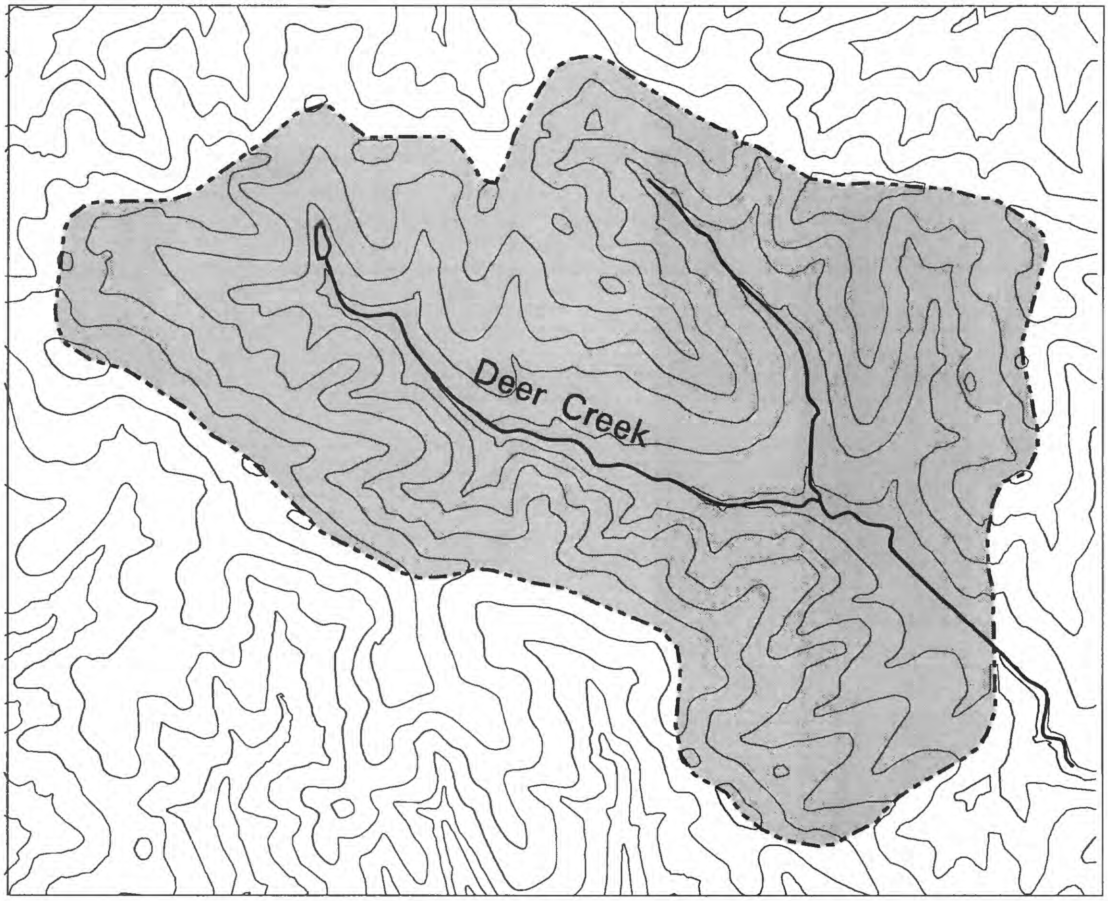
AGRICULTURAL CHEMICALS IN GROUND AND SURFACE WATER IN A SMALL WATERSHED IN CLAYTON COUNTY, IOWA, 1988-91

U. S. GEOLOGICAL SURVEY
Water-Resources Investigations Report 95-4158



Prepared in cooperation with
IOWA DEPARTMENT OF NATURAL RESOURCES
(GEOLOGICAL SURVEY BUREAU)

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

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By Stephen J. Kalkhoff and Bryan D. Schaap

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1995

U. S. DEPARTMENT OF THE INTERIOR
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For additional information write to:

District Chief
U.S. Geological Survey
Rm. 269, Federal Building
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CONVERSION FACTORS, ABBREVIATIONS, AND VERTICAL DATUM

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
	Area	
acre	4,047	square meter
acre	0.4047	hectare
square foot (ft^2)	929.0	square centimeter
square mile (mi^2)	2.590	square kilometer
	Velocity	
foot per second (ft/s)	0.3048	meter per second
foot per day (ft/d)	0.3048	meter per day
	Mass	
pound (lb)	0.4536	kilogram (kg)
pound per acre (lb/acre)	1.121	kilogram per hectare
pound per square mile (lb/mi^2)	0.1751	kilogram per square kilometer
ton, short	.9072	megagram
ton per day (t/d)	.9072	megagrams per day
	Flow	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second
	Pressure	
bar	100	kilopascal
	Temperature	
degree Fahrenheit ($^{\circ}F$)	$5/9(^{\circ}F)- 32$	degree Celsius ($^{\circ}C$)

Sea level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929 --a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Water Year: The 12-month period October 1 through September 30. The water year is designated by the calendar year in which it ends. Thus, the year ending September 30, 1991, is called the "1991 water year."

Agricultural Chemicals in Ground and Surface Water in a Small Watershed in Clayton County, Iowa, 1988-91

by Stephen J. Kalkhoff and Bryan D. Schaap

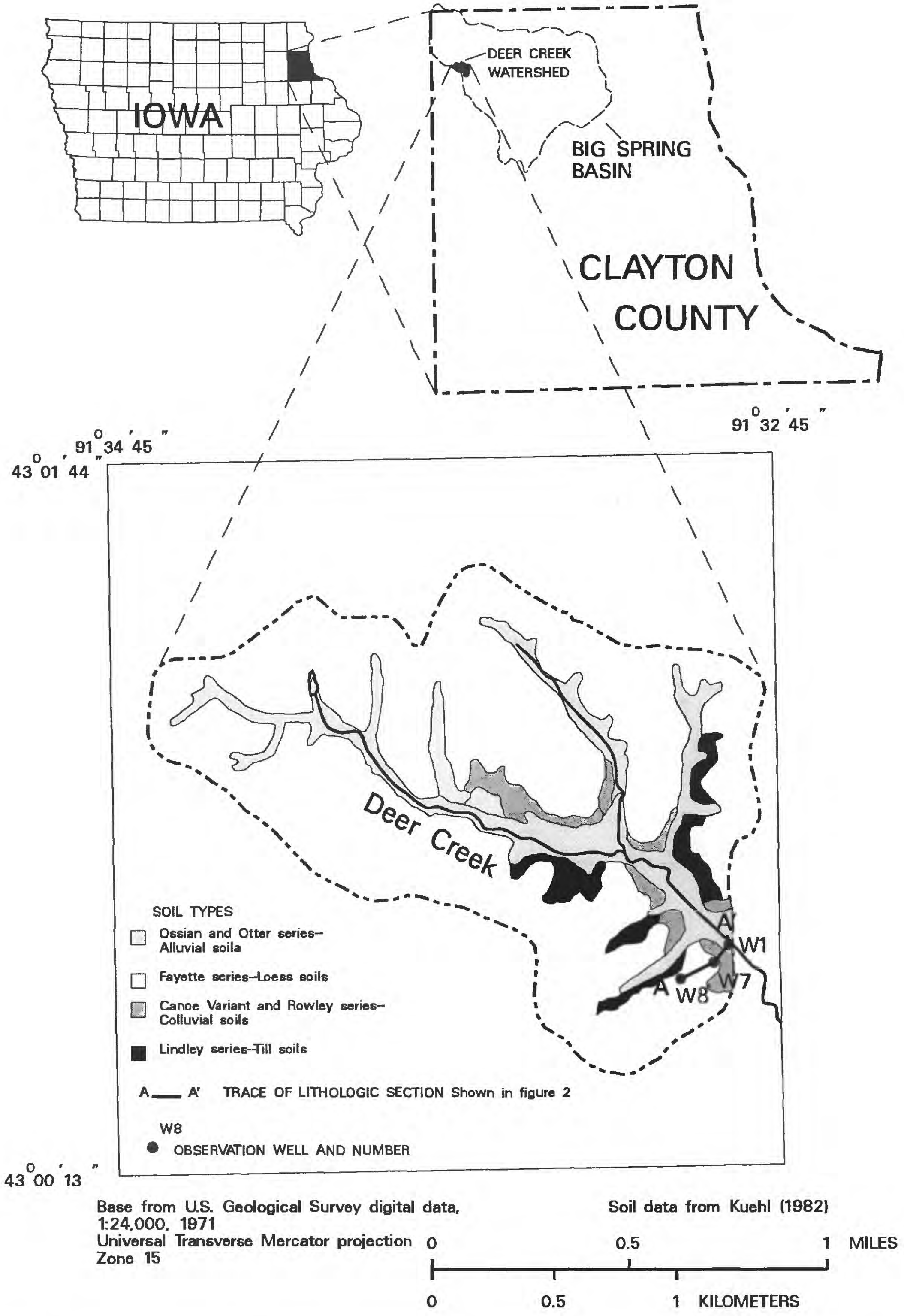
ABSTRACT

An investigation was conducted from October 1988 through September 1991 to (1) describe the quality of water in shallow, unconsolidated materials in the 1.09-square-mile Deer Creek watershed in Clayton County, Iowa, and to (2) define the quantity and seasonal distribution of selected agricultural chemicals in water from this watershed. Surficial unconsolidated aquifer materials that discharge water to Deer Creek include alluvium, loess, and glacial till. More than 80 percent of the watershed is used for row and cover crops. Median nitrate concentrations ranged from 16 mg/L (milligrams per liter) in water from the top of the 10-foot thick alluvial aquifer to less than 0.10 mg/L near the bottom. Atrazine was detected in more than 85 percent of the ground-water samples collected at or less than 5.5 feet below land surface. Only one sample collected at 7.0 feet below land surface in the alluvial aquifer had an atrazine concentration greater than the detection limit of 0.10 µg/L (micrograms per liter). Nitrogen and herbicide concentrations were largest in late spring and early summer. Sources of agricultural chemicals in the alluvial aquifer include vertical infiltration through the soil and lateral transport from upslope unconsolidated materials.

Nitrogen was present in all water samples from Deer Creek. Nitrate concentrations ranged from 0.70 to 17 mg/L. Alachlor was detected in 11 percent of the samples, atrazine in 69 percent, cyanazine in 19 percent, and metolachlor in 33 percent. Alachlor concentrations ranged from less than 0.10 to 0.53 µg/L, atrazine ranged from less than 0.10 to 55 µg/L, cyanazine ranged from less than 0.10 to 12 µg/L, and metolachlor ranged from less than 0.10 to 69 µg/L. Herbicide detections occurred most frequently in late spring and early summer during or just following chemical application. Overland flow is an important source of nitrogen and herbicides to Deer Creek. Substantial amounts of agricultural chemicals are transported from the watershed. As much as 4,700 pounds, or 6.7 pounds per acre, of nitrogen were estimated to be transported from the watershed in 1 year. Nitrogen loads transported from the Deer Creek watershed were less during dry years than during years with average or greater than average rainfall.

INTRODUCTION

Agricultural chemicals such as inorganic fertilizers and herbicides are important in the production of crops in Iowa. Inorganic fertilizers are applied to supplement nitrogen from natural mineralization and herbicides are applied to control competing vegetation. All chemicals applied may not be used by crops due to a variety of climatic and economic factors, with the result that excess chemicals may be available for transport to ground and surface water (Detroy and others, 1988). In the Big Spring Basin, a karst area of northeastern Iowa (fig. 1), Hallberg and others (1984; 1989) estimated that in the early 1980's, from 27 to 43 lb/acre of nitrogen were transported from



Base from U.S. Geological Survey digital data, 1:24,000, 1971
Universal Transverse Mercator projection
Zone 15

Soil data from Kuehl (1982)

Figure 1. Map showing location and soil types in the Deer Creek watershed, Clayton County, Iowa.

the basin through both surface- and ground-water discharge. Atrazine, the most consistently detected herbicide in the Big Spring Basin, was discharged from Big Spring in annual loads ranging from about 18 lb in 1987 to about 48 lb in 1985 (Hallberg and others, 1989).

The hydrologic system in the karstic Big Spring Basin is complex. Streams generally gain water in headwaters areas in the western part of the basin (Kalkhoff, 1993) and lose water to the karstic Galena aquifer in the eastern part of the basin (Hallberg and others, 1983, p. 26; Kalkhoff and others, 1992, p. 25). Thus, surface water flowing out of the headwaters areas may be one source of agricultural chemicals that could adversely affect the quality of water in the Galena aquifer, a major source for rural and domestic supplies in the Big Spring Basin.

Thus, there is a need to define the quantity and seasonal distribution of agricultural chemicals originating in headwaters of gaining streams in the Big Spring Basin and to relate stream-water quality to ground-water quality in the watershed. These data are needed to improve the understanding of the hydrologic cycle in the Big Spring Basin and the agricultural-chemical transport processes in the surface- and ground-water systems. This knowledge also will contribute to the understanding of the fate of agricultural chemicals once applied.

Purpose and Scope

The purpose of this report is to describe the results of a study done by the U.S. Geological Survey in cooperation with the Iowa Department of Natural Resources, Geological Survey Bureau, to define the source, quantity, and seasonal distribution of agricultural chemicals in a small representative headwaters stream in the Big Spring Basin in Clayton County, Iowa. The study was conducted from October 1988 through September 1991. The quantity and quality of the surface water discharged from the 1.09-mi^2 Deer Creek watershed was measured. Shallow ground water was monitored in a field adjacent to Deer Creek. Quantifying agricultural chemicals from individual sources in Deer Creek was beyond the scope of this study.

Acknowledgments

This study was supported, in part, by the Iowa Department of Natural Resources, Geological Survey Bureau, through the Big Spring Basin Demonstration Project, with funds provided from the Iowa Ground-water Protection Act. George Hallberg, Coordinator of the Big Spring Basin Demonstration Project, and other members of the Iowa Department of Natural Resources, Geological Survey Bureau, Robert Libra, John Littke, Debra Quade, and Robert Rowden, provided technical advice and field support.

DESCRIPTION OF THE STUDY AREA

A 1.09-mi^2 or about 700-acre watershed in the headwaters of Deer Creek (fig. 1) was selected as representative of small headwaters streams that gain water from ground-water inflow in the western part of the Big Spring Basin (Kalkhoff, 1993). The Deer Creek watershed is characterized by gently rolling to hilly topography. Land-surface altitudes range from about 1,060 ft above sea level near the outlet of the watershed to 1,220 ft above sea level at the southwest edge of the watershed. Deer Creek and several intermittent tributaries drain the study area. The density of these streams is 1.3 mi of streams per square mile of watershed. The channel of Deer Creek slopes about 48 feet per mile from the basin boundary to the outlet.

Geology and soils

Wind, glaciers, and water have deposited unconsolidated material to form the present-day topographic features in the Deer Creek watershed. Subsurface unconsolidated materials include recent alluvial deposits, Wisconsinan loess, colluvium, and pre-Illinoian glacial till. Soil development in the Deer Creek watershed (fig. 1) is directly related to the near-surface presence of these deposits. An Ordovician-age shale bedrock unit underlies the unconsolidated materials.

