stratification of atrazine in wells down-gradient from irrigated corn fields in Nebraska reveals an essentially non-point-source distribution.

The U.S. Department of Agriculture reports that 10.6 million tons of nitrogen fertilizer is 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 was an eightfold increase in the use of all classes of fertilizers. In Kansas 500,000 tons of nitrogen fertilizer was 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 Kansas farmstead wells (used for domestic and farm purposes), Heiman et al. (1987) showed that 3% of the wells had atrazine but that 28% had nitrate levels above the recommended level of 45 mg/L as nitrate. Their study suggested that wells in northeast, north-central, and south-central Kansas had a higher probability of nitrate contamination than those in 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 to the number 2 carbon atom of a triazine ring (composed of three nitrogen atoms and three carbon atoms with double bonds at the 2, 4, and 6 positions of the ring; fig. A.1), the ethylamino group ($-NH-C_2H_5$) is attached to the number 4 carbon atom, and the isopropylamino group ($-NH-C_3H_7$) is attached to the number 6 carbon atom (Hassall, 1982; Sheets, 1970; 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 chlorine 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), the charge distribution on the organic molecule, and the shape and configuration of the molecule (Bailey and White, 1970; Sheets, 1970). Various researchers have reported conflicting results on whether the solubility of the compound has a primary influence on movement through or adsorption onto 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 adsorb the tightest to montmorillonite. The triazines and their relative solubilities in order of decreasing adsorption capability are simetone (3200 mg/L), atratone (1654 mg/L), prometone (750 mg/L), atrazine (33 mg/L), trietazine (20 mg/L), and propazine (8.6 mg/L). Rodgers (1962) found a distinct lack of correlation between solubility and leachability. He also found that soil type can alter the order of leachability of triazines. In his studies, atrazine, with a solubility of 33 mg/L, moved farther than simazine (5 mg/L), atratone (1654 mg/L), or ipatone (100 mg/L). 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 the 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 catalyzed by 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 herbicidal characteristics. 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 onto montmorillonite-type clays depends on the surface acidity on the clay, not on the pH of the suspension.

Armstrong and Chesters (1968) and Harris (1967) also emphasize the role of catalysis resulting from adsorption onto 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 nitrogen 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 ≈ 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 nucleophilic H_2O to replace the chlorine.

Skipper et al. (1978) indicated that under acidic field conditions smectite-type clays are expected to enhance the chemical hydrolysis of atrazine. Russell et al. (1968) indicated 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, the atrazine degradation rate increases 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 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 60 µmol/L atrazine mixed with 0.2 g humic acid per 10 ml H_2O decomposed much faster than it did in solutions without 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.

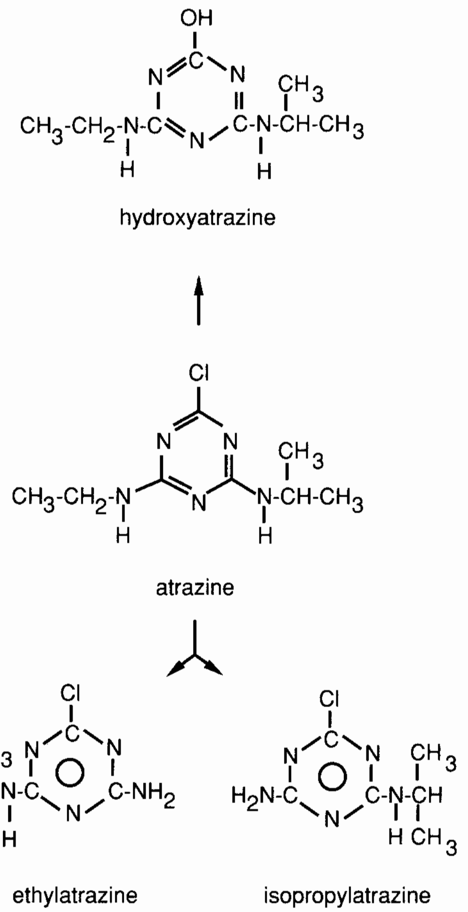

FIGURE A.1—STRUCTURE AND NOMENCLATURE FOR ATRAZINE and its degradation by-products.

