

Movement of Agricultural Chemicals Between Surface Water and Ground Water, Lower Cedar River Basin, Iowa

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Movement of Agricultural Chemicals Between Surface Water and Ground Water, Lower Cedar River Basin, Iowa

By PAUL J. SQUILLACE, JAMES P. CALDWELL,
PETER M. SCHULMEYER, and CRAIG A. HARVEY

Prepared as part of the
Toxic Substances Hydrology Program

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CONVERSION FACTORS, ABBREVIATIONS, AND VERTICAL DATUM

| Multiply | By | To obtain |
|--|----------|-----------------------------------|
| millimeter (mm) | 0.03937 | inch |
| centimeter (cm) | 0.3937 | inch |
| meter (m) | 3.281 | foot |
| kilometer (km) | 0.6214 | mile |
| square meter (m ²) | 10.76 | square foot |
| square kilometer (km ²) | 0.3861 | square mile |
| cubic meter (m ³) | 264.2 | gallon |
| liter (L) | 0.2642 | gallon |
| meter per kilometer (m/km) | 5.280 | foot per mile |
| meter per day (m/d) | 3.281 | foot per day |
| cubic meter per second (m ³ /s) | 35.3145 | cubic foot per second |
| cubic meter per second per square kilometer [(m ³ /s)/km ²] | 91.4646 | cubic foot per record square mile |
| grams per day (g/d) | 0.002205 | pound per day |
| cubic meter per day (m ³ /d) | 264.2 | gallon per day |
| cubic meter per year per day per meter [(m ³ /d)/m] | 1 | cubic foot per day per foot |
| cubic meter per year (m ³ /yr) | 264.2 | gallon per year |
| meter squared per day (m ² /d) ¹ | 10.76 | foot squared per day |
| gram (g) | 0.002205 | pound |
| kilogram (kg) | 2.205 | pound |
| megagram (Mg) | 1.102 | ton |

¹The standard unit for transmissivity (T) is cubic meter per day per square meter times meter of aquifer thickness [(m³/d)/m²]m. This mathematical expression reduces to meter squared per day (m²/d), which is the unit of measurement used in this report.

Convert degrees Celsius (°C) to degrees Fahrenheit (°F) by using the formula:

$$^{\circ}\text{F} = 1.8 \times ^{\circ}\text{C} + 32.$$

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

Movement of Agricultural Chemicals Between Surface Water and Ground Water, Lower Cedar River Basin, Iowa

By Paul J. Squillace, James P. Caldwell, Peter M. Schulmeyer, and Craig A. Harvey

Abstract

Movement of agricultural chemicals alachlor, atrazine, cyanazine, deethylatrazine, deisopropylatrazine, and metolachlor between surface water and ground water is documented by data collected from May 1989 through July 1991 at an unfarmed study site adjacent to the Cedar River in Iowa. During periods of runoff, these chemicals moved from the Cedar River into the alluvial aquifer with bank-storage water. Results of simulation of ground-water flow conditions during March–April 1990 indicated that bank-storage water moving through the river bottom accounted for 70 percent of the total bank-storage water, whereas the remaining 30 percent moved through the riverbank. The largest concentrations of the chemicals in bank-storage water during 1990 were: alachlor, 2.1 micrograms per liter ($\mu\text{g/L}$); atrazine, 4.7 $\mu\text{g/L}$; cyanazine, 3.2 $\mu\text{g/L}$; deethylatrazine, 0.54 $\mu\text{g/L}$; deisopropylatrazine, 0.33 $\mu\text{g/L}$; and metolachlor, 2.2 $\mu\text{g/L}$. Larger concentrations of some herbicides and their metabolites were detected in the ground water after the study site was inundated by floodwater between June and August 1990. The concentrations in a water sample from one well after this flooding on February 5, 1991, were: alachlor, 0.06 $\mu\text{g/L}$; atrazine, 18 $\mu\text{g/L}$; cyanazine, 1.3 $\mu\text{g/L}$; deethylatrazine, 1.4 $\mu\text{g/L}$; deisopropylatrazine, 0.40 $\mu\text{g/L}$; and metolachlor, 7.0 $\mu\text{g/L}$.

During base-flow conditions, the movement of agricultural chemicals from ground water to surface water was quantified for two periods of

time in 1989 and 1990 along a 117-kilometer reach of the Cedar River. The principal source of atrazine, deethylatrazine, deisopropylatrazine, and metolachlor in the Cedar River during base flow was ground water discharged directly from the alluvial aquifer adjacent to the Cedar River. This discharge exceeded the combined tributary inflow of the chemicals along the entire reach.

Bank storage is probably an important source of agricultural chemicals discharged from the alluvial aquifer but becomes depleted with time after surface runoff. Herbicides discharged from the alluvial aquifer during periods of extended base flow entered the alluvial aquifer with ground-water recharge at some distance from the river. The movement of nitrate between surface water and ground water is minor, when compared to the herbicides, even though nitrite was detected in the Cedar River during runoff.

INTRODUCTION

The application of agricultural chemicals on row crops is a major cause of nonpoint-source contamination of surface water and ground water in the Midwestern United States (Frank and others, 1982; Gilliom and others, 1985; Squillace and Engberg, 1988; Thurman and others, 1991). Agricultural chemicals used in Midwestern States include nutrients (nitrogen, potassium, and phosphorus) and synthetic organic compounds (including the herbicides alachlor, atrazine, cyanazine, metolachlor, metribuzin, and simazine). About 136,000 Mg of herbicides (active ingredients) are applied annually to cropland and

pasture in the Midwest to control undesirable competing vegetation in the production of corn, soybeans, and sorghum (Goolsby and others, 1991).

During the spring, the concentrations of alachlor, atrazine, and simazine in Midwest rivers are frequently 3 to 10 times greater (Thurman and others, 1991) than the Maximum Contaminant Levels for drinking water established by the U.S. Environmental Protection Agency. These water-soluble chemicals are not removed by conventional water-treatment practices and thus may be found in drinking water (U.S. Environmental Protection Agency, 1991a).

Herbicides can be transported to streams by overland flow, through field drainage tiles, or by ground water. Once contaminants are transported to a stream, dynamic surface- and ground-water interaction affects their storage and further distribution in the environment. Alluvial aquifers adjacent to large rivers are particularly vulnerable to these surface- and ground-water interactions because of bank storage and flooding. During periods of snowmelt or rainfall, runoff to a river can cause an increase in river stage. Because of the increased river stage, river water may move through the river bottom and riverbank into the adjacent aquifer. As the stage declines, some of this same water returns to the river. The volume of water stored and released is referred to as bank storage. Floodwater originating from the river or tributaries to the river also can recharge the alluvial aquifer.

Pesticides can degrade during their transport to ground water. Pesticide compounds are degraded in the soil and water to produce new compounds referred to as metabolites (Paris and Lewis, 1973). These metabolites may become more abundant than the parent compound as degradation progresses. Preliminary results from current research indicate that concentrations of atrazine metabolites (deethylatrazine and deisopropylatrazine, for example) in ground water may be several times larger than the concentration of the parent compound (Kross and others, 1990; Adams and Thurman, 1991; Kolpin and others, 1994)

Purpose and Scope

This report describes results of a study of the movement of selected agricultural chemicals between surface water in the Cedar River and ground water in an adjacent alluvial aquifer in east-central Iowa. This study was supported by the Toxic Substances Hydrology Program of the U.S. Geological Survey, which

was implemented to provide the Earth-science information needed to understand the movement and fate of hazardous substances in the Nations' surface and ground water.

Water-quality analyses of surface-water and shallow ground-water samples collected during various flow regimes of the Cedar River are presented and interpreted in this report. The selected chemicals include: nitrate, alachlor, ametryn, atrazine, cyanazine, deethylatrazine, deisopropylatrazine, metolachlor, metribuzin, prometon, prometryn, propazine, simazine, and terbutryn. On a small scale, chemical movements were investigated using data from observation wells in the alluvial aquifer adjacent to the river at an unfarmed site (hereafter referred to in this report as the Palisades site) 10 km southeast of Cedar Rapids in Linn County, Iowa (fig. 1). Ground-water samples from these wells, as well as river and other surface-water samples, were collected during base-flow conditions and during selected periods of runoff from May 1989 through July 1991. Water-level data also were collected from the wells, and the river stage was monitored at the Palisades site. A two-dimensional, ground-water flow model was used to quantitatively describe the movement of water into and out of the alluvial aquifer in response to rising and falling river stages. On a large scale, the movement of agricultural chemicals from ground water to surface water was quantified for two periods of time in 1989 and 1990 along a 117-km reach of the Cedar River.

Previous Investigations

Geologic, hydrologic, and geochemical studies by previous investigators provide useful information on the geohydrology of the study site. Hansen (1970), Bunker and others (1985), and Wahl and Bunker (1986) summarize the geology and ground-water resources in and around Linn County, Iowa.

Previous and current investigations of the Cedar River provide useful information about the distribution of agricultural chemicals in surface and ground water. Squillace and Engberg (1988) and Squillace and Thurman (1992) evaluated the occurrence and transport of herbicides in the Cedar River Basin. Schulmeyer (1991) described the relation of alachlor, atrazine, cyanazine, deethylatrazine, deisopropylatrazine, and metolachlor to river stage in the Cedar River. Squillace and others (1991) investigated the source of selected triazine compounds in the Cedar River Basin

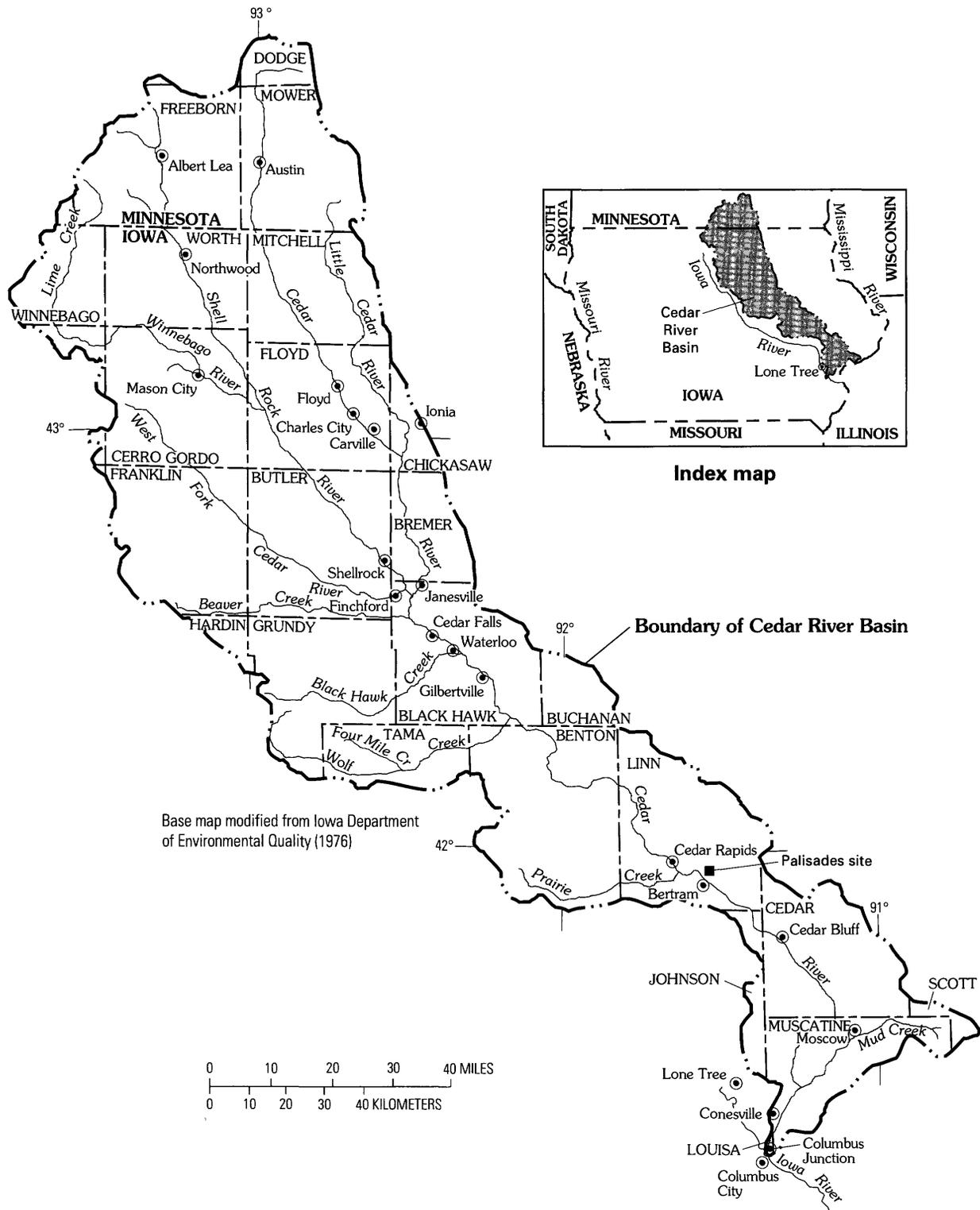


Figure 1. Location of Cedar River Basin and Palisades site in east-central Iowa.

during base-flow conditions. Goldberg and others (1991) investigated photolytic degradation of atrazine in the Cedar River. Surface- and ground-water interaction during the transport and storage of atrazine in the

Cedar River is reported by Liszewski and Squillace (1991). A report by Schulmeyer and others (1995) contains much of the data for the investigation that is interpreted in this report.

Acknowledgments

James Snyder, owner of the land on which the Palisades site is located, generously provided access to his property for the installation and monitoring of the observation wells. Mr. Snyder assisted throughout the course of the study by maintaining road access to the site and assisting with equipment transportation.

DESCRIPTION OF STUDY AREA

Cedar River Basin

The Cedar River Valley varies considerably in width, ranging from a constricted bedrock valley to a broad flood plain and extending from south-central Minnesota to southeastern Iowa (fig. 1). The basin has a drainage area of 20,242 km², of which 87 percent is in Iowa (Iowa Department of Environmental Quality, 1976). The description of the study area is limited to the Cedar River Basin within the State of Iowa.

Land and Water Use

Land use in the Cedar River Basin is primarily agricultural (81 percent), with corn and soybeans as the major crops (U.S. Department of Agriculture, 1976). Alachlor, atrazine, cyanazine, and metolachlor are among the most commonly used herbicides for corn production; the amount of active ingredients applied in 1990 in Iowa were 2.8, 3.5, 2.3, and 4.3 thousand Mg, respectively (Iowa State University, 1991). Alachlor and metolachlor also are used for soybean production. The usages for soybeans were 700 and 260 Mg, respectively (Iowa State University, 1991). Livestock raised in the basin include beef and dairy cattle, hogs, and sheep. Several urban areas are in the basin, including the municipalities of Albert Lea, Minnesota, and Cedar Falls, Cedar Rapids, and Waterloo, Iowa.

