AGRICULTURAL CHEMICAL INTERCHANGE BETWEEN GROUND WATER AND SURFACE WATER, CEDAR RIVER BASIN, IOWA AND MINNESOTA--A STUDY DESCRIPTION

By Paul J. Squillace, Michael J. Liszewski, and E.M. Thurman

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CONVERSION FACTORS AND VERTICAL DATUM

Multiply	*By*	*To obtain*
	Length	
micrometer (μm)	0.00003937	inch
centimeter (cm)	0.3937	inch
millimeter (mm)	0.03937	inch
meter (m)	3.281	foot
kilometer (km)	0.6214	mile
	Area	
hectare (ha)	2.471	acre
square kilometer (km^2)	0.3861	square mile
cubic meter per second (m^3/s)	35.3145	cubic foot per second
cubic meter per year (m^3/yr)	264.2	gallon per year
	Volume	
microliter (μL)	0.000338	ounce
milliliter (mL)	0.0338	ounce
liter (L)	0.2642	gallon
	Mass	
kilogram (kg)	2.205	pound

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.

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ABSTRACT

A review of the data collected in the Cedar River basin, Iowa and Minnesota, indicates that atrazine is consistently detected in the main-stem river at concentrations greater than 0.10 microgram per liter even during periods of extended base flow. The primary source of atrazine in the river during these periods of base flow is not known. This study is designed to determine how atrazine and other agricultural chemicals move between ground water and surface water in an alluvial aquifer adjacent to a river. A site has been selected in an unfarmed area adjacent to the Cedar River near Bertram, Iowa, to determine how the concentrations of agricultural chemicals in the alluvial aquifer change as a result of bank storage of surface water. Research also is planned to determine the contribution of agricultural chemicals discharged by the alluvial aquifer into the river during base flow.

INTRODUCTION

Nonpoint-source (NPS) contamination is a major water-quality concern in the Midwest. Humenik and others (1987) state, "Nonpoint source contamination is a principal source of water-quality problems...and that agricultural activities are a major cause." Assessing the severity of NPS contamination is difficult. Many hydrologic and geochemical factors are thought to affect the severity of NPS contamination, and knowledge of these factors may provide a means of assessing the susceptibility of a drainage basin to this type of contamination. Some of these factors are: (1) local ground- and surface-water interactions between the stream and the adjacent alluvial aquifer; (2) runoff characteristics of the basin; and (3) the chemical properties and characteristics of contaminants in the alluvial aquifer and surface water. Knowledge of these factors will be valuable to policy makers for establishing regulations, to State and Federal regulatory agencies, and to research scientists for defining new research areas.

Alluvial aquifers and rivers, major sources of freshwater in many parts of the Nation, are vulnerable to NPS contamination. In the United States, 77 percent of the total freshwater withdrawals and 65 percent of public-water supplies are from surface water (U.S. Geological Survey, 1988). As the demand for freshwater increases, alluvial aquifers may supply larger quantities of water. For example, surficial aquifers, which in Iowa predominately are alluvial aquifers, provide 60 percent of the ground water used in the State (Clark and Thamke, 1988).

Agricultural activity is the third most important source of ground-water contamination and is a moderate or severe problem in 36 States (U.S. Department of Agriculture, 1989). Agricultural chemicals used in the Midwest include nitrate and the following major herbicides: atrazine and cyanazine for corn, alachlor and metolachlor for corn and soybeans, and metribuzin for soybeans. These compounds are soluble, have moderate to large mobility in soil (table 1), and have been identified as having a large potential to move into ground water through various pathways.

Field-dissipation studies on hectare-sized plots indicate that about 1 to 4 percent of the applied herbicides are removed by direct runoff, depending on the tillage practice and the slope of the fields (Hall and others, 1972; Hall, 1974; Ritter and others, 1974; Triplett and others, 1978; Leonard and others, 1979; Rhode and others, 1981; Glotfelty and others, 1984). Furthermore, most of the herbicide transport occurs between 2 and 6 weeks after application (Wauchope, 1978; Glotfelty and others, 1984).

Table 1. *Chemical properties of major herbicides used in the Midwest*

[mg/L, milligrams per liter; Log Kow, the logarithm of the partition coefficient of the herbicide between n-octanol and water; --, no data]

Herbicide	Class	Relative mobility in soils[1]	Solubility[2] (mg/L)	Persistence[3] (months)	Log Kow[2]
Alachlor	Acetamide	Large	240	2	3.1
Atrazine	Triazine	Moderate	[1]33	12	[4]2.8
Cyanazine	Triazine	Moderate	171	12	2.2
Metolachlor	Acetamide	Large	530	--	--
Metribuzin	Triazine	Large	1,200	5	5.0

[1] Helling (1971); Jury and others (1987).

[2] U.S. Environmental Protection Agency (1987).

[3] Approximate time for 90-percent disappearance from soil; time may vary by 50 percent (Wauchope, 1978).

[4] Cohen and others (1984).

The scope of past studies has been limited to test plots or to slightly larger basins of 10 to 100 km^2. For example, Frank and Sirons (1979) measured atrazine runoff in Quebec, Canada, from basins of 18 to 79 km^2 and determined that from 0.3 to 1.9 percent of the applied herbicide was lost on an annual basis. The smaller percentages were for sandy soils, and the larger percentages were for clayey soils. Mean loss for all basins was slightly less than 1 percent. Frank and others (1982) reported that atrazine and simazine were the only herbicides detected throughout the year in surface water in the Canadian Great Lakes basin. Muir and others (1978) estimated that 1.7 percent of the applied atrazine was lost from a 22- to 129-km^2 area in Quebec, Canada. Golfelty and others (1984) stated that 2 to 3 percent of the atrazine applied in the Wye River basin (10 km^2) in Maryland was lost in runoff to Chesapeake Bay; the loss mainly occurred during 2 weeks immediately after application. They reported the transport of atrazine by direct runoff decreased substantially within 4 to 6 weeks after application. A similar response has not been documented for drainage areas greater than 500 km^2. Furthermore, the fate and transport of agricultural chemicals once they enter the hydrologic system are largely unknown.

Herbicide compounds degrade by chemical and microbial processes in the soil and water to produce new compounds or metabolites (Paris and Lewis, 1973). These degradation products ultimately may become the more abundant species as transport progresses. Preliminary results from recent research (W.F. Pereira, U.S. Geological Survey, oral commun., 1989) indicate that the concentration of atrazine metabolites (for example, deethylatrazine and deisopropylatrazine) in ground water in some areas may be several times larger than the concentration of the parent compound. The ratio of the metabolite to the parent compound may be different than that in surface water. Understanding these degradation processes and how they relate to the hydrologic system is important to understanding the evolution and effect of NPS contamination on alluvial aquifers and surface water.

Herbicides may be transported to the streams directly from overland flow, through field-drainage tile, by shallow bedrock and alluvial aquifers that are already contaminated with these chemicals, or by precipitation. Research is needed to determine the partitioning of herbicide transport to streams into overland-flow and ground-water components. An analysis of the water quality of rivers during different flow regimes may provide a means of understanding the partitioning process. During large run-off events, the concentration of herbicides in the rivers may provide an indication of the susceptibility of a drainage area to herbicide transport by overland flow. During base flow, the concentration of herbicides and their metabolites in the rivers may provide an indication of the extent and type of ground-water contamination in a basin.

This report provides an interpretation of some of the data previously collected in the Cedar River basin by the U.S. Geological Survey and a study description for an additional study in the basin. The study is designed to investigate the interchange of agricultural chemicals between ground water and surface water.

STUDY AREA

The Cedar River basin in Iowa and Minnesota (fig. 1) has been selected for study. Farming practices in the basin are extensive, and previous hydrologic investigations provide an excellent data base for this area.

Geology

The bedrock of the Cedar River basin consists of Devonian and Silurian dolomite, limestone, and lesser quantities of shale, which generally are covered by a layer of glacial drift of Quaternary age (Anderson, 1983). The bedrock is exposed in the river bottoms in some areas. Approximately 80 percent of the basin is overlain by glacial drift called the Iowan Erosion Surface (Anderson, 1983), which is Illinoian and pre-Illinoian in age (fig. 1). The glacial drift ranges in thickness from 0 to 120 m and is thickest in buried, preglacial bedrock valleys (D.R. Soller, U.S. Geological Survey, written commun., 1986). However, the glacial drift is less than 15 m thick in most of the basin north of Waterloo. The upstream part of the basin is covered by the Wisconsin Cary Drift (Des Moines Lobe) (fig. 1).

Precipitation

Mean annual precipitation in the basin ranges from 76 to 84 cm but varies considerably from year to year (Waite, 1969, p. 4). The southern part of the basin normally receives the largest quantity of precipitation.

Surface-Water Hydrology

The Cedar River is the largest tributary to the Iowa River (fig. 1). The average discharge of the Cedar River near Conesville is 135 m^3/s and exceeds the average discharge of the Iowa River near Lone Tree (fig. 1) of 82 m^3/s (Miller and others, 1985). The drainage area for the Cedar River near Conesville is 20,163 km^2. The principal tributaries of the Cedar River are in the northwestern one-half of the basin (fig. 1). Downstream from Cedar Falls, only five tributaries have drainage areas that exceed 500 km^2, and none exceed 1,000 km^2 (Schwob, 1963).

The quantity of runoff that results from a single storm varies substantially with subbasin size and topography in the Cedar River basin. The discharge per unit area of the peak annual discharge generally decreases with increasing subbasin size (Lara, 1987). However, even for subbasins with similar drainage-area size, such as the subbasins upstream of the streamflow-gaging stations near Northwood and Ionia (fig. 2), the flood peak for the 10-year recurrence interval can vary by more than a factor of three (Lara, 1987). Topography may explain the difference in runoff between subbasins of similar size. The two principal topographic areas within the Cedar River basin coincide with the location of the two glacial-drift deposits shown in figure 1. The relief within the area covered by the Wisconsin glacial drift is less than in the rest of the basin and results in a poorly developed drainage system.