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

Biologic degradation

Biologic degradation of atrazine results in two daughter products: deethylated atrazine (2-chloro-4-amino-6-isopropylamino-*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 (pH = 7) composed of 32% clay and 4.8% organic matter; the CEC was 22.8 meq/100 g. The pH is much higher than the pH found in studies of chemical hydrolysis (pH = 3.5–4.5). Sirons et al. (1973) failed to detect hydroxyatrazine in their products, leading them to believe that microbial degradation was the primary pathway. Most studies involving microbial degradation of atrazine use soils in the neutral to alkaline pH range (Sheets, 1970).

The effects of temperature are also important. Harris and Warren (1964) indicated that adsorption of atrazine increases with decreasing temperature, atrazine being more available 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 (Sheets, 1970). Roeth et al. (1969) found that chemical hydrolysis occurs 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.

Sheets (1970) best summarizes the debate on chemical and biologic degradation. 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 temperatures and low moisture levels are unfavorable for both routes of breakdown. Physical characteristics of the soil, aeration, amount of inorganic and organic nutrients, and quantity of clay and organic matter also play major roles in determining which process 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, agricultural practices (type of tillage used, for example), 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). Models, field experiments, and laboratory studies indicate 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 percentage of organic matter in the soil are two primary controls in the breakdown process of herbicides. Armstrong et al. (1967) indicated that hydrolysis of atrazine (replacement of the chlorine atom attached to the number 2 carbon atom in the triazine ring with a hydroxyl group) into the hydroxyatrazine daughter product is controlled by pH and the percentage 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 the section on chemistry of atrazine).

Hiltbold and Buchanan (1977) found that with each unit increase in soil pH atrazine persisted 9–29 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 have high organic matter and clay contents and is highest in light-textured soils. Burnside et al. (1963) found that atrazine leaches the most in sandy soils with low organic matter content and pH of 6.8 and least in soils with high clay and organic matter contents and low pH. Soils with low pH tend to cause increased adsorption onto clays or organic matter and thus encourage chemical hydrolysis (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 and 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 a 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 onto 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 that 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 researchers 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 occurs with the mineral system. The percentage of recovery of atrazine from humic acid increases when the pH increases to 7 but is small when the pH is low.

Dao and Lavy (1978) found that increased temperature results 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 researchers have found. Hayes (1970) found that more atrazine is adsorbed at low temperatures (20°C) than at high temperatures (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-grained 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. Only 0.07% of the chemical applied reaches the aquifer. The researchers postulate that the rest is removed by chemical hydrolysis.

Nitrate

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

$$NH_4^+ + \tfrac{3}{2}O_2 \rightarrow NO_2^- + 2H^+ + H_2O. \qquad (A.1)$$

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, to nitrogen gas, or even to ammonium ion. 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 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 are measurable differences between irrigated areas with non–point sources of contamination, areas with point-source contamination (such as septic systems or feedlots), and areas with pristine ground water. Additional evaluation of the water chemistry from areas with non-point-source contamination 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 salts (KCl and K_2SO_4), and sulfamag ($MgSO_4$–K_2SO_4). The positive correlation between sulfate and nitrate and between chloride and 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

Hurlburt (1988), in a feature article in a recent issue of *Water Well Journal*, used interviews with various investigators to discuss the problem of nitrate contamination in ground water. Researchers in Canada, Arizona, and Nebraska all indicate that agricultural use of nitrogen fertilizers may be a major contributor to 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 subsurface karst. There is a direct correlation between 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 (18 m) through fine-grained sediments and that up to 1200 lb (540 kg) nitrogen per acre had accumulated in the vadose zone beneath a test site treated with 400 lb (180 kg) nitrogen per acre per year. The storage of this amount of nitrate in fine-grained sediments indicates probable future non-point-source nitrate contamination 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 spatial 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 denitrification.