Ground water is the principal source of supply for commercial, domestic, industrial, and agricultural water users (Clark and Thamke, 1988). Approximately 135,000,000 m³ of surface and ground water were used in the basin during 1990 (E.E. Fischer, U.S. Geological Survey, written commun., 1992). Domestic use, both self- and public-supplied, was about 46,200,000 m³ from ground water. Estimated agricultural water use was 19,700,000 m³, which

consisted of about 76-percent ground water and 24-percent surface water. The quantity of surface and ground water withdrawn in 1990 by principal users (excluding electric power generation) and by source in the Cedar River Basin is shown in figure 2.

Climate

The climate of Iowa typically is continental and is characterized by large seasonal (commonly as high as 38 °C in the summer and as low as -28 °C in the winter) and daily temperature variations. Average annual precipitation in the Cedar River Basin ranges from 76 to 92 cm, but large variations can occur (Iowa Department of Environmental Quality, 1976). Annual precipitation at Cedar Rapids during the study was 62 cm in 1989, 109 cm in 1990, and 103 cm in 1991 (Harry Hillaker, State Climatologist, Iowa Department of Agriculture and Land Stewardship, oral commun., 1992). The median monthly precipitation during calendar years 1989–91 was greatest during May, June, and August. The average annual temperature at Cedar Rapids is 9.4 °C, the average annual snowfall is 87.4 cm, and the average length of the growing season is 161 days (Harry Hillaker, State Climatologist, Iowa

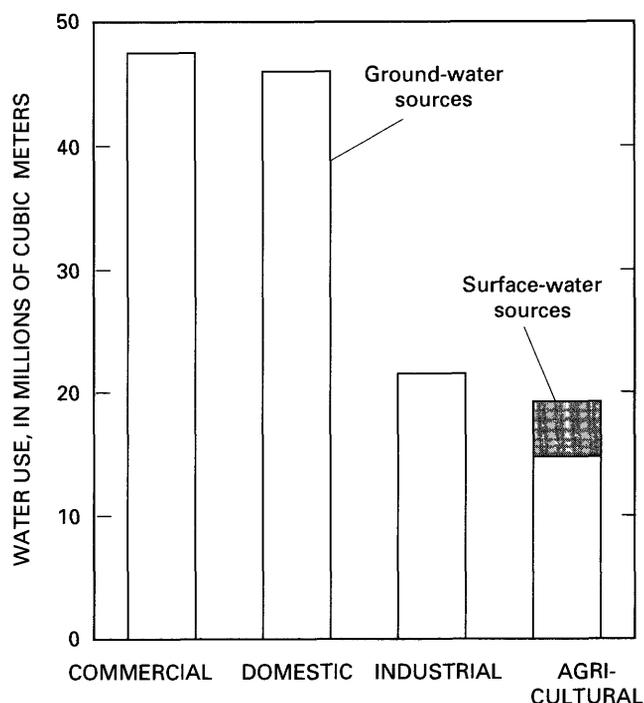
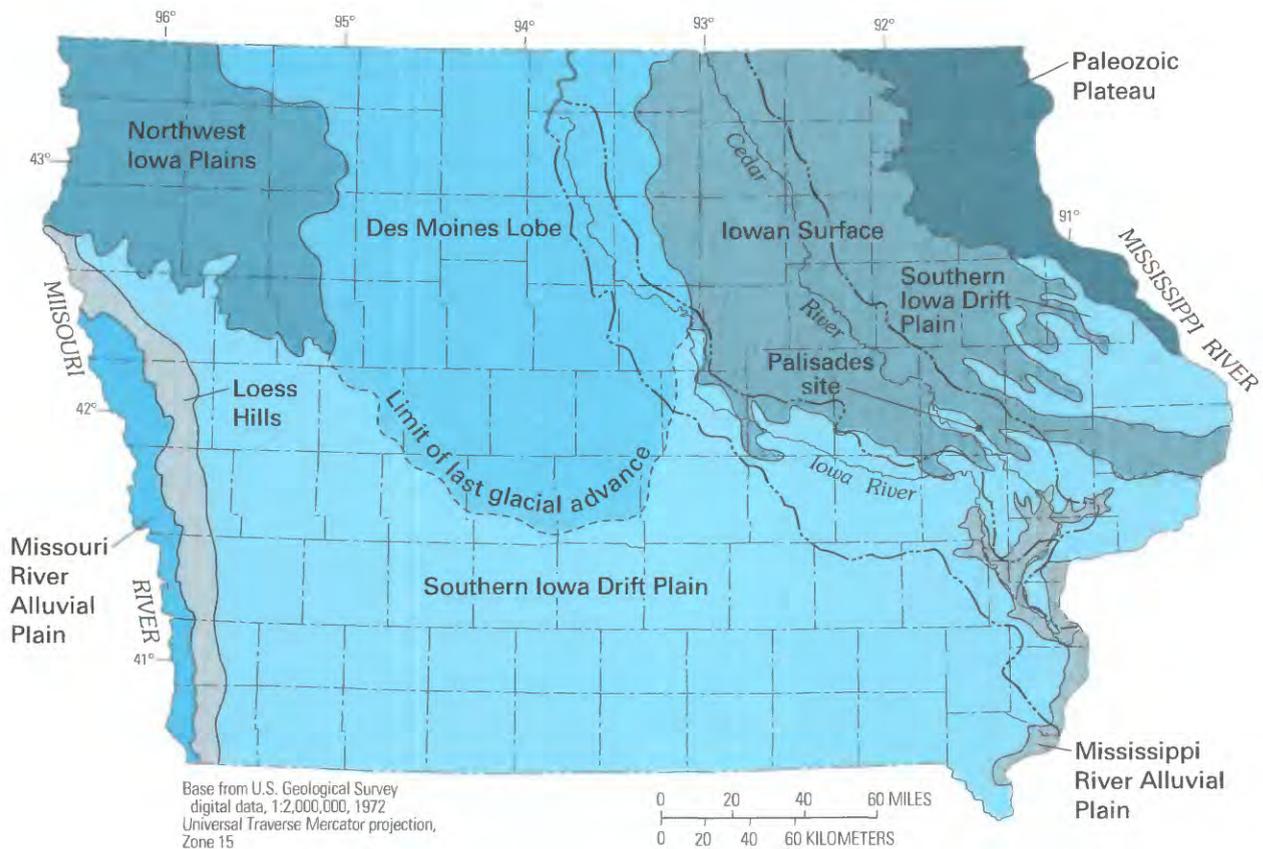


Figure 2. Water use in the Cedar River Basin, 1990 (Source: E.E. Fischer, U.S. Geological Survey, written commun., 1992. Figures do not include nonconsumptive use by electric-power generating facilities. Agricultural use includes irrigation withdrawals; commercial, domestic, and industrial use includes self- and public-supplied sources).



EXPLANATION

- Boundary of drainage basin
- Boundary of physiographic province

Figure 3. Physiographic provinces of Iowa and location of Cedar and Iowa River drainage basins (modified from Prior, 1991).

Department of Agriculture and Land Stewardship, written commun., 1992).

Physiography

The Cedar River Basin is characterized by four physiographic provinces that correspond to areas of glacial-drift deposits (fig. 3 and Prior, 1991). The rivers and streams in the basin traverse surfaces whose features and sediment deposits are the result of multiple episodes of continental glaciation and subsequent erosion. The major physiographic provinces recognized in the Cedar River Basin are the Des Moines Lobe, the Iowan Surface, the Southern Iowa Drift

Plain, and the Mississippi River Alluvial Plain (Prior, 1991).

The Des Moines Lobe represents the most recent advance of continental glaciation into Iowa. The lobe essentially is a constructional or depositional glacial terrain that is characterized by Wisconsin-age glacial drift, undulating topography, and poorly established drainage. Radiocarbon dating indicates that the drift material was deposited about 14,000 years before present (Prior, 1991). Sediments of the Des Moines Lobe consist chiefly of glacial till, with alluvium in the river valleys and gravel-and-sand outwash deposits along the margin of the province. The headwaters of several major streams of the Cedar River Basin begin

on the poorly drained, undulating surface of the Des Moines Lobe.

The physiographic features of the Des Moines Lobe blend rapidly with the gently rolling, low-relief, boulder-strewn Iowan Surface. The Iowan Surface is considered to be a widespread erosion-surface complex that evolved from normal processes of erosion acting on a landscape of pre-Illinoian-age glacial drift. Drainage networks generally are well established in the province, although stream gradients usually are slight and some scattered areas of poor drainage and wetlands occur. The major streams have broad valleys and are flanked by low, rolling hills that merge with the moderately dissected stream divides. The tributary valleys have slight relief that are barely incised into the Iowan Surface. The southern margin of the Iowan Surface is marked by the sharp contrast of its low-relief topographic features with those of the more highly dissected Southern Iowa Drift Plain. The glacial deposits in the northern two-thirds of the Iowan Surface physiographic province are quite thin; the effect of shallow limestone bedrock on the land surface is seen in the form of karst features, especially sinkholes. These karst features make this extensively cultivated region especially vulnerable to ground-water contamination by agricultural chemicals. In areas of thin glacial drift, the flow of the major streams and rivers on the Iowan Surface is maintained during dry periods by ground-water discharge from bedrock aquifers.

The Southern Iowa Drift Plain, Iowa's largest physiographic province, is characterized by a variety of landscapes—steeply rolling hills, flat-topped uplands of uniform elevation, and lowland valley floors. Glaciers were present in the headwater of the Cedar and Iowa River Valleys during the time the Des Moines Lobe province was ice covered. The valleys in the Southern Iowa Drift Plain obtained much of their present width, depth, and alluvial fill during melt-water flooding as the Wisconsin ice sheet receded from north-central Iowa (Prior, 1991). The landforms of this physiographic province result primarily from a deepening network of rivers and streams flowing on surfaces composed mostly of pre-Illinoian glacial drift. Well-integrated, dendritic drainage, with bedrock exposed in the lower stream valleys, is characteristic of the province. Locally, broad, relatively flat upland areas are present where the areas between the major streams are wide.

The Mississippi River Alluvial Plain is among the youngest of the State's physiographic provinces. As the name implies, the topographic features in this area are the result of alluvial processes. Physiographic features of the Mississippi River Alluvial Plain include flood plains, stream terraces, sand dunes, and river valleys. The flood plains, terraces, and river valleys contain stratified deposits of sand, gravel, clay, and silt. These generally porous deposits allow rapid infiltration and subsurface movement of water. A large area is dominated by backwater sloughs and meander scars created by the ancestral and present Mississippi River as it shifted across the valley surface. The province is characterized by generally flat surfaces and wetlands.

Maximum topographic relief in the Cedar River Basin is 238 m, ranging from an elevation of 415 m above sea level in western Winnebago County, Iowa, to 177 m above sea level at the confluence of the Cedar and Iowa Rivers at Columbus Junction, Iowa (fig. 1). Local topographic relief, from the upland drainage divides to the valley surface, is about 30 m.

Geology

Precambrian-age igneous and metamorphic rocks form a crystalline basement complex. The overlying sedimentary bedrock consists principally of carbonate rocks, with lesser quantities of shale and sandstone, and dips to the southwest at about 2.4 m/km (Horick and Steinhilber, 1973). The ages of these sedimentary rocks are primarily Cambrian through Devonian. The uppermost bedrock is Ordovician-age rock along the eastern fringe of the basin. Rocks of Silurian age occur immediately beneath the glacial drift along the Cedar River Valley in most of Linn and Cedar Counties, Iowa. However, Devonian-age bedrock subcrops throughout most of the Cedar River Basin. There are some isolated subcrops of Cretaceous-age rocks in the northern part of the basin. The surface of these bedrock units was eroded, and an incised drainage system was established before deposition of the overlying glacial drift.

The topography of the Cedar River Basin developed on glacial materials deposited over the sedimentary rocks. The glacial drift, which mantles nearly the entire area, filled the incised bedrock valleys with outwash and till deposits and preserved much of the bedrock topography. The glacial drift is thin or absent as a result of erosion in some of the northern areas of the

Iowan Surface but increases in thickness to 120 m in the Des Moines Lobe physiographic province.

Surface-Water Hydrology

The Cedar River is the largest tributary of the Iowa River (fig. 3); the average discharge of the Cedar River at the confluence with the Iowa River is $136 \text{ m}^3/\text{s}$, which exceeds the average discharge of the Iowa River ($82 \text{ m}^3/\text{s}$) at the confluence (Squillace and Engberg, 1988). The largest tributaries of the Cedar River are located in the northwestern half of the basin. Downstream from the community of Cedar Falls, Iowa, only five tributaries have subbasin drainage areas that exceed 520 km^2 , and none exceed $1,040 \text{ km}^2$ (Iowa Department of Environmental Quality, 1976). The river discharge is considered unregulated as no major artificial impoundments are located on the Cedar River.

Peak runoff rates in the Cedar River Basin vary substantially depending on subbasin drainage area and topography. Upstream from Northwood (fig. 1), in the Des Moines Lobe physiographic province, which is characterized by slight topographic relief and poorly developed drainage systems, the peak runoff rate for the gaged period of record is $0.33 \text{ (m}^3/\text{s)/km}^2$. In the remainder of the Cedar River Basin, which has a well-established drainage system, peak runoff for the period of record is $1.41 \text{ (m}^3/\text{s)/km}^2$ (Lara, 1987). Flood runoff consists predominantly of overland flow and, to a lesser extent, drainage conveyed by field-drainage tile from agricultural areas and ground water (Squillace and Engberg, 1988). The source of water during stream base flow is ground water.

Ground-Water Hydrology

Bedrock and unconsolidated aquifers are present within the study area. Carbonate rocks of Silurian-Devonian age and sandstone of Cambrian-Ordovician age are the most extensively used sources of water for municipal, domestic, and industrial supplies in the basin (Horick and Steinhilber, 1973; Horick, 1984). Other bedrock aquifers are present in the Cedar River Basin, but they are not used extensively because of small yields or unsuitable water quality. Although the Silurian-Devonian aquifer system is comprised of several distinct rock formations, often they are referred to as one hydrologic unit when they are in hydraulic connection (Horick, 1984). However, well yields and other related information suggest that the Silurian

rocks are the principal water-bearing units in this system (Hansen, 1970). In ascending order, the principal water-bearing units that make up the Cambrian-Ordovician aquifer system are the Jordan Sandstone and the St. Peter Sandstone (Burkart and Buchmiller, 1990). The Cambrian-Ordovician aquifer system is overlain by 90 to 180 m of shale and argillaceous carbonate of Ordovician age that form confining layers and provide hydraulic separation from the overlying Silurian-Devonian aquifer system. Unconsolidated aquifers above the bedrock surface are divided into three types on the basis of their occurrence and lateral distribution—alluvial aquifers, drift aquifers, and buried-channel aquifers (Buchmiller and others, 1985).