A hydrogeologic section across the outlet of the watershed is shown in figure 2. The

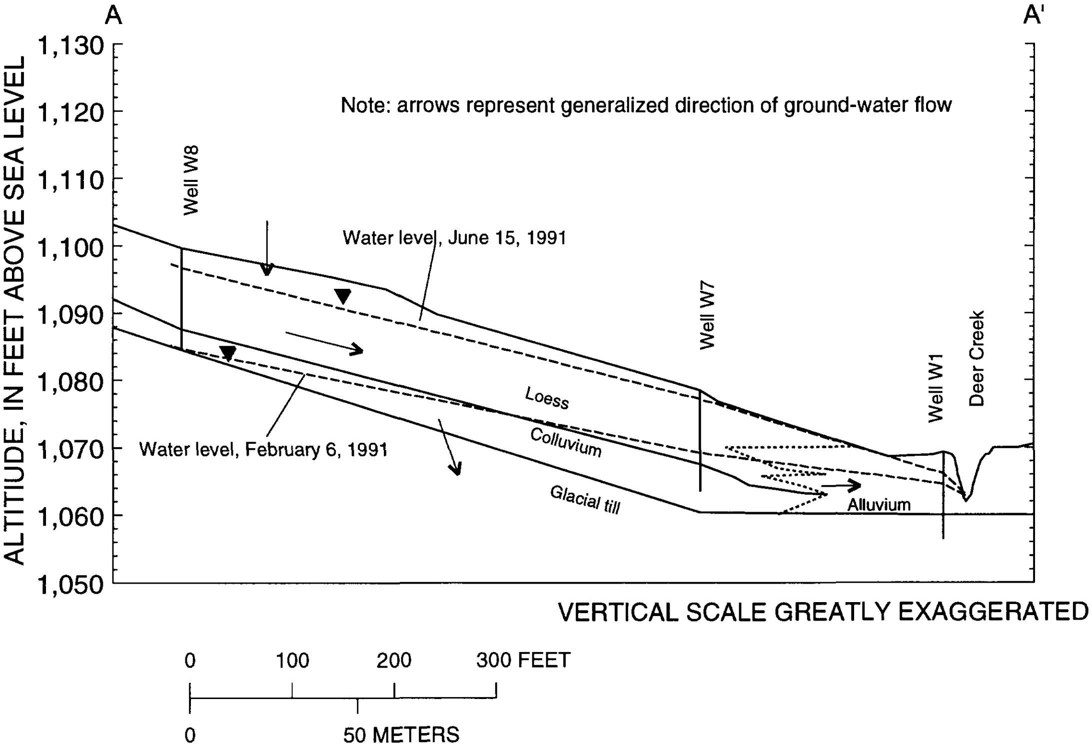


Figure 2. Hydrogeologic section showing water levels in unconsolidated material in the Deer Creek watershed, Clayton County, Iowa.

section includes observation wells W1, W7, and W8. The descriptive logs for wells W7 and W8 in table 1 show a lithology that is typical of much of the study area, with loess overlying the colluvium, which overlies the glacial till.

Water has formed two types of alluvial deposits along Deer Creek and its tributaries. The first is silty alluvium located in the bottom lands, in the lower part of upland drainages, and in low stream benches. Soils that have developed on silty alluvium belong to the Ossian and Otter series of soils (Kuehl, 1982). The Ossian and Otter soils cover about 15 percent of the watershed in the valleys near the streams, are moderately permeable, and contain five to seven percent organic matter.The second type of alluvial deposit, a fluvial bench deposit, consists of silty and sandy alluvium. The soils that developed on the bench deposits belong to the Canoe Variant and Rowley series (Kuehl, 1982). These soils cover about three percent of the watershed, are moderately permeable, and contain two to four percent organic matter. The alluvium is about 10 ft thick near the outlet of the watershed and probably thins upstream along Deer Creek and its tributaries.

About 78 percent of the Deer Creek watershed is covered by Fayette series soils, which formed on loess deposits. The Fayette series soils are found mostly on the uplands and stream benches, are moderately permeable, and contain five to seven percent organic matter. The wind-deposited loess, composed of angular clay and silt-sized particles, ranges from 0 to about 20 ft thick, with the thickest deposits on the ridges near the upstream basin boundaries (Kuehl, 1982).

Glacially deposited till underlies the loess and the soils that formed on the outcrops of mainly clayey glacial till belong to the Lindley

Table 1. --Descriptive logs of observation wells W7 and W8 in the Deer Creek watershed, Clayton County, Iowa

[Samples collected and described on June 14, 1992, by John Littke of the Iowa Department of Natural Resources, Geological Survey Bureau]

Lithologic unit	Depth below land surface (inches)	Description
		Well W7
Loess	0 to 11	Olive-brown silt loam, firm, noneffervescent, abrupt boundary.
	11 to 25	Yellowish brown silt loam, weak very fine to fine subangular blocky, firm, noneffervescent, olive-brown thin discontinuous cutans, clear boundary.
	25 to 37	Yellowish brown silt loam, moderate fine to medium subangular blocky, firm, noneffervescent, olive-brown thin continuous cutan, clear boundary.
	37 to 54	Light olive-brown silt loam, moderate coarse prismatic breaking to coarse subangular blocky, firm, noneffervescent, olive-brown thin continuous cutans, distinct boundary.
	54 to 84	Olive-yellow silt loam, massive, firm, noneffervescent, many fine olive gray mottles, clear boundary.
	84 to 131	Olive gray silt loam, massive, firm, common coarse olive-yellow mottles, slight effervescence, clear boundary.
Colluvium	131 to 143	Alternating thin beds of light olive-brown silt loam and yellowish brown sandy loam, noneffervescent, firm, clear boundary
	143 to 157	Dark grayish-brown silty clay loam, massive, firm, noneffervescent, clear boundary
	157 to 178	Dark olive-gray loam, massive, firm, noneffervescent, clear boundary
	178 to 218	Brownish yellow sandy loam with large pebbles and small cobbles up to two inches in diameter, firm, noneffervescent, abrupt boundary
Pre-Illinoian till	218 to 245	Very dark-gray loam, massive, very firm, violently effervescent, unoxidized, unleached

Table 1. --Descriptive logs of observation wells W7 and W8 in the Deer Creek watershed, Clayton County, Iowa

[Samples collected and described on June 14, 1992, by John Littke of the Iowa Department of Natural Resources, Geological Survey Bureau]

Lithologic unit	Depth below land surface (inches)	Description
		Well W8
Loess	0 to 10	Dark-brown silt loam, friable, noneffervescent, abrupt boundary.
	10 to 31	Yellowish brown silt loam, moderate medium to coarse subangular blocky, firm, noneffervescent, thin continuous dark yellowish brown cutans, common iron and manganese oxidized in 0.25-inch diameter pipestems, gradual boundary.
	31 to 55	Yellowish brown silt loam, moderate medium to coarse prismatic breaking to moderate medium to coarse subangular blocky, firm, noneffervescent, thin continuous dark yellowish-brown cutans, thin continuous dark yellowish-brown cutans, common fine yellowish-brown mottles, gradual boundary.
	55 to 95	Olive-brown silt loam, friable, occasional joints and worm tubes coated with thin continuous dark yellowish-brown cutans, manganese oxides in pipestems, common fine olive-yellow mottles, noneffervescent, gradual boundary.
	95 to 145	Light olive-gray silt loam, friable, iron oxides in pipestems, common medium yellowish-brown and light olive-brown mottles, violently effervescent, abrupt boundary.
Colluvium	145 to 149	Strong brown clay loam with pebbles up to one inch in diameter, common fine light olive-brown mottles, abundant iron oxides, noneffervescent, clear boundary.
	149 to 182	Yellowish-brown loam with pebbles, weak fine grading to medium subangular blocky, firm, common medium strong brown and common fine light olive brown mottles thin (0.25 to 0.50 inch) strong brown interbeds of gravely sand with iron oxides, noneffervescent, gradual boundary
Pre-Illinoian till	182 to 187	Brownish-yellow loam with pebbles, very firm, common fine strong brown mottles, noneffervescent

series (Kuehl, 1982). The Lindley soils cover about four percent of the watershed on the side slopes, have low permeability, and contain less than 0.5 percent organic matter.

The glacial till in the watershed also includes sand and gravel deposits. These deposits are similar to the pre-Illinoian outwash deposits described by Steinhilber and others (1961, p. 93). The characteristically iron-stained red deposits may be locally extensive as similar deposits were encountered in a test hole about 1.5 mi north of the watershed (Rowden and Libra, 1990, p. 19).

Bedrock underlying the unconsolidated material in the Deer Creek watershed was not observed during test drilling for the study. In the test hole mentioned above, an Ordovician shale was encountered at 1,050 ft above sea level (Rowden and Libra, 1990).

Hydrology

Precipitation, the principal source of water in the Deer Creek watershed, generally was less than the 30-year average (1961-90) during part of 1988 and 1989 (fig. 3). Rainfall in August 1989 was an exception to the dry trend. During 1990, precipitation was near normal, and in the first nine months of 1991 the precipitation was substantially above normal for northeastern Iowa (fig. 3). Precipitation in the Deer Creek watershed was estimated for October 1, 1988 through May 23, 1990, from rainfall recorded at a site (Unnamed Creek near Luana, Iowa; not shown) about 3 mi east of the Deer Creek watershed (Kalkhoff and Kuzniar, 1991; Kalkhoff and others, 1992). Precipitation was measured in the watershed from May 23, 1990 to the end of the study except for June, July, and August, 1990. Rainfall data for June, July, and August, 1990 are National Oceanic and Atmospheric Administration (1990a) divisional data for northeastern Iowa. Rainfall in northeastern Iowa during this period was substantially greater than normal (National Oceanic and Atmospheric Administration, 1990 b,c,d).

When rainfall intensity is greater than the saturated hydraulic conductivity of the soil surface and the rainfall duration exceeds the time required for the soil surface to become saturated, water will begin to pond on the surface and will be available for overland flow

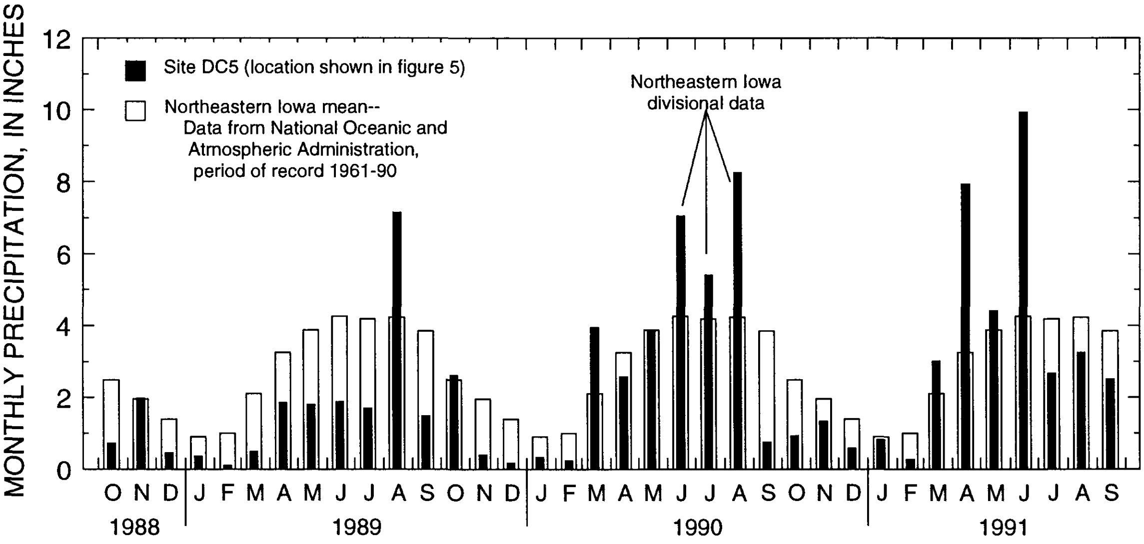


Figure 3. Monthly precipitation in the Deer Creek watershed, Clayton County, Iowa.

to streams (Freeze and Cherry, 1979). Water infiltrating into the unconsolidated material can move horizontally through the shallow soil horizon (subsurface storm-flow) created by agricultural tillage or vertically through the unsaturated zone to the water table. The subsurface storm-flow is probably a minor ground-water component of flow to Deer Creek as Freeze (1972) found that this component is quantitatively significant only on convex hillslopes that feed deeply incised channels and when permeabilities of the soils are in the very highest bracket of the reasonable range. The topography of the Deer Creek watershed, hillslopes with shallowly incised channels, is generally not conductive to subsurface stormflow. Most water infiltrating the soil moves vertically to the water table in the loess or alluvial deposits. The presence of a low-permeability material such as glacial till underlying the loess causes most water in the loess material to move downslope to the alluvial material and finally into the stream. Some water migrates downward through the relatively impermeable till to interbedded sand lenses within this material.

Land use

Land in the watershed is used primarily for row-crop agriculture (fig. 4). Row crops (mostly corn) are grown on about 65 percent of the watershed. Cover crops, such as alfalfa and small grain, are grown on about 16 percent of the watershed. Grassland covers about 11 percent of the watershed. In the spring, summer, and fall, some of the grassland along Deer Creek was used to pasture cattle. The remainder of the watershed is forests, farmsteads, or roads. A variety of soil-conservation practices are used to reduce erosion in the watershed. Grass buffer strips, sometimes used for pastures, were present along Deer Creek and several of the intermittent tributaries. On some of the steeper slopes, terraces have been constructed and strip-cropping practices are used. Strip cropping is evident in figure 4 by the narrow alternating bands of row and cover crops. Figure 4 illustrates land use in the watershed during 1990. Although minor land-use changes generally occur from year to year, there were no major changes during the study period.

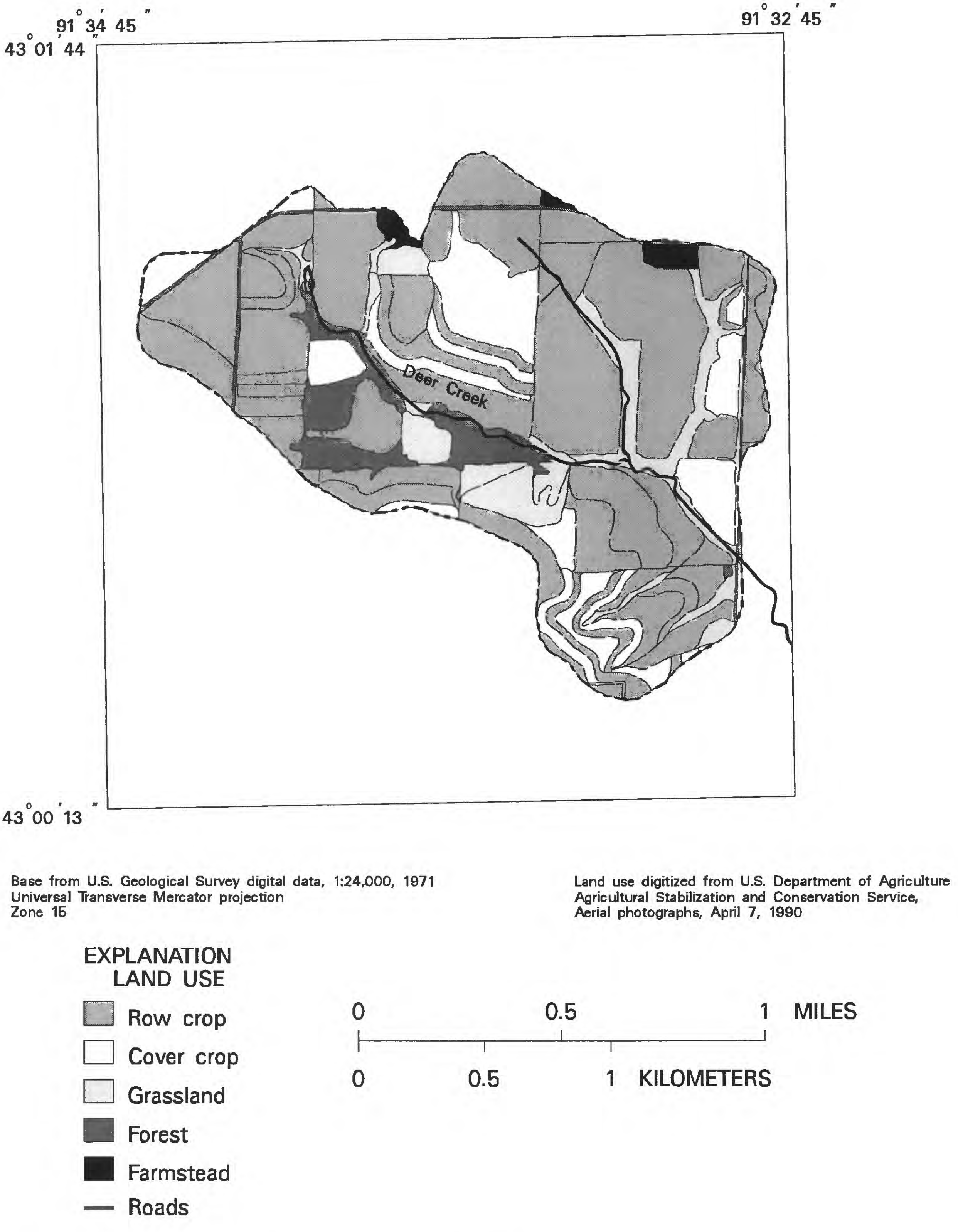
Inorganic fertilizer and herbicides are applied to row crops in the Deer Creek watershed to enhance crop yields. Nitrogen was applied to corn at a rate of about 125 lb/acre in 1989 (Mary Craig, Iowa Department of Natural Resources, Geological Survey Bureau, written commun., 1993). Herbicide application information is available only by farm and not by individual fields, thus exact usage numbers are not available for the Deer Creek watershed. However, application rates for four inventoried farms with land in the basin may be used to estimate the amount of herbicides applied to row crops in the watershed. Alachlor was applied at a rate of 2.2 lb/acre to about 9 percent of the corn, atrazine was applied at a rate of 1.5 lb/acre to about 94 percent of the corn, cyanazine was applied at a rate of 2.3 lb/acre to about 5 percent of the corn, and metolachlor was applied at a rate of 1.7 lb/acre to about 80 percent of the corn (Mary Craig, Iowa Department of Natural Resources, Geological Survey Bureau, written commun., 1993).