A survey of nitrate-nitrogen concentrations 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 levels 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 that the concentration of nitrate in the soil beneath the irrigated site was an order of magnitude higher than the concentration at the native rangeland site (Hergert, 1982). In another study in Nebraska on management of nitrogen in sandy soils, Hergert (1978) 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 susceptible to leaching (nitrate movement). Two keys for nitrogen management in sandy soils were offered: The quantity of nitrogen applied must be adjusted 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

Geologic nitrate-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 migration to ground water (Boyce et al., 1976). Boyce et al. found nitrate at depths of 7–30 m (23–98 ft). Nitrate-nitrogen values ranged from 25 mg/kg to 45 mg/kg but values up to 87 mg/kg (5.6 tons/acre to 91-ft depth) have been reported. 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, generation of nitrate in surface soils during periods of drought in which nitrification rates were greater than plant uptake and after which leaching occurred, and fixed ammonium released and nitrified over the recent geologic past.

Strathouse et al. (1980) in the San Joaquin Valley of California 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 of nitrogen. Total nitrogen and nitrate concentrations increased from older to younger geologic sediments. The other basin consisted of coarse clastic sediments with a high total nitrogen concentration; the nitrogen 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 and soil and water conservation practices, such as terracing, has caused increased movement of nitrate in dryland farming areas of Texas, Nebraska, and California.

Nitrate and chloride profiles as indicators of movement

Various researchers 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. Others 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 what follows. Investigators who use the ratio method for determination of denitrification processes usually deal with either 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/d (16–18 in/d) under a 2.5-cm (1-in) 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 spatial 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 (30 m) 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 indicates that fine-grained and vadose sediments do not adequately prevent contamination of ground water. Spalding and Kitchen (1988) showed that in 15 years nitrate moved vertically at least 60 ft (18 m) through fine-textured unsaturated sediments in Nebraska.

Smith and Davis (1974) showed that bromide and nitrate move at similar rates unless some denitrification 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 is not similar as a result of mineralization of the nitrogen or denitrification. In the subsoils the breakthrough curves for both anions are similar. Autoclaving the surface soils results in breakthrough curves similar to those for the subsoils, 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 nitrate loss. Because both nitrate and chloride are anions, 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, the 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 with coarse-textured sandy soils and three sites with fine clayey soils. Soil-moisture samplers were used to collect the water. The coarse-textured soils had high redox potentials throughout and low denitrification potential. Nitrate moved downward in these profiles as a result of irrigation. The Cl/NO_3-N ratio for the coarse soils was fairly constant with depth, indicating that the primary source of 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 by denitrification. 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 concentrations were significantly higher than background levels. 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. Saffigna and Keeney 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 Cl/NO_3-N ratio 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 in 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 effect on the ratio and the movement of nitrate into the aquifer.

Appendix B: Chemical analysis methodology

Determination of atrazine in soil

Reference method 3550 was used to determine the concentration of atrazine in soil. The method is described by the U.S. Environmental Protection Agency (1986b). Analyses performed according to this method use 50.0 g of sample, which 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 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 set specifically for atrazine.

Determination of atrazine in water

Reference method 507 was used to determine the concentration of atrazine in water. The method is described by the U.S. Environmental Protection Agency (1986a). In this 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 testing positive for atrazine are reconfirmed and quantitated using a Hewlett Packard (HP) 5890A Gas Chromatograph with an HP 5970 Mass Selective Detector in the single-ion monitoring mode set specifically for atrazine.

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

Reference method CHR–2.1 was used to determine the concentration of atrazine and its metabolites in soil. The method was developed by the Minnesota Valley Testing Laboratories (1986a). In this method atrazine and its dealkylated metabolites are extracted from soil by refluxing with a solution of acetonitrile and 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 mg/kg of soil.