Although narrow bedrock valleys contain little alluvial material, the broad flood plains of the Cedar River and its larger tributary streams have extensive alluvial aquifers consisting of sand and gravel interbedded with less-permeable silt and clay. Recharge to the alluvial aquifer occurs by vertical infiltration through the soil, and the area adjacent to the river can be recharged by bank storage. Furthermore, in some areas alluvial aquifers can be recharged by upward seepage from the underlying bedrock aquifers. Generally, the alluvial aquifers discharge ground water to the Cedar River; the Cedar River is a gaining stream. Cedar Rapids withdraws about $110,000 \text{ m}^3/\text{d}$ from wells located in the alluvium along the Cedar River in Linn County (Thomas Noth, Cedar Rapids Water Department, oral commun., 1992).

Palisades Site

The Palisades site is an unfarmed, wooded area, located in sec. 11, T. 82 N., R. 6 W., Linn County, Iowa. The City of Cedar Rapids (population 108,751, U.S. Department of Commerce, 1991) is 10 km northwest of the study site (fig. 1). The site is located in the Southern Iowa Drift Plain just south of its irregular boundary with the Iowan Surface (fig. 3).

Physiography

The Palisades site is on a flood plain, bounded to the south and southwest by the Cedar River, on the southeast by intermittently inundated backwater sloughs of the Cedar River, and to the north by glacial-drift-mantled uplands. Local topographic relief is about 30 m from the uplands 0.5 km north of the

Palisades site to the Cedar River on the south. The maximum relief at the site is about 3 m.

Most of the flood plain at the site is covered by a 0.5- to 3.0-m thick surficial layer of laminated, organic-rich, silty, fine-grained sand with a number of surficial, channel-like, topographic depressions. These depressions may be the result of scouring of the flood plain by overbank streamflow (flood thalweg), or they simply may represent meander scars or accretion ridges that have been incompletely filled in by overbank deposition. The silty sand layer is generally thinner in the topographically low areas, possibly the result of scouring during flooding.

Soils in the Cedar River Valley in southern Linn County are principally of the Fayette series, which consists of well-drained soils that formed in loess, whereas the soils at the Palisades site are categorized as "loamy alluvial land" (Schermerhorn and Highland, 1975).

Hydrology

The three hydrogeologic units of interest at the study site: (1) the confined or semiconfined Silurian-Devonian carbonate aquifer system, (2) an intermediate confining unit of glacial till, and (3) the unconfined, sand-and-gravel alluvial aquifer. Although not confirmed by fossil evidence, the uppermost bedrock at the Palisades site is believed to be Silurian dolomite; fossil correlation was not possible from the sample collected. A deep reconnaissance boring near the river's edge (in the vicinity of the 10-m well nest) encountered bedrock at a subsurface elevation of 180 m above sea level or about 32 m below land surface. Cuttings recovered during drilling were described lithologically as dolomite. The geologic log from another reconnaissance borehole drilled by the Geologic Survey Bureau, Iowa Department of Natural Resources, 1.5 km north of the Palisades site, in NE 1/4, sec. 10, T. 82 N., R. 6 W., described the Gower Formation (uppermost Silurian) at a subsurface elevation of 189 m above sea level. It is inferred, therefore, from well control that the Devonian aquifer is absent because of erosion and that the uppermost bedrock at the site is of Silurian age. The uppermost bedrock (Silurian-Devonian aquifer system; Bunker and others, 1985) is confined by 10 to 15 m of low permeability glacial till at the site and is not a significant contributor to shallow ground-water flow.

Surface drainage at the Palisades site is to the south-southeast. Several small ephemeral streams

carry runoff from the uplands north of the site onto the flood plain. This surface-water runoff drains to several topographic depressions on the generally flat flood plain. During wet periods these depressions retain surface water and form ephemeral ponds. The largest of these ephemeral ponds has a maximum area of 4,500 m² (fig. 4). These ponds function as areas of focused ground-water recharge.

The hydrologic aspects of this study are concerned primarily with recharge to and discharge from the shallow ground-water system and with the water-level fluctuations in the alluvial aquifer along the Cedar River. Recharge to the ground-water system is from precipitation, leakage from ephemeral streams and ponds, bank storage from the Cedar River, and flooding of the Cedar River and ephemeral streams. Discharge from the ground-water system is by evapotranspiration and discharge to streams.

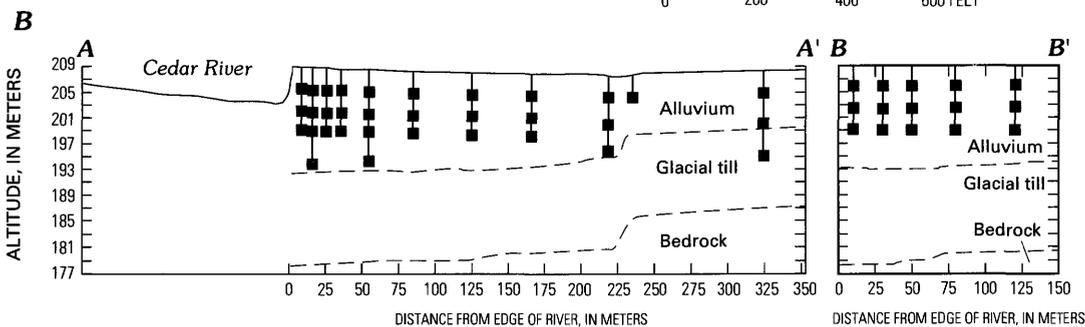
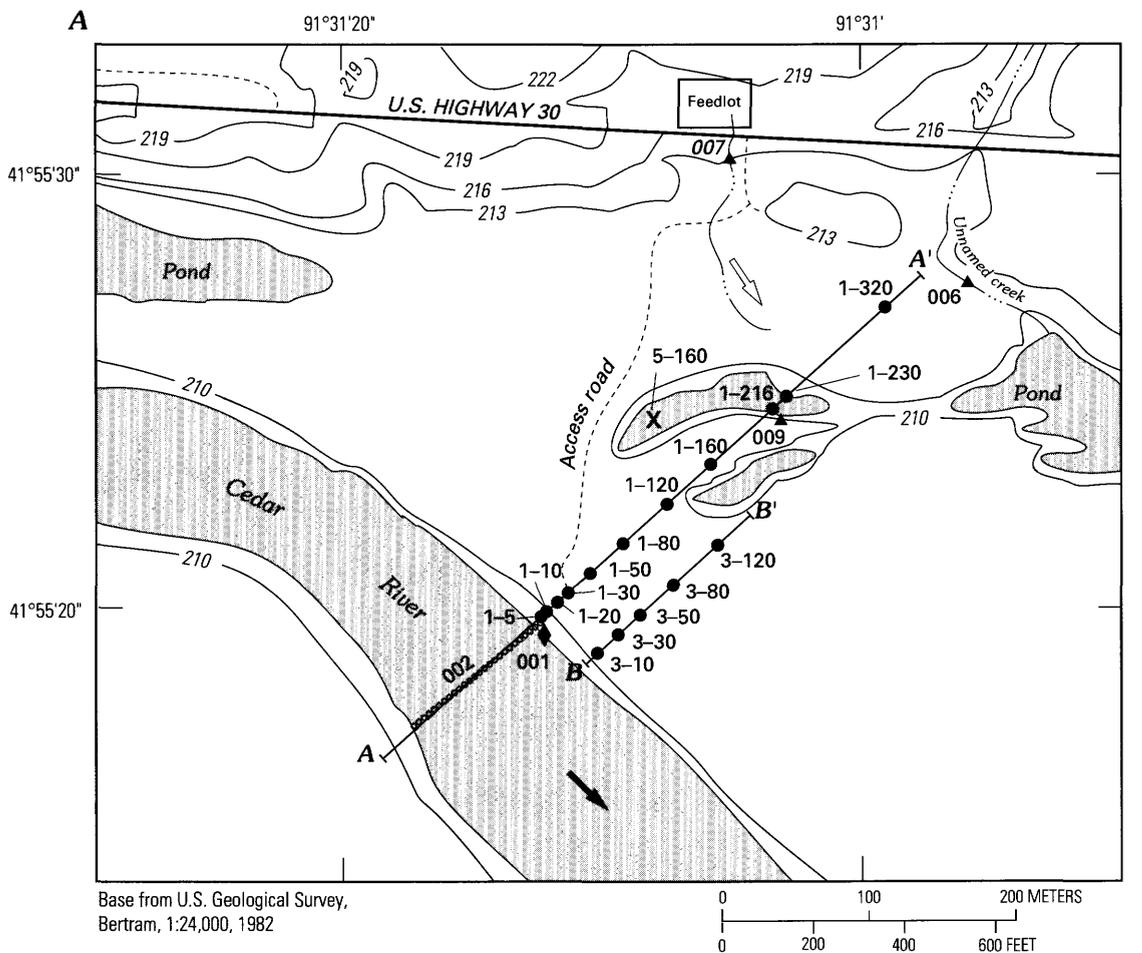
FIELD AND LABORATORY METHODS

Observation-Well Construction

Drilling was begun in the spring of 1989 to delineate the geologic and hydrologic characteristics of the Palisades site and to install observation wells for water-quality sampling and water-level measurements. A preliminary analysis of the unconsolidated material in the area, coupled with a review of available well logs, facilitated the design of the observation-well network.

The observation-well network, comprising 54 wells, was installed as a series of well nests perpendicular to the Cedar River (fig. 4). Map numbers in figure 4 consist of a prefix indicating line location and distance from the river's edge; 1-10 refers to the well nest on section A-A' located 10 m from the river, whereas 3-30 refers to the well nest on section B-B' located 30 m from the river. Well numbers (Schulmeyer and others, 1995) have a third component representing the depth of the top of the 76-cm-long screened interval. For example, Palisades well 1-5-3 is located on section A-A' and is 5 m from the river's edge, and the top of the screen is 3 m below land surface.

The observation wells were installed at selected distances from the river's edge on the basis of river stage at the time of installation. As the river stage changes, the distance from the river's edge to the well



EXPLANATION

- 219 — **Topographic contour**— Shows altitude of land surface. Contour interval 3 meters. Datum is sea level
- - - - **Geologic contact**
- A — A' **Trace of section**
- 002 **Minipiezometer line**
- ➔ **Direction of streamflow**
- 007 ▲ **Surface-water sampling site and number**
- 001 ◆ **Surface-water sampling site and location where river stage was monitored**
- 5-160 X **Single observation well**—First number is location. Second number is distance from edge of river, in meters
- 1-30 ● **Observation-well nest**—First number is location. Second number is distance from edge of river, in meters
- **Well nest**—Each square indicates screened depth of individual observation wells in nest

Figure 4. (A) Location of observation-well nests at Palisades site as installed in 1989 and (B) hydrogeologic sections showing depths of screened intervals.

varies because the riverbank is not vertical. Therefore, the location of the observation wells from the river's edge is somewhat dependent on river stage. Furthermore, between the spring of 1989 and the completion of the field activities in 1991, lateral erosion of the riverbank by the Cedar River at the Palisades site removed nearly 20 m of bank sediment. Along section A–A', the 5- and 10-m well nests were destroyed by this erosion, and by the completion of field activities (1991), the 20-m well nest was near the river's edge. The 10-m well nest along section B–B' was at the river's edge on July 9, 1991.

Each well nest consists of three, single-riser, limited-interval wells, closely spaced so as to provide data from different stratigraphic levels at approximately the same location. The wells were screened at depths approximately 3, 6, and 9 m below land surface. The 1-10 m and 1-50 m well nests also had an additional well screened at a depth greater than 9 m below land surface. Ten of the well nests were oriented in a line perpendicular to the channel of the river. At the time of installation, these wells were located 5, 10, 20, 30, 50, 80, 120, 160, 216, and 320 m from the river's edge (section A–A'). A second line of five well nests (section B–B'), parallel to the A–A' section and located 50 m downstream, was installed to help define the ground-water flow system at the site. These wells are configured as in the A–A' section and were located 10, 30, 50, 80, and 120 m from the riverbank. Five additional single (non-nested) wells were installed at sites numbered 1–12, 1–19, 1–195, 1–230, 1–5–4, 5–160 (fig. 4) and were used to monitor specific features at the site, such as the ephemeral pond (observation well 5–160).

Well borings were advanced using 8.25-cm inside-diameter, continuous-flight, hollow-stem augers. The shallow, unconsolidated alluvial sediment was described visually from cuttings returned to the surface by the auger flights during penetration. When drilling in the saturated zone, samples were collected by a split-spoon soil sampler at the screened interval of the well. These samples were described and preserved for laboratory grain-size analysis and determination of total organic carbon, atrazine, and deethylatrazine concentrations.

The casing and screen for the observation wells consisted of 5.1-cm outside-diameter, schedule-80, flush-threaded polyvinyl chloride pipe. The screen slot size was 0.25 cm, and screen length was 76 cm. Prior

to installation, well screens and casing materials were steam cleaned.

To prevent collapse of the borehole wall during penetration of unconsolidated materials, the hollow-stem auger assembly was used as a temporary casing during well construction. The string of well casing with attached screen was installed inside the auger column, and the auger flights were counter-rotated while being slowly withdrawn, thus allowing the formation materials to collapse around the well screen and act as a natural filter pack. In boreholes where the well was screened in glacial till, an artificial filter pack consisting of clean, coarse sand was emplaced by trickling the sand into the annulus between the well casing and the interior of the hollow-stem augers. In all the remaining wells, the annular space between the borehole wall and the solid riser was backfilled with native aquifer material. Annular seals above the filter pack were not used because the relatively homogeneous alluvial sand did not have discernible, laterally continuous interstratified silt and clay that could be vertically isolated. However, granular bentonite was used as a seal in the upper 1 m of the borehole to prevent the infiltration of surface water along the outside of the well casing.

The observation wells were developed by pumping until the water ran clear. Each well was capped with a vented cap and surveyed for vertical and horizontal control. The elevations are referenced to sea level.

Aquifer Characterization

The river stage of the Cedar River was continuously monitored at the Palisades site (fig. 4; Schulmeyer and others, 1995), and periodic water-level data were collected from the wells (Schulmeyer and others, 1995). River stage and well water-level data are given in Schulmeyer and others (1995). The accuracy of the river-stage measurements and the water levels in the wells is 3 mm.