A modified version of a computer program by Pettyjohn and Henning (1979) was used to calculate ground-water contribution to surface-water discharge. River hydrographs for the 1985 water year (October 1, 1984, to September 30, 1985) were analyzed using three methods of hydrograph separation--local minimum, fixed interval, and sliding interval (Pettyjohn and Henning, 1979). The statewide average precipitation for this period was 107 percent of the long-term average (Melcher and others, 1986). Estimates of ground-water contribution to river discharge were calculated for 10 streamflow-gaging stations in the Cedar River basin and ranged from 56 to 80 percent of the total annual river discharge (fig. 2). Some of this variation may result from the method of hydrograph

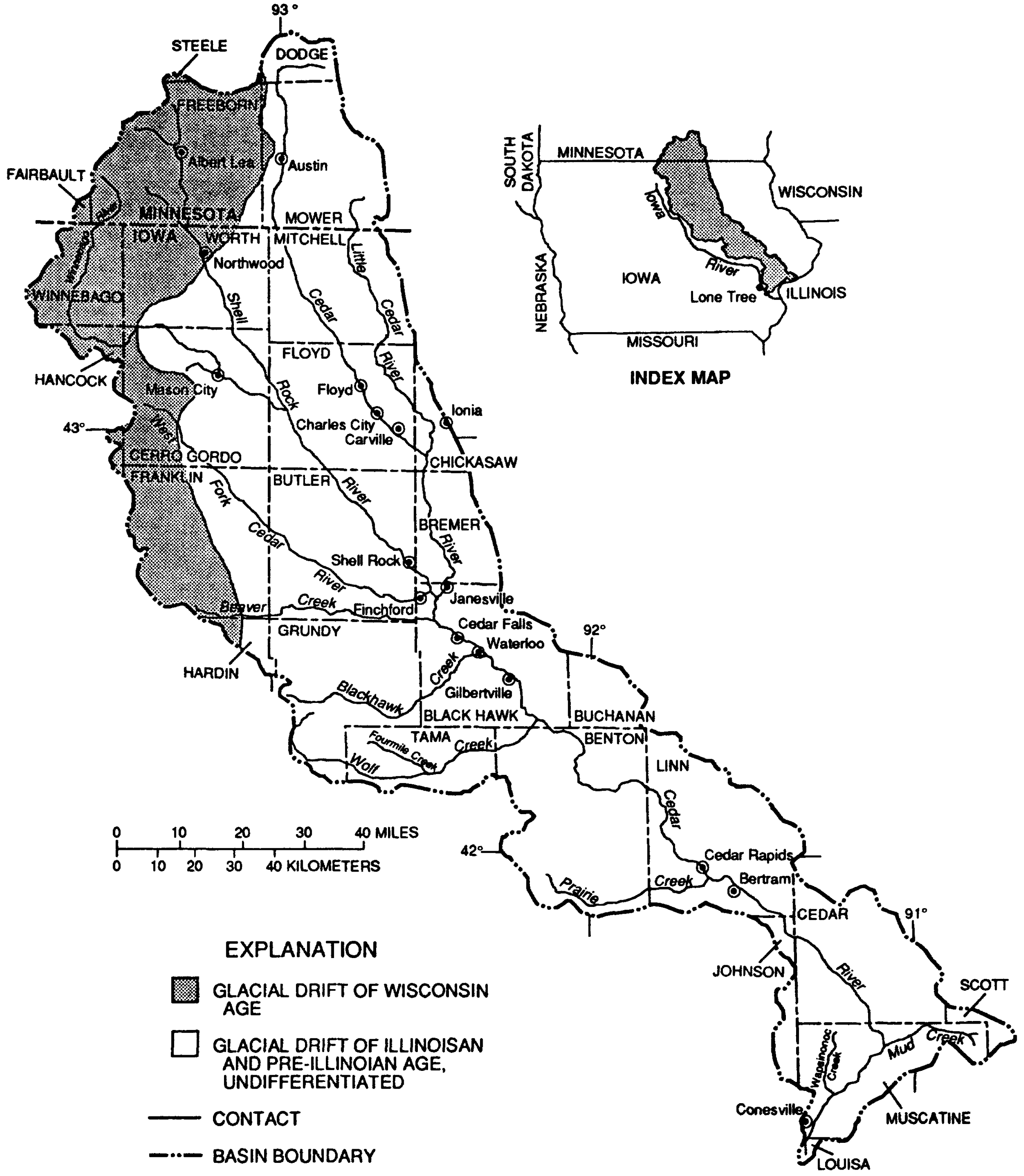

Figure 1. Glacial drift in the study area (modified from Anderson, 1983, p. 221 and 222.)

separation, or it could represent actual differences in the quantity of ground-water contribution (Squillace and Engberg, 1988).

The separation of overland flow from ground-water flow for the gaging stations at Northwood and Mason City (fig. 2) was more uncertain than for the rest of the stations in the Cedar River basin because of the poorly developed surface-drainage system within their drainage basins. Surface drainage within these two subbasins includes numerous lakes and swamps that may store or retard overland flow. In addition, field-drainage tile is installed at a

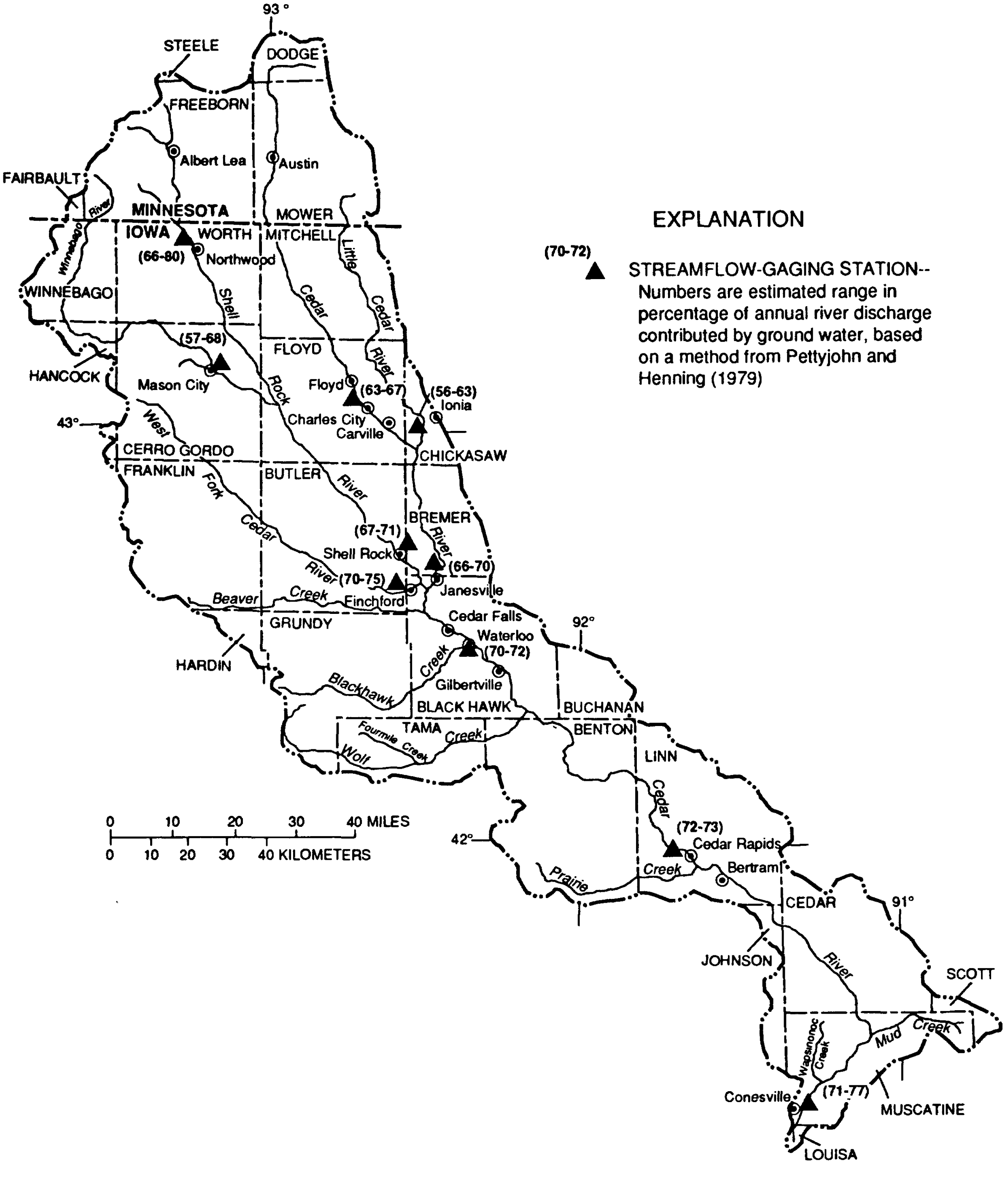

Figure 2. Location of U.S. Geological Survey streamflow-gaging stations and estimated percentage of ground-water contribution to annual river discharge, 1985 water year.

depth of 1 to 2 m in several locations in the subbasin to lower the water table. Discharge from field-drainage tile may constitute a substantial part of the overall river discharge during periods of base flow. Drainage tile also intercepts some recharge to deeper aquifers. During a summer when precipitation is greater than average, discharge from tile drains can continue throughout the entire summer. The hydrograph separation of tile-drain flow from overland flow and deeper ground-water flow in estimating ground-water contributions is difficult and can affect the percentage calculations.

Land and Water Use

Land use in the Cedar River basin consists of 81-percent cropland, 7-percent pasture, and 12-percent forest and urban areas (U.S. Department of Agriculture, 1976). Corn and soybeans are the principal grain crops and are grown on 88 percent of the cropland (Skow and Holden, 1986). Nitrate and herbicides for corn and soybean production are the principal agricultural chemicals used in the basin.

Data on estimated and reported water use for the Cedar River basin in 1985 indicate that municipalities provided about 83 million m^3/yr of water, almost all of which was from ground-water sources (fig. 3; data on file with the U.S. Geological Survey, Iowa City, Iowa). The principal water uses in the Cedar River basin and the quantity contributed by ground and surface water for 1985 are shown in figure 3. Estimated nonirrigation agricultural water use was 37 million m^3/yr, about 75 percent of which was from ground water. Self- and public-supplied water for industrial uses was about 24 million m^3/yr, of which 36 percent was from surface water and 64 percent was from ground water. Domestic use, self- and public-supplied, was about 13 million m^3/yr, which was almost entirely ground water.

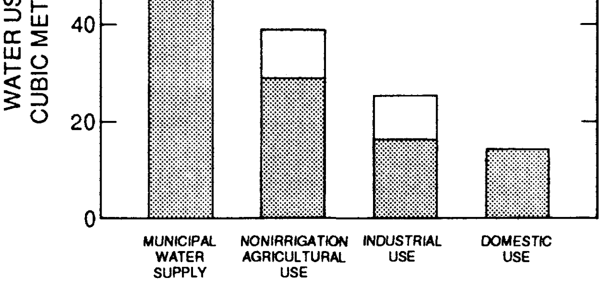

Figure 3. Water supply and use for Cedar River basin, 1985.