Determination of hydroxyatrazine (G–34048) in soil

Reference method CHR–3 was used to determine the concentration of hydroxyatrazine in soil. The method was developed by the Minnesota Valley Testing Laboratories (1986b). In this method hydroxyatrazine is extracted from soil by Soxhlet extraction using a solution of methanol and water (80:20). The extract is cleaned by solvent partitions and column chromatography to remove nonpolar triazines and other interferences. The final aqueous solution containing the hydroxyatrazine is chromatographed by using paired-ion reversed-phase high-performance liquid chromatography. Residues are quantitated by ultraviolet absorption at 240 nm. The method is sensitive to 0.05 mg/kg of soil.

Bromide determination

We used an automated colorimetric method to measure bromide concentration in water. In earlier determinations in our study we had followed the automated phenol red method involving segmented-flow analysis described by Basel et al. (1982) and further modified by Whittemore (personal communication, 1987). For later measurements we used the automated fluorescein method of the U.S. 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, a proportioning pump, an appropriate analytical cartridge, a spectrophotometer, and a 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 µg/L.

Inorganic analyses

The inorganic analyses (except bromide determination) were performed by the Analytical Services Section of the Kansas Geological Survey. The calculated standard deviation in the analytical methods is based on individual duplicate analyses of water samples collected in the Equus beds region of Kansas in 1980 (Hathaway et al., 1980). Duplicate samples were not collected for the current study.

Initial nitrate concentrations were obtained using ultraviolet absorption spectroscopy with an analytical error of ±3–4 mg/L (L. R. Hathaway, personal communication, 1988). Once the initial level was established, we used standard colorimetric autoanalyzer techniques to determine nitrate

(±0.2 mg/L), sulfate (±1.5 mg/L), chloride (±2.1 mg/L), and sometimes phosphate (±0.03 mg/L) and ammonia concentrations. Cations (Ca^{2+}, ±0.08 mg/L; Mg^{2+}, ±0.04 mg/L; Na^+, ±2.2 mg/L; K^+, ±0.2 mg/L) were measured with a Jarrel–Ash inductivity-coupled plasma (ICP) unit, and bicarbonate (±0.4 mg/L) was measured by potentiometric titration using an autotitrimeter. We measured pH at the same time. Specific conductance (1 1 µS/cm) was measured in the laboratory with a Labline meter at 25°C.

Sample collection

We collected water samples for major and minor ion analysis in a 500-ml unacidified polyethylene bottle and, for nitrate determination, in a 200 ml acidified polyethylene bottle. All samples were stored on ice in the field and transported that way to the laboratory. The samples were refrigerated until analyzed. We collected atrazine samples from the wells in 1-gal acid-washed bottles supplied by the Kansas State Board of Agriculture and 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 (mo-d-yr)	Depth (ft)	Lab or field spec. cond. (µS/cm)	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
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 water		660		8.2	359		72	5.3	61	4.1	0.3	224	18	77	11	0.1	<0.1	
8-6-87 Stafford water		975												157				0.14
9-3-87 Stafford water		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 well		990		7.9			63	6.1	137	3.1	0.4	265	28	162	<0.1			
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 Bromide solution		1450	7.45			23.5								381				376
9-16-87																		
Peace Creek upstream		615	8.65	8.15	334	21.0	48	5.5	69	14	0.3	149	22	102	0.1	0.67	0.1	
Peace Creek downstream		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

All analyses except bromide performed by the KGS Analytical Services Section.

TABLE C.2—SITE 7 WATER CHEMISTRY.

Date (mo-d-yr)	Depth (ft)	Lab or field spec. cond. (µS/cm)	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																		
6-23-87	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 Irrigation well		500		7.7	277		69	5.4	26	3.1	0.3	200	13	33	29			<0.05
Lysimeters																		
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
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

All analyses except bromide performed by the KGS Analytical Services Section.