In-situ hydraulic-conductivity (slug) tests were performed on 23 selected observation wells at the Palisades site (table 1). The slug tests were performed in September 1991 using the technique described by Lohman (1972). The observation wells were developed by purging and were sampled numerous times before the slug tests were performed. Slug tests were performed by quickly displacing water in the wells using a solid cylinder with a known volume. The

Table 1. Summary of hydraulic-conductivity test results for selected observation wells at Palisades site, Linn County, Iowa

| Well number ¹ (fig. 4) | Geologic material adjacent to screen (from drill cuttings and split-spoon samples) | Hydraulic conductivity (meters per day) |
|--------------------------------------|---|--|
| Section A-A' (fig. 4) | | |
| 1-20-6 | Medium-to-coarse clean sand | 27 |
| 1-20-9 | Coarse clean sand | 53 |
| 1-30-6 | Medium-to-coarse pebbly sand | 51 |
| 1-30-9 | Coarse, clean pebbly sand | 36 |
| 1-50-6 | Medium-to-coarse clean sand | 26 |
| 1-50-9 | Fine-to-coarse poorly sorted sand | 8 |
| 1-50-12 | Silty clayey coarse sand | .3 |
| 1-80-6 | Coarse, poorly sorted pebbly sand | 40 |
| 1-80-9 | Medium-to-coarse poorly sorted sand | 7 |
| 1-120-6 | Medium to very coarse poorly sorted silty sand | 30 |
| 1-120-9 | Medium to very coarse silty clay, pebbly sand | 3 |
| 1-160-6 | Very coarse poorly sorted clean pebbly sand | 36 |
| 1-160-9 | Medium-coarse silty clay, pebbly sand | 8 |
| 1-216-9 | Medium-to-coarse sand with clay interbeds | .6 |
| 1-320-3 | Medium-to-coarse sand with clay interbeds | 5 |
| Section B-B' (fig. 4) | | |
| 3-10-9 | Medium-coarse sand | 19 |
| 3-30-9 | Medium-coarse silty sand | 38 |
| 3-50-6 | Coarse sand | 23 |
| 3-50-9 | Coarse sand | 20 |
| 3-80-6 | Coarse sand | 23 |
| 3-80-9 | Very coarse sand | ² 2 |
| 3-120-6 | Very coarse sand | 47 |
| 3-120-9 | Medium-to-coarse silty clayey sand | 3 |

¹Well numbers consist of the distance from river's edge and the depth below land surface, in meters.

²Well probably screened in silty, clayey coarse sand on the basis of hydraulic-conductivity results.

recovery rates for wells screened in coarse alluvium were rapid, requiring that the initial change in water level in the test well be at least 1 m in order to record a

sufficient water-level recovery versus time relationship. For this reason, only wells that had water levels at least 1 m above the top of the well screen were

selected for tests. With the exception of one well (1-320-3), this criteria eliminated the 3.0-m deep wells from the test procedure because the water levels in the shallow wells were too low as a result of the dry weather during the summer of 1991. The slug-test data were analyzed following the method described by Hvorslev (1951) to solve for the hydraulic conductivity of an unconfined aquifer adjacent to the well screen of a partially penetrating well.

Sample Collection

Following is a summary of the protocol used in sampling surface water and ground water, which is described in detail by Squillace, Liszewski, and Thurman (1992). The discharge of agricultural chemicals in surface water was calculated by measuring stream discharge and determining the concentrations of these chemicals in the water. Stream discharges were measured using current-meter methods (Buchanan and Somers, 1969). In the Cedar River, a depth-integrated (DI) sample was collected from the deepest, swiftest section of the river, and a composite sample was collected at 10 equal-discharge sections across the width of the river (equal discharge increment, EDI) (Guy and Norman, 1970). In the tributary streams, EDI samples were collected when the streams were sufficiently wide for the technique.

Water from the alluvial wells at the Palisades site was sampled using a Keck submersible pump equipped with Teflon tubing; however, during the study an inflatable packer was added to the pump to isolate the screened interval of the well. The packer was used only during collection of some of the water samples. Prior to the addition of the packer, the sampling procedure was to lower the pump to about 1 m below the water table and withdraw at least three casing volumes of water from the well. The pump then was lowered to near the screened interval of the well, and a sample was collected. After the addition of the packer, the procedure was to lower the pump into the well to just above the screened interval. The packer was inflated to isolate the screened interval from overlying water in the well casing, and about 10 L of water from the well was purged before sampling. Between samples, the Teflon tubing, packer, and pump were flushed with deionized, organic-free water.

Water samples for analysis of herbicides and selected metabolites were filtered using baked Whatman GF/F glass-fiber filters and a stainless-steel

holder and collected in baked glass bottles (450 °C). The filters have a nominal pore size of 0.7 μm (micrometer). Water samples for nitrate analysis were filtered using an acetate filter with a 0.45- μm pore size, collected in brown plastic bottles, and preserved with mercuric chloride. Samples were chilled until they were analyzed. Filters were flushed with sample water before collecting the sample.

Ground-water samples also were collected beneath the riverbed using a modified stainless-steel minipiezometer (fig. 4) as described by Winter and others (1988). Samples were collected along a line designated as 002, which transects the Cedar River at 1- to 3-m depths beneath the riverbed. Individual minipiezometer locations are designated in a similar manner to observation wells. For example, location 002-15-2 consists of three parts: the first number indicates the minipiezometer line; the second number indicates the distance from the northeast riverbank, in meters; and, the third number indicates the sampling depth below the riverbed surface, in meters. The difference in hydraulic head between the ground water and the river was determined at the time of sampling using a manometer attachment (Winter and others, 1988). The sampling equipment was rinsed with deionized organic-free water between samples.

Aquifer and soil sediment was collected with a split-spoon sampler, which was cleaned between samples. The samples were placed in a baked glass jar and chilled or frozen until extraction for atrazine and deethylatrazine and analyses for total organic carbon were performed.

Sample Analysis

The selected herbicides and metabolites were extracted from the water samples by solid-phase cartridges and then analyzed using gas chromatography/mass spectrometry according to the method described by Thurman and others (1990). The samples were analyzed at the U.S. Geological Survey laboratory in Lawrence, Kansas.

Nitrate concentration was determined by an automated colorimetric procedure at the U.S. Geological Survey's National Water-Quality Laboratory in Arvada, Colorado. An aliquot of the sample was passed through a cadmium column on which nitrate was chemically reduced to nitrite (Fishman and Friedman, 1989). The resulting solution, containing both the original nitrite present in the sample plus the nitrite

produced from the reduction of nitrate, was analyzed colorimetrically. A second aliquot of the sample that was not passed through the cadmium column also was analyzed for nitrite. The concentration of nitrate in the sample then was calculated from the difference between these two determinations.

Aquifer sediment was analyzed for concentrations of atrazine and deethylatrazine and for organic-carbon content according to the method described by Squilace and others (1993). The sediment sample was placed in a baked glass jar and chilled or frozen until extraction for atrazine and deethylatrazine and analysis for total organic carbon.

RESULTS OF AQUIFER CHARACTERIZATION AND SAMPLE ANALYSIS

Hydrogeologic Subunit Delineation

Unconsolidated sediment that constitutes the alluvial aquifer varies considerably in grain size and is underlain by 15 m of glacial till. At the edge of the river, the alluvial aquifer is about 15 m thick. The alluvial aquifer is composed of a fining-upward, sand-rich, alluvial sequence. A test hole drilled near the river's edge and a domestic well located just off the flood plain indicate that the area is underlain by 15 m of glacial till. The glacial till becomes more shallow toward the edge of the flood plain as indicated by these two drill holes and observation well 1-320-8 drilled for this study.

The unconsolidated sediment was divided into eight subunits on the basis of grain-size distribution (fig. 5) that correspond to the subunits observed at the study site (fig. 6). The grain-size analysis in figure 5 supports the interpretation of the descriptive geologic logs made from drill cuttings as well as the hydraulic-conductivity test results—that the unconsolidated sediment at the site is composed of clay-rich glacial till overlain by a fining-upward alluvial sequence. In figure 5 there are no grain-size analyses for subunit 1, which is the surficial material in the study area.

Aquifer Characteristics and Property Determination

Water levels in alluvial aquifers fluctuate throughout the year and are highest in the spring and fall.

During summer, water levels usually decline because of increased evapotranspiration. Observations at the Palisades site show that water levels in the alluvial aquifer tend to respond rapidly to precipitation and changing river stage in the Cedar River (Schulmeyer and others, 1995).

The results of the in-situ hydraulic-conductivity test for each well, in meters per day, is shown in table 1. Values of hydraulic conductivity ranged from as much as 53 m/d in the coarse-grained alluvial sand to as little as 0.3 m/d. The range of hydraulic-conductivity values is comparable with the values published by Freeze and Cherry (1979) for the various geologic materials.

The aquifer diffusivity (ratio of the transmissivity to the coefficient of storage) was determined by comparing the response of the aquifer to fluctuations in the river stage using the method described by Pinder and others (1969). This diffusivity then was used to estimate the average hydraulic conductivity of the coarse-grained sand. Aquifer diffusivity also can be determined by comparing the response of one well adjacent to the river with one farther from the river's edge. Diffusivity values are only estimates because this method assumes a homogeneous isotropic aquifer with a fully penetrating river, which according to the observed geologic conditions is not valid for the Palisades site. The Cedar River only partially penetrates the alluvial aquifer at the Palisades site, the observation wells are not screened throughout the entire thickness of the aquifer, and the aquifer sediment is not homogenous and isotropic. During a 20-hour period between October 31 and November 1, 1989, the Cedar River stage rose and fell about 120 cm due to a malfunction in the flood-control gates of an upstream dam at Cedar Rapids (Schulmeyer and others, 1995). Water-level changes in the aquifer were recorded in the three wells along section A-A' that were 10, 30, and 50 m from the river's edge and had screened intervals of 76 cm at about 9 m below land surface. Recorded ground-water levels increased 70 cm at a distance of 10 m from the river's edge and about 25 cm at 50 m from the river's edge. The calculated diffusivity ranged from 1,000 to 3,000 m²/d. Hydraulic conductivity was estimated to range from 20 to 70 m/d by assuming an aquifer thickness of 9 m and a coefficient of storage of 0.2.

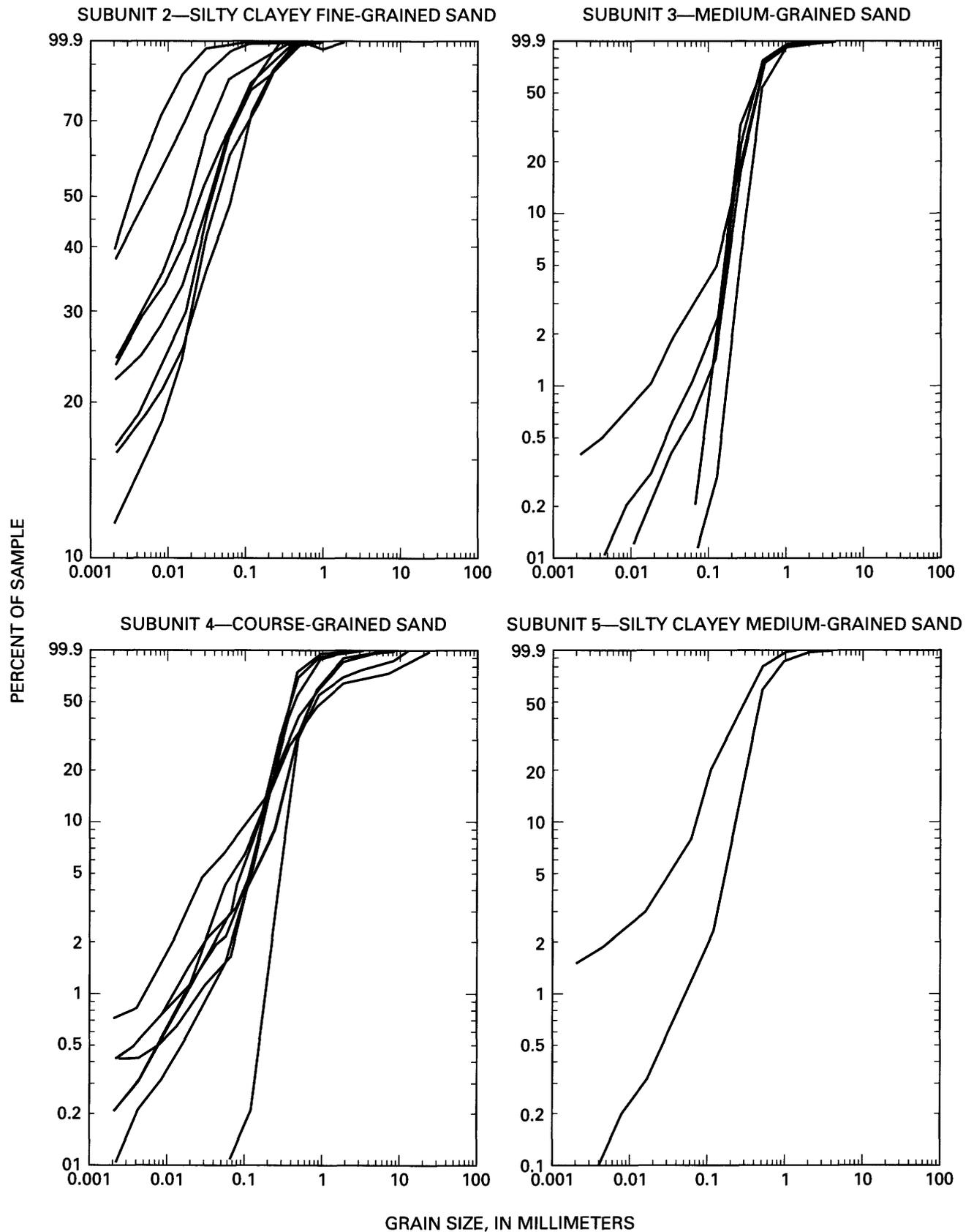


Figure 5. Grain-size distributions of unconsolidated sediment collected at Palisades site, Iowa.