PREVIOUS COLLECTION AND INTERPRETATION OF HERBICIDE DATA

A large surface-water-quality data set was collected for the Cedar River basin study in Iowa and Minnesota during 1984 and 1985 (Squillace and Engberg, 1988). A total of 105 herbicide samples were collected at six water-quality sampling sites from May 1984 through November 1985 (fig. 4). Concentrations of alachlor, atrazine, cyanazine, metolachlor, and metribuzin in the dissolved and whole-water phases were determined for each sample. The data collected are unique because large subbasins (780 to 15,500 km^2) were monitored within the Cedar River basin. Also, 50 percent more precipitation than normal was received in June 1984, (Waite, 1984) while the spring of 1985 was the driest since 1936 (Waite, 1985).

Additional surface- and ground-water-quality data were collected in the Cedar River basin during 1988. Seven surface-water sites and two drainage-tile sites were sampled weekly for a period of 3 months (May, June, and July 1988) for nitrate (the abbreviated form of nitrite plus nitrate as nitrogen used in this report) and herbicide concentrations (fig. 4). Four well nests consisting of three wells each also were installed in alluvium in an unfarmed area near Bertram (fig. 4). Samples from these wells were used to determine whether or not herbicides in the river move into the alluvial aquifer during high river stage and then are released during base flow (figs. 5 and 6). The well nests were located from 10 to 80 m perpendicular to the river, and the three wells at each nest ranged from 3 to 10 m deep. These wells were sampled three times between April and November 1988.

During base flow, the geographic contribution of nitrate and herbicides to the river was determined by water-quality sampling and the measurement of discharge at 51 sites throughout the entire basin (fig. 4). This low-flow seepage investigation was conducted in July 1988, and water samples were collected at each measurement site in conjunction with the seepage investigation. The period of investigation was part of the driest January through July in 116 years of record in Iowa (Hillaker, 1988).

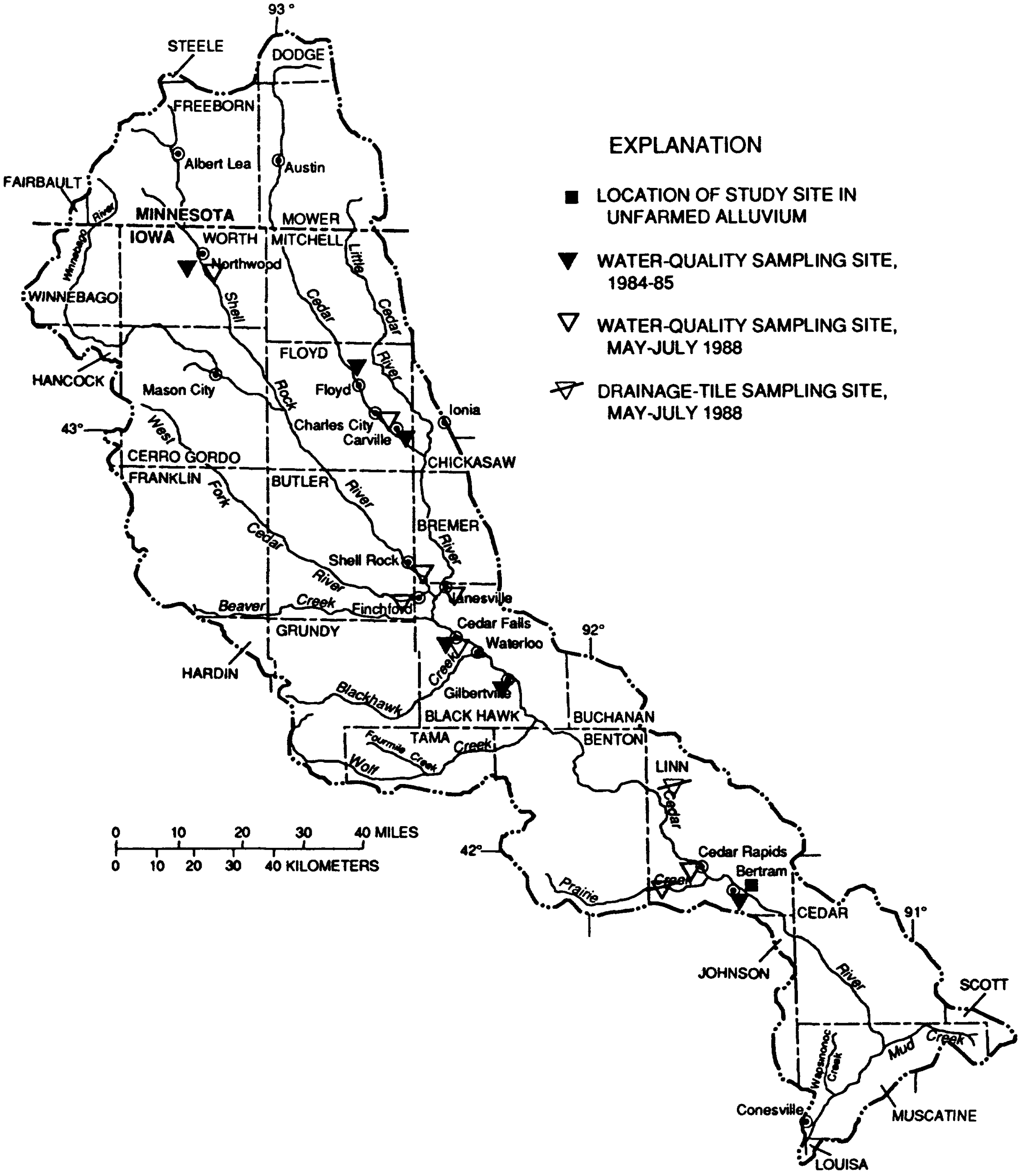

Figure 4. Location of water-quality sampling sites, May 1984 through November 1985 and May through July 1988, and location of study site in unfarmed alluvium.

Dominant Herbicide Transport

Herbicides were detected only in the dissolved phase in surface-water samples collected from the Cedar River basin in 1984 and 1985 (Squillace and Engberg, 1988). The concentrations of herbicides detected in the whole-water samples (unfiltered samples) were generally within 10 to 20 percent of concentrations detected in the dissolved phase. This variation in the reported concentrations is within the laboratory error and indicates that

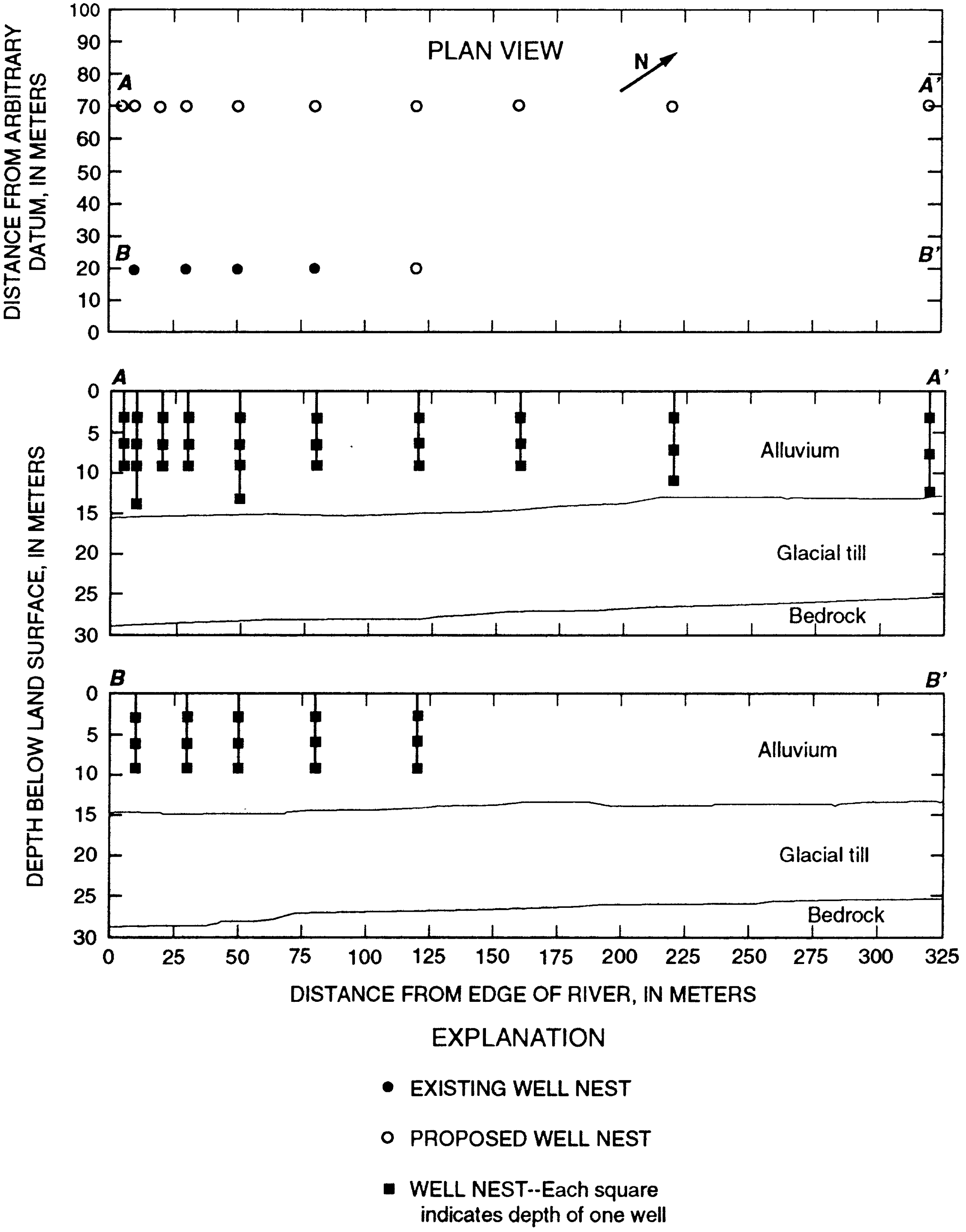

Figure 5. Approximate location and depth of wells in an area of unfarmed alluvium. Location of sections A-A' and B-B' is shown in figure 6.