TABLE C.3—SITE 10 WATER CHEMISTRY.

Date (mo-d-yr)	Depth (ft)	Lab or field spec. cond. (µS/cm)	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)
Wells																	
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

Analyses performed by the KGS Analytical Services Section.

TABLE C.4—Additional chloride and bromide data for site 6.

Date (mo-d-yr)	Depth (ft)	Cl (mg/L)	Br (mg/L)
Wells			
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
Lysimeters			
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
Lysimeters (cont.)			
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

Chloride analyses performed by the KGS Analytical Services Section.

TABLE C.5—ADDITIONAL CHLORIDE AND BROMIDE DATA FOR SITE 7.

Date (mo-d-yr)	Depth (ft)	Cl (mg/L)	Br (mg/L)
Wells			
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
Lysimeters			
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)	1[a]		0.11
10-7-87(a)	2[a]		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)	1[a]		0.32
10-7-87(b)	2[a]		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)	1[a]		0.3
10-8-87(a)	2[a]		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)	2[a]		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	1[a]		0.06
10-10-87	2	44	21
Lysimeters (cont.)			
10-10-87	3	54	90
10-10-87	4	61	173
10-10-87	6	49	3.9
10-10-87	1[a]		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
10-13-87	1[a]		0.16
10-15-87	3	73	144
10-15-87	5	42	78
10-15-87	6	41	2.5
10-15-87	1[a]		0.06
10-15-87	2[a]		0.11
10-20-87	3	81	168
10-20-87	6	41	5.6
10-20-87	1[a]		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	1[a]		0.04
11-10-87	6	52	17
11-10-87	1[a]		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 Bromide solution 1		103	430
10-7-87 Stafford water		132	0.07
10-7-87 Bromide solution 2		140	457

Chloride analyses performed by the KGS Analytical Services Section.

[a] Outside flooded perimeter.

TABLE C.6—Application schedule for chemicals at site 7, Pratt County.

Chemical type	Chemical name	Quantity applied	Date (mo-d-yr)
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.
Information from Servi-tech, Inc., Dodge City, Kansas.

Appendix D: Atrazine analyses in soil and water

TABLE D.1—Atrazine in water samples, site 6, Stafford County.

Sample	Well depth (ft)						Lysimeter depth (ft)													
date	20.0		34.0		45.0		0.5		1.0		2.0		3.0		4.0		5.0		6.0	
(mo-d-yr)	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[a]											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																		

Atrazine analyses performed by the Division of Laboratories, Kansas State Board of Agriculture.

a. 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.