METHODS

Ground Water

Ground-water data from the unconsolidated material was obtained by installing observation wells and lysimeters near Deer Creek and in an adjacent field that was considered representative of the geology and land use in the watershed. Ground-water flow was determined by mapping the water levels measured in the wells. Ground-water quality was determined from samples collected at observation wells and lysimeters.

Two shallow observation wells, W1 and W10 (fig. 5), were installed to allow continual measurement of water levels. Well-construction information is given in table 2. Well W1 was installed about 30 ft from Deer Creek to measure water-level fluctuations and to compare the altitude of the alluvial water table to the altitude of water in the creek. Well W10 was installed on the hillslope to record water-



Base from U.S. Geological Survey digital data, 1:24,000, 1971
Universal Transverse Mercator projection
Zone 15

Land use digitized from U.S. Department of Agriculture
Agricultural Stabilization and Conservation Service,
Aerial photographs, April 7, 1990

Figure 4. Landuse in the Deer Creek watershed, Clayton County, Iowa, 1990.

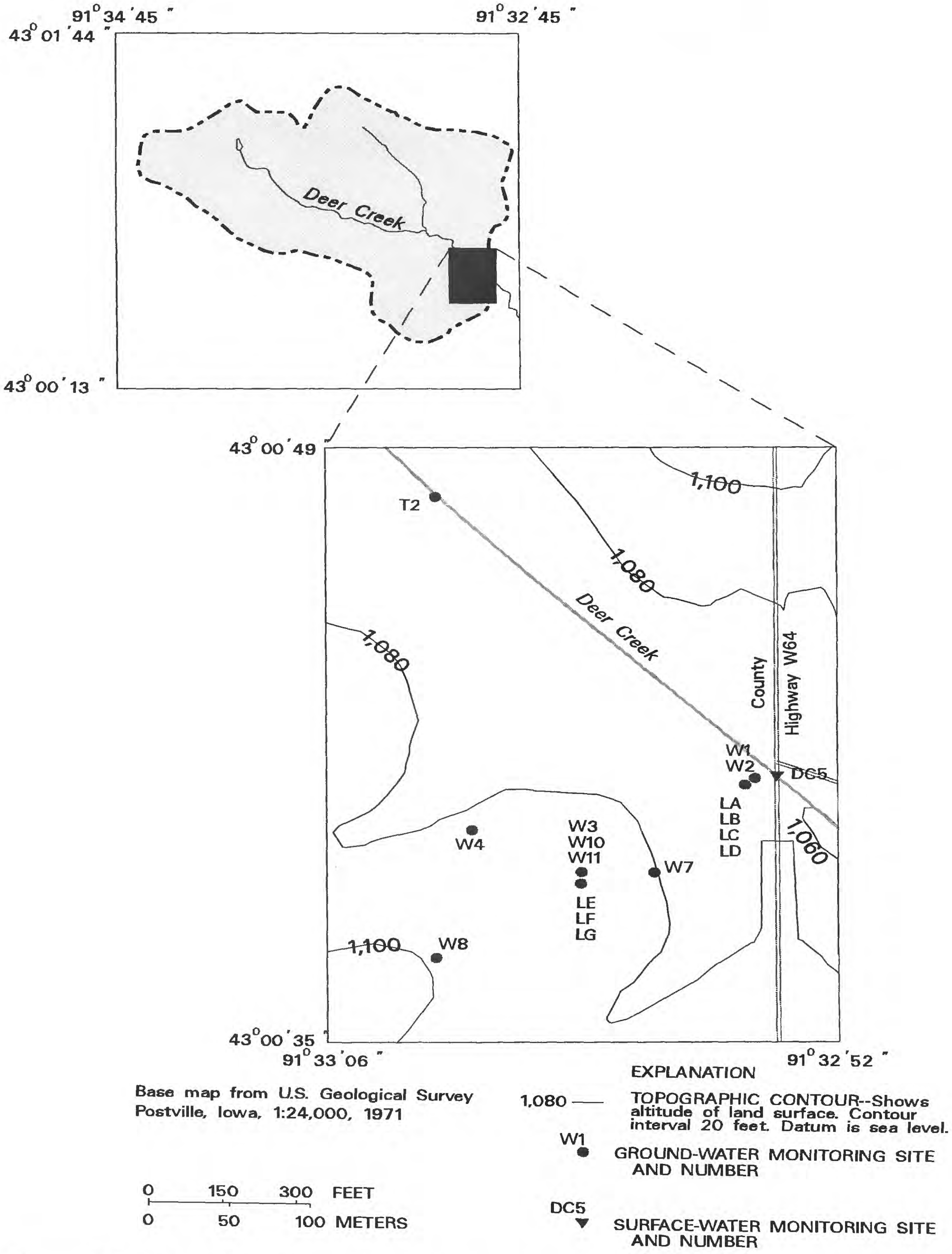


Figure 5. Location of monitoring sites in the Deer Creek study area, Clayton County, Iowa.

Table 2.--Information on selected monitoring wells, lysimeters, and tile lines in the Deer Creek watershed, Clayton County, Iowa

[ft, feet; --,data not available; NA, not applicable]

Site number (fig. 5)	Monitoring site	Site identification number	Land-surface altitude (ft above sea level)	Well depth (ft below land surface)	Sampling interval (ft below land surface)	Unconsolidated material
W1	well	430040091325402	1,070	13	11-13	Alluvium
W2	well	430040091325403	1,070	11	8-11	Alluvium
W3	well	430040091325410	1,083	15	13-15	--
W7	well	430040091325414	1,078	15	13-15	Loess and colluvium
W8	well	430040091325415	1,100	15	10-15	Loess and colluvium
W10	well	430040091325417	1,083	15	11-15	Loess
W11	well	430040091325418	1,083	23	18-23	Glacial till
LA	lysimeter	430040091325404	1,069	NA	8.5	Alluvium
LB	lysimeter	430040091325405	1,069	NA	7.0	Alluvium
LC	lysimeter	430040091325406	1,069	NA	5.5	Alluvium
LD	lysimeter	430040091325407	1,069	NA	4.0	Alluvium
LE	lysimeter	430040091325419	1,084	NA	10.0	Loess
LF	lysimeter	430040091325420	1,084	NA	7.0	Loess
LG	lysimeter	430040091325421	1,084	NA	4.0	Loess
T2	tile-line discharge	430040091325408	1,070	NA	NA	Alluvium

level fluctuations in the loess deposits and to determine the relation of the water-table altitude on the hillslope to the water-table altitude near Deer Creek. A hollow-stem auger was used to drill holes to the desired depth. A 4 in.-diameter polyvinyl chloride (PVC) casing in which slots had been cut for a screen then was lowered into the hole. Sand was backfilled around the casing to a height of about 1 ft above the slotted interval. Drill cuttings then were backfilled to the surface. Water levels were sensed by a float and then recorded hourly on paper tape for subsequent storage in the U.S. Geological Survey's National Water Data Storage and Retrieval System (WATSTORE). The water-level altitude was calculated by subtracting the water level in feet below land surface from the altitude of the land surface. The altitude of land surface at the wells was determined by differential levels from a benchmark about 1.5 mi from the study area.

Four observation wells, W2, W3, W8, and W11(fig.5) were installed specifically to obtain water samples. PVC casing (2-in. diameter) with 2 ft of PVC screen, was lowered into the hole and aquifer material then was allowed to collapse around the screen. Sand and gravel were used to backfill around the screen. The remainder of the borehole was backfilled with native material. Well W2 was screened in alluvial material, well W3 in a sand lens in glacial till, and wells W8 and W11 at the base of the loess deposits.

Two lysimeter nests (fig. 5) were installed to collect water samples at discrete depths in the unconsolidated alluvium and loess. The lysimeter nests were located about 25 ft into the field. Suction and sample collection tubes were trenched to the edge of the field. Individual lysimeters were installed in holes hand augered to the specific depth. Silica flour was poured around the lysimeters to reduce plugging of the pores. One nest of four suction lysimeters was installed in the fall of 1988 to sample water in the alluvial material near Deer Creek. The ceramic cups of lysimeters LA, LB, LC, and LD (table 2), were set at 8.5, 7.0, 5.5, and 4.0 ft below land surface, respectively. A second lysimeter nest was installed in the fall of 1990 to collect water from loess material on the hillslope. Three lysimeters, LE, LF, and LG, were set at 10.0, 7.0, and 4.0 ft below land surface, respectively.

Water samples were collected monthly from the observation wells, lysimeters and a tile line. Occasionally samples were collected after substantial rainfall. Before sample collection, the water level in each well was measured and recorded. To obtain a representative water sample from the aquifer, samples were collected from wells after a minimum of three casing volumes had been pumped from the well or the well had been pumped dry and allowed to recover. Water was collected unfiltered into glass and polyethylene sample containers. Additional water was pumped into a Teflon[1] container for onsite water-quality measurements. Water temperature was measured in the pump discharge with a standard mercury thermometer that had been compared with a laboratory-grade thermometer for accuracy. Specific conductance and pH were measured immediately upon sample collection with instruments that were calibrated with two specific conductance and two pH reference solutions. Before sample collection, the lysimeters were evacuated to a vacuum of 0.60 to 0.70 bar by a hand pump and allowed to equilibrate for 24 hours, allowing water to flow into the lysimeter under partial-vacuum conditions. The samples were removed by purging the lysimeters with air. Samples for analysis of nitrogen species were preserved with sulfuric acid and chilled. Samples for the analyses of selected herbicides were chilled for shipment to the laboratory.

Tile lines generally are installed to lower the water table in a relatively large area of the alluvial aquifer adjacent to Deer Creek to make the land suitable for modern agricultural practices. Water discharged from the tile lines is a composite of the water in the upper part of the alluvial aquifer in a relatively large area in comparison to the water from the lysimeters or observation wells. The water discharging from a tile line at siteT2 (fig.5) upstream from lysimeters LA-LD was sampled to determine alluvial water quality in this area.

Water samples were analyzed by the University of Iowa Hygienic Laboratories (UHL) in Iowa City and Des Moines, Iowa. Samples were analyzed for herbicides by U.S. Environmental Protection Agency (EPA) Method 81.40, modified to use dual capillary columns, and nitrite plus nitrate was analyzed by EPA Method 353.2 (U.S. Environmental Protection Agency, 1983). The detection limit for all herbicides was 0.10 µg/L (micrograms per liter); the detection limit for nitrite plus nitrate was 0.10 mg/L (milligrams per liter) as nitrogen. No attempt was made to correct for the recovery rate in herbicide concentrations. Nitrite concentrations in most samples were less than the detection limit, therefore, nitrite plus nitrate as nitrogen is referred to as nitrate-N in this report. Ammonia in water samples is reported as ammonia-N, and organic nitrogen in water samples is reported as organic-N.

Surface Water

The surface water discharged from the Deer Creek watershed was gaged at monitoring site DC5 (fig. 5). An artificial control, a V-notch thin-plate weir, was installed to improve the

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[1] The use of trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

accuracy of the stream discharge record. The level of the water pooled upstream of the weir was recorded hourly using a float sensor and an electronic datalogger. Discharge was calculated using the standard-discharge equation for a 90^0 V-notch weir (Rantz and others, 1982, p. 305) and was verified using standard current-meter methods (Buchanan and Somers, 1969). Current-meter measurements also were used to develop the stage-discharge rating when the water level was higher than the top of the weir.

Selected physical properties and water-quality constituents in surface water were measured on-site and water samples were collected monthly or during substantial rains at site DC5 on Deer Creek. Specific conductance, pH, water temperature, and dissolved-oxygen (DO) concentration were measured in a flowing section of the stream. During base-flow, water samples for the analyses of chemical constituents were collected from the discharge through the weir. During storms or snowmelt, samples were collected by grab samples in the center of flow. Immediately after sample collection, specific conductance and pH of the water were measured with respective meters. Water temperatures were measured with a standard mercury or alcohol thermometer that had been compared to a laboratory grade thermometer for accuracy. DO was measured in the stream with a dissolved-oxygen meter. Water samples were preserved and analyzed by methods described previously in the ground-water methods section of this report.

Data Analysis

Several analytical techniques were used to help interpret and understand the data produced by field measurements and chemical analyses of water samples. Nonparametric statistical procedures were used to summarize and compare the data. Two hydrographic separations techniques were used to understand where the water flowing in Deer Creek originated so that the transport processes can be better understood.

One of the basic assumptions in determining measures of central tendency (mean) and variability (standard deviation) of constituent concentrations is that the data are normally distributed. Based on the "univariate" procedure with the "normal" option of the SAS statistical software system (SAS Institute, Inc., 1990), only the pH and dissolved-oxygen concentrations of the samples collected from Deer Creek were normally distributed. Thus, the mean and standard deviation of the remaining data may be skewed and may not accurately represent the quality of the stream and the ground water. Alternative nonparametric procedures (based on rank), which does not rely on the presence of normally distributed data, were used to prepare a descriptive statistical summary and to test the differences between data sets. The nonparametric equivalent of the mean is the median, and the nonparametric equivalent of the standard deviation is the interquartile range. One-half of the data values are less than or equal to the median, and one-half of the values are equal to or greater than the median. The interquartile range is the range of values between the 25th percentile and the 75th percentile. Twenty-five percent of the values are less than or equal to the 25th percentile, and 75 percent of the values are less than or equal to the 75th percentile. The relation between constituents were tested using Spearman's rank correlation and the Kruskal-Wallis test (Helsel and Hirsh, 1992). Spearman's rank correlation is a measure of the monotonic relation between two continuous variables. The Kruskal-Wallis one-way analysis by ranks is an extension of the Mann-Whitney rank sum test than can test for differences in the medians of two or more groups.

Hydrographic (Sloto, 1991) and isotopic separation (Sklash and others, 1986) techniques were used to determine the source of water to Deer Creek and thus help explain the source of agricultural chemicals in the stream. Several computerized empirical methods that separate the discharge hydrograph into the ground-water and overland-flow components were used.