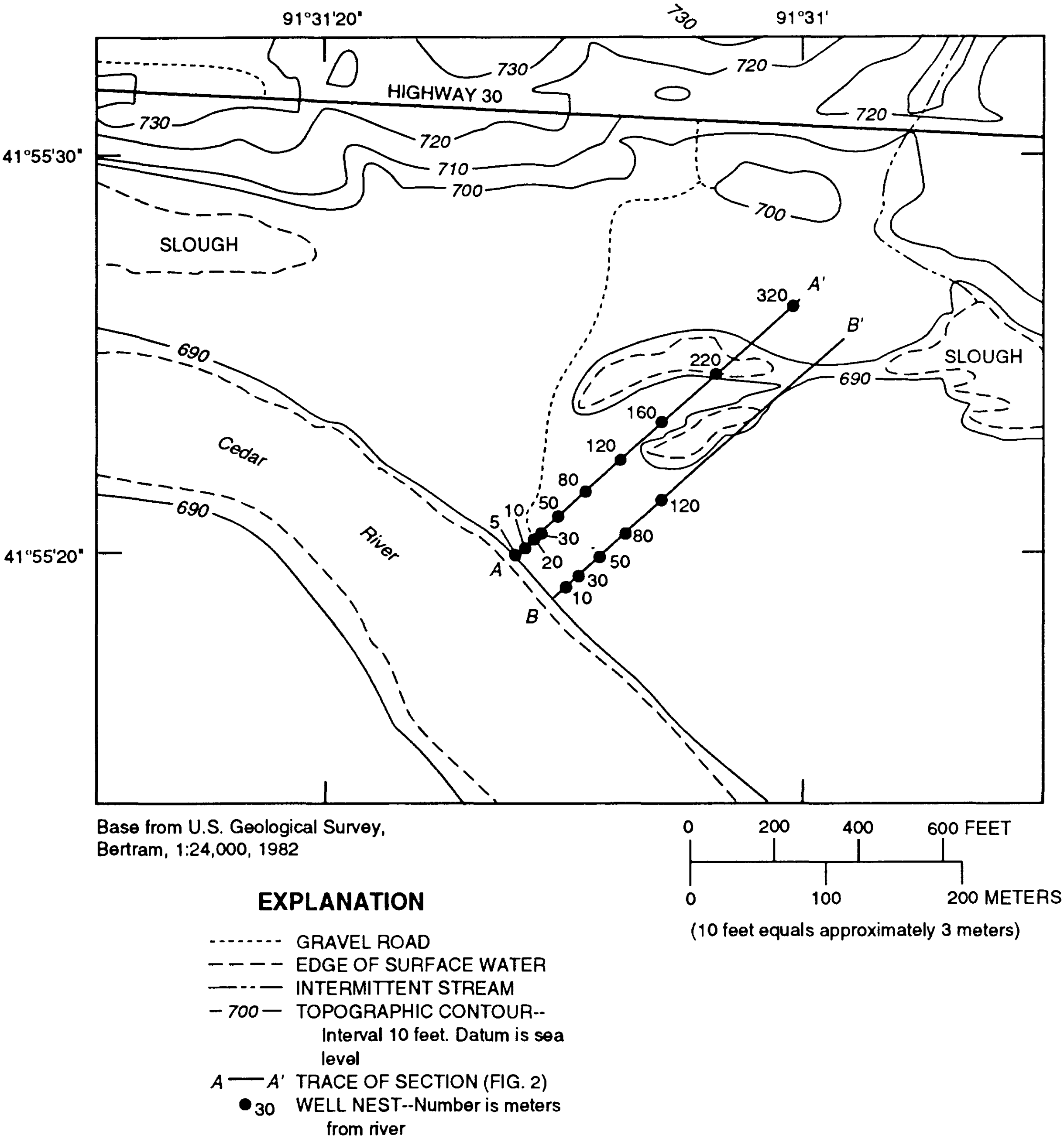

Figure 6. Study site in unfarmed alluvium near Bertram.

the herbicides were not sorbed to suspended sediment in substantial quantities. However, the data collection and analysis were not designed for optimum determination of herbicide transport by suspended sediment.

On the basis of theoretical considerations and the literature, nonionic water-soluble herbicides are not likely to be sorbed to suspended sediment in major river systems to any substantial degree. Rao and Davidson (1979) reported that the soil-water sorption coefficients for several pesticides showed large variations with three soil types they tested. Another parameter, the organic-carbon coefficient (K_{oc}), which normalizes the quantity of organic carbon in soil, varied much less from soil type to soil type. Similarly, Glotfelty and others (1984) reported that distribution coefficients (K_d) for suspended sediment were 1.5 to 7 times larger than those obtained for bottom sediment. K_d can have units of milligrams per gram and is defined as:

$$K_d = C_s/C_e, \qquad (1)$$

where C_s = the concentration of a contaminant sorbed to a specific weight of sediment, and

C_e = the concentration of the same contaminant dissolved in an equal weight of water.

However, the K_{oc} values varied by about one-half as much as the K_d values. It is generally accepted that the sorption of nonionic organic compounds occurs primarily on the organic fraction of soils and sediment (Chiou and others, 1979, 1983, 1985; Karickhoff and others, 1979; Witkowski and others, 1987).

The reported average K_{oc} value for atrazine is 160 (Jury and others, 1987), with variations between 150 and 250. K_{oc} is related to K_d by

$$K_{oc} = K_d/f_{oc}, \qquad (2)$$

where K_d = the distribution coefficient, and

f_{oc} = the organic carbon fraction in the suspended sediment.

If 2-percent organic carbon and a K_{oc} value of 160 are assumed, then:

$$K_d = K_{oc} \bullet f_{oc} \qquad (3)$$

$$= 160\ (0.02)$$

$$= 3.2\ \text{mL/g}.$$

If a dissolved-atrazine concentration of 1.0 µg/L (0.001 µg/mL) is assumed, the concentration of atrazine on the suspended sediment can be calculated as follows:

$$C_s = (K_d)\ (C_e) \qquad (4)$$

$$= 3.2\ \text{mL/g}\ (0.001\ \mu\text{g/mL})$$

$$= 0.0032\ \mu\text{g/g}.$$

Suspended-sediment concentrations (S_s) in the Cedar River during June (month of maximum concentration) can be as much as 0.25 g/L (grams per liter). The concentration of atrazine on the suspended sediment (X) in 1 L of river water can be calculated using the following equation:

$$X = C_s\, S_s \qquad (5)$$

$$= (0.0032\ \mu\text{g/g})\ (0.25\ \text{g/L})$$

$$= 0.0008\ \mu\text{g/L}.$$

Thus, 0.0008 µg/L of atrazine is in the suspended phase, and 1 µg/L is in the dissolved phase. Therefore, on the basis of this calculation, only 0.08 percent of the total atrazine is present in the suspended phase.

If the percentage of organic carbon (f_{oc}) is increased from 2 to 4 percent (maximum observed value), the organic-carbon coefficient (K_{oc}) is increased to 250 (also maximum), and the quantity of suspended sediment is increased to 700 mg/L (maximum concentration detected in the Cedar River), then the quantity of atrazine on the suspended sediment is only about 1 percent, whereas 99 percent is dissolved. Thus, hypothetical K_d calculations and chemical analyses both indicate that atrazine is transported mainly in the dissolved phase.

The percentage of water-soluble herbicides transported on the suspended sediment can increase when the drainage area is reduced. If rainfall is intense, then there is a mixture of sediment and water transported from the field. The largest concentrations of suspended sediment are found in the stream adjacent to the fields and then decrease downstream. When the suspended-sediment concentrations are large, more of the herbicides can be transported with the sediment. For example, Buttle (1989) stated that concentrations of suspended sediment can be as large as 800,000 mg/L, and as much as 77 percent of the metolachlor can be transported on the suspended sediment from field-size plots. The Four Mile Creek agricultural subbasin (5,505 ha) in the Cedar River basin was studied for 3 years, and the percentage of herbicides (alachlor, atrazine, cyanazine, metribuzin, and propachlor) lost from the subbasin during storms (May through August) was less than 0.2 percent of that applied (Johnson and Baker, 1980). More than 80 percent of herbicide losses occurred in the dissolved phase during storms. For atrazine, dissolved-phase losses during a storm were greater than 92 percent of the total loss. For a particular sample collected during a storm, the percentage of atrazine on the sediment can be larger (Johnson, 1977). During 1976, a sample collected by Johnson from Four Mile Creek had a suspended-sediment concentration of 12,320 mg/L and a concentration of atrazine on the sediment of 600 µg/kg (micrograms per kilogram). The concentration of atrazine in the dissolved phase was 60 µg/L. Therefore, about 12 percent of the atrazine transported in the stream was carried on the sediment.

As the concentration of suspended sediment decreases in the river channel, a new equilibrium between the concentration of herbicides in the solid phase and in the dissolved phase is achieved rapidly. Desorption of atrazine and linuron approaches 75 percent of equilibrium values within 3 to 6 minutes after the system has been disturbed (Wauchope and Myers, 1985). This rapid desorption and the small suspended-sediment concentration explains the fact that 99.5 percent of the triazine herbicides and metolachlor are transported in the dissolved phase in the Mississippi River during base-flow conditions (W.F. Pereira, U.S. Geological Survey, oral commun., 1989). These data are substantiated by Leung and Richard (1982) and Frank and others (1979).

Herbicides Transported During Base Flow

The transport of herbicides from ground water into surface water is indicated by the persistent occurrence of atrazine at detectable concentrations (greater than 0.10 µg/L) throughout the year in the surface water, even during periods when no substantial overland flow has occurred for almost 2 months (Squillace and Engberg, 1988). The presence of atrazine in ground water has been substantiated by data collected from municipal wells in Iowa. From 1982 through 1987, 24 percent of the samples collected from municipal wells less than 15 m deep had concentrations of atrazine greater than 0.10 µg/L (Detroy and others, 1988). Furthermore, unpublished water-quality data collected by the U.S. Geological Survey (Iowa City, Iowa) indicate that ground water in an alluvial aquifer beneath an unfarmed stretch of land adjacent to the Cedar River contained concentrations of atrazine greater than 0.10 µg/L. These data indicate that atrazine is detected in the ground water and that atrazine in the ground water eventually may be discharged into the river system.