	Depth (in)							
	0–3		3–6		6–9		9–12	
Date (mo-d-yr)	**mg/kg**	**limit (mg/kg)**	**mg/kg**	**limit (mg/kg)**	**mg/kg**	**limit (mg/kg)**	**mg/kg**	**limit (mg/kg)**
6-23-87	ND	0.04	ND	0.04	ND	0.04	ND	0.04
7-16-87	0.04	0.04	ND	0.04	ND	0.04	ND	0.04
8-6-87A	ND	0.04	ND	0.03	ND	0.04	ND	0.03
8-6-87B	0.13	0.04	ND	0.04	ND	0.04	ND	0.03
9-10-87A	0.06	0.04	ND	0.04	ND	0.03	ND	0.03
9-10-87B	0.04	0.04	0.06	0.04	ND	0.03	ND	0.03
9-16-87	0.54	0.04			0.21	0.04	0.26	0.03
9-16-87RE[a]								
9-17-87	0.62	0.04	0.23	0.04	0.09	0.03	0.03	0.03
9-18-87	0.63	0.04	0.35	0.03	0.12	0.03	0.08	0.03
9-22-87	0.18	0.04	ND	0.03	0.05	0.04	ND	0.03
9-25-87	0.14	0.04	ND	0.03	ND	0.04	ND	0.03
10-1-87	0.43	0.04	0.05	0.04	ND	0.03	ND	0.03
10-6-87	0.13	0.03	0.08	0.03	ND	0.04	ND	0.03
10-9-87	0.36	0.04	0.05	0.04	ND	0.04	ND	0.03
10-14-87	0.18	0.04	0.07	0.04	ND	0.03	ND	0.03
10-20-87	0.06	0.04	ND	0.03	ND	0.05	ND	0.04
10-27-87	0.08	0.03	ND	0.04	ND	0.04	ND	0.03
11-10-87	0.14	0.04	0.08	0.03	ND	0.04	ND	0.03
12-1-87[c]	ND	0.03	ND	0.03	ND	0.04	ND	0.03
12-17-87	0.27	0.05	0.36	0.04	0.29	0.04	0.20	0.03
2-25-88	0.10	0.03	ND	0.04	ND	0.04	ND	0.04
5-4-88A[d]	ND	0.03	ND	0.03	ND	0.04	ND	0.03
5-4-88D[e]	0.24	0.03	0.05	0.03	ND	0.03	ND	0.03
8-3-88B	0.17	0.03	0.06	0.03	0.07	0.05	0.04	0.03
9-13-88	0.07	0.04	0.07	0.03	0.03	0.03	ND	0.04
11-2-88	ND	0.05	ND	0.04	ND	0.05	ND	0.05

(Table D.2, continued)

	Depth (in)							
	12–18		**18–24**		**24–30**		**30–36**	
Date (mo-d-yr)	**mg/kg**	**limit (mg/kg)**	**mg/kg**	**limit (mg/kg)**	**mg/kg**	**limit (mg/kg)**	**mg/kg**	**limit (mg/kg)**
6-23-87	ND	0.04	ND	0.04	ND	0.04	ND	0.04
7-16-87	ND	0.04						
8-6-87A								
8-6-87B								
9-10-87A	ND	0.04						
9-10-87B	ND	0.04						
9-16-87	0.30[b]	0.04	0.04	0.04	ND	0.04	ND	0.04
9-16-87RE[a]	0.21[b]	0.04	0.12[b]	0.03				
9-17-87	ND	0.04	ND	0.04	ND	0.04	ND	0.04
9-18-87	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[c]								
12-17-87	0.19	0.04	0.09	0.04	ND	0.04	0.09	0.04
2-25-88	ND	0.04	ND	0.04	ND	0.04	ND	0.04
5-4-88A[d]	ND	0.04	ND	0.04	ND	0.04	ND	0.04
5-4-88D[e]	0.24	0.04	ND	0.04	0.28	0.04	ND	0.04
8-3-88B	0.1[b]	0.04	ND	0.04				
9-13-88	ND	0.04	ND	0.04	ND	0.04	ND	0.03
11-2-88	ND	0.04	ND	0.04	ND	0.04	ND	0.04

Atrazine analyses performed by the Division of Laboratories, Kansas State Board of Agriculture.

a. Repeat analysis.
b. Sample probably contaminated.
c. Field (and plot) plowed *after* this date.
d. Outside cornfield but within flooded site.
e. Inside cornfield and within flooded site.

TABLE D.3—ATRAZINE IN WATER SAMPLES, SITE 7, Pratt County.