Ground water and precipitation commonly have distinct isotopic compositions due to fractionation by physical and chemical processes in nature (Faure, 1977). This difference allows the isotopic compositions to be used as tracers to determine the source of water (Sklash and others, 1986). On the basis of this theory, a limited number of water samples from rainfall, ground water, and Deer Creek discharge were collected for the analyses of oxygen-18/oxygen-16 ($^{18}O/^{16}O$) isotopic ratios. The individual components of stream discharge (ground-water inflow and overland flow) were determined using $^{18}O/^{16}O$ isotopic ratios in precipitation during a storm (new water), in ground water collected before the storm (old water), and in Deer Creek. Assuming that the isotopic ratio in the ground water is homogeneous, the fraction of stream discharge contributed by each source was calculated with the following equations;

$$Po = \left(\frac{Rs - Rn}{Ro - Rn}\right) x100 \ , \qquad (1)$$

where Po = percentage of stream discharge from old water;

Rs = $^{18}O/^{16}O$ ratio in Deer Creek;

Rn = $^{18}O/^{16}O$ ratio in precipitation during storm; and

Ro = $^{18}O/^{16}O$ ratio in ground water before storm.

$$Pn = \left(\frac{Rs - Ro}{Rn - Ro}\right) x100 \ , \qquad (2)$$

where Pn = percentage of stream discharge from new water;

Rs = $^{18}O/^{16}O$ ratio in Deer Creek;

Ro = $^{18}O/^{16}O$ ratio in ground water before storm; and

Rn = $^{18}O/^{16}O$ ratio in precipitation during storm.

AGRICULTURAL CHEMICALS IN GROUND WATER

Because ground water is an important source of water to Deer Creek, the occurrence of agricultural chemicals in ground water may substantially affect the water quality of Deer Creek. The most immediate affect would be from water in the alluvial aquifer adjacent to the stream. Water in the alluvium adjacent to Deer Creek contained nitrogen and several herbicides in concentrations that varied by depth and by season.

Occurrence and Variability with Depth

Agricultural chemicals were detected most frequently, and concentrations were the greatest in water from the upper 5 ft of the alluvium. Statistical summaries of the nitrogen species and selected herbicide concentrations in ground-water samples are listed in tables 3 and 4. Individual results of sample analyses are published in Kalkhoff and Kuzniar (1991; 1994) and Kalkhoff and others, 1992.

Nitrate-N, the major nitrogen species in solution, was detected in less than 10 percent of the alluvial samples from 7.0 ft and 8.5 ft (LB and LA) below land surface. In contrast nitrate N was detected in more than 90 percent of the alluvial samples from 4.0 and 5.5 ft (LD and LC) below land surface (table 3). The median nitrate concentration decreased from 16 mg/L at 4.0 ft to less than the detection limit (0.10 mg/L) at 8.5 ft. These results are similar to other studies (Thompson, 1986, 1987; Detroy and others, 1990; Hansen and others, 1992), which found that nitrate concentrations were largest near the top of alluvial aquifers in Iowa. Although the frequency of detection was less than 20 percent at all depths, ammonia-N was detected more uniformly throughout the vertical section (table 3) than was nitrate. The maximum ammonia-N concentrations were less than or equal to 0.40 mg/L. Organic-N was commonly detected at all depths in the aquifer but did not exceed 1.1 mg/L. Organic-N concentrations were larger in the samples from the shallower (4.0 and 5.5 ft) lysimeters than in samples from the deeper (7.0 and 8.5 ft) lysimeters. This trend suggests that the organic N is derived from the surface or shallow soil zone. The organic-N may be from organic compounds that resulted from the degradation of plant materials or that were produced biochemically in the soil zone (Freeze and Cherry, 1979, p. 241).

Identification of individual nitrogen species is important in understanding the transformation and transport processes of nitrogen. Discussion of the total nitrogen concentrations and loads (nitrate-N plus ammonia-N plus organic-N) is useful to summarize the distribution and movement of nitrogen in the environment irrespective of the form. Nitrogen was rarely transported deeper than about 6.0 ft in the alluvial aquifer near Deer Creek. Total nitrogen concentrations were similar to nitrate-N and organic-N concentrations in the alluvial aquifer. The largest total nitrogen concentrations were in the shallowest sampled part of the aquifer (fig. 6). Total-N concentrations were commonly larger than 10 mg/L in samples from 4.0 ft below land surface. With the exception of samples collected in 1991, the total nitrogen concentration in samples from 5.5 ft below land surface ranged from 0.1 to 3.0 mg/L. Total nitrogen concentrations were rarely greater than 0.10 mg/L in water 7.0 ft or more below land surface.

Atrazine and metolachlor, the most commonly used herbicides on the watershed, were most frequently detected in the upper part of the alluvial aquifer (fig. 7, table 4). Alachlor and cyanazine were rarely (less than 10 percent) detected throughout the aquifer. Atrazine was detected in more than 85 percent of the samples from the two shallowest lysimeters at 4.0 and 5.5 ft (table 4). Maximum concentrations were 0.96 µg/L at 5.5 ft and 3.6 µg/L at 4.0 ft. In contrast, atrazine was detected in only 3 and 11 percent of the alluvial samples and the maximum atrazine concentrations were 0.10 and 0.25 µg/L at 7.0 and 8.5 ft, respectively. Metolachlor was detected in 32 and 15 percent of the samples from 4.0 and 5.5 ft below land surface. Metolachlor was not detected in lysimeters at 7.0 and 8.5 ft. The maximum metolachlor concentration was 0.83 µg/L.

A possible explanation for the stratification of agricultural chemicals in the alluvial aquifer near Deer Creek is the flow system. Theoretically, a stream is considered to be a discharge point for a homogeneous alluvial aquifer. Near the discharge point there is a component of the flow that is upward towards the stream (Freeze and Cherry, 1979). This upward flow would prevent movement of water and agricultural chemicals from the unsaturated zone to the base of the aquifer. Water that infiltrated locally would mix only with the uppermost water in the aquifer before being transported laterally to Deer Creek. The water deeper in the aquifer has infiltrated through the soil and entered the aquifer farther up the hillside. The water in the lower part of the aquifer contains little detectable nitrogen or herbicides because either none were present at the point and time of infiltration or because degradation, sorption, or dilution has occurred since infiltration.

The water quality of samples collected from well W2 was different than the quality of samples collected from the lysimeters. Lysimeters were used to determine water quality at discrete depths in the alluvial aquifer. In contrast, water quality data obtained from well W2 represents a mix of waters through the screened interval (3 ft.) of the well and water drawn into the well from shallower parts of the alluvial aquifer by pumping. The median concentrations of the nitrogen species and selected herbicides in samples from well W2 were similar to those from lysimeters LA and LB (table 3 and 4). Well W2 was screened at an altitude of about 1,059 to 1,062 feet above sea level. This corresponds to the altitude of the deepest alluvial lysimeters, LA and LB.

The quality of water in the alluvial aquifer discharged at T2 is similar to that in the upper part of the aquifer at lysimeters LA-LD. Concentrations of nitrate, ammonia, atrazine, and metolachlor were in samples from T2 were similar to concentrations in samples from lysimeter LC and LD . There were an insufficient number of samples with detectable alachlor and cyanazine concentrations to make a similar comparison. The organic nitrogen concentrations in the tile line samples were greater than in the alluvial aquifer at lysimeter LC and LD. Differences in organic nitrogen concentrations may be caused by the variability of the organic content of the alluvial soils. The organic matter content of the alluvial soil

Table 3.--Statistical summary of nitrogen in ground water from the Deer Creek watershed, October 1988 through September 1991

[Concentrations in milligrams per liter; <, concentration less than detection limit; --, not applicable]

Monitoring site (fig. 5)	Sampling depth (feet below land surface)	Number of samples	Samples with detections (percent)	Concentration				
				Minimum	25th percentile	Median	75th percentile	Maximum
				Nitrite plus nitrate as nitrogen				
W2	8-11	42	60	< 0.10	<0.10	0.15	1.3	28
W3	13-15	30	27	< .10	<.10	<.10	.10	.60
W8	10-15	6	100	19	29	30	30	33
W11	18-23	8	38	<.10	<.10	< .10	.10	1.4
LA	8.5	35	9	<.10	<.10	<.10	<.10	.10
LB	7.0	34	6	< .10	<.10	< .10	<.10	.70
LC	5.5	33	94	< .10	.20	.40	.50	8.3
LD	4.0	28	100	1.8	5.8	16	33	63
LE	10.0	7	100	13	13	14	16	16
LF	7.0	7	100	39	40	40	46	47
LG	4.0	5	100	100	110	110	120	140
T2	--	31	100	.60	3.7	7.4	19	43
				Ammonia as nitrogen				
W2	8-11	42	40	< .10	<.10	< .10	.20	1.5
W3	13-15	30	83	< .10	.10	.20	.20	.30
W8	10-15	6	50	< .10	<.10	< .10	.10	.50
W11	18-23	8	88	< .10	.20	.20	.35	.60
LA	8.5	35	14	< .10	<.10	< .10	<.10	.40
LB	7.0	34	18	< .10	<.10	< .10	<.10	.30
LC	5.5	33	15	< .10	<.10	< .10	<.10	.30
LD	4.0	26	12	< .10	<.10	< .10	<.10	.30
LE	10.0	7	29	< .10	<.10	< .10	.10	.30
LF	7.0	7	43	< .10	<.10	< .10	.10	.30
LG	4.0	5	40	< .10	<.10	< .10	.10	.40
T2	--S	31	26	< .10	<.10	< .10	.10	.50
				Organic nitrogen as nitrogen				
W2	8-11	42	81	< .10	.10	.20	.40	8.8
W3	13-15	30	80	< .10	.10	.20	.40	1.0
W8	10-15	6	83	< .10	.30	.60	.90	1.2
W11	18-23	8	75	< .10	<.10	.25	2.7	7.3
LA	8.5	35	63	< .10	<.10	.10	.20	.40
LB	7.0	34	74	< .10	<.10	.10	.20	.40
LC	5.5	33	91	< .10	.20	.30	.40	.80
LD	4.0	28	100	.10	.40	.65	.80	1.1
LE	10.0	7	86	< .10	.10	.20	.30	.40
LF	7.0	7	86	< .10	.20	.30	.50	.50
LG	4.0	5	80	< .10	.40	.40	.50	.90
T2	--	31	100	.60	.70	1.3	1.6	3.3

Table 4.--Statistical summary of selected herbicides in ground water from the Deer Creek watershed, October 1988 through September 1991

[Concentrations in micrograms per liter; <, concentration less than detection limit; --, not applicable]

Monitoring site (fig. 5)	Sampling depth (feet below land surface)	Number of samples	Samples with detections (percent)	Concentration				
				Minimum	25th percentile	Median	75th percentile	Maximum
				Alachlor				
W2	8-11	42	0	<0.10	<0.10	<0.10	<0.10	<0.10
W3	13-15	30	3	<.10	<.10	<.10	<.10	.20
W8	10-15	5	20	<.10	<.10	<.10	<.10	.23
W11	18-23	8	0	<.10	<.10	<.10	<.10	<.10
LA	8.5	37	3	<.10	<.10	<.10	<.10	.13
LB	7.0	37	8	<.10	<.10	<.10	<.10	.46
LC	5.5	34	3	<.10	<.10	<.10	<.10	.35
LD	4.0	31	6	<.10	<.10	<.10	<.10	.60
LE	10.0	7	0	<.10	<.10	<.10	<.10	<.10
LF	7.0	7	0	<.10	<.10	<.10	<.10	<.10
LG	4.0	3	0	<.10	<.10	<.10	<.10	<.10
T2	--	31	0	<.10	<.10	<.10	<.10	<.10
				Atrazine				
W2	8-11	42	21	<.10	<.10	<.10	<.10	2.4
W3	13-15	30	17	<.10	<.10	<.10	<.10	4.0
W8	10-15	5	100	.18	.33	.61	1.2	8.3
W11	18-23	8	12	<.10	<.10	<.10	<.10	.15
LA	8.5	37	11	<.10	<.10	<.10	<.10	.25
LB	7.0	37	3	<.10	<.10	<.10	<.10	.10
LC	5.5	34	88	<.10	.10	.16	.46	.96
LD	4.0	31	97	<.10	.44	.58	1.1	3.6
LE	10.0	7	57	<.10	<.10	.10	.14	.19
LF	7.0	7	100	.29	.38	.63	.70	.91
LG	4.0	3	100	.28	.28	.40	.73	.73
T2	--	31	71	<.10	<.10	.19	.30	.54
				Cyanazine				
W2	8-11	42	5	<.10	<.10	<.10	<.10	.23
W3	13-15	30	3	<.10	<.10	<.10	<.10	.34
W8	10-15	5	0	<.10	<.10	<.10	<.10	<.10
W11	18-23	8	0	<.10	<.10	<.10	<.10	<.10
LA	8.5	37	3	<.10	<.10	<.10	<.10	.14
LB	7.0	37	8	<.10	<.10	<.10	<.10	.92
LC	5.5	34	6	<.10	<.10	<.10	<.10	1.4
LD	4.0	31	6	<.10	<.10	<.10	<.10	.23
LE	10.0	7	0	<.10	<.10	<.10	<.10	<.10
LF	7.0	7	0	<.10	<.10	<.10	<.10	<.10
LG	4.0	3	0	<.10	<.10	<.10	<.10	<.10
T2	--	31	0	<.10	<.10	<.10	<.10	<.10

Table 4.--Statistical summary of selected herbicides in ground water from the Deer Creek watershed, October 1988 through September 1991

[Concentrations in micrograms per liter; <, concentration less than detection limit; --, not applicable]

Monitoring site (fig. 5)	Sampling depth (feet below land surface)	Number of samples	Samples with detections (percent)	Concentration				
				Minimum	25th percentile	Median	75th percentile	Maximum
				Metolachlor				
W2	8-11	41	5	< .10	<.10	< .10	<.10	.82
W3	13-15	30	6	< .10	<.10	< .10	<.10	.15
W8	10-15	5	60	< .10	<.10	.21	.73	4.0
W11	18-23	8	0	< .10	<.10	< .10	<.10	< .10
LA	8.5	37	0	< .10	<.10	< .10	<.10	< .10
LB	7.0	37	0	< .10	<.10	< .10	<.10	< .10
LC	5.5	34	15	< .10	<.10	< .10	<.10	.50
LD	4.0	31	32	< .10	<.10	< .10	.24	.83
LE	10.0	7	0	< .10	<.10	< .10	<.10	< .10
LF	7.0	7	14	< .10	<.10	< .10	<.10	.27
LG	4.0	3	0	< .10	<.10	< .10	<.10	< .10
T2	--	31	16	< .10	<.10	< .10	<.10	.85

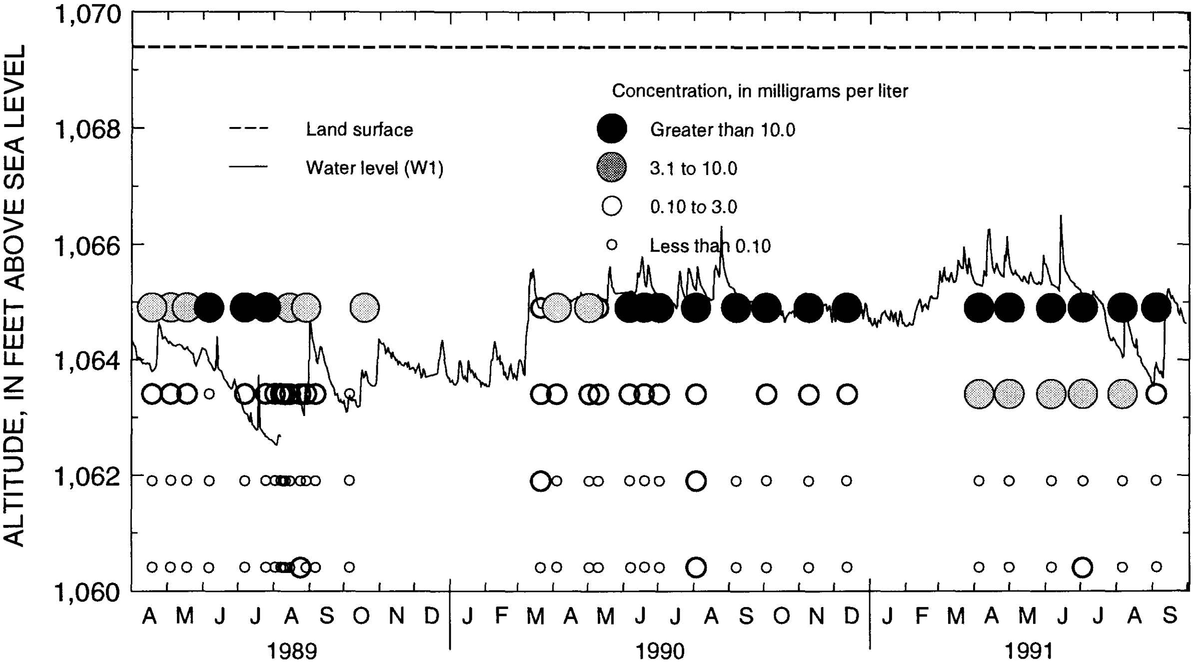

Figure 6. Total nitrogen concentrations in the alluvium near Deer Creek, Clayton County, Iowa.