These data also indicate other modes of herbicide transport to the river, in addition to ground water, are possible during base-flow conditions. Atrazine is the only commonly (but not exclusively) detected herbicide in ground water (Detroy and others, 1988); however, there are numerous herbicides in the river during periods of base flow in the spring (Squillace and Engberg, 1988). This would seem to indicate that at least during certain times of the year other processes or transport mechanisms also may deliver herbicides to the river during base flow. Some possible processes and transport mechanisms include discharge from drainage tile, desorption from sediment in the riverbed, bank storage of surface water in alluvial aquifers adjacent to the river, precipitation falling on the stream, and small quantities of overland flow that may contain large concentrations of herbicides.

Vertical and Horizontal Concentration Gradients in Alluvial Aquifers

The alluvial aquifers adjacent to the main-stem rivers may be a source of atrazine during periods of base flow. Surface-water data collected during base-flow conditions in the summer of 1988 indicate that detectable concentrations of atrazine (about 0.30 µg/L) are found predominately in the major tributaries and along the main stem of the Cedar River. Alluvial aquifers are more extensive and well-developed along the main-stem river and adjacent to larger streams. These aquifers contribute water to the river and may be the source of much of the atrazine in the river during base flow.

Data from samples collected in 1988 indicate that the vertical-concentration gradients of herbicides in an unfarmed alluvial aquifer can change within a period of 7 months. This area has never been farmed, and there was no adjacent farming activity. During base-flow conditions, water samples were collected from well nests 10, 30, 50, and 80 m from the edge of the water and from 3 to 10 m deep in the alluvial aquifer. These wells are shown in figure 5 on section B-B' as "existing well nests." The analyses of water samples from these wells indicated that herbicides (parent compounds) can be vertically stratified and that herbicide concentrations ranged from less than 0.10 to 0.40 µg/L. On May 13, 1988, the smallest concentrations of atrazine were detected at the top of the aquifer, while on November 22, 1988, the largest concentrations of atrazine were detected at the top of the aquifer. On July 8 and 23, 1988, no vertical stratification of atrazine concentrations was apparent in the aquifer. The reversed concentration gradient between May and November 1988 may be related to changes in the river stage that occurred between the times of sample collection. More research is needed to explain the cause of this concentration-gradient reversal.

These data also indicate that a horizontal concentration gradient was present in the alluvial aquifer and that atrazine concentrations decreased away from the river. Analyses of samples collected on May 13, July 8, and July 23, 1988, indicate that atrazine concentrations remained fairly constant from 10 to 80 m from the river, whereas analyses of samples collected on November 22, 1988, indicate that atrazine concentrations decreased with distance from the river. Atrazine was consistently detected at all the well nests, whereas cyanazine was detected (greater than 0.10 µg/L) in only the well nests 10 and 50 m from the river on May 23, 1988. Water samples collected from the alluvial aquifer in November 1988 were analyzed, and concentrations of atrazine and deethylatrazine and deisopropylatrazine (metabolites of atrazine) generally decreased with distance from the Cedar River (W.F. Pereira, U.S. Geological Survey, oral commun., 1989). Furthermore, wells that were completed in bedrock located next to the alluvium also contained atrazine and deethylatrazine. It is not known if the bedrock is hydrologically connected to the alluvium and if these contaminants in the bedrock contribute to their presence in the alluvial aquifer.

Estimated Load From Ground Water

Six percent of the total annual atrazine load in the Cedar River at Cedar Rapids during April 1984 through March 1985 was associated with ground-water flow (Squillace and Thurman, 1992). Atrazine is the only herbicide that was consistently detected in the Cedar River throughout the year (Squillace and Engberg, 1988). Total annual atrazine load was estimated from monthly samples collected from the Cedar River at the Bertram sampling site from June 1984 through March 1985 (Squillace and Engberg, 1988). Loads for April and May 1984 were conservatively estimated at 320 kg/month (kilograms per month). The Bertram sampling site is 15 km (kilometers) downstream from Cedar Rapids (fig. 4), and for the purpose of this calculation, the atrazine concentrations were assumed to be equal to those at the Cedar Rapids gaging station. These loads were calculated also by assuming that the atrazine concentration and discharge at the time of the sample collection were representative of the entire month. This assumption was made because the samples were collected representatively throughout the water-discharge hydrograph, except for June 1984 when the median of three discharges and sample concentrations was used for the entire month. The annual load of atrazine calculated from these data was 14,500 ± (plus or minus) 2,000 kg/yr (kilograms per year). In 1 month, June 1984, 70 percent of the total annual load of atrazine was transported.

An estimate of the annual ground-water flow into the Cedar River (April 1984 through March 1985) was determined using the local-minimum hydrograph-separation method in the computer program developed by Pettyjohn and Henning (1979). The concentration of atrazine associated with the ground-water flow was assumed to be constant at a concentration of 0.20 µg/L on the basis of data from Squillace and Engberg (1988). This concentration was typical of the Cedar River during base flow in 1984 and 1985 (Squillace and Engberg, 1988). Therefore, a conservative estimate of atrazine associated with the ground-water component of river discharge at the Cedar Rapids gaging station is 800 kg/yr (± 100 kg/yr), which is about 6 percent of the total atrazine transported. If the large June flush had not occurred, the annual ground-water contribution would have been about 16 percent of the total annual surface-water load.

Storage Capacity Of Alluvial Aquifers

Quantities of atrazine (parent compound) stored in the alluvial aquifer adjacent to the Cedar River is estimated at about 200 to 400 kg (kilograms). This estimate is based on ground-water concentrations of atrazine of 0.20 to 0.40 μg/L and assumes a sand aquifer 0.50 km wide and 12 m deep in the valleys of the larger tributaries north of Waterloo and 1 km wide and 18 m deep south of Waterloo to the Cedar Rapids gaging station. The specific yield of the alluvial aquifer was assumed to be 22 percent, which is typical for sand aquifers (Heath, 1983). The atrazine in storage is about one-fourth to one-half of the estimated 800 kg/yr associated with the ground-water flow component of the river discharge at Cedar Rapids.

These calculations indicate that if ground water in the alluvial aquifer is the primary source of atrazine to the river during base flow, then this aquifer is recharged throughout the year (because atrazine is detected throughout the year during base flow). Recharge of atrazine to the alluvial aquifer can occur by: (1) ground- and surface-water interaction adjacent to the river; (2) runoff from valleys adjacent to the alluvial aquifer that infiltrates into the alluvial aquifer; (3) flooding of small streams flowing over the alluvial aquifer; (4) flooding of the main-stem river over the alluvial aquifer; (5) bedrock-aquifer water containing atrazine moving into the alluvial aquifer; or (6) herbicide use on the land surface above the alluvial aquifer.

Herbicide Concentration In Stream Versus Discharge Per Unit Area

Surface-water concentrations of atrazine detected at sampling sites in the Cedar River basin in 1984 and 1985 can be estimated from the unit-discharge values during May, June, and July by the equation shown in figure 7. All sampling sites from the previous study by Squillace and Engberg (1988) were compared on a logarithm plot of atrazine concentration versus logarithm of discharge per unit drainage area (fig. 7). When all sample points are plotted on this diagram, including those from drainage areas as small as 800 km^2 to as large as 15,000 km^2, there is a linear trend ($p<0.05$) with correlation coefficient $r=0.86$. When the entire year, except May, June, and July, is considered in the regression, the correlation coefficient is small and not significant statistically. Further research is needed to determined what processes affect this apparent relation.

Need for Additional Research

There is a need to further define the degradation and movement of NPS agricultural contaminants from the fields to the streams. Some of these contaminants moving from the field to the streams by overland flow may be introduced into the ground-water system. Types of research that may help understand the movement and degradation of NPS contaminants include investigation of tillage practices, methods of pesticide application, soil types, soil moisture, basin slope, water chemistry (ground water, surface water, and precipitation), and microbial and physiochemical degradation.

STUDY WORK PLAN

Little is known about how agricultural chemicals move between alluvial aquifers and rivers. The objectives stated in this section examine the significance of this interchange by focusing on two questions: (1) To what extent does the water quality of a river affect the water quality of the alluvial aquifer during periods of recharge, and (2) what is the contribution of NPS agricultural contamination to the river by alluvial aquifers during base-flow conditions?

Objective 1-Determination of Movement of Agricultural Chemicals as a Result of Change in River Stage

Work for this objective is designed to define some of the factors that affect the movement of agricultural chemicals between surface water and ground water in an alluvial aquifer. The agricultural chemicals that will be investigated are nitrate and alachlor, atrazine, cyanazine, metolachlor, and metribuzin, and the atrazine metabolites deethylatrazine and deisopropylatrazine.