Sample date (mo-d-yr)	Well depth (ft) 30.0 µg/L	limit (µg/L)	50.0 µg/L	limit (µg/L)	70.0 µg/L	limit (µg/L)	Lysimeter depth (ft) 0.5 µg/L	limit (µg/L)	1.0 µg/L	limit (µg/L)	2.0 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
10-5-87	ND	0.5					ND	7.7				
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		
10-8-87/2B							121	6.3				
10-9-87/3A	ND	1.0					24.9	5.6				
10-10-87/4A	ND	1.0							ND	50.0	ND	16.7
10-12-87/6A	ND	0.5									ND	7.1
10-13-87	ND	0.5	ND	0.5	ND	0.5						
10-15-87	ND	0.5									ND	33.3
10-20-87	ND	0.5	ND	0.5								
10-22-87												
10-28-87	ND	0.5	ND	0.5								
11-10-87	ND	0.5	ND	0.5								
1-20-88	ND	0.5										
2-17-88	ND	1.0	ND	1.0	ND	1.0						
3-3-88							53	4.5	28	2.9	20	6.7
5-4-88	ND	0.4									36.3	0.8
8-3-88	ND	0.4	ND	0.4	ND	0.4						
9-12-88							8.8	2.3			3.4	0.9
9-14-88	ND	0.4	ND	0.4					3.9	2.2		
9-16-88							5.3	2.2	3.4	1.6	ND	2.4
11-1-88	ND	0.4					ND	4.5				
11-3-88							ND	2.7	ND	3.6		

(Table D.3, continued)

Sample date (mo-d-yr)	Lysimeter depth (ft) 3.0 µg/L	limit (µg/L)	4.0 µg/L	limit (µg/L)	5.0 µg/L	limit (µg/L)	6.0 µg/L	limit (µg/L)	1E[a] µg/L	limit (mg/L)	2E[a] µg/L	limit (mg/L)	1S[a] µg/L	limit (mg/L)
6-23-87														
9-3-87	ND	3.8	ND	3.8	ND	3.8	ND	3.8						
10-5-87					ND	5.0								
10-7-87/1A														
10-8-87/2A	ND	3.3	ND	5.6	ND	12.5	ND	20.0	ND	12.5	ND	8.3		
10-8-87/2B	ND	12.5							ND	16.7	ND	10.0		
10-9-87/3A	ND	10.0	ND	16.7									ND	12.5
10-10-87/4A	ND	11.1	ND	20.0										
10-12-87/6A	ND	8.3			ND	10.0	ND	16.7						
10-13-87									ND	10.0				
10-15-87	ND	6.7					ND	9.1	ND	5.0	ND	10.0		
10-20-87	4.9	4.5					ND	11.1	ND	2.3				
10-22-87	ND	10.0												
10-28-87							ND	16.7	ND	2.5				
11-10-87							ND	11.1	ND	3.8				
1-20-88														
2-17-88							ND	7.7						
3-3-88														
5-4-88	48.7	0.4	48.0	0.4	57.8	0.8	1.0	0.8						
8-3-88			28.1	1.1	21.1	0.8	2.9	1.7						
9-12-88	7.9	1.6	9.2	1.9	6.0	2.9	ND	1.7						
9-14-88	6.3	1.6												
9-16-88	6.1	1.8	13.7	1.8	4.9	3.2	ND	4.7						
11-1-88			18.7	0.4	3.4	0.8								
11-3-88	ND	4.4					ND	3.5						

Atrazine analyses performed by the Division of Laboratories, Kansas State Board of Agriculture.

a. Outside the perimeter of the flooded area.

TABLE D.4—Atrazine in soils, site 7, Pratt County.