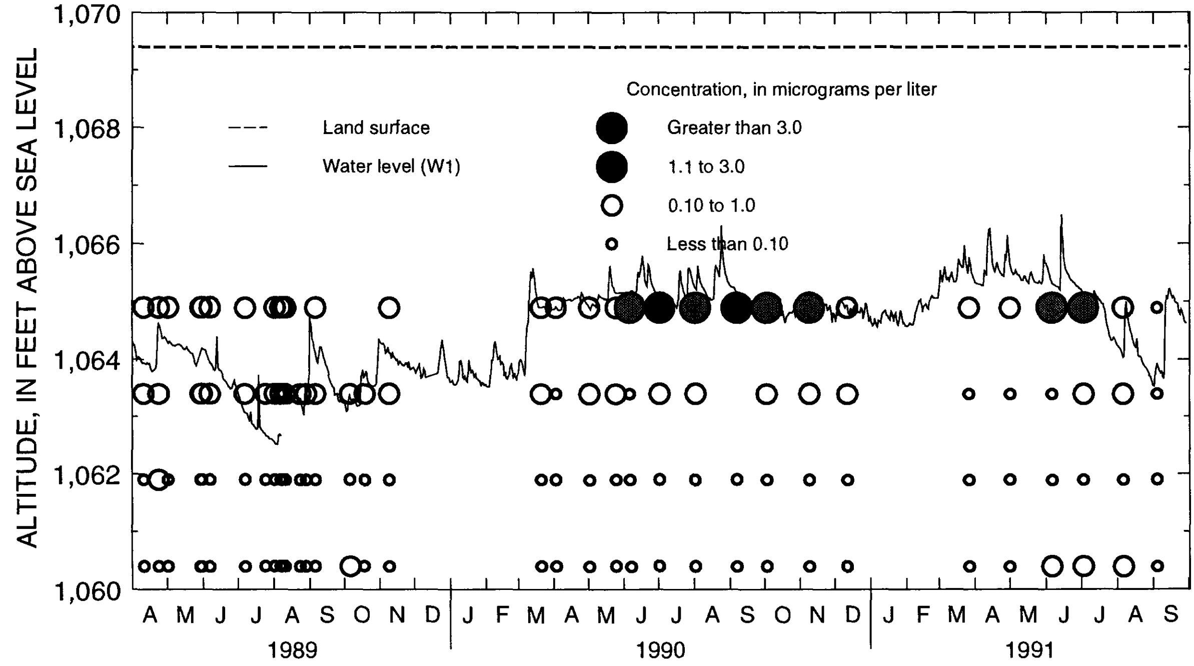

Figure 7. Atrazine concentrations in the alluvium near Deer Creek, Clayton County, Iowa.

(Ossian silt loam) in the study area varies from five to seven percent (Kuehl, 1982). Similar concentrations of several agricultural chemicals in shallow water at the lysimeters LA-LD and in the area drained by the tile line may indicate that water quality of the alluvial aquifer is relatively homogeneous in the study area.

Water samples were collected to determine the concentration of nitrogen and selected herbicides in water from the unconsolidated loess on the hillslope which may be a potential source of these compounds to the alluvial aquifer. Samples from well W8 (fig. 5) were collected from December 1990 to June 1991. At lysimeters LE, LF, and LG, which are downslope from well W8 (fig. 5), additional samples were collected from March through September 1991.

Nitrate-N was detected in 100 percent of the loess water samples. The W8 samples, from 10 to 15 ft below land surface, had a median concentration of 30 mg/L (table 3). The samples from LE, LF, and LG, had decreasing median concentrations with depth; median concentrations decreased from 110 to 40 to 14 mg/L as sampling depth increased from 4.0 to 7.0 to 10 ft below land surface (table 3). On each date of sample collection from these lysimeters, the nitrate-N concentrations decreased with depth (fig. 8). Ammonia-N was detected in 50 percent of the W8 samples, but in only 37 percent of the lysimeter samples (table 3). For W8 and the lysimeters, the median ammonia-N concentration was less than the detection limit of 0.10 mg/L. The maximum ammonia-N concentrations in samples from loess were less than or equal to 0.50 mg/L.

Organic-N was detected in more than 80 percent of the loess water samples. The W8 samples had a median concentration of 0.60 mg/L, with a maximum concentration of 1.2 mg/L and a minimum concentration less than the detection limit of 0.10 mg/L. The lysimeter samples again had decreasing concentrations with depth. Median concentrations were 0.40, 0.30, and 0.20 mg/L for lysimeters LG, LF, and LE, respectively. Maximum concentrations decreased from 0.90 to 0.40 mg/L with depth.

As in the alluvial samples, atrazine and metolachlor were the most frequently detected herbicides in the loess. Alachlor was detected in one W8 sample and cyanazine was not detected in any of the loess samples. Atrazine was

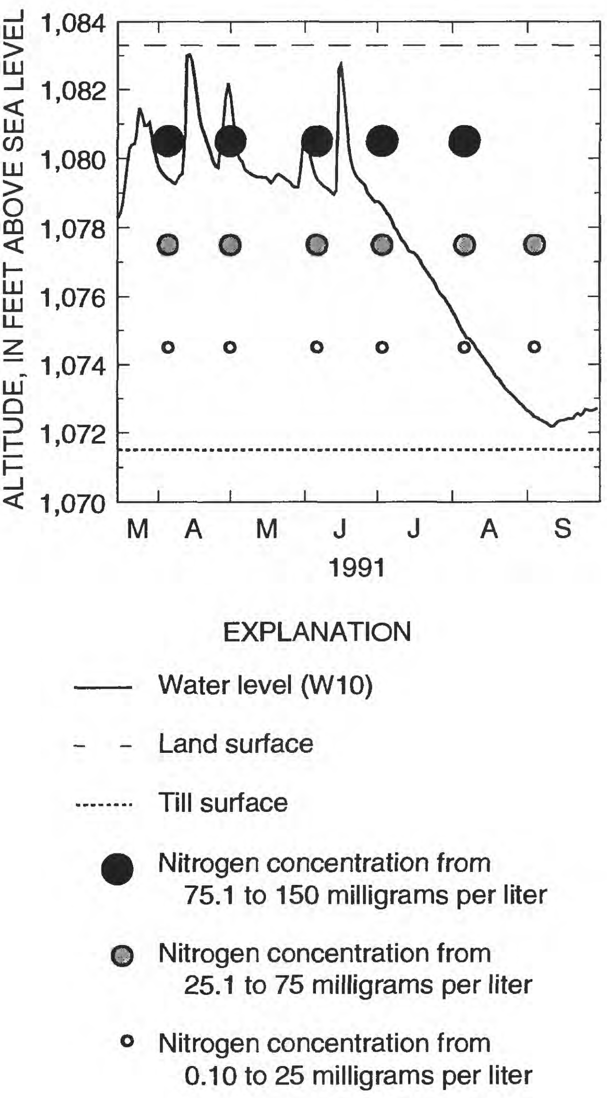

Figure 8. Total nitrogen concentrations in the hillslope loess near Deer Creek, Clayton County, Iowa.

detected in 100 percent of the W8, LG, and LF samples and in 57 percent of the LE samples (table 4). The atrazine concentrations ranged from 0.18 to 8.3 µg/L with a median concentration of 0.61 µg/L in samples from W8. For atrazine, the largest median concentrations were from the middle lysimeter, LF; the intermediate median concentrations were from the upper lysimeter, LG; and the smallest median concentrations were from the deepest lysimeter, LE (fig. 9). Metolachlor was detected in 60 percent of the W8 samples, with concentrations ranging from less than 0.10 to 4.0 µg/L and a median concentration of 0.21 µg/L. One lysimeter sample from the hillside loess had a metolachlor concentration of 0.27 µg/L. No metolachlor was detected in the remainder of the lysimeter samples from the loess.

Seasonal Variability

Nitrate-N concentrations varied seasonally in the alluvial aquifer near Deer Creek. Seasonal variability was not evident in the concentrations of ammonia-N and organic N (fig. 10). The monthly median nitrate N concentrations in January and February were less than the detection limit of 0.10 mg/L but increased in the spring and peaked at 2.0 mg/L in April. After April, the monthly median nitrate-N concentrations decreased to less than detection limits in September. The spring nitrate peak may be due to decomposing plants and winter-applied manure. All monthly median ammonia-N concentrations were less than 0.10 mg/L, the detection limit, and October had the largest 75th percentile concentration of any month, only 0.30 mg/L. Monthly median organic-N concentrations were all between 0.20 and 0.40 mg/L, with the greatest median concentrations in February and July.

Seasonal variability was not apparent for alachlor or cyanazine concentrations in the alluvial aquifer, but it appears that atrazine concentrations varied seasonally (fig. 11). Alachlor was detected only in June and even then the 75th percentile was less than the detection limit of 0.10 µg/L. Monthly median atrazine concentrations in alluvial ground-water samples ranged from 0.14 µg/L in June to less than 0.10 µg/L in several other months, but it appears that concentrations gradually increased until they peaked in June and July, and then gradually decreased. Atrazine concentrations in the alluvial aquifer increased after application in April and May and decreased as degradation and transport via

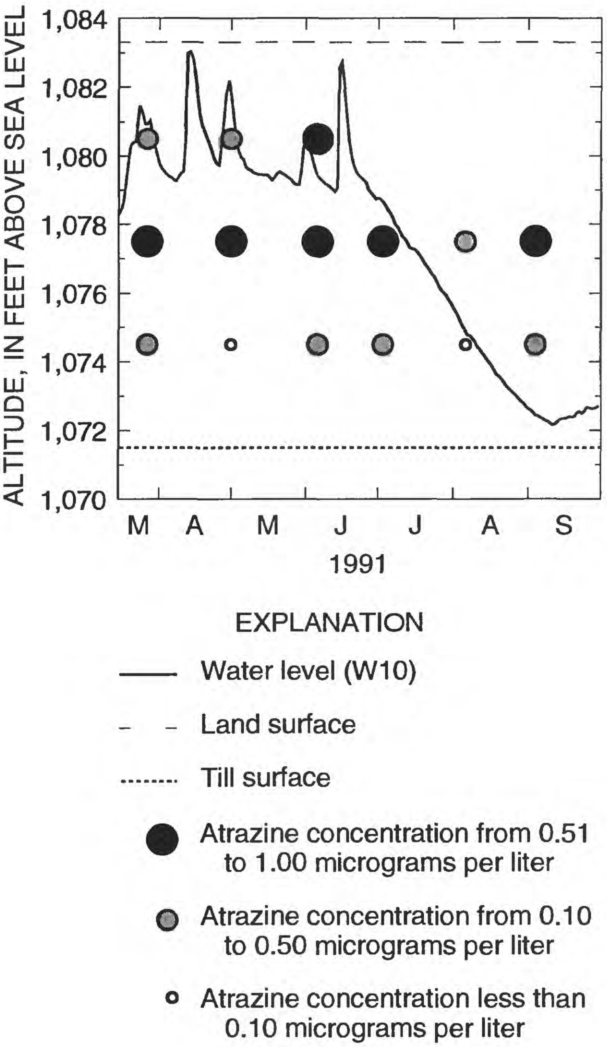

Figure 9. Atrazine concentrations in the hillslope loess near Deer Creek, Clayton County, Iowa.

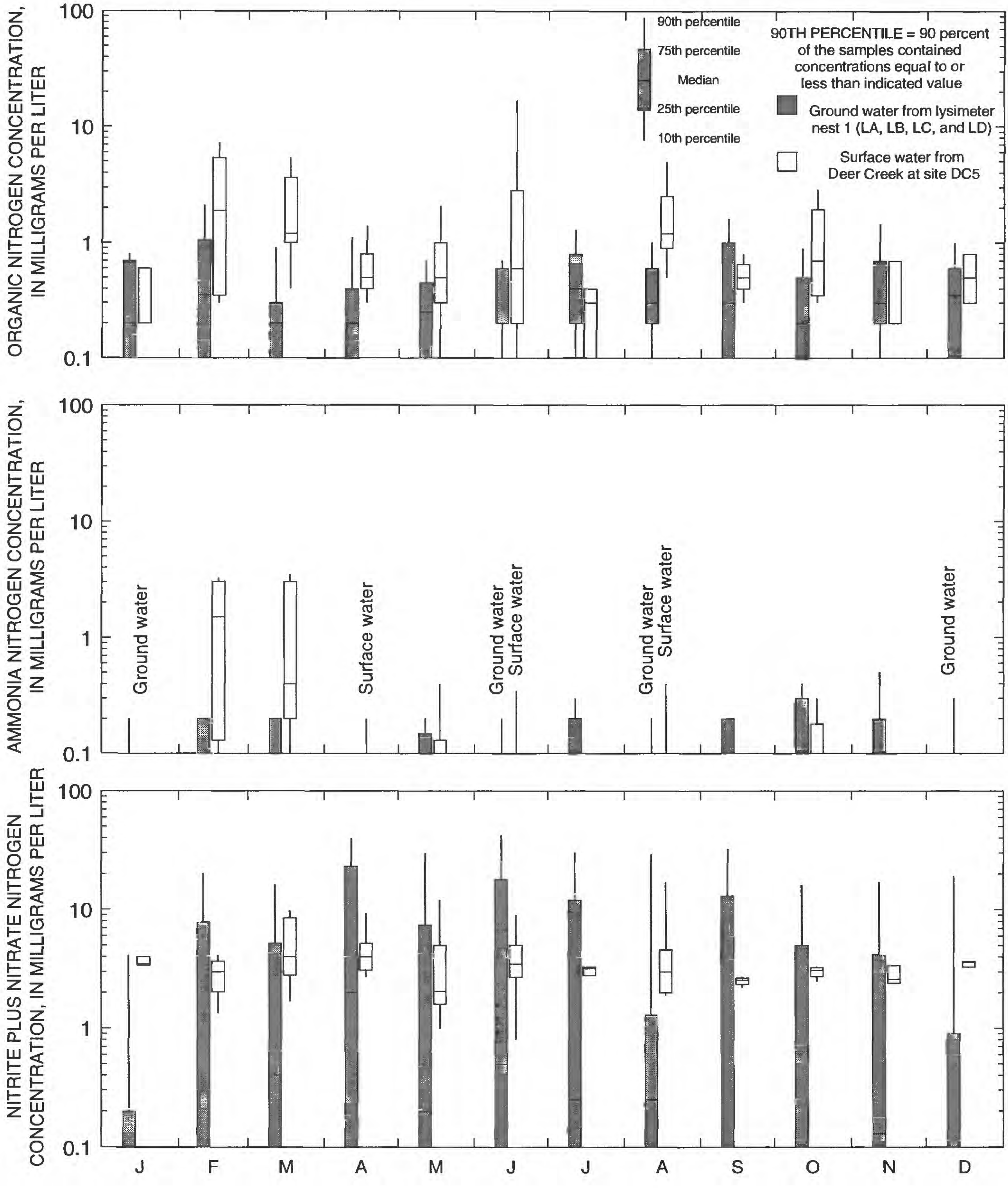

Figure 10. Monthly nitrogen concentrations in ground water and surface water in the Deer Creek watershed, Clayton County, Iowa, 1988-91.