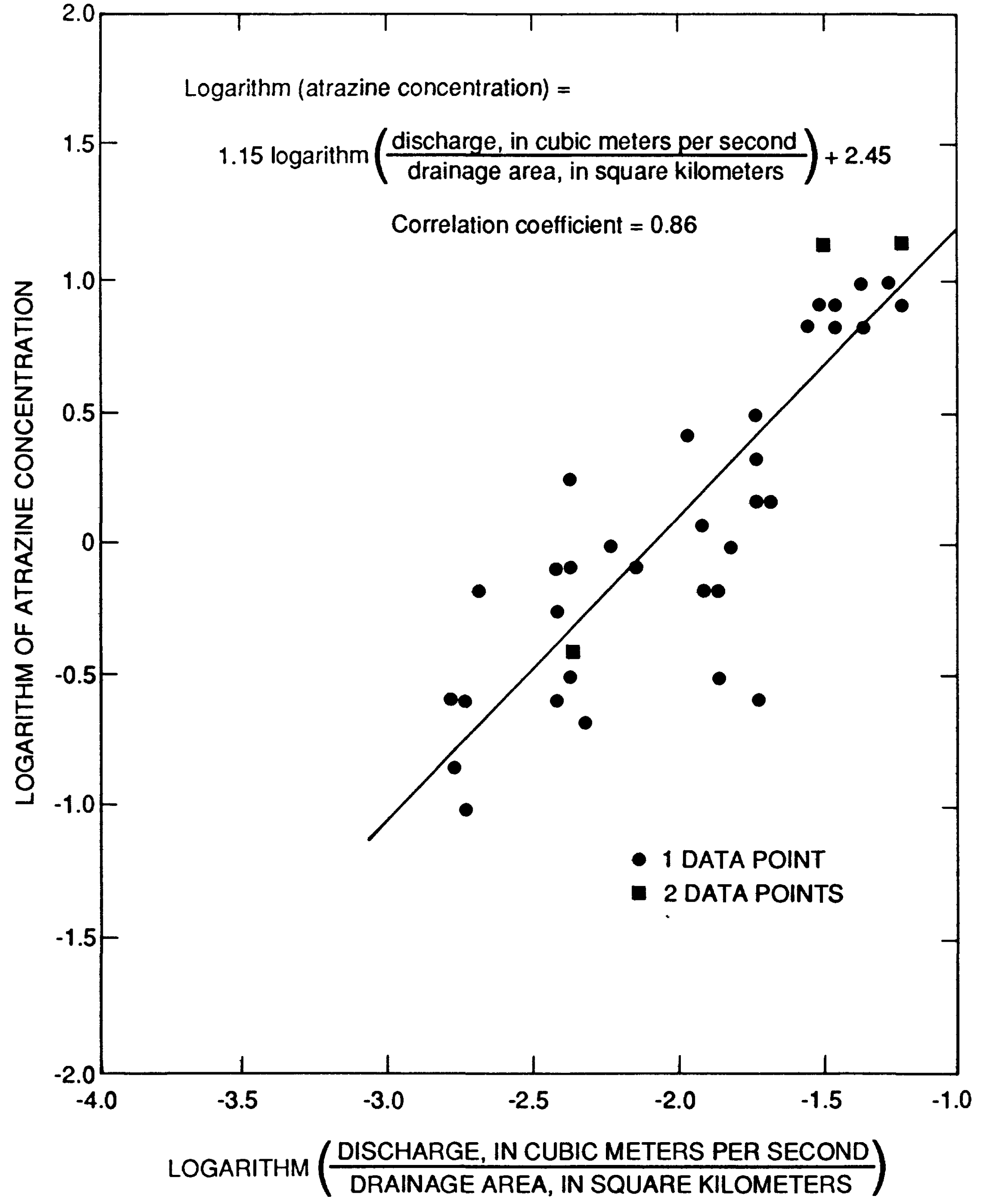

Figure 7. Linear regression of the logarithm of atrazine concentration to logarithm of discharge per unit drainage area.

The location of the study site is shown in figures 4 and 6. This site is about 18 km south of the Cedar Rapids gaging station. It was selected as the study site for four reasons. First, the steep riverbank allows for the study of ground- and surface-water interaction without the surface of the aquifer being inundated with river water during high river stage. Furthermore, a steep riverbank consisting of fine- to medium-grained sand commonly occurs within the Cedar River basin. Second, data from wells drilled for this study indicate that glacial till lies under the alluvium. If this glacial till is continuous, the alluvial aquifer in this area is, for all practical purposes, isolated from ground-water input from the underlying bedrock. Further drilling and geophysical data will be used to define the extent and thickness of the glacial till. Third, buried river channels are not located near the study area (Hansen, 1972) and, therefore, should not substantially affect the direction of ground-water flow within the study area. Fourth, the study site is unfarmed. This eliminates the input of NPS contaminants to the alluvial aquifer by farming practices on the land surface.

Hypotheses To Be Tested

Two hypotheses will be tested for this objective: First, that during a large runoff event in the spring and early summer (April through July), recharge water from the river carries the nitrate and herbicides into the alluvial aquifer through the riverbank. Runoff during the remaining months also causes recharge of nitrate and herbicides and some degradation products, but the concentrations are much smaller. Second, that the organic-carbon content and sediment-size distribution of the alluvial-aquifer material greatly affects the presence of nitrate and herbicides in ground water.

Work Elements

Locate Well Nests

Well nests for a previous investigation were already located at 10, 30, 50, and 80 m perpendicular to the Cedar River (figs. 5 and 6). Additional wells at the specified depths will be installed as shown in figure 5. These wells will provide water-level information and a means of sampling the alluvium. These wells will give a three-dimensional view of how water and agricultural chemicals move between the river and the aquifer and from the valley walls to the alluvial aquifer. A bedrock test hole will be drilled to verify the thickness of the underlying till. The Geologic Division of the U.S. Geological Survey will conduct geophysical tests to determine the thickness of the glacial till at the study site and to further define the geology between the well nests.

Monitor Water Levels

Water levels will be monitored continuously in three wells, 7 m deep, located 10, 30, and 50 m from the river. These are the shallowest wells that do not go dry during periods of low river stage. The water levels in all the wells will be measured by U.S. Geological Survey personnel daily as river stages change during runoff. The river stage also will be monitored continuously, and a rain gage will be installed at the study site to monitor precipitation.

This water-level information will be used to document the hydraulic gradient between the river and the alluvial aquifer. Defining the conditions that are necessary to cause a reverse of the gradient will help in determining the importance of bank storage in alluvial aquifers.

Collect Water-Quality Samples

Water samples from the aquifer wells will be collected during four runoff events and during stable conditions within 3 years to determine how concentrations of nitrate and selected herbicides vary with time. The wells will be sampled before the rising river stage (pre-event sampling), at the peak stage, and when the river stage drops after the peak. The wells shown in figure 6 along sections A-A' and B-B' will be sampled during the first two runoff events. During the remaining two runoff events, only wells along A-A' will be sampled. The data collected along section B-B' will serve to confirm data collected along A-A'.

The pre-event samples will be collected in February-March and April-May. These pre-event samples will be collected with the expectation that runoff will occur soon after the sampling. The timing of these pre-event samplings were selected for two reasons: (1) statistically, the months of March and June provide the maximum change in river stage for the year and (2) June generally has large concentrations of NPS contaminants associated with runoff that may be available for recharge to the alluvial aquifer because of application of herbicides after planting of corn and soybeans. For the period of record at Cedar Rapids from 1903 through 1988, March and June provide the maximum change in discharge and river stage for a 1-month period. On the basis of a 10- and 90-percent exceedence probability, the river stage at Cedar Rapids increases 1.2 m in March, 0.88 m in June, and 0.58 m in September. This would indicate that March and June are probably the best months to study the influx of water from the river into the alluvial aquifer. Furthermore, snowmelt in March generally causes a sustained increase in river stage, which would allow larger volumes of water to enter the alluvial aquifer than would runoff in June. If runoff occurs within 2 months of the pre-event sampling, the wells will be sampled at the river peak and after the river stage drops. If no runoff occurs after the first April-May sampling (1989), the wells will be sampled three times at 1-month intervals. Additional samples will be collected in September and November if no runoff occurs.

At the time well samples are collected, stainless-steel minipiezometers will be used to sample the ground water in the alluvium beneath and adjacent to the river at a depth of 1 and 2 m. A minipiezometer is essentially a small-diameter pipe that is pushed into the alluvium (Winter and others, 1988). Hydraulic head in the minipiezometers will be measured in relation to the river water level, and samples will be collected to determine concentrations of nitrate, herbicides, and herbicide metabolites. The depth-profile samples are designed to provide information on the first 2 m of the alluvial aquifer with regard to storage, transmission, and degradation of contaminants. Furthermore, the minipiezometer information will be used to complete the concentration contours from the wells to the river. Collection of the minipiezometer samples is dependent on the river stage; that is, if the river depth is greater than 2 m, the minipiezometers are not long enough to collect a sample. The concentrations of contaminants from the minipiezometer samples will be compared to those in the alluvium farther from the river and also to river samples.

A depth-integrated river sample will be collected daily during the rise and fall of the river stage, and concentrations of nitrate and selected herbicides and some of their degradation products determined. The specific conductance, pH, water temperature, and dissolved-oxygen concentrations in river water will be measured daily.

Additional wells may be installed during the second year of the study to complete the coverage. Drill locations for the subsequent year of this study will be determined after the first year of the study.

Collect Supporting Data

Biological and physiochemical properties of the alluvial aquifer may be important in understanding the occurrence of NPS contaminants and their degradation products. The specific conductance, pH value, water temperature, oxidation-reduction potential, and dissolved-oxygen concentration will be determined for water in each well at the time it is sampled. These physical properties also may help distinguish the source of the well water.

Grain-size distribution, organic-carbon content, and clay and grain analysis will be determined for each major lithologic unit in the alluvial aquifer and for two samples of bed material in the river. A total of 28 samples will be collected at the well nests 10, 80, 160, and 320 m from the river. About five thin sections will be made from sediment samples (about five samples), and the thin sections will be described by U.S. Geological Survey personnel. If the mineralogy varies substantially between samples, then point-count analysis will be done to quantify those differences.

Objective 2 - Determination of Agricultural Chemicals Discharged During Base Flow

The quantity and variability of the concentrations of agricultural chemicals being discharged from the alluvial aquifer to the river during base flow will be defined by the second objective. Data can be compared to the site-specific data collected for objective 1. Furthermore, data will be collected and compared from a large river and a small stream.

Seepage investigations will be repeated twice during the study (fig. 8). During a seepage investigation, stream-discharge measurements and water-quality samples will be collected from almost all of the tributaries and in the Cedar River within a selected reach of the Cedar River. A seepage investigation identifies "gaining" and "losing" reaches of a stream and, consequently, helps to delineate where agricultural chemicals enter the river and the quantity of that input.