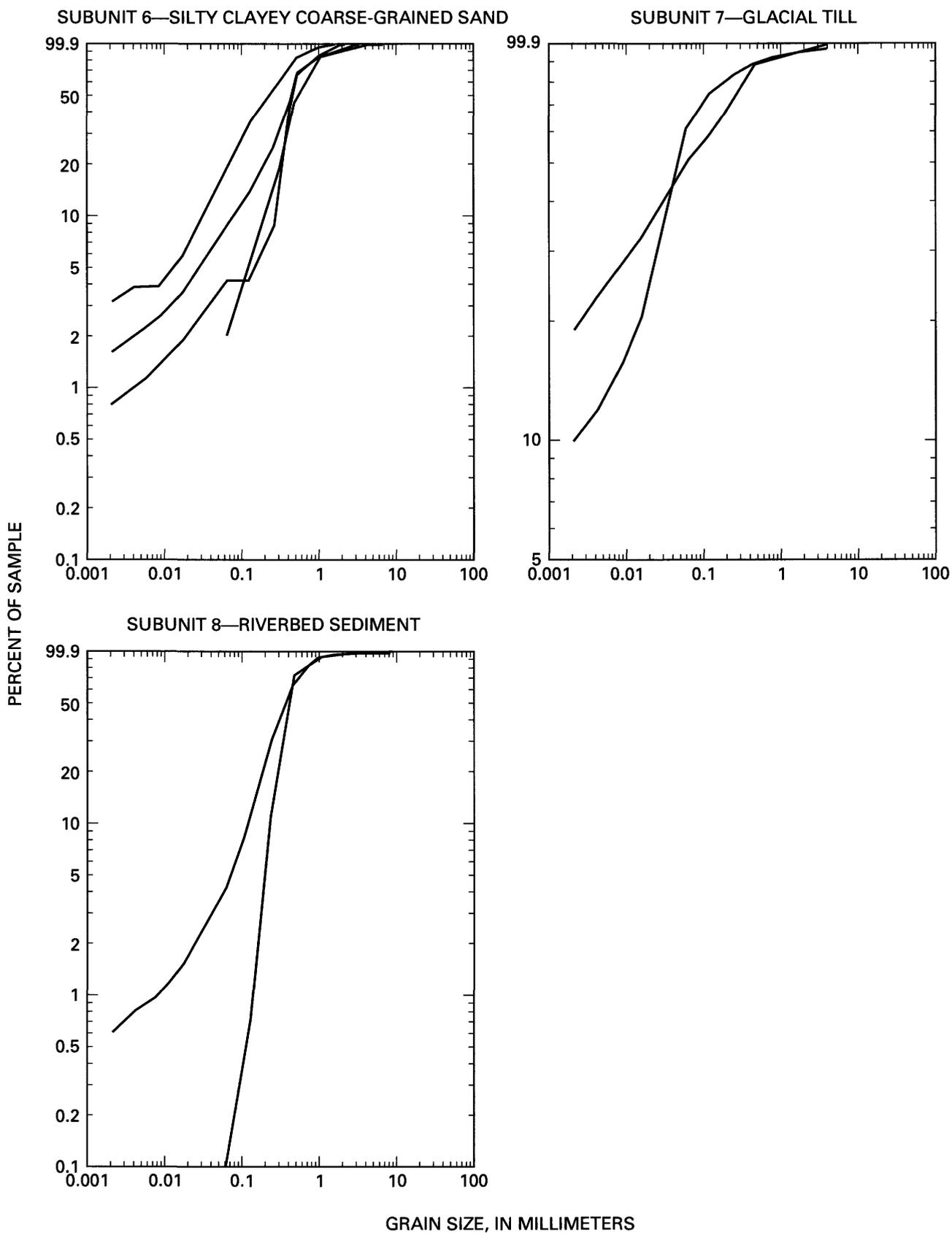


Figure 5. Grain-size distributions of unconsolidated sediment collected at Palisades site, Iowa—Continued.

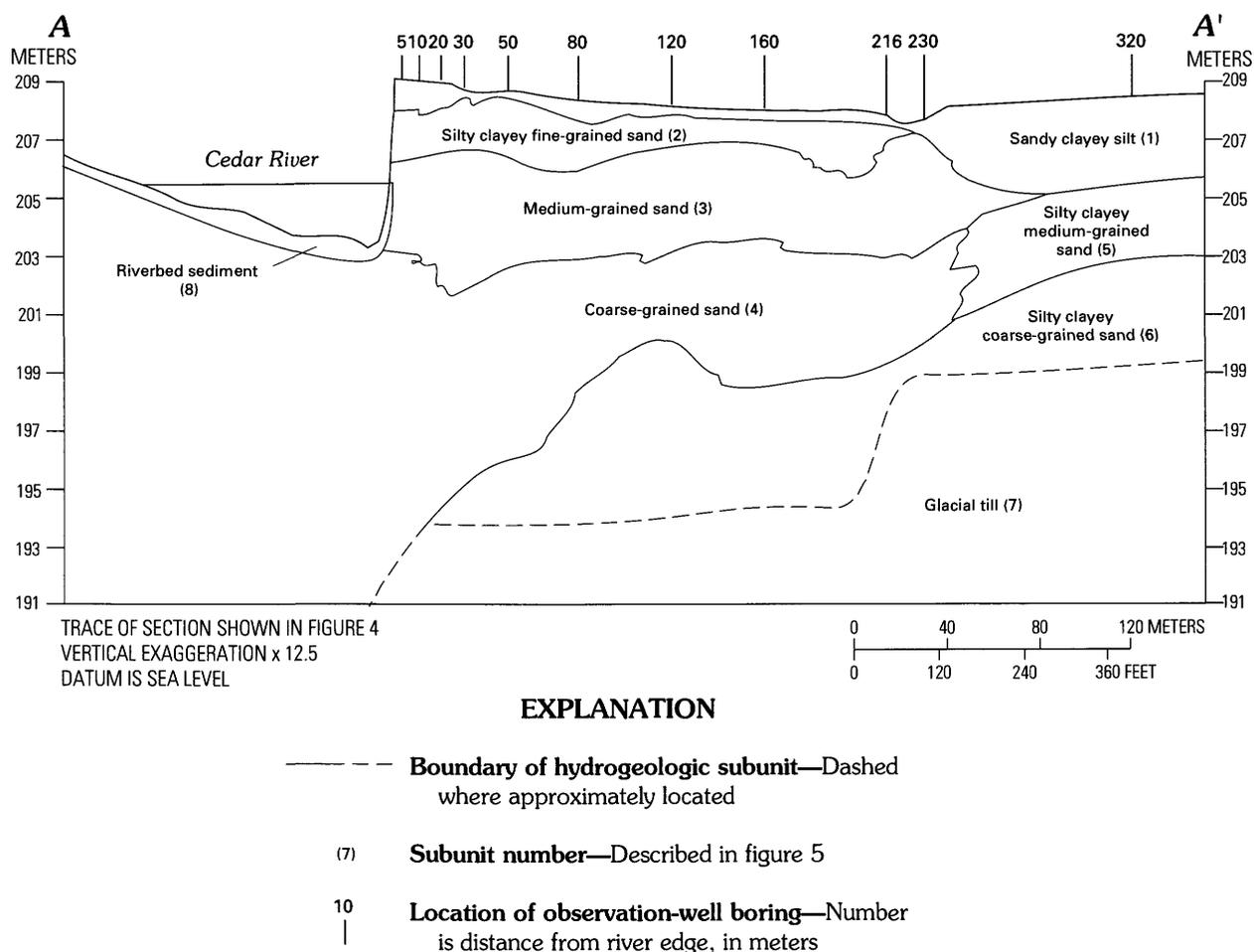


Figure 6. Distribution of hydrogeologic subunits at Palisades site.

Sediment Analyses

A total of 26 sediment samples collected at various times from the alluvial aquifer, soil, and riverbed at the Palisades site contained no detectable concentrations of atrazine and deethylatrazine sorbed to the sediment (table 2) even though these compounds were consistently detected in the ground water (fig. 7). The detection levels for atrazine and deethylatrazine on the sediment ranged from 0.05 to 0.10 $\mu\text{g}/\text{kg}$ (microgram per kilogram) (table 2).

Because the actual concentrations of atrazine and deethylatrazine on the sediment were not known, a theoretical approach was used to estimate the amount of atrazine that may be sorbed to the aquifer sand. Only atrazine was considered in these calculations because the large mobility of deethylatrazine in the soil indicates that sorption of deethylatrazine would be less than atrazine (Muir and Baker, 1978). The other herbicides included in this study have organic-carbon

coefficients (K_{oc}) that are similar to atrazine (Becker and others, 1989), which would indicate that sorption of these chemicals should be similar to atrazine.

There are two equations that can be used to estimate the amount of atrazine that is sorbed to the aquifer material. The first equation quantifies the extent to which an organic compound is sorbed to a given sediment by its distribution (sorption) coefficient, K_d , which is defined as:

$$K_d = \frac{C_s}{C_e}, \quad (1)$$

where C_s is the concentration of a contaminant sorbed to a specific weight of sediment, and C_e is the concentration of the contaminant dissolved in an equal weight of water (Olsen and others, 1982). The concentrations of atrazine in at least some of the ground water were assumed to be 0.4 $\mu\text{g}/\text{L}$ (microgram per liter) when the sediment samples were collected in the spring of 1989. This assumed concentration lies within the upper

Table 2. Atrazine and deethylatrazine concentrations, fraction of organic carbon, and particle-size analysis of sediment collected during 1989–90

[foc, fraction of organic carbon in sediment; µg/kg, microgram per kilogram; <, less than detection level indicated]

| Sample location (meters from) | | Date sample (month/ day/year) | Concentration (µg/kg) | | | Particle size analysis (percent) | | | |
|---|-----------------|--|-----------------------|----------------------|--------|----------------------------------|------|------|--------|
| River's edge | Land surface | | Atrazine | Deethyl- atrazine | foc | Clay | Silt | Sand | Gravel |
| Alluvial sediment collected along A–A' shown in figure 4 | | | | | | | | | |
| ¹ 10 | 3.0 | 3/21/89 | ² <0.10 | ² <0.10 | 0.0014 | 0.5 | 2.4 | 92.0 | 5.1 |
| | 15.2 | 3/22/89 | <.10 | <.10 | .0012 | 11.6 | 49.6 | 34.4 | 4.4 |
| ¹ 20 | 3.0 | 7/18/90 | <.10 | <.10 | .0005 | <.2 | <.2 | 98.1 | 1.7 |
| | 6.1 | 7/18/90 | <.10 | <.10 | .0005 | <.1 | <.1 | 66.6 | 33.3 |
| ¹ 80 | 3.0 | 3/30/89 | <.10 | <.10 | .0008 | .1 | 1.0 | 96.6 | 2.3 |
| | 6.1 | 3/30/89 | <.10 | <.10 | .0007 | .3 | 1.3 | 95.8 | 2.6 |
| | 9.1 | 3/30/89 | <.10 | <.10 | .0006 | .3 | 2.4 | 93.1 | 4.2 |
| ¹ 120 | 6.1 | 3/31/89 | <.10 | <.10 | .0006 | <2.5 | <2.5 | 94.9 | 2.0 |
| | 9.1 | 3/31/89 | <.10 | <.10 | .0028 | <2.0 | <2.0 | 91.6 | 6.4 |
| | 14.0 | 4/3/89 | <.10 | <.10 | .0006 | 3.8 | 15.1 | 79.9 | 1.2 |
| ¹ 160 | 3.0 | 4/4/89 | <.10 | <.10 | .0007 | .1 | .6 | 98.9 | .4 |
| | 6.1 | 4/4/89 | <.10 | <.10 | .0006 | .5 | 1.7 | 93.7 | 4.1 |
| | 9.1 | 4/6/89 | <.10 | <.10 | .0006 | .2 | 1.4 | 95.9 | 2.5 |
| 216 | .6 | 4/7/89 | <.10 | <.10 | .0245 | 46.1 | 48.8 | 4.1 | 0 |
| | 1.2 | 4/7/89 | <.10 | <.10 | .0067 | 17.9 | 30.6 | 51.5 | 0 |
| 230 | .6 | 2/13/90 | <.10 | <.10 | .0113 | 24.1 | 42.9 | 33.0 | 0 |
| 320 | .9 | 4/18/89 | <.10 | <.10 | .0088 | 17.7 | 39.7 | 24.4 | 18.2 |
| | 1.5 | 4/18/89 | <.10 | <.10 | .0096 | 29.1 | 55.8 | 15.0 | .1 |
| | 3.0 | 4/12/89 | <.10 | <.10 | .0169 | 18.7 | 47.6 | 33.7 | 0 |
| | 3.4 | 4/12/89 | <.10 | <.10 | .0021 | 1.8 | 6.4 | 91.5 | .3 |
| | 3.7 | 4/12/89 | <.10 | <.10 | .0008 | .1 | 1.1 | 95.6 | 3.2 |
| | 7.6 | 4/12/89 | <.10 | <.10 | .0019 | 1.0 | 3.2 | 87.1 | 8.7 |
| | 10.7 | 4/12/89 | <.10 | <.10 | .0028 | 2.0 | 6.6 | 89.3 | 2.1 |
| | 11.0 | 4/12/89 | <.10 | <.10 | .0057 | 22.7 | 27.7 | 45.9 | 3.7 |
| Site-identification number (fig. 24) | | | | | | | | | |
| Bed sediment from the Cedar River | | | | | | | | | |
| 002 | | 4/18/89 | <0.10 | <0.10 | 0.0027 | 0.8 | 3.1 | 91.3 | 4.8 |
| | | 11/01/90 | <.10 | <.10 | .004 | <.1 | <.1 | 96.8 | 3.1 |
| 470 | | 10/31/90 | <.10 | <.10 | .0070 | <5.3 | <5.3 | 61.3 | 33.4 |
| 570 | | 11/01/90 | <.10 | <.10 | .0024 | <2.6 | <2.6 | 90.7 | 6.7 |
| 610 | | 11/02/90 | <.10 | <.10 | .0041 | 6.3 | 10.2 | 73.8 | 9.7 |
| 660 | | 10/31/90 | <.10 | <.10 | .0006 | <.7 | <.7 | 82.0 | 17.3 |
| 890 | | 11/02/90 | <.10 | <.10 | .0023 | <5.6 | <5.6 | 92.7 | 1.7 |

¹Principal aquifer sand. ²Detection limits varied between 0.05 to 0.10 µg/kg.