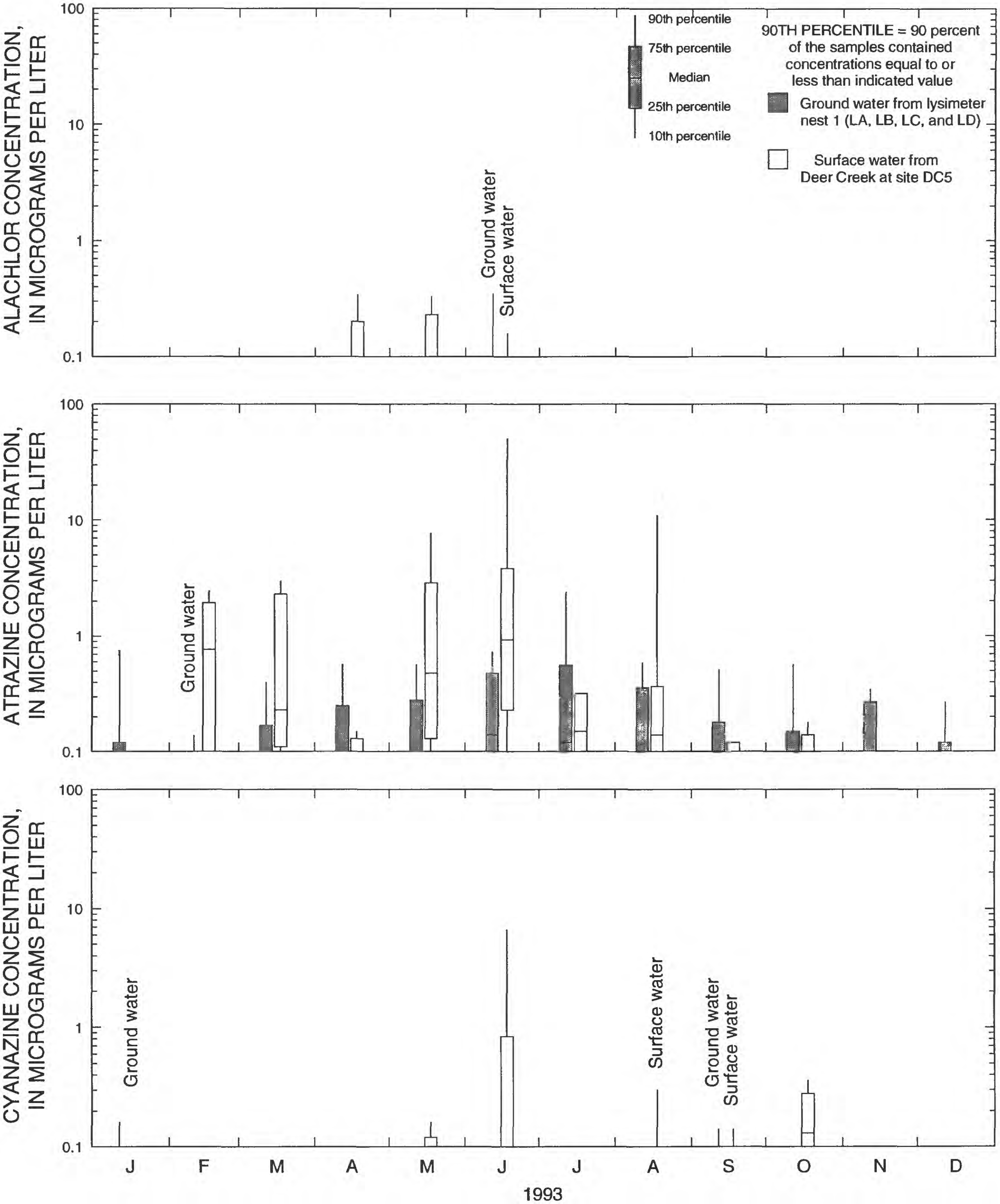

Figure 11. Monthly herbicide concentrations in ground and surface water in the Deer Creek watershed, Clayton County, Iowa, 1988-91.

Deer Creek removed the atrazine from the watershed. Cyanazine was detected only in January and September and for both months the 90th percentile concentration was less than 0.20 µg/L.

Source

The source of agricultural chemicals in the alluvial aquifer is most likely from direct infiltration of fertilizers and herbicides transported from the soil by precipitation to the water table and from water moving to the aquifer from upgradient unconsolidated material on the hillslopes. Measurable quantities of nitrogen and herbicides also originate from rainfall (Nations and Hallberg, 1992).

Transport of agricultural chemicals by precipitation infiltrating through the soil is the most direct source of agricultural chemicals to the alluvial aquifer. Rapid infiltration of rain water may occur along preferential flow paths, primarily through macropores (Shuford and others, 1977; Thomas and Phillips, 1979). This conclusion is supported by data which indicate that the water level in the alluvial aquifer responded in less than one hour after intense rainfall (0.46 in. within 15 minutes) on May 29, 1991 (fig. 12). During a longer, less-intense rain on April 12, 1991, the water level peaked in less than 18 hours after the start of rain. Atrazine concentrations in the shallowest part of the aquifer increased from 0.74 µg/L on May 1, 1991, to 1.1 µg/L about one month later on June 6, 1991(Kalkhoff and Kuzniar, 1994) even though atrazine had not been applied to the field in 1991. The combination of a rapid water level increase with rainfall and an increase in atrazine concentration during a one-month period suggests that rain infiltrating through the soil transported residual atrazine to the aquifer.

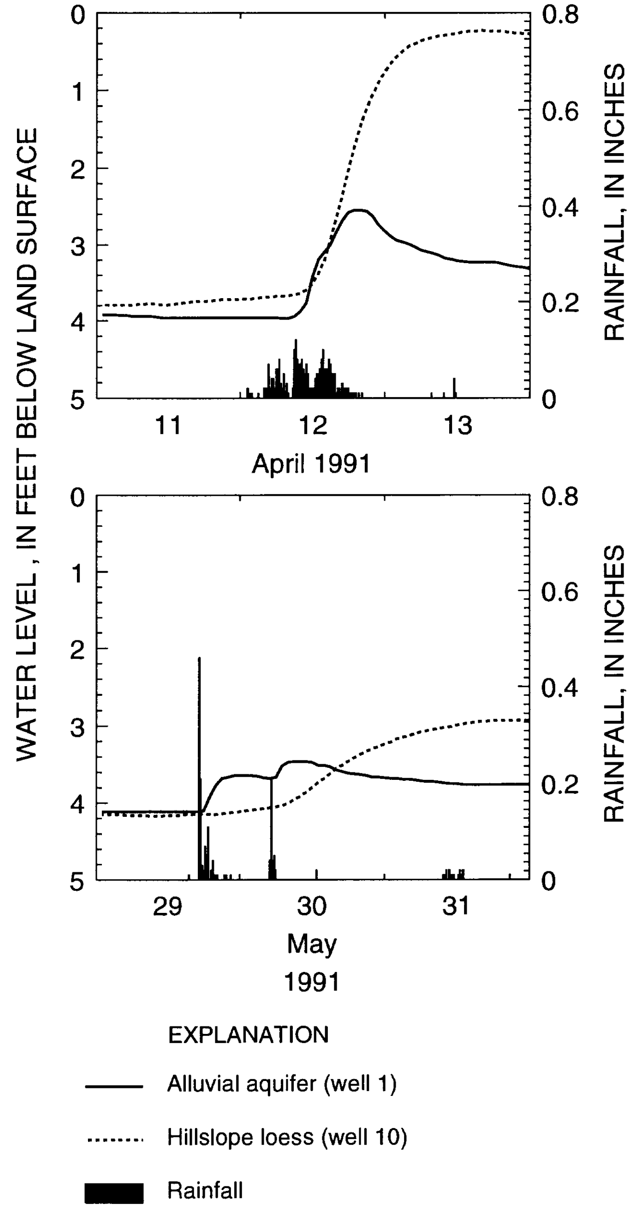

Figure 12. Relation between rainfall and water levels in shallow unconsolidated materials in the Deer Creek watershed.

The unconsolidated loess may be another persistent source of agricultural chemicals to the alluvial aquifer. The loess deposits on the hillslope were recharged in the spring after snowmelt and periodically by rains during the summer (fig. 8). The water table in the hillslope loess deposits responded rapidly after longer duration low-intensity rains and, in contrast, showed no apparent response to short-duration intense rain on May 29, 1991 (fig. 12). During intense rainfall, the soil rapidly becomes saturated, limiting infiltration. Once the soil surface is saturated, additional rainfall runs off the hillslope. Infiltration of water and agricultural chemicals is dependent on the rate of precipitation on the hillslope loess. When rainfall decreased in late summer, the water level in well W10 gradually decreased. Water in the unconsolidated loess material on the hillslope moves slowly downslope to the alluvial aquifer (fig. 2). Estimated rates of movement based on a gradient of about 18 ft in the 508 ft distance from well W8 to well W7 on July 2, 1991, and on a range of hydraulic conductivities for silt of 3.28×10^{-7} ft/s and 3.28×10^{-5} ft/s (Freeze and Cherry,1979, p. 29) were 2.5×10^{-3} to 0.25 ft/d. On the basis of these rates, it would require from about 8.2 to 820 years for water to travel from well W8 to Deer Creek. These slow estimated rates of movement do not appear to be consistent with the rapid water-level declines in the hillslope loess (fig.8). Results of particle-size analyses (Carol Anderson, U.S. Geological Survey, written commun., 1991) indicate that the colluvial layer at the base of the loess contains as much as 50 percent sand-sized material and thus is substantially more conductive than the silt-sized loess material. An estimated rate of movement using the same gradient as above and a hydraulic conductivity for silty sand of 3.28×10^{-4} ft/s (Freeze and Cherry,1979, p. 29) is about 25 ft/d. Based on this estimate, water moving through the colluvial material would require about 30 days to travel from well W8 to Deer Creek. Undoubtedly, evapotranspiration accounted for some of the decline in the water table in the hillslope loess, but the water containing nitrogen and atrazine also moved downslope to the alluvial aquifer. Analysis of this limited data raises many questions about rates and processes of nitrogen and herbicide transport in loess deposits and additional studies would improve our understanding of this potentially important source of agricultural chemicals to alluvial aquifers and streams.

Small but measurable quantities of nitrogen and herbicides were input into the Deer Creek watershed from precipitation. During 1989 through 1991, about 5 to 6 lb/acre of nitrogen were contributed to the watershed from precipitation (National Atmospheric Deposition Program, 1990, 1991, and 1992). Ammonia-N deposition generally was greater than nitrate-N deposition. Nations and Hallberg (1992) reported that the atrazine load contributed to the Big Spring Basin (of which the Deer Creek watershed is a part) by precipitation was about 2.12 and 0.81 lb/mi^2 in 1989 and 1990 respectively. Alachlor, cyanazine, and metolachlor also were detected in rainfall.

AGRICULTURAL CHEMICALS IN SURFACE WATER

Water samples for the analysis of agricultural chemicals were collected from a surface-water environment that had a moderate amount of dissolved solids as indicated by the specific conductance (median of 554 microsiemens per centimeter), that was slightly basic (median pH of 7.7 standard units), that was relatively cool (median water temperature of 9.5 °C), and that was well oxygenated (median dissolved-oxygen concentration of 12.0 mg/L) (table 5). The water was a calcium-magnesium-bicarbonate type (Kalkhoff and Kuzniar, 1991, p. 7). Seventy-five percent of the samples were collected from Deer Creek when the stream discharge was less than 1.0 ft^3/s.

Occurrence

Nitrogen, which originates from natural mineralization, chemical fertilizers, and animal wastes was present in some form in all surface-water samples (table 5). Nitrate-N was detected in all samples in concentrations that ranged from 0.70 to 17 mg/L. About half the samples had nitrate concentrations greater than about 3.0 mg/L, which is generally considered to be indicative of human influence (Madison and Brunett, 1985). Ammonia-N was detected in 40 percent of the samples. Concentrations ranged from less than 0.10 to 4.9 mg/L. However, ammonia-N concentrations were 0.30 mg/L or less in 75 percent of the samples. Organic-N was detected in 99 percent of the samples. Concentrations ranged from less than 0.10 mg/L to 17 mg/L.

Precipitation in the watershed

Table 5.--Statistical summary of selected surface-water quality constituents at site DC5 on Deer Creek, Clayton County, Iowa, October 1988 through September 1991

[Concentration of nitrogen species in milligrams per liter and concentration of herbicides in micrograms per liter; --, not applicable; µS/cm, microsiemens per centimeter; °C, degrees Celsius; mg/L, milligrams per liter; N, Nitrogen; <, concentration less than detection limit indicated]

Constituent	Number of samples	Samples with detections (percent)	Concentration				
			Minimum	25th percentile	Median	75th percentile	Maximum
			On-site measurements				
Specific conductance (µS/cm)	72	--	145	448	554	586	760
pH (standard units)	71	--	7.1	7.5	7.7	7.9	8.2
Water temperature (°C)	76	--	0	1.0	9.5	16.0	22.0
Dissolved oxygen (mg/L)	41	100	6.2	9.5	12.0	13.8	20.0
			Nitrogen species				
Nitrite plus nitrate-N	76	100	.70	1.9	2.9	4.0	17
Ammonia-N	76	40	<.10	<.10	.10	.30	4.9
Organic-N	75	99	<.10	.40	.80	2.7	17
			Herbicides				
Alachlor	75	11	<.10	<.10	<.10	<.10	.53
Atrazine	75	69	<.10	<.10	.15	1.3	55
Cyanazine	75	19	<.10	<.10	<.10	<.10	12
Metolachlor	75	33	<.10	<.10	<.10	.43	69

significantly affected the nitrate-N concentration in water from Deer Creek. Nitrate-N concentrations were significantly less ($p<0.05$: Kruskal-Wallis test) during 1988 and 1989 when precipitation was below normal in northeastern Iowa as compared to 1990 and 1991 when precipitation was near or slightly above normal (National Oceanic and Atmospheric Administration, 1988, 1989, 1990a, and 1991) in northeastern Iowa. Reduced runoff and leaching during dry periods may allow the buildup of nitrogen in the soil (Lucey and Goolsby, 1993). The additional nitrogen then would be available for transport during subsequent years. The median nitrate concentration was 2.7 mg/L in samples collected during 1988 and 1989 and 4.8 mg/L in samples collected during 1990 and 1991. Total

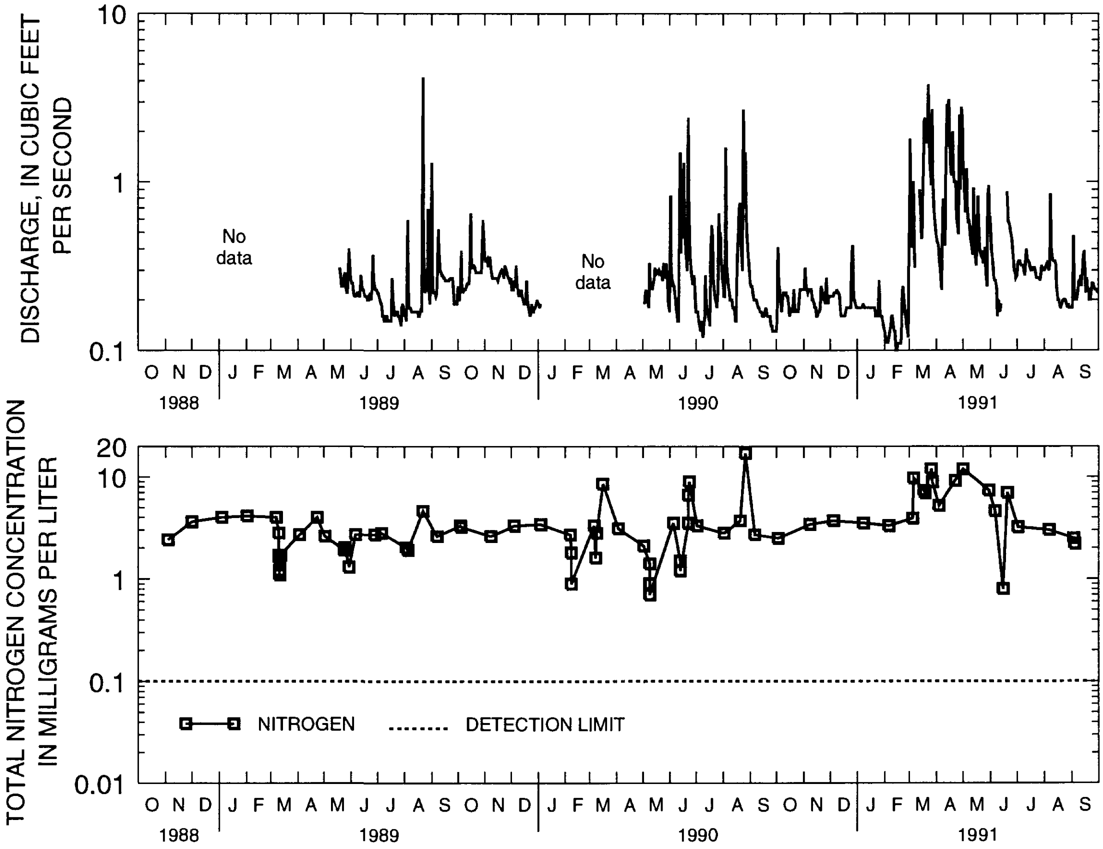

Figure 13. Stream discharge and total nitrogen concentrations in Deer Creek at site DC5, Clayton County, Iowa.

nitrogen concentrations also were significantly larger ($p<0.05$: Kruskal-Wallis test) during 1990 and 1991 (fig. 13).