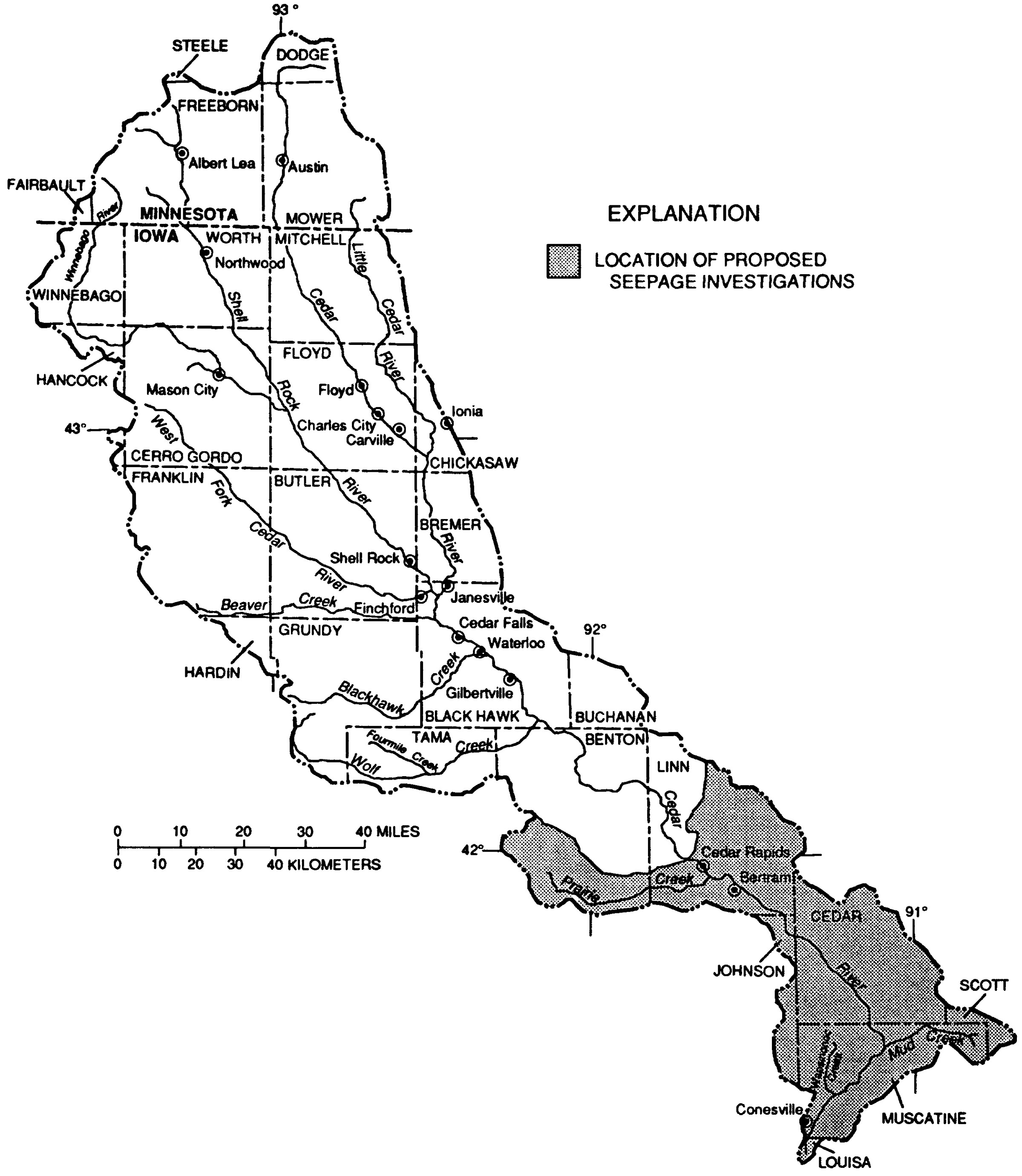

Figure 8. Location of proposed seepage investigations.

The seepage investigations will be done in the summer during the first 2 years of the study. A strong correlation exists between base-flow discharge on a selected day and the discharge 10 days later (fig. 9) for 14 rivers throughout Iowa with basins ranging from 2,000 to 17,000 km^2 (data on file with the U.S. Geological Survey, Iowa City, Iowa). This relation would seem to indicate a similarity of the hydraulic characteristics of aquifers that discharge water to rivers in Iowa during base flow. Therefore, the hydrologic and chemical processes investigated during this study should be qualitatively transferrable to other major rivers in Iowa.

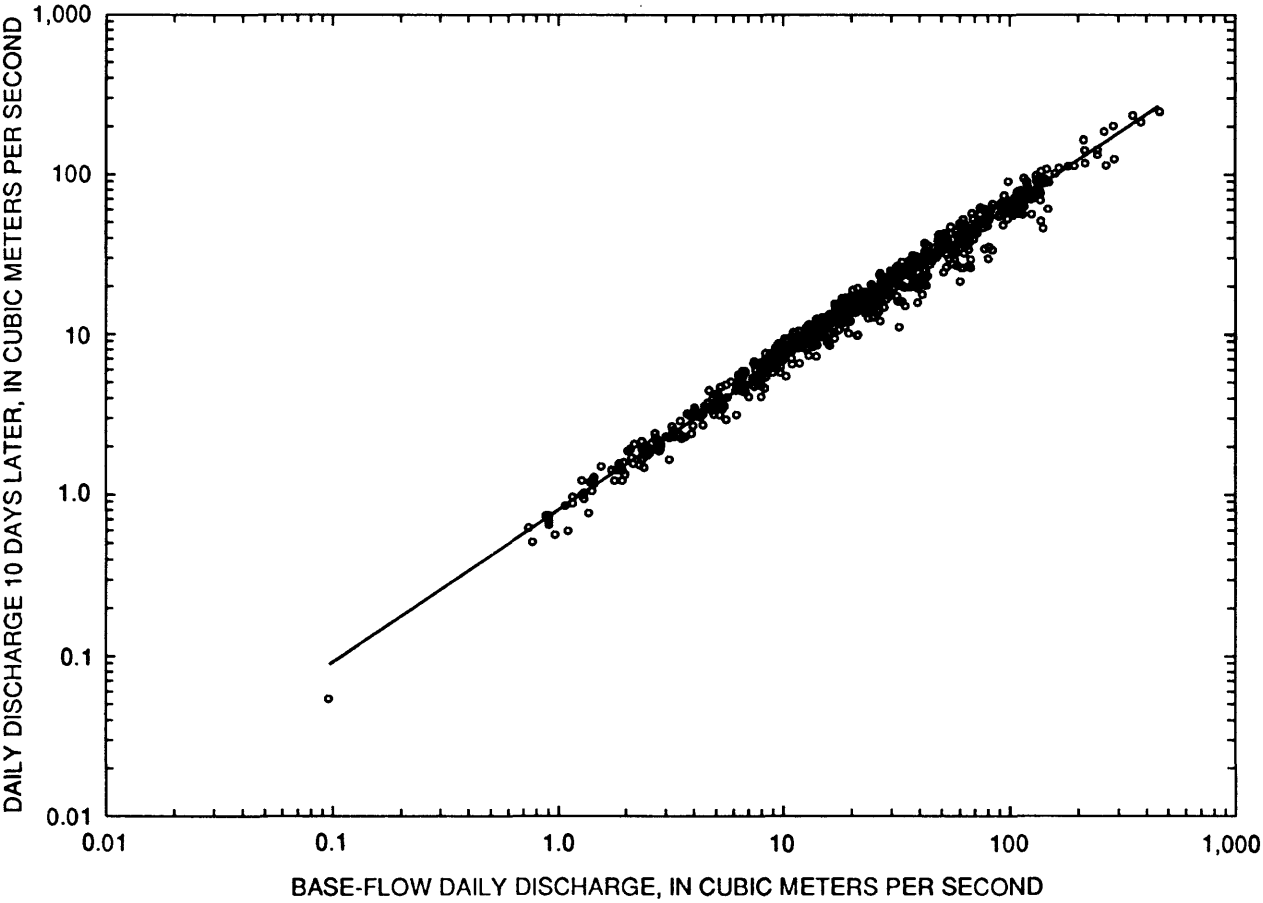

Figure 9. Relation between base flow on a selected day and 10 days later based on a composite of data from 14 rivers in Iowa.

Hypotheses To Be Tested

Two hypotheses will be tested for objective two. First, during base-flow periods, the release of NPS agricultural chemical contaminants from the alluvial aquifer affects the water quality of the river. Second, small tributaries flowing into the main stem are not major contributors of contamination load in the main-stem river during base flow.

Work Elements

Quantify Increased Contaminant Load

The increased contaminant load as a result of discharge from the alluvial aquifer will be measured in the Cedar River. Discharge and the concentration of NPS contaminants will be determined at four main-stem locations along the Cedar River. The upstream site will be at Cedar Rapids, and the downstream site will be near Conesville, 117 river km downstream (fig. 4). Two additional sites will be located approximately equidistant between Cedar Rapids and Conesville. This reach is characterized by a well-developed alluvial aquifer and an absence of reservoirs.

The discharge and concentration of contaminants from tributaries entering the main stem between Cedar Rapids and Conesville will be measured where they enter the Cedar River. Depth- and flow-integrated samples will be collected at all surface-water locations. Sampling of the tributaries will start at the upstream reaches and progress downstream so as to coincide with the flow of river water. The total load contribution of the tributaries will be determined and will be subtracted from the load increase along the main stem of the river. The remaining load is that which is being discharged from the alluvial aquifer. Drainage-tile discharge directly into the main-stem river is not a factor because the soil on top of the alluvium is sandy and does not require the use of tile to drain soil water.

It takes about 2.5 days for water to travel from Cedar Rapids to Conesville. Discharge measurements and sampling of the main-stem sites will be repeated over a period of 2.5 days so that load calculations can be made considering the time of travel or by assuming equilibrium of the river system.

The sampling schedule will be determined by the occurrence of targeted flow conditions. It is anticipated that low base-flow sampling will take place in the fall, and that high base-flow sampling will take place in the spring.

Determine Conservative Nature of Herbicides

At the beginning of each seepage investigation, a sample of river water collected at the upstream main-stem site will be divided into two equivalent subsamples. One subsample will be filtered and chilled, while the other subsample will be put in a sealed glass jar with an adequate air space for aerobic conditions to be maintained and then returned to the river. At the end of the seepage investigation, the jar will be retrieved, and the sample will be processed following the normal procedures. The concentrations of contaminants in these two samples will be compared. This comparison may help define in-stream degradation of contaminants during the period of sample collection.

Atrazine did not degrade within the Mississippi River from St. Louis to the Gulf of Mexico during a 40-day traveltime (W.E. Pereira, U.S. Geological Survey, written commun., 1988). This conclusion was based on the fact that the ratio of deethylatrazine to atrazine did not change significantly from St. Louis to the Gulf of Mexico. Ratios of the concentration of deethylatrazine to atrazine will be computed for the Cedar River between Cedar Rapids and Conesville to determine any changes in the ratio. If rapid degradation of atrazine occurs within the stream channel, it should be apparent from this comparison.

Assess Concentration Variability of Agricultural Chemicals in the Alluvial Aquifer

Variability in the concentrations of the contaminants that are discharged from the alluvial aquifer will be determined at selected cross sections using minipiezometers. A maximum of six samples per section will be collected by temporary installation of the minipiezometer at three cross sections along the Cedar River.

At the edge of the water, a shallow profile will be sampled at a depth of 1 and 2 m. These samples will help determine how the contaminant concentrations may vary with depth next to the river.

Determine Possible Variability of Agricultural Chemicals With Time

To relate ground- and surface-water sampling events together in time, a sample from the Cedar River will be collected monthly at the unfarmed study site (fig. 6) during base-flow conditions. These samples will help determine the variability of the contaminants and their degradation products with time.