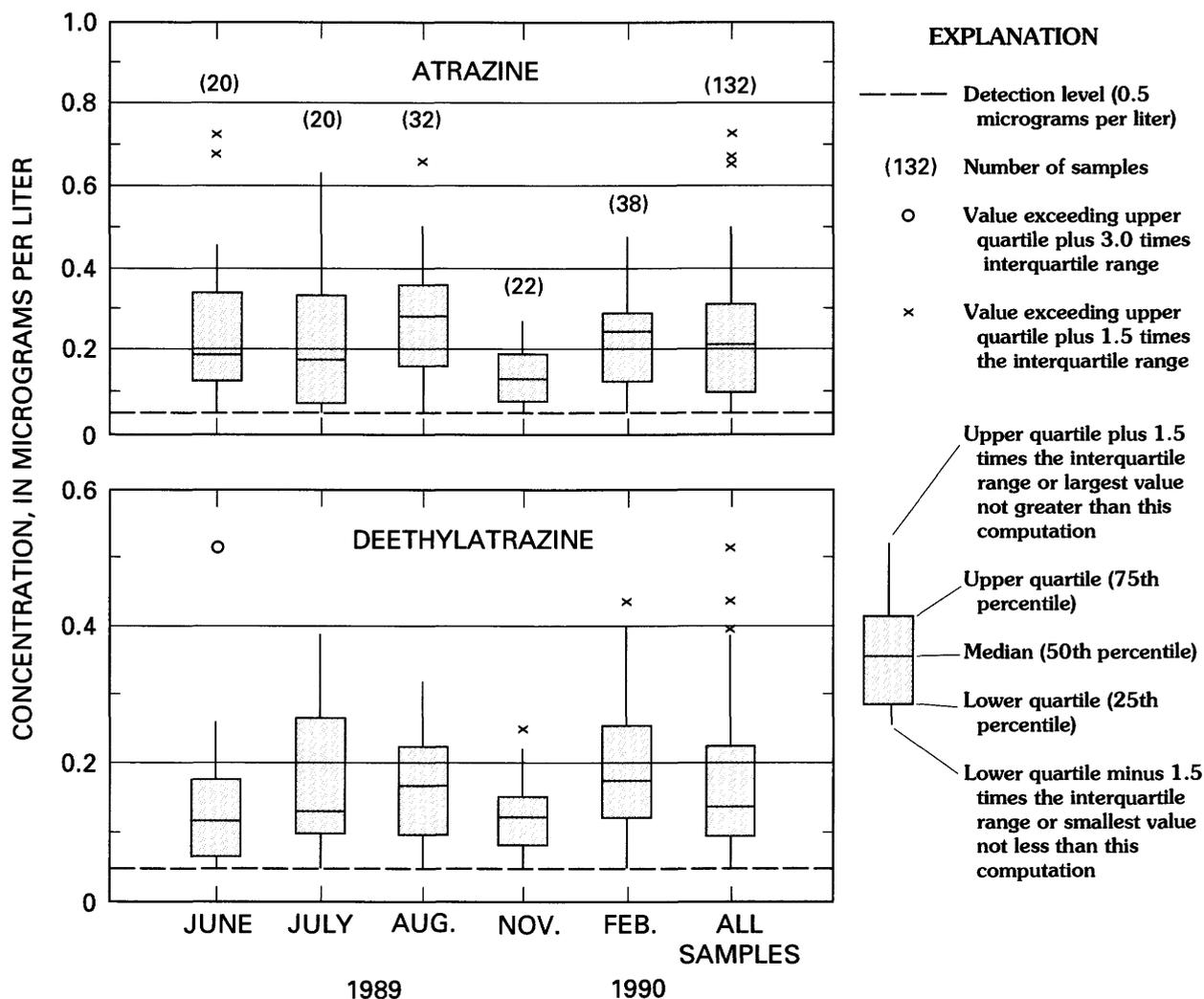


Figure 7. Statistical summary of atrazine and deethylatrazine concentrations in water samples collected from wells at Palisades site, June 1989 through February 1990.

quartile of the concentrations measured in the ground water from June 1989 through February 1990 (fig. 7) when there was no major runoff. Using a detection level of 0.05 $\mu\text{g}/\text{kg}$ for the sediment and the assumed concentration in the ground water, the measured K_d of the aquifer sand is less than 0.13 for atrazine.

The second equation defines the organic carbon coefficient (K_{oc}) on the basis of K_d and the fraction of organic carbon (f_{oc}) in the sediment and is defined as:

$$K_{oc} = \frac{K_d}{f_{oc}} \quad (2)$$

When the f_{oc} in the sediment is greater than 0.001, the amount of organic carbon has been shown to be important in the sorption of some organic compounds (Schwarzenbach and Westall, 1981; Karickhoff, 1984; Mackay and others, 1986).

Theoretical calculations, described below, indicate that a relatively small part of the total atrazine present would be sorbed to the aquifer material, and the percentage could be much less. Using published values for K_{oc} , the amount of atrazine that is sorbed to the aquifer material can be estimated. K_{oc} values for atrazine range from 45 in a sandy loam (Singh and others, 1990) to 160 as an average value for various soil types (Jury and others, 1987). The measured f_{oc} for the principal aquifer sand at the Palisades site is generally 0.001, or less; however, for these calculations a f_{oc} of 0.001 was assumed. Using equation 2, the K_d is 0.16 or 0.045 depending on the value of K_{oc} , but it has already been estimated that the measured K_d of the sediment is less than 0.13, and therefore the K_{oc} of 160 is too large. Using a K_d of 0.045, the concentrations of atrazine on the sediment would be 0.018 $\mu\text{g}/\text{kg}$. This

concentration is less than the detection level for the sediment samples; therefore, the assumed K_d (0.045) appears reasonable. In 1 L of aquifer material there is about 2.0 kg of sand and 0.25 kg of water. Multiplying the concentrations of atrazine (0.018 $\mu\text{g}/\text{kg}$ on sediment and 0.4 $\mu\text{g}/\text{L}$ in water) by the quantity of water and sediment, there is 0.036 μg of atrazine on the sediment and 0.10 μg of atrazine in the water. Thus, about 25 percent of the total atrazine present would be sorbed to the aquifer material. It is important to remember that even the atrazine sorbed to the sediment could have entered the aquifer only in the water phase.

Results of Water-Quality Analyses

Location of sampling sites and analytical results for herbicides and other water-quality constituents are presented in Schulmeyer and others (1995). Approximately 10 percent of the samples were water blanks, duplicates, or spikes. These samples were collected for quality-control and assurance purposes. No herbicides were detected in the blank samples, indicating no

carryover of herbicides between the collection of water samples. The concentrations of nitrate in the blank samples were at or below the detection level. The coefficients of variation (standard variation divided by the mean) of atrazine and deethylatrazine in 13 duplicate samples were 3.7 and 7.1 percent, respectively. These values were small, attesting to the precision of the analyses.

RELATION OF RIVER STAGE TO SAMPLING PERIODS

The hydrograph for the Cedar River at the Palisades site during the study from May 1989 through July 1991 is shown in figure 8, and the data are in Schulmeyer and others (1995). Water-quality samples were collected 22 times, and the sequentially numbered dates are shown in figure 8. On the basis of the river stage, the 22 sampling dates are grouped into five periods. During sampling period 1, May 1989 through February 1990, the river stage was low and stable due to prolonged dry weather lasting almost 10 months.

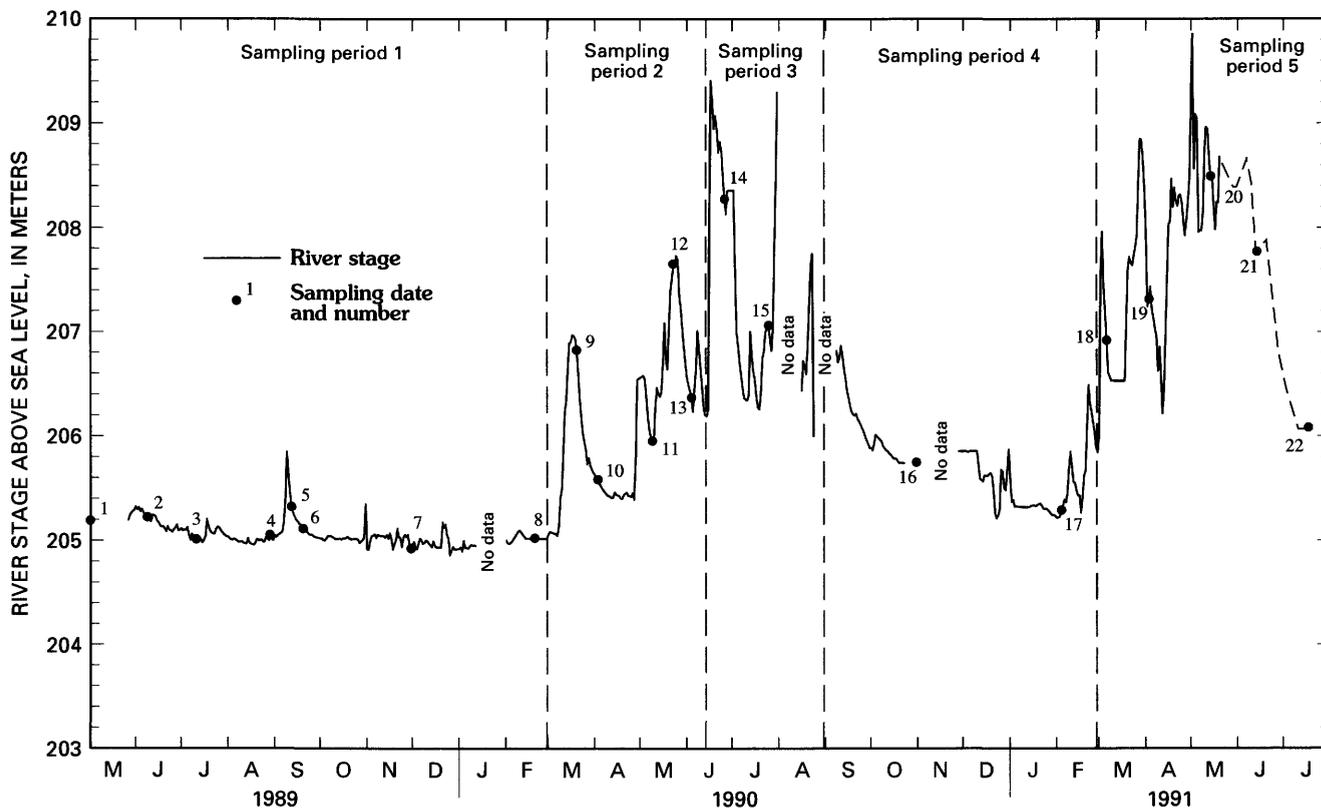


Figure 8. Stage of the Cedar River at Palisades site for five sampling periods, May 1989 through July 1991 (dashed line indicates intermittent stage data).

The river was in base-flow conditions for almost this entire sampling period.

During sampling period 2, March to mid-June 1990, the river stage increased substantially twice, but the Cedar River remained within the riverbank. Sampling dates 9 and 12 were collected during high-flow conditions as shown in figure 8. During sampling period 3, mid-June through August 1990, the river stage increased and resulted in flooding at the Palisades site; a major storm caused the river to rise 3 m in a short time, and the Cedar River overflowed the riverbank at 208 m above sea level. The study site was inundated for more than 2 weeks, and water samples were collected when floodwater receded (sampling dates 14 and 15).

During sampling period 4, September 1990 through February 1991, the river stage was low and stable. The river was in base-flow conditions during most of this sampling period. During sampling period 5, March 1991 through July 1991, the river stage increased, which once again resulted in flooding at the Palisades site. The combined effects of a major storm and snowmelt in early March 1991 caused flooding during sampling date 18. Discussion in the next major section will focus on concentrations of selected agricultural chemicals in the alluvial aquifer during a range in flow conditions.

MOVEMENT OF SELECTED AGRICULTURAL CHEMICALS WITH BANK-STORAGE WATER

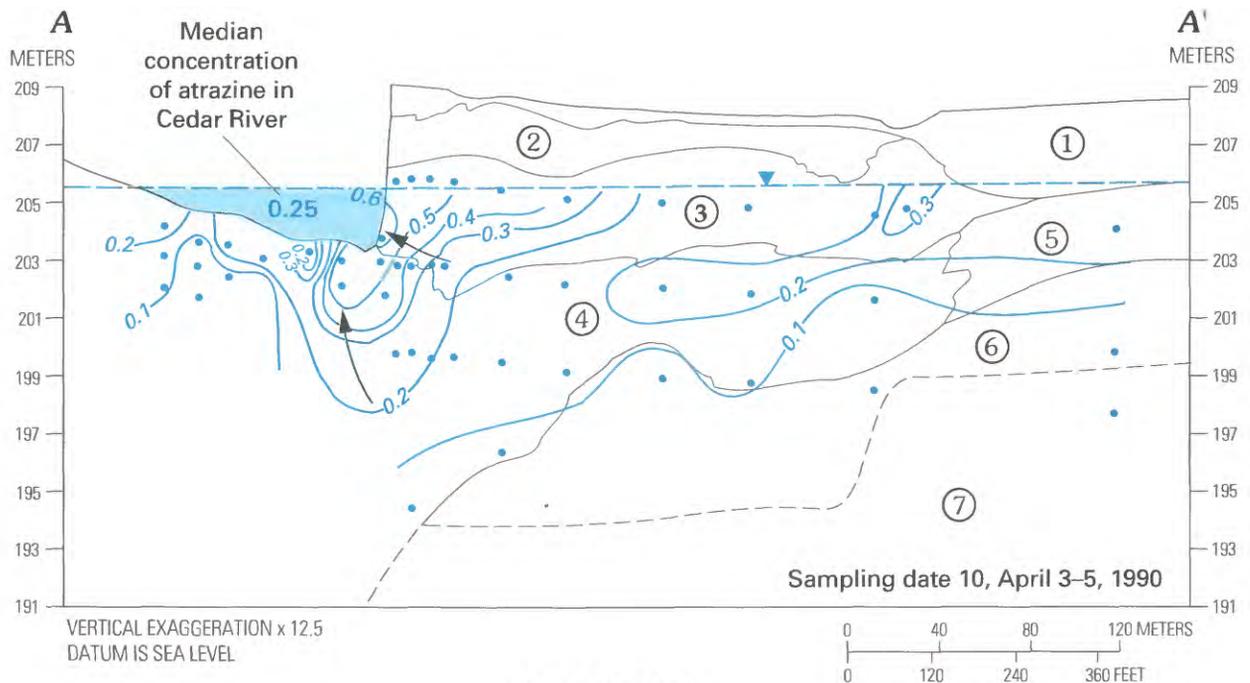
Bank storage and its role as a "reservoir" for river water is well known (Freeze and Cherry, 1979), whereas the movement of agricultural chemicals with bank-storage water has been discussed only recently (Squillace and Engberg, 1988; Squillace and others, 1991; Thurman and others, 1991). In this section, the movement of bank-storage water between surface water and ground water will be described using chemical and hydrologic data collected at the Palisades site. Concentrations of selected agricultural chemicals including nitrate-nitrogen as N (nitrate-nitrogen), alachlor, ametryn, atrazine, cyanazine, deethylatrazine, deisopropylatrazine, metolachlor, metribuzin, prometon, prometryn, propazine, simazine, and terbutryn, will be discussed.

The hydrologic data collected at the Palisades site show how bank-storage water moved between surface water and ground water; however, the actual

movement of bank-storage water that occurs at any specific location along a large reach of a river will vary. This movement is affected by two important factors: (1) the hydraulic conductivity of the riverbed and the alluvial aquifer and (2) the hydraulic gradient between the river and the aquifer. The hydraulic gradient is dependent on the amount of recharge that the alluvial aquifer receives and the river stage. A rise in the river stage can cause bank-storage water to move into the alluvial aquifer. During runoff, however, the river stage generally does not increase uniformly along a long reach of the river because of variations in the channel geometry and slope of the river bottom. A river channel that is wide with a steep, river-bottom slope can carry additional discharge with a small change in the river stage, whereas a narrow river channel with little slope will show a substantial change in the river stage with the same increase in discharge. For example, the river channel at the Palisades site is relatively narrow. As a consequence, during runoff, the river stage typically increases three-fold as compared to the stage increase at the gaging station at Cedar Rapids where the river channel is wider.