Alachlor, atrazine, cyanazine, and metolachlor were detected in samples collected from Deer Creek. Alachlor was detected in 11 percent of the samples, atrazine in 69 percent, cyanazine in 19 percent, and metolachlor in 33 percent (table 5). The frequency of herbicide detection generally coincides with the number of acres that received the particular herbicide. Alachlor concentrations ranged from less than 0.10 to 0.53 µg/L, atrazine ranged from less than 0.10 to 55 µg/L, cyanazine ranged from less than 0.10 to 12 µg/L, and metolachlor ranged from less than 0.10 to 69 µg/L. The atrazine concentration was greater than 3.0 µg/L in nine percent of the samples and cyanazine concentration was greater than 10 µg/L in one sample.

Seasonal Variability

The concentrations of nitrogen discharged from the Deer Creek watershed varied seasonally and from year to year. Although nitrate-N concentrations were largest during April, generally after fertilizers were applied, the median concentration was not significantly different ($p>0.05$: Kruskal-Wallis test) than in other months. The median monthly nitrate-N concentration during the study in April was 4.0 mg/L. The median monthly nitrate-N concentration during the remaining months ranged from 1.9 mg/L in May to 3.6 mg/L in December. Ammonia-N and organic-N concentrations were largest in February and March (fig. 10), possibly due to decomposition of plants and the winter application of manure. Organic-N concentrations were positively correlated (table 6) with stream discharge indicating organic-N was washed into the stream by runoff.

Herbicides commonly were detected in late spring and early summer during or just following application (fig. 14). The peak atrazine (55 µg/L), cyanazine (12 µg/L), and metolachlor (69 µg/L) concentrations were in surface-water samples collected in June 1990. Atrazine and metolachlor also peaked in May and June 1989 and 1991, and cyanazine concentrations also increased to above detection levels in 1989. Because the herbicide concentrations increased during increased stream discharge due to rainfall runoff, some of

Table 6. --Spearman correlation coefficients of selected hydrologic and water-quality data collected at site DC5 on Deer Creek, Clayton County, Iowa, October 1988 through September 1991

[Significant correlations ($P<0.05$) are in bold print; ft^3/s, cubic feet per second; N, Nitrogen; mg/L, milligrams per liter; µg/L; micrograms per liter]

	Discharge (ft^3/s)	Percentage of ground water	Precipitation	Nitrate-N concentration (mg/L)	Ammonia-N concentration (mg/L)	Organic-N concentration (mg/L)	Atrazine concentration (µg/L)	Cyanazine concentration (µg/L)	Metolachlor concentration (µg/L)
Discharge (ft^3/s)	**1.00**								
Percent ground water	**-.69**	**1.00**							
Precipitation	**.37**	**-.45**	**1.00**						
Nitrate-N concentration (mg/L)	.25	-.22	-.13	**1.00**					
Ammonia-N concentration (mg/L)	**.63**	**-.61**	.20	.01	**1.00**				
Organic-N concentration (mg/L)	**.73**	**-.52**	**.50**	-.06	**.65**	**1.00**			
Atrazine concentration (µg/L)	**.65**	**-.52**	**.38**	-.02	**.63**	**.67**	**1.00**		
Cyanazine concentration (µg/L)	.15	-.14	**.39**	-.22	.15	.15	**.39**	**1.00**	
Metolochlor concentration (µg/L)	**.47**	**-.33**	.34	-.23	**.37**	**.47**	**.71**	**.39**	**1.00**

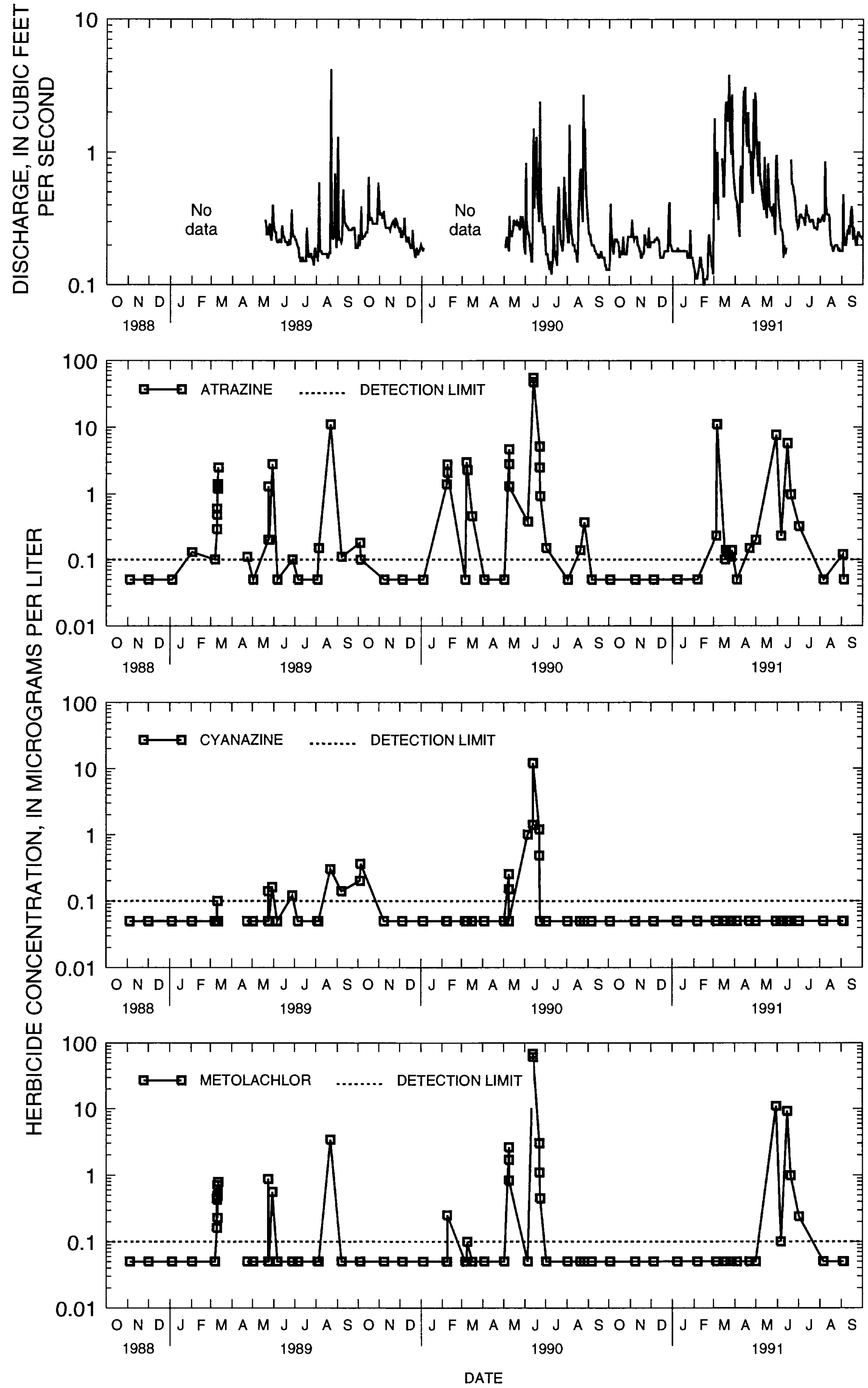

Figure 14. Stream discharge and selected herbicide concentrations in Deer Creek at site DC5, Clayton County, Iowa (note: concentrations less than the detection limit are arbitrarily plotted as one half the detection limit).

the newly applied herbicides probably were transported to Deer Creek by overland flow.

At times, herbicides were detected in late summer and early fall and in the spring before application (fig. 14) Atrazine concentrations increased in August during storms. Additional atrazine was detected consistently in late winter and early spring during snowmelt. This atrazine may have originated from ground-water inflow or from residues remaining in the soil from the previous year's application. Wu (1980) estimated that in Maryland, 5 to 13 percent of the atrazine applied remained in the soil until the next growing season.

Cyanazine and metolachlor were detected in spring and in fall of 1989 when rainfall was below normal but were not detected in the fall of 1990 and spring of 1991 during normal or above-normal rainfall. This contrast suggests that the transport and degradation processes for cyanazine and metolachlor are affected by rainfall. Drought conditions after application would reduce the leaching of herbicides into ground water or overland transport to the stream. The dry soil also would not provide optimal conditions needed for the microbial degradation of the herbicides (Esser and others, 1975). With reduced transport and degradation due to below-normal precipitation, herbicides may be more readily available for transport to Deer Creek during runoff after the growing season in late fall and the following spring.

Agricultural chemicals in ground and surface water have similar seasonal trends and variability in concentrations in the Deer Creek watershed. Nitrate-N concentrations peaked in spring in the alluvial aquifer, while the Deer Creek samples had no apparent seasonal variability. The ground-water samples had greater variability from month to month and within each month than did the surface-water samples, but the surface-water concentrations were consistently greater than the ground-water concentrations. There did not appear to be any seasonal variability in the alluvial aquifer ammonia-N concentrations, but the surface water samples had much greater concentrations in February and March than at any other time of the year. Organic-N in the alluvial aquifer varied little from month to month and median concentrations were only a few tenths of mg/L larger than the detection level of 0.10 mg/L. In water from Deer Creek, organic-N concentrations showed a seasonal trend as previously described and concentrations generally were larger than those in the alluvial aquifer.

Alachlor was detected in surface water more often than in the alluvial aquifer, but all detections were in April, May, and June. In ground water and surface water, atrazine concentrations generally increased from winter to summer and decreased from summer to winter, but the surface water concentrations were usually larger than those in the ground water. Cyanazine was detected more often and at larger concentrations in surface water than in the water from the alluvial aquifer.

Source

Hydrograph-separation methods (Sloto, 1991) indicated that 73 to 78 percent of the yearly-mean discharge from the Deer Creek watershed originated from ground water (table 7) during the 1989-91 water years. These percentages are in the upper part of the range (33 to 90 percent) found for ground-water inflow during a 6-year study of five small watersheds (75 to 389 acres) in western Iowa that also have loess overlying relatively impermeable till (Saxton and others, 1971).

Water moved from the alluvial aquifer to Deer Creek during most of the study period. Except for parts of July and August 1989, and for several hours during June 1991, the water level in the alluvial aquifer at well W1 near the outlet of the watershed was higher than that in Deer Creek at site DC5 (fig. 15). The average head difference in the 30 ft of horizontal distance between the well and the stream was 1.74 ft. Water levels in the alluvial aquifer were substantially lower in 1989 during the period of below normal precipitation than during 1990 and 1991. Subsequently, the head difference was significantly less in 1989 (mean 0.75 ft) than in 1990 (2.19 ft) and 1991 (2.04 ft). Because the water level in the aquifer generally was higher

Table 7.--Percentage of water discharged from Deer Creek that originated from ground-water inflow, 1989-91

[Determined using hydrograph separation methods (Sloto and others, 1991); FI, fixed interval; SI, sliding interval; LM, local minimum; --, insufficient data]

Method	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Yearly mean
						1989 water year							
FI	--	82	89	--	--	--	--	84	94	93	50	84	78
SI	--	80	82	--	--	--	--	81	94	93	51	82	77
LM	--	75	78	--	--	--	--	75	93	93	50	80	75
Mean	--	79	83	--	--	--	--	80	94	93	50	82	77
						1990 water year							
FI	87	96	94	97	--	--	--	85	55	75	67	96	78
SI	88	96	94	73	--	--	--	88	56	78	60	97	77
LM	87	96	94	80	--	--	--	83	57	76	61	98	76
Mean	87	96	94	83	--	--	--	85	56	76	63	97	77
						1991 water year							
FI	90	93	92	97	90	67	61	80	8	95	90	89	75
SI	90	93	92	97	90	65	66	77	17	96	90	88	76
LM	91	94	92	97	84	57	68	73	4	96	89	87	73
Mean	90	93	92	97	88	63	65	77	10	96	90	88	75

than in Deer Creek, water was moving from the alluvial aquifer to the stream during the study period.

Water levels in the alluvial aquifer were higher than in Deer Creek during storm runoff that increased stream discharge and stream elevation. This is in contrast to the relation at a main-stem site on the larger Cedar River (Squillace and others, 1993) where the altitude of the river remained higher than the altitude of the adjacent alluvial aquifer and where water from the river infiltrated into the aquifer. Water levels in the Deer Creek alluvial aquifer responded rapidly to rainfall and rose to remain higher than the altitude in Deer Creek. The stream-level altitude rapidly returned to base-flow levels after each rain.