Date (mo-d-yr)	Depth (in)											
	0–3		3–6		6–9		9–12		12–18		18–24	
	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)
6-23-87	ND	0.04	ND	0.04	ND	0.04	ND	0.04	ND	0.04	ND	0.04
8-6-87	ND	0.04	ND	0.03	ND	0.03	ND	0.03				
9-10-87	ND	0.04	ND	0.04	ND	0.04	ND	0.04				
10-6-87	ND	0.03	ND	0.04	ND	0.03	ND	0.03				
10-8-87[a]	0.25	0.04	0.28	0.03	0.13	0.03	0.04	0.03	0.12	0.04	ND	0.04
10-8-87[b]	0.42	0.04	0.29	0.03	0.20	0.03	0.09	0.03	0.26	0.04	0.17	0.04
10-9-87	0.44	0.04	0.11	0.03	ND	0.03	ND	0.03				
10-10-87	0.32	0.04	ND	0.03	ND	0.04	ND	0.03	ND	0.04	ND	0.04
10-12-87	0.47	0.08	0.30	0.03	0.21	0.05	0.15	0.03	0.16	0.04	0.19	0.04
10-13-87	0.41	0.06	0.27	0.03	0.20	0.03	0.12	0.03	0.20	0.04	0.22	0.04
10-20-87	0.14	0.03	0.19	0.03	ND	0.03	ND	0.03				
10-28-87	0.08	0.05	0.21	0.04	0.12	0.03	0.05	0.03	ND	0.04	ND	0.04
11-10-87	0.27	0.04	0.21	0.03	0.06	0.03	0.04	0.03	0.08	0.04	0.08	0.04
11-30-87	0.30	0.04	0.14	0.04	ND	0.03	0.05	0.03	0.15	0.04	0.12	0.04
12-17-87	0.28	0.04	0.18	0.03	ND	0.03	ND	0.03	ND	0.04	0.04	0.04
2-24-88	0.12	0.03	ND	0.04	ND	0.03	ND	0.03	ND	0.04	ND	0.04
5-4-88	0.11	0.03	0.11	0.04	0.21	0.04	0.09	0.03	0.09	0.04	ND	0.04
8-2-88	0.03	0.03	ND	0.03	ND	0.03	ND	0.03	ND	0.03	ND	0.04
9-14-88	ND	0.03	ND	0.03	ND	0.03	ND	0.04	ND	0.04	ND	0.04
11-2-88	ND	0.04	ND	0.04	ND	0.04	ND	0.04	ND	0.04	ND	0.04

(Table D.4, continued)

Date (mo-d-yr)	Depth (in)											
	24–30		30–36		36–42		42–48		48–54		54–60	
	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)
6-23-87	ND	0.04	ND	0.04								
8-6-87												
9-10-87												
10-6-87												
10-8-87[a]	0.19	0.04	0.06	0.04								
10-8-87[b]												
10-9-87												
10-10-87	ND	0.04	ND	0.04								
10-12-87	0.06	0.04	ND	0.04	0.19	0.04	0.12	0.04	0.04	0.04	ND	0.04
10-13-87	0.18	0.04	0.17	0.04	0.16	0.04	0.05	0.04	0.05	0.04	ND	0.04
10-20-87												
10-28-87												
11-10-87	0.06	0.04	0.06	0.04	0.11	0.04	0.05	0.04	0.07	0.04	ND	0.04
11-30-87	0.13	0.04	0.13	0.04	0.12	0.04	0.12	0.04	0.04	0.04	ND	0.04
12-17-87												
2-24-88	ND	0.04	ND	0.04								
5-4-88	0.10	0.04	0.05	0.04	ND	0.04	ND	0.04	ND	0.04	ND	0.04
8-2-88	ND	0.04	ND	0.04	ND	0.04	ND	0.04	ND	0.04	ND	0.04
9-14-88	ND	0.04	ND	0.04	ND	0.04	ND	0.04				
11-2-88	ND	0.04	ND	0.04	ND	0.04	ND	0.04	ND	0.04	ND	0.04

a. Sample drawn at 10:30 A.M.

b. Sample drawn at 5:00 P.M.

Appendix E: Determination of atrazine degradation by-products

TABLE E.1—DETERMINATION OF ATRAZINE DEGRADATION BY-PRODUCTS FOR SITES 6 AND 7.

			Biodegradation by-products[a]		
Sampling date (mo-d-yr)	**Depth (in)**	**Parent atrazine (mg/kg)**	**G–34048 hydroxy-atrazine (mg/kg)**	**G–28279 ethyl-atrazine (mg/kg)**	**G–30033 isopropyl-atrazine (mg/kg)**
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

a. Moisture-corrected residues. Detection limit 0.05 mg/kg. Analyses by Minnesota Valley Testing Laboratories, Inc.

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