Background Concentrations

The Palisades site is an unfarmed, wooded area that has no history of herbicide application; therefore, any herbicides detected in the ground water were transported to the study site by ground water or surface water. During sampling period 1 (fig. 8), the concentrations of alachlor, cyanazine, metolachlor, propazine, simazine, and the atrazine metabolite deisopropylatrazine in the river water and all ground-water samples were generally less than the detection level. The small concentrations of atrazine and its metabolite deethylatrazine detected in ground water during the first sampling period are considered background concentrations at the Palisades site. No major influx of water and herbicides occurred during this dry period from either flooding or bank storage. The only known source of the background atrazine and deethylatrazine is ground-water recharge from ephemeral and perennial streams that drain the upland areas. Data collected during February 20–22, 1990 (fig. 9), is typical for this first sampling period. The atrazine distribution in the aquifer was stratified, and the concentrations ranged from less than 0.10 to 0.66 $\mu\text{g/L}$. The concentration in the river was 0.12 $\mu\text{g/L}$ (fig. 9). Figure 7 summarizes median monthly concentrations of



EXPLANATION

- ① --- Boundary of hydrogeologic subunit—
Dashed where approximately located. Number refers to subunit: 1, sandy clayey silt; 2, silty clayey fine-grained sand; 3, medium-grained sand; 4, coarse-grained sand; 5, silty clayey medium-grained sand; 6, silty clayey coarse-grained sand; 7, glacial till
- 0.1— Line of equal atrazine concentration—
Interval 0.10 microgram per liter
- Direction of ground-water movement
- ▼— Water table
- Location of minipiezometer or well sampling point—Location of well sampling point is at the top of the well screen

Figure 9. Distribution of atrazine in the alluvial aquifer on the basis of atrazine concentrations in ground-water samples collected at Palisades site, February through April 1990—Continued. Trace of section shown in figure 4.

aquifer during high flow in March 1990. Snowmelt and rainfall combined to gradually increase the river stage, which peaked during March 17–18 (fig. 10 and Schulmeyer and others, 1995) and then began to decline. Figure 10 shows the hydraulic gradient along A–A' (fig. 4A) between two wells that were 10 and 30 m from the river's edge and both screened at 6 m below land surface (water-level data rounded to nearest 0.01 m are presented in Schulmeyer and others, 1995). The hydraulic gradients between these wells are a good estimate of the hydraulic gradient between the river and the ground water because the aquifer responds very quickly to changes in the river stage. The hydraulic gradients between these two wells were used because the exact distance between

these two wells was known, whereas the distance to the river's edge changes somewhat with river stage and with erosion of the riverbank. According to maps of the water-table surface (fig. 11), these wells also are located along the ground-water flow path; that is, ground water is expected to move parallel to A–A' (fig. 4A). During March 8 to 21, the hydraulic gradient was from the 10-m well to the 30-m well and is designated as a negative value in figure 10. On March 22, the gradient was zero, and thus momentarily, an equilibrium was reached between these two wells. Thereafter, the ground-water gradient was from the 30 m well to the 10-m well and is designated as a positive value in figure 10.

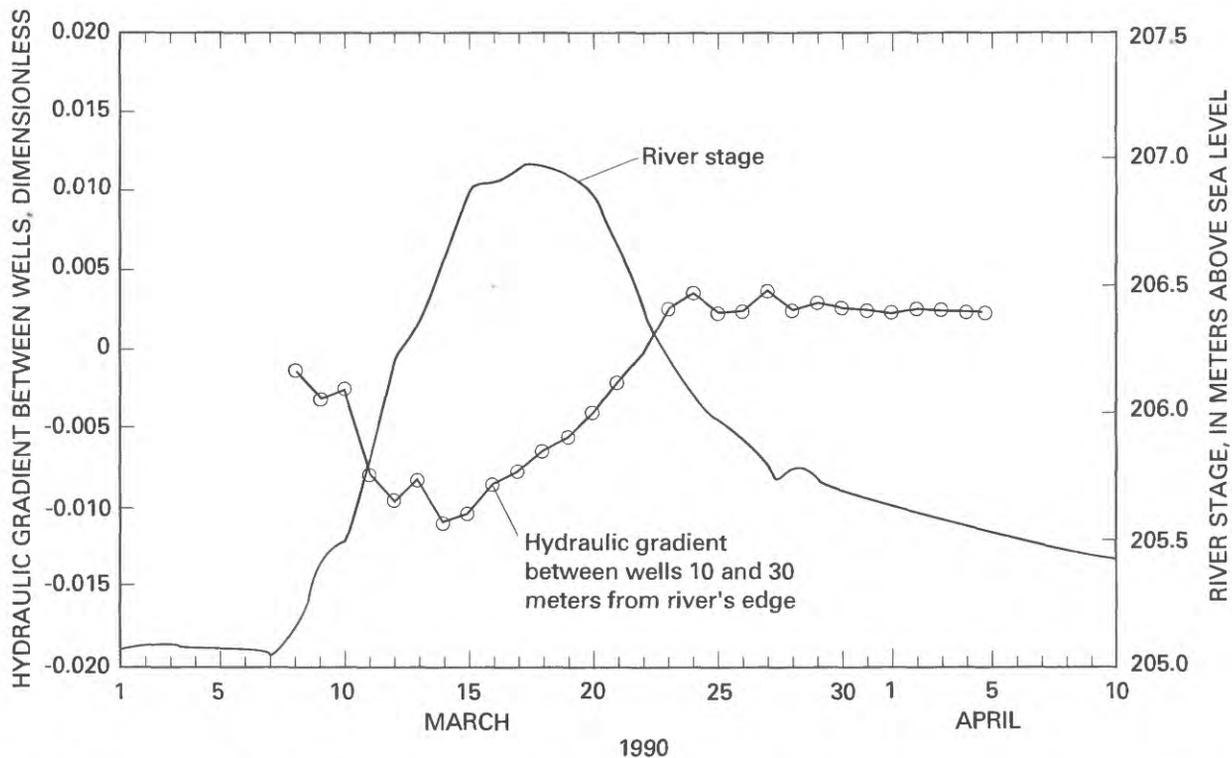


Figure 10. Horizontal hydraulic gradient between wells 10 and 30 meters from river's edge along section A–A', both screened at 6 meters below land surface, and river stage at Palisades site, March and April 1990.

Chemical data show that bank-storage water displaced the resident water with larger concentrations of herbicides that originated from the river. During the high flow in March 1990, the river stage and concentrations of selected herbicides in the river peaked concurrently. These herbicides were alachlor, atrazine, deethylatrazine, and metolachlor (fig. 12). The concentrations of alachlor increased slightly during the runoff (fig. 12A). Atrazine concentrations in the river water increased from 0.12 $\mu\text{g/L}$ on February 20 to 0.82 $\mu\text{g/L}$ on March 17 (Schulmeyer and others, 1995). Concurrently, atrazine concentrations at a well 5 m from the river's edge and 6 m deep changed from 0.26 $\mu\text{g/L}$ on February 20 to 0.68 $\mu\text{g/L}$ on March 20 (fig. 9). Alachlor and metolachlor also exhibited changes in concentration in ground water. The concentrations of deisopropylatrazine increased during the runoff but did not peak with the river stage. Concentrations of all other herbicides were less than their detection levels in the river.

The atrazine data shown in figure 9 (sampling date March 20–22, 1990) indicate the greatest intrusion of bank-storage water occurred at a shallow depth of about 3 m where the aquifer material is finer grained. There was only one sample collected during February

20–22, 1990, in which the concentration of atrazine was greater than 0.4 $\mu\text{g/L}$, and it was collected 1 m beneath the river bottom along the river's edge. Therefore, assuming that the 0.4- $\mu\text{g/L}$ contour line for the March 20–22, 1990, data defines the maximum movement of bank-storage water into the aquifer, it appears that bank-storage water moved about 80 m and 30 m into the aquifer at a depth of 3 m and 6 m, respectively. This distribution of bank-storage water would not be expected on the basis of texture alone; because the aquifer material is medium-grained sand at a depth of 3 m and a coarse-grained sand at 6 m, one would expect greater intrusion of bank-storage water at a depth of 6 m.

A well-developed tree-root system that extends horizontally to the riverbank (fig. 13) may have allowed greater intrusion of bank-storage water at shallow depths. The shallow root system (fig. 13), especially when dead and decayed, could provide macropores that could substantially increase the horizontal hydraulic conductivity of the medium-grained sand and the overlying silty clayey fine sand. This increased hydraulic conductivity would allow greater intrusion of river water into the alluvial aquifer during

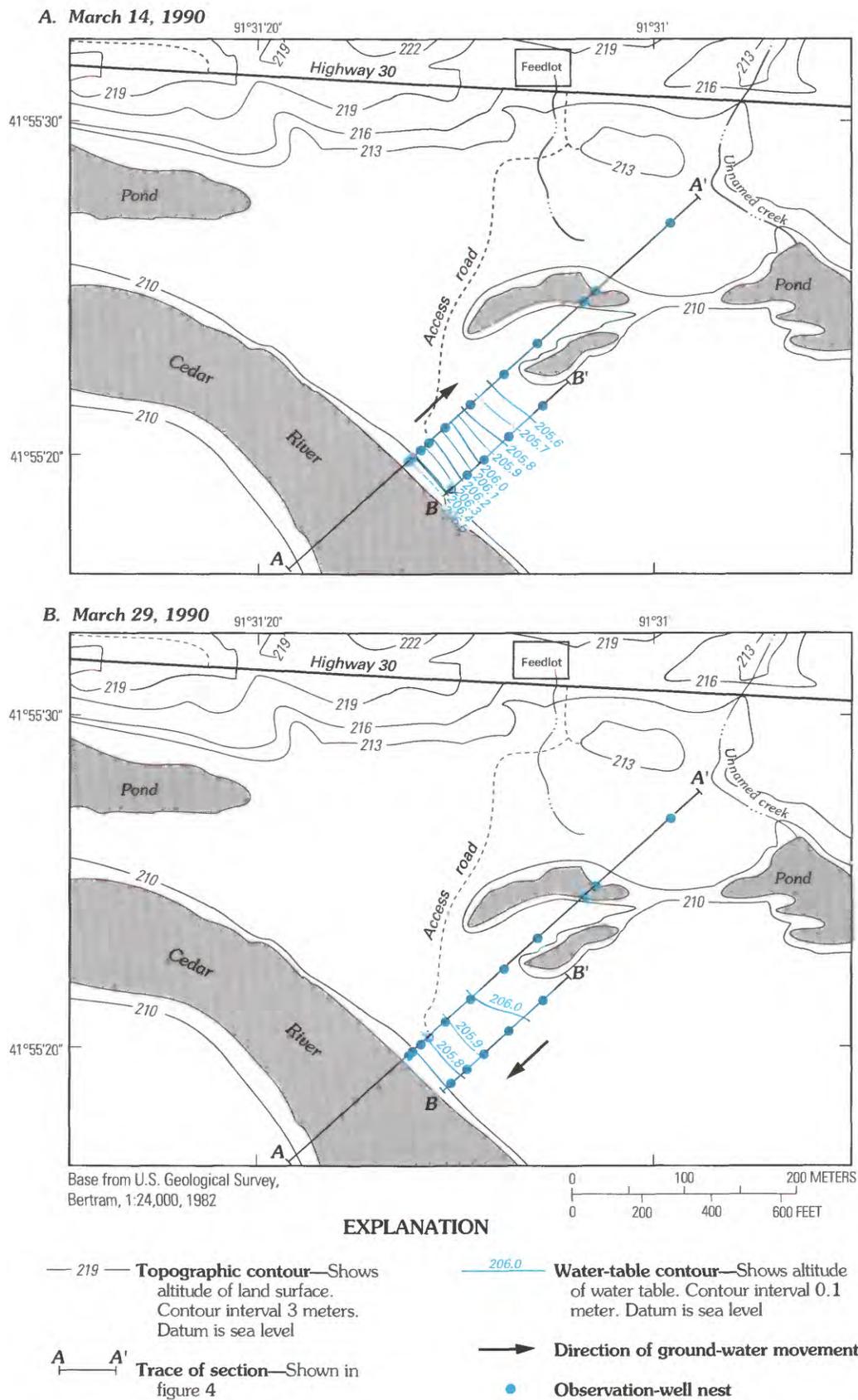


Figure 11. Water-table surface at Palisades site, (A) March 14 and (B) March 29, 1990.

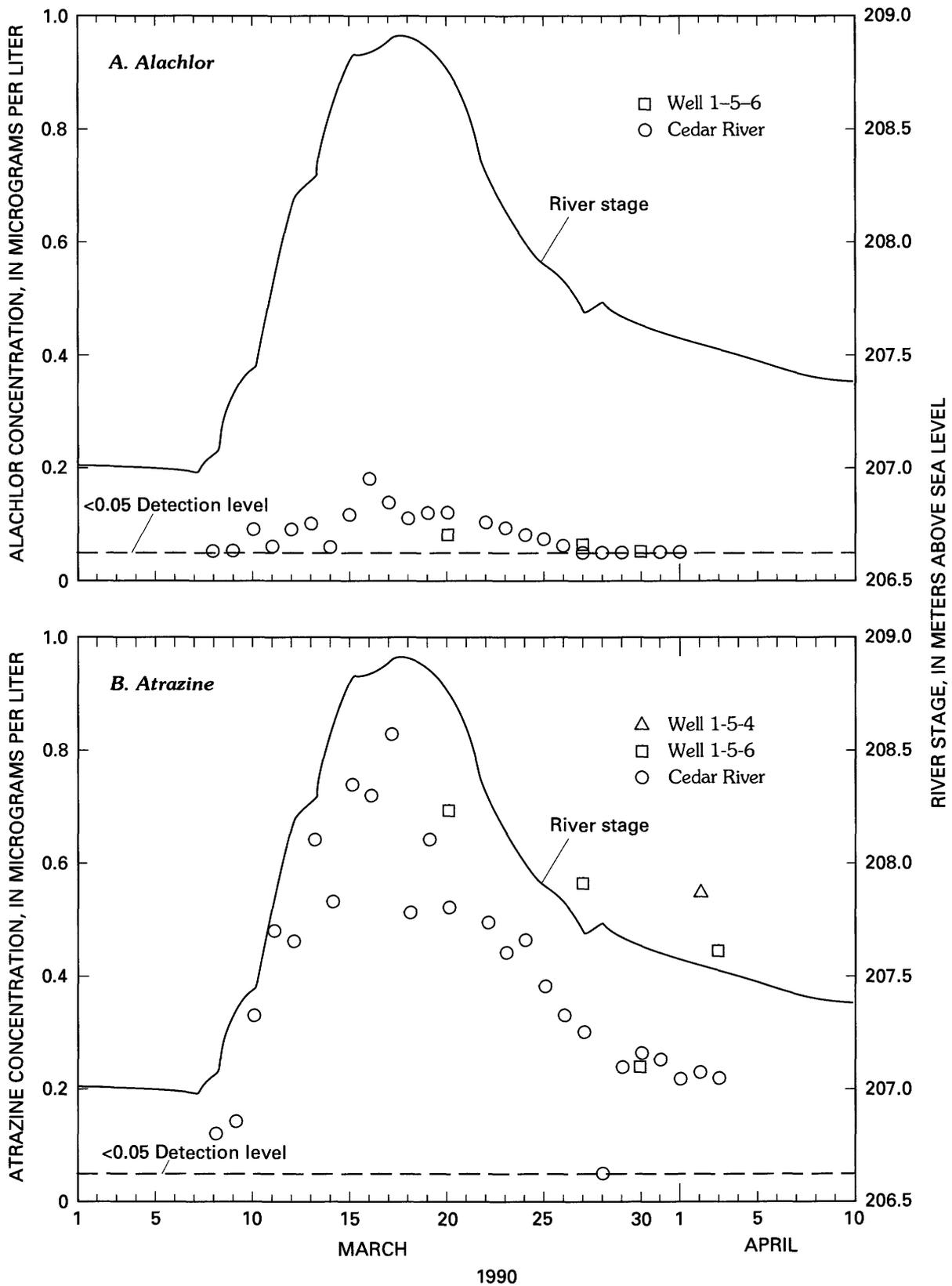


Figure 12. River stage and selected herbicide concentrations in water samples from the Cedar River and selected wells at Palisades site, March and April 1990.