A limited amount of isotopic data also suggest that the source of water in Deer Creek during rainfall is variable, but during some periods of rain much of the water in Deer Creek originates from ground-water inflow. Results from the isotopic hydrographic-separation methods (described in the Methods section) indicate that, during two rains in August 1989 and May 1990, more than 65 percent of the water discharged from Deer Creek originated from ground-water inflow (table 8). During another rain in June 1990, the ground-water contribution to discharge in Deer Creek was only 19 percent.The differences in the results probably are due to antecedent rainfall and infiltration. On August 4-5, 1989, and May 9, 1990, rains of 1.87 and 1.11 in., measured at a site about 3 mi east of the Deer Creek watershed, increased the daily mean discharge from less than 0.20 ft^3/s to 0.59 and 0.33 ft^3/s, respectively (Kalkhoff and Kuzniar, 1991; Kalkhoff and others,1992). Rainfall during the 10 days before these two rains was only about 0.30 in. In contrast, the rainfall on June 22, 1990 (1.34 in.), increased the daily mean discharge at site DC5 from 0.30 to 2.4 ft^3/s (Kalkhoff and others, 1992). Rainfall during the 10 days before this rain was about 3.1 in., which may have saturated the soil. Much of the additional rain then may have become runoff to the stream, accounting for the high percentage of "new" water in the stream discharge on June

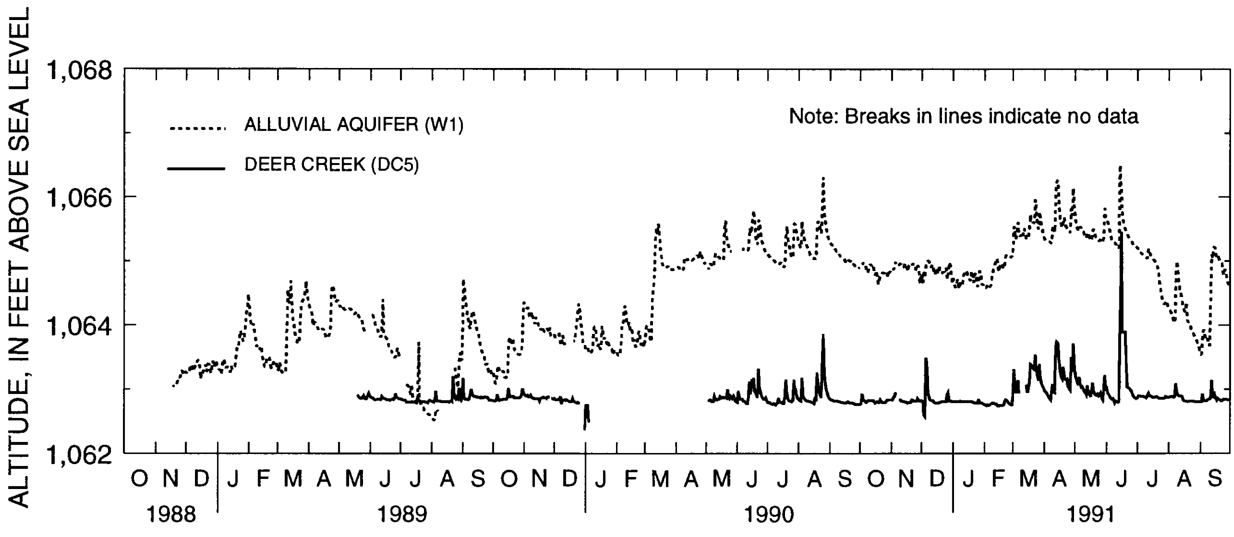

Figure 15. Altitude of the water level of water in the alluvial aquifer and the stream surface of Deer Creek, Clayton County, Iowa.

22, 1990. Although there is a limited amount of isotopic data for a few periods of rain, the data generally agree with previous studies, summarized by Hooper and Shoemaker (1986), that indicate "new" water usually contributes less than one-half of the peak runoff during storms.

Because ground water is a major source of water to Deer Creek and because substantial concentrations of agricultural chemicals are present in ground water (discussed previously) some nitrogen and herbicides in Deer Creek are contributed by ground-water inflow. Although ground water is an important source of chemicals, the largest loads of several constituents appear to originate from overland flow. Ammonia-N, organic-N, atrazine, and metolachlor concentrations increased during periods of greater discharge (table 6) when a smaller percentage of streamflow was contributed by ground-water inflow. Nitrate-N concentrations do not significantly correlate with either stream discharge or percentage of streamflow contributed by ground water. These results suggest that both ground-water inflow and overland flow are important sources of nitrate-N to Deer Creek.

Nitrogen Transport from the Watershed

The results of this study indicate that surface water discharged from the headwaters of Deer Creek contains substantial amounts of nitrogen that are available for transport downstream to karstic areas of the Big Spring Basin. Total-nitrogen concentrations are related to stream discharge in Deer Creek (fig. 16): thus, daily nitrogen loads were estimated from the mean daily discharge using two simple regression equations. Separate equations were developed, using log base 10 transformed data, to account for the substantial rainfall differences between the dry part of the study (1989) and the normal to above-normal rainfall period (1990-91). Total nitrogen concentrations in Deer Creek were significantly correlated ($r=0.35$, $p<0.05$) to precipitation recorded in or near the study area. Daily total nitrogen concentration was estimated using the following regression

Table 8.--Isotopic separation data for selected periods of precipitation in the Deer Creek watershed, Clayton County, Iowa

[$^{18}O/^{16}O$, Mean oxygen-18/oxygen-16 ratio]

Date	Deer Creek $^{18}O/^{16}O$ ratio (Rs)	Precipitation $^{18}O/^{16}O$ ratio (Rn)	Ground-water $^{18}O/^{16}O$ ratio (Ro)	Percent stream water from groundwater	Percent stream water from overland flow
August 4-5, 1989	-7.10	-4.67	-8.20	69	31
May 9, 1990	-8.12	-7.53	-8.35	72	28
June 22, 1990	-9.92	-10.31	-8.30	19	81

equations:

$$\mathrm{NIT} = 5.05 \times Q^{0.295}, \qquad (3)$$

$$\mathrm{NIT} = 6.25 \times Q^{0.270}, \qquad (4)$$

where NIT = daily total (nitrite plus nitrate, organic, and ammonia) nitrogen concentration, in mg L;

Q = daily mean stream discharge, in ft^3/s;

Equation 3 best estimated nitrogen concentrations during the period of below-normal rainfall in 1989. Equation 4 best predicted the nitrogen concentrations in Deer Creek during the normal to greater than normal rainfall period during 1990 and 1991. The two separate equations account for differing climatic factors that affect the delivery of nitrogen to Deer Creek. Separate equations, based on rainfall, were found to provide the best estimates of nitrogen concentrations. However, analyses of the regression residuals indicated that these models underestimated the nitrogen concentration for discharges greater than about 10 ft^3/s. Other factors, not measured, probably affected the nitrogen concentration during periods of greater runoff.

Once the daily nitrogen concentration was calculated, the daily-nitrogen load was calculated using the following equation:

$$L = (Q \times NIT) \times 5.4, \qquad (5)$$

where L = nitrogen load, in lb per day;

Q = daily mean stream discharge, in ft^3/s;

NIT = daily total nitrogen concentration, in mg/L.

The estimated nitrogen load was about 1,200 lb for about 7 months in 1989, about 1,900 lbs for 8 months in 1990, and about 4,300 lbs for 9 months in 1991. Nitrogen loads were variable from year to year because of rainfall variations.The estimated annual nitrogen load leaving the Deer Creek watershed is less than reported in other similar studies. For example, during the 1991 water year (October 1989-September 1991), about 4,700 lb or 6.7 lb acre of nitrogen were transported from the watershed. This compares to a nitrogen discharge of 12.6 lb/acre of nitrogen as nitrate for the Mississippi River Basin upstream of Clinton, Iowa (Battaglin and others,1993); and 11 to 34 lb/acre of nitrogen as ammonia and nitrate (Johnson, and Baker, 1984) for the Four Mile Creek Basin in Tama County, Iowa; and about 11 lb/acre (Hallberg and others, 1983) to about 23 lb/acre (Hallberg and others, 1984) of nitrogen as nitrate for Roberts Creek in Clayton County, Iowa.

The load differences may be caused by differences in land use, application rates, and

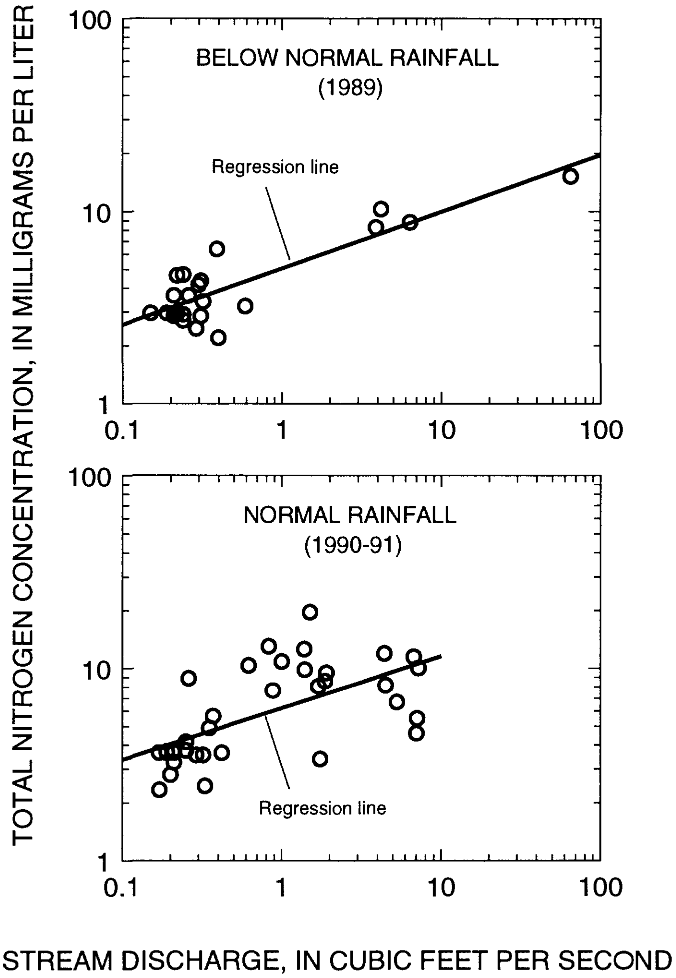

Figure 16. Relation between stream discharge and the total nitrogen concentration in Deer Creek at site DC5, Clayton County, Iowa, 1989-91.

error in the regression equations used to estimate nitrogen concentrations. Conservation-tillage practices (contour farming and terraces) used in the Deer Creek watershed may substantially reduce the amount of nitrogen transported from a watershed (Johnson and others, 1979). The amount of nitrogen applied in the Deer Creek watershed may be less due to differing application rates and a smaller percentage of the basin planted in row crops. Another reason for the differing results may be the underestimation of the nitrogen load by the regression equations at larger stream discharges. Nitrogen loads transported during high stream discharge have been reported to be much greater than that transported during low-flow conditions (Taylor and others, 1994) and may account for a large part of the annual nitrogen transport. Data collected during the study are not sufficient to fully evaluate the reasons for the apparent smaller nitrogen transport from the Deer Creek watershed than from other watersheds that have been studied in the past.

Even though it is probably underestimated, the nitrogen loads determined for this study show a substantial relation to precipitation. The amount of nitrogen transported from the watershed was much less during periods of below-normal precipitation. During dry years, less nitrogen is transported from the fields or leached into ground water and more is retained in the soil. These results agree with those reported by numerous other researchers (Johnson and others, 1979; Johnson, and Baker, 1984; and Lucey and Goolsby, 1993). The largest nitrogen concentrations are found in Deer Creek during periods of rainfall runoff.

Nitrogen transported from the Deer Creek watershed varies seasonally. In spring during snowmelt and rainfall, substantial amounts of nitrogen are transported in the form of organic compounds and ammonia in addition to nitrate.

SUMMARY AND CONCLUSIONS

An investigation to define the quantity and seasonal distribution of agricultural chemicals in a small headwaters stream, Deer Creek, in the Big Spring Basin in Clayton County, Iowa, and to describe the quality of water in shallow unconsolidated material that is the source of water to this headwaters stream, was conducted from October 1988 through September 1991.A 1.09 mi^2 watershed in the headwaters of Deer Creek was selected as representative of small headwater streams that gain water from ground-water inflow in the Big Spring Basin. The Deer Creek watershed is characterized by gently rolling to hilly topography. Subsurface unconsolidated materials include recent alluvial deposits, Wisconsinan loess, colluvial deposits, and pre-Illinoian glacial tills. An Ordovician-age shale bedrock unit underlies the unconsolidated materials.

About 65 percent of the land in the watershed is used for row-crop (mainly corn) agriculture. Cover crops such as alfalfa and small grain are grown on about 16 percent of the watershed, grassland covers about 11 percent of the watershed, and the remainder of the watershed is forests, farmsteads, or roads. Soil-conservation practices that include grass buffer strips and terraces are used in parts of the watershed to reduce soil erosion.

Precipitation generally was below normal from the beginning of the study in October 1988 until September 1989. During 1990 and 1991, precipitation was at or slightly above normal.

Water in the alluvium that is adjacent to Deer Creek contained nitrogen and several common herbicides in concentrations that varied with depth and with season. The median nitrate concentration decreased from 16 mg/L at 4.0 ft. below land surface to less than 0.10 mg/L at 8.5 ft below land surface. The maximum ammonia-N concentrations in all samples were less than or equal to 0.40 mg/L. Organic-N concentrations were larger in the samples from shallower 4.0- and 5.5-ft-deep lysimeters than in samples from deeper (7.0 and 8.5-ft-deep) lysimeters. Atrazine was detected in more than 85 percent of the samples from the two shallowest lysimeters at 4.0 and 5.5 ft. below land surface. Maximum concentrations were 3.6 µg/L at 4.0 ft and 0.96 µg/L at 5.5 ft. In contrast, atrazine was detected in only 3 and 11 percent of the samples and the maximum atrazine concentrations were 0.10 and 0.25 µg/L at 7.0 and 8.5 ft, respectively. Metolachlor was detected in 32 and 15 percent of the samples from 4.0 and 5.5 ft, respectively. Metolachlor was not detected at 7.0 and 8.5 ft. Agricultural-chemical concentrations varied seasonally in parts of the alluvial aquifer and generally increased in late spring or early summer and decreased through the summer.

Water levels in the alluvial aquifer were higher than in Deer Creek during storm runoff that increased stream discharge and stream-level altitude. Water levels in the alluvial aquifer responded within 1 hour of major rainfall indicating that water and agricultural chemicals can potentially move rapidly to the water table. Also, concentrations of nitrate ranged from 14 to more than 100 mg/L in water in loess materials on the hillslope. This nitrogen may be transported downslope to the alluvial aquifer during the summer.

Water samples for the analysis of agricultural chemicals were collected from Deer Creek which had a moderate amount of dissolved solids as indicated by the specific conductance (median of 554 microsiemens per centimeter), was slightly basic (median pH of 7.7 standard units), a median water temperature of 9.5 °C, and had a median dissolved-oxygen concentration of 12.0 mg/L. The water was a calcium-magnesium-bicarbonate type. Seventy-five percent of the samples were collected from Deer Creek when the stream discharge was less than 1.0 ft^3/s.

Nitrogen was present in some form in all samples collected from Deer Creek. Nitrate-N was detected in all samples in concentrations that ranged from 0.70 to 17 mg/L. Ammonia-N was detected in 40 percent of the samples in concentrations that ranged from less than 0.10 to 4.9 mg/L. Organic-N was detected in 99 percent of the samples in concentrations that ranged from less than 0.10 mg/L to 17 mg/L.

Alachlor, atrazine, cyanazine, and metolachlor were detected in samples collected from Deer Creek. Alachlor was detected in 11 percent of the samples; atrazine in 69 percent; cyanazine in 19 percent; and metolachlor in 33 percent. Alachlor concentrations ranged from less than 0.10 to 0.53 µg/L; atrazine ranged from less than 0.10 to 55 µg/L; cyanazine ranged from less than 0.10 to 12 µg/L; and metolachlor ranged from less than 0.10 to 69 µg/L.

Herbicide detections commonly occurred in late spring and early summer, during or just following chemical application and were detected in the fall and following spring after a dry growing season. Apparent reductions of leaching into ground water, of overland flow, and possibly of microbial degradation during drought conditions increased the availability of chemicals for transport to Deer Creek after the growing season. Larger herbicide concentrations were positively correlated with higher stream discharge and negatively correlated with the percentage of discharge due to ground-water inflow, which indicates that overland flow is an important source of herbicides to Deer Creek.

The results of this study indicate that surface-water discharged from the headwaters of Deer Creek contained substantial amounts of nitrogen that were available for transport downstream to karstic areas. During the 1991 water year (October 1989-September 1991), about 4,700 lbs or 6.7 lb/acre of nitrogen were transported from the study area. Nitrogen loads transported from the Deer Creek watershed were less in dry years than in years with average or greater than average rainfall.

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