PLANNED REPORTS

Several journal articles and papers are planned for this study. These articles will address the results of the seepage investigations and the movement of agricultural chemicals between ground water and surface water. The articles will be published during and at the conclusion of the study. A final, comprehensive report is planned for publication as a U.S. Geological Survey report.

SAMPLING PROCEDURES AND QUALITY-ASSURANCE PLAN

Sampling in general is subject to many sources of error, beginning at the point of collection and continuing to the point of receiving analytical results. To ensure the integrity of data generated during the study, a rigorous quality-control and assurance program will be implemented. Results of the samples collected for the quality-assurance part of the study will reflect the sum of the sources of error. In addition, a methods-comparison study will be conducted to assess the comparability of data generated at the laboratory performing the herbicide analysis to that of the U.S. Geological Survey National Water-Quality Laboratory.

Sampling Procedures

Sampling procedures are designed to obtain samples of water that accurately represent the targeted water source, effectively preserve the samples, and minimize the chance of sample contamination. Selection of appropriate sampling equipment and containers is necessary to achieve these goals and to ensure proper maintenance and decontamination of the equipment. All of the sampling equipment selected for this study contains stainless-steel, Teflon[1], or otherwise noncontaminating components in areas that come in contact with sample material. A source of deionized-organic-free (DIOF) water has been located for decontamination purposes.

Separate sampling and quality-control procedures have been developed for ground- and surface-water samples. A modified ground-water sampling procedure will be used for samples collected using the minipiezometer. Each procedure will be described separately.

Observation Wells

The sampling procedure for the observation wells includes techniques consistent with obtaining samples from the specific horizons within the aquifer. The procedure used for this type of sampling is as follows:

1. Before sampling begins
    a. Wash and load equipment truck.
    b. Replace membrane on dissolved-oxygen meter probe.
    c. Prepare worksheets.
    d. Record water levels of all wells.
2. Sample wells
    a. Calculate the depth to water table and three well volumes of water on the basis of levels and depth of well.
    b. Assemble sampling apparatus and calibrate instrumentation.
    c. Lower pump to 0.5 m below the water level and begin pumping.
    d. Continue pumping until three volumes of water are removed from the well.
    e. Lower pump to 0.5 m from the bottom of the well and remove an additional 4 to 8 L of water. Try not to disturb sediment at bottom of well while doing this.
    f. Let flow stabilize and record specific conductance, pH, oxidation-reduction potential, water temperature, and dissolved-oxygen concentration.
    g. Switch tubing from flow-through chamber to filter apparatus.
    h. Flush 200 mL of sample water through filter containing 0.4 µm acetate filter. Use tweezers to handle filter.
    i. Collect nitrate sample by first rinsing the bottle with 30 to 50 mL of sample, dumping, and then collecting sample to within a few milliliters of the top. Add 1 ampule of mercuric chloride.
    j. Remove nylon filter, rinse apparatus with DIOF water, install 0.7-µm burned glass fiber filter (and pre-filter if necessary), and reassemble. Use forceps to handle filter.
    k. Pump additional 200 mL of sample through apparatus and collect herbicide sample. If additional filters are needed due to large sediment load, repeat above.
    l. Immediately place samples on ice.

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

    m. Place pump in recirculator. Pump an air pocket in tubing to mark the end of sample water, fill recirculator with DIOF water, and pump until sample water is evacuated.
    n. Set switch to "reverse" and return approximately one-third of the water to the recirculator.
    o. Pump water from recirculator a second time. Continue pumping until all DIOF water is removed from recirculator.
    p. Rinse tubing with DIOF water.
    q. Disassemble filter apparatus and rinse with DIOF water.
    r. Rinse out any sediment remaining in the flow-through chamber.
3. End-of-day maintenance and decontamination
    a. Check the meter calibrations at the end of the day. If there is greater than 5-percent error, meters may have to be calibrated at several intervals throughout the day.
    b. Fill recirculator with water, add 1 teaspoon of laboratory detergent, place discharge hose in recirculator and pump for at least 5 minutes. Set pump to "reverse" for a few minutes to flush intake chamber.
    c. Remove any detergent in recirculator and rinse both pump and recirculator with DIOF water. Fill recirculator with DIOF water and flush detergent from tubing. Pump additional 25 to 30 L of DIOF water through pump and tubing. Reverse low to rinse out intake chamber.
    d. Disassemble and scrub filter apparatus with detergent. Rinse with several liters of DIOF water and leave disassembled overnight to dry.
    e. Evacuate water from tubing by pumping air through pump.

Maintain a smooth, constant flow during the meter-reading and sampling process. Consistency in sampling, maintenance, and decontamination is necessary and will reduce variations in the data. The sampling area should be kept clean and free of extraneous sample material that may spray from leaky joints in the tubing or leak around the fittings of the filter apparatus due to excess pressure.

Minipiezometers

The sampling procedure for minipiezometer samples is similar to that for ground-water samples with the following exceptions and additions.

1. Run tag-line across river.
2. Insert minipiezometer at selected sites a minimum of 1 m into the bottom sediment and open screen.
3. Assemble manometer and sampling apparatus and connect appropriate tube to the minipiezometer. Submerse the other tube into the river water.
4. Draw water into the manometer and equilibrate. Record difference in millimeters.
5. Draw additional water from the minipiezometer into the sample flask. Draw several volumes of water from the minipiezometer and tubing at a slow, steady rate. Fill enough 1-L bottles with sample water for physical properties (about 250 mL), TOC (total organic carbon, about 150 mL), herbicide (about 500 mL), nitrate (about 500 mL), and tritium (about 1,000 mL). Immediately record water temperature on sample worksheet.
6. Filter sample by pumping through filter apparatus.
7. Decontaminate minipiezometer and manometer.

Streams

A depth-integrated sample will be collected from the deepest, swiftest part of the stream. Equal discharge-interval (EDI) samples will be composited from depth-integrated samples from 10 sections. Dip samples are acceptable when discharge or stream characteristics do not permit depth integration. Surface-water samples will be collected as described by Guy and Norman (1970). Sample bottles will be rinsed with methanol and dried before use. Sampling equipment will be disassembled and decontaminated with several rinsings of DIOF water.

Quality-Assurance Plan

The quality-assurance plan consists of the analysis of blank, duplicate, and when possible, spiked water samples prepared onsite to assess the effectiveness of the sampling procedures. Spiked water samples will be collected if standard solutions for herbicides are available. The quality-assurance plan will be carried out in cooperation with the U.S. Geological Survey laboratories in Lawrence, Kansas, and Denver, Colorado.

Quality assurance will vary according to the sample property being determined and the sampling technique used to collect it. Each of the sampling techniques will have a quality-assurance plan appropriate for the type of equipment and personnel being used. Each type of sample will be discussed separately.

Herbicide-sample quality assurance will consist of the analysis of blank, matrix spike, and duplicate samples. These samples will represent about 10 percent of all samples submitted for analysis. Nitrate and TOC will consist of blank and duplicate samples only. A matrix spike is a duplicate water sample spiked with a known amount of the constituent being analyzed. Quality-assurance samples will be collected at pre-selected sites during each sample collection. Blank samples will be collected at the sample location selected for duplicates and spikes. Blank samples will consist of DIOF water pumped through the sampling apparatus. Additional blank samples will be collected if the pump blanks are unsatisfactory or if contamination is suspected. Matrix spikes will be prepared subsequent to the original sample and then adding 15 μL of spiking solution prepared by the servicing laboratory with a 50–μL syringe. A graduated syringe will be designated for this purpose. The syringe will be rinsed five times with methanol before and after spiking and three times with spiking material before spiking. The bottles used for matrix spikes will be weighed before and after filling so that an exact amount of spiked water can be calculated. Spiking levels will be approximately 0.5 μg/L, or 10 times the detection level (0.05 μg/L). Duplicate samples will be collected by decontaminating the apparatus and taking another sample as if at another site.

Ground-Water Samples

Quality-assurance samples will be collected for each sampling session. Blank samples will be collected by pumping DIOF water from the recirculator through the filtering apparatus. Matrix spikes will be composed of aquifer water spiked with an appropriate quantity of spiked solution. Duplicate samples will be collected by decontaminating the filter apparatus and resampling.

Minipiezometer Samples

One suite of quality-assurance samples will be collected for every sampling session requiring minipiezometer samples. Blank samples will be collected by pumping DIOF water through the minipiezometer from a 4-L jar. The sampling apparatus (not including the minipiezometer) will be decontaminated between duplicate samples.

Surface-Water Samples

One suite of quality-assurance samples will be collected for every 10 surface-water samples collected. Blank samples will be collected by pouring water down the spout of the sampler into the sample bottle. Matrix spikes will not be prepared for nitrate and TOC determination. The sampling apparatus and sample bottles will be decontaminated between duplicates.

Seepage Samples

During the seepage investigation, one suite of quality-assurance samples will be collected from the streams by every seepage-sampling crew. Blank samples will consist of collecting rinsings of DIOF water poured through the sampling apparatus and collected. Duplicate samples will be collected by resampling the same location as before, decontaminating between samples.

Main-Stem Samples

One suite of quality-assurance samples will be collected by every main-stem sampling crew. Blank samples will be collected by collecting rinsings of DIOF water poured through the sampling apparatus. Duplicates will be collected by resampling the same location as before, decontaminating between samples.

Sample Filtration

One filter blank sample will be collected at the end of each sampling day. DIOF water will be pumped through the filter apparatus after decontamination but before final cleaning. The blank samples will be analyzed for all constituents.

Methods Comparison

A methods-comparison study will be done to aid in assessing the comparability of data generated by the U.S. Geological Survey laboratory in Lawrence, Kansas, and the U.S. Geological Survey National Water-Quality Laboratory in Denver, Colorado. An additional 1-L sample will be collected along with the quality-assurance samples. This sample will be sent to the National Water-Quality Laboratory for analysis. The servicing laboratory will analyze for alachlor, ametryn, atrazine, cyanazine, deethylatrazine, deisopropylatrazine, metolachlor, metribuzin, prometon, prometryn, propazine, simazine, and terbutryn. The National Water-Quality Laboratory will analyze for alachlor, ametryn, atrazine, cyanazine, metolachlor, metribuzin, prometon, prometryn, propazine, simazine, simetryn, and trifluralin. Results for analytes in common will be reviewed for comparability.

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