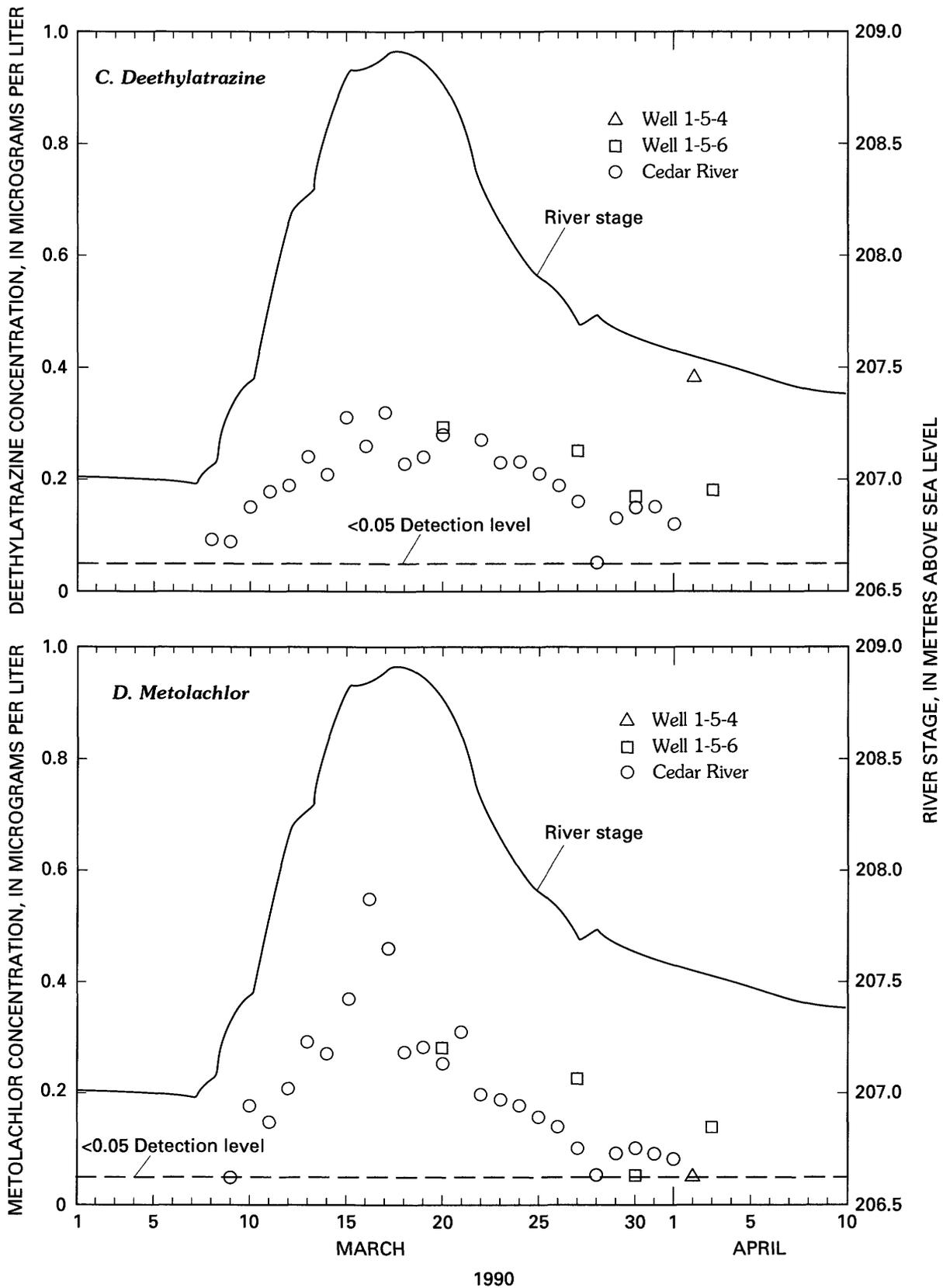


Figure 12. River stage and selected herbicide concentrations in water samples from the Cedar River and selected wells at Palisades site, March and April 1990—Continued.

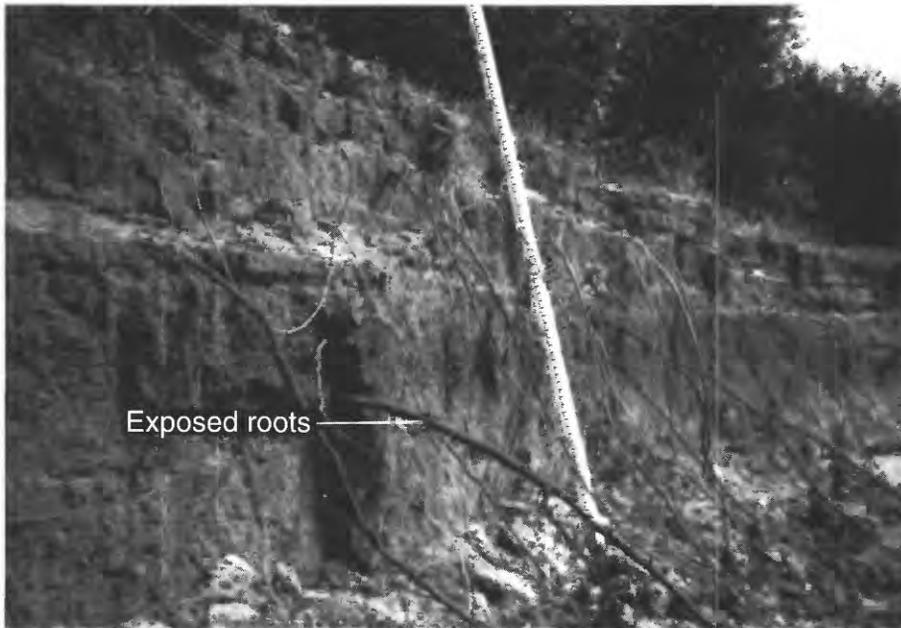


Figure 13. Tree roots exposed along riverbank at Palisades after a section of the bank was eroded during flooding of the Cedar River in January 1991. Divisions on rod are 0.1-foot (0.03-meter) intervals.

high flow and could transport large atrazine concentrations in the process.

On the basis of herbicide analyses given in Schulmeyer and others (1995), the maximum intrusion of bank-storage water into the alluvial aquifer was detected during March 1990 at 80 m from the river. Elevated concentrations of alachlor, atrazine, deisopropylatrazine, and metolachlor were detected at a maximum of 20, 80, 80, and 10 m from the river, respectively. It is possible that all these constituents moved 80 m from the river, but the smaller concentrations in the river and laboratory detection levels preclude identification of all constituents throughout the bank-storage water. After March 22, 1990, the hydraulic gradient was toward the river (fig. 10), which indicates that bank-storage water was being discharged back into the river. Because the herbicides are in the dissolved phase, they are returned to the river with the bank-storage water. Minipiezometer samples collected within 1 to 3 m of the river bottom during April 3–5, 1990 (fig. 9) had elevated concentrations of herbicides compared to those before the runoff (Schulmeyer and others, 1995), indicating that bank-storage water returned larger concentrations of herbicides to the river than previous ground-water discharge.

During February 20–22, 1990, the background concentrations of nitrate-nitrogen were very small, 0.10 mg/L (milligram per liter) or less. During the high streamflow of March 20–22, 1990, nitrate-nitrogen concentrations of 6.1, 5.5, 0.77, and 1.5 mg/L (Schulmeyer and others, 1995) were detected in water from wells at 5, 10, 20, and 30 m from the river's edge along section A–A', all screened at a depth of 3 m. These increased concentrations confirm the movement of bank-storage water into the aquifer. After the runoff, however, elevated concentrations of nitrate were not being discharged back to the river with the herbicides in the bank-storage water; during April 3–5, 1990, concentrations of nitrate in the minipiezometer samples collected within 1 to 3 m of the river bottom were generally less than 0.10 mg/L. These and other data for different sampling periods (Schulmeyer and others, 1995) indicate that nitrate typically is not discharged back into the river with bank-storage water, probably due to denitrification within the aquifer.

May 1990 Data

The high-flow period, which occurred during May 1990, was hydrologically more complex than the March high flow because bank-storage water moved

into the aquifer three separate times, as shown in figure 14. The river stage is a composite of tributary contributions in the river basin and can rise and fall depending on rainfall intensity, distribution, duration, and antecedent soil-moisture conditions. The rise and fall of the river stage three times caused a corresponding change in the ground-water hydraulic gradient between the wells 10 and 30 m from the river's edge (fig. 14).

Larger concentrations of all herbicides were detected in surface water and ground water during May 1990 when compared with those measured during March 1990 because the later samples were collected after spring application of herbicides. For example, the largest atrazine concentrations in the river water were 3.0 µg/L on May 23 and 0.82 µg/L on March 17 (Schulmeyer and others, 1995). Other herbicide concentrations in river water measured during May 23 and 24 also were larger than those reported during March 1990; the median concentrations during May 23 and 24 for alachlor, cyanazine, and metolachlor were 3.9, 2.5, and 4.6 µg/L, respectively.

The largest concentrations of herbicides in bank-storage water during sampling period 2 were detected

in a minipiezometer sample collected beneath the river bottom on May 23, 1990. The concentrations of herbicides at 2 m beneath the riverbed at the north edge of the river channel were: alachlor, 2.1 µg/L; atrazine, 4.7 µg/L; cyanazine, 3.2 µg/L; deethylatrazine, 0.54 µg/L; deisopropylatrazine, 0.33 µg/L; and metolachlor, 2.2 µg/L (Schulmeyer and others, 1995). These concentrations were verified by the large concentrations of atrazine and its metabolites, deethylatrazine and deisopropylatrazine, which were detected in well samples collected on May 23 at wells 5 m from the river's edge screened at depths of 3 and 6 m.

Chemical data indicate that the maximum intrusion of bank-storage water into the alluvial aquifer during May 23–24, 1990, was 50 m; however, the various herbicides were not detected an equal distance from the river, and they moved at different levels within the aquifer. This may be explained by the accumulation of bank-storage water from multiple runoff events and differences in the concentrations of herbicides in the river. Large concentrations of herbicides were detected in the aquifer at 20, 50, 10, and 20 m for alachlor, atrazine, cyanazine, and metolachlor, respectively. These large concentrations were detected at 6 m

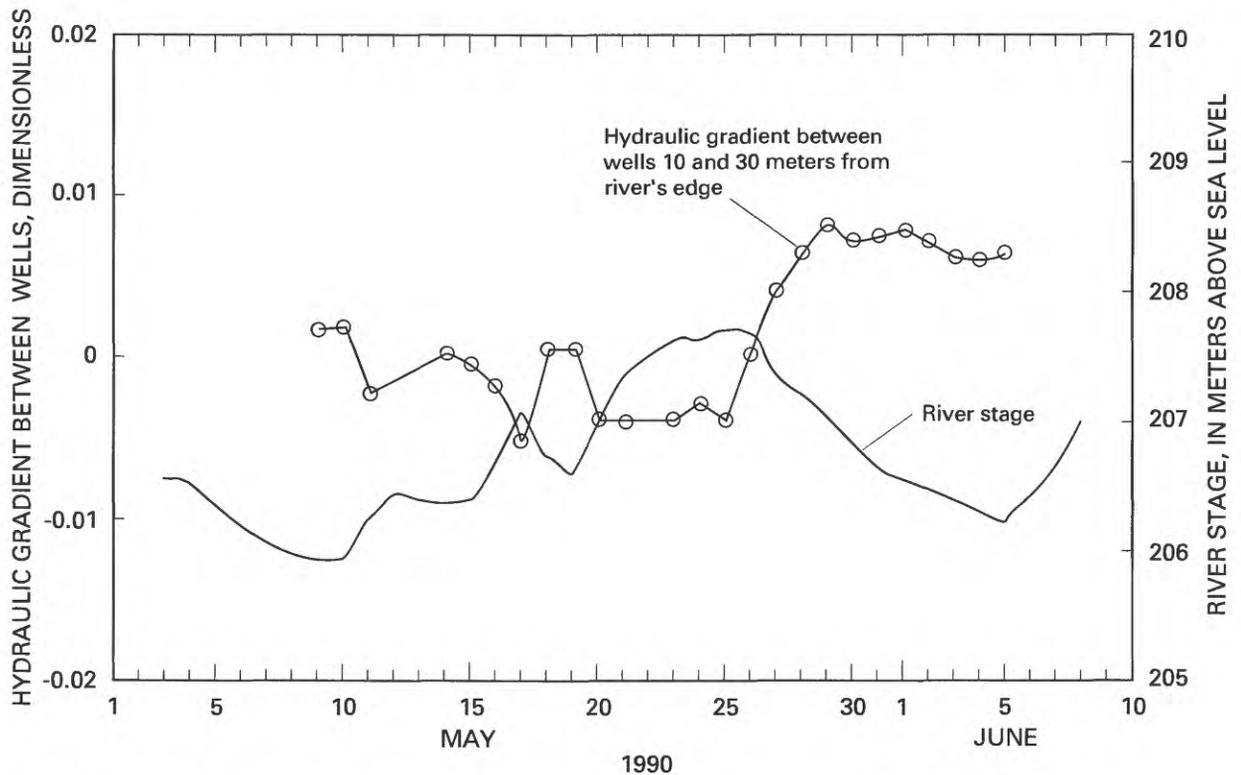


Figure 14. Hydraulic gradient between wells 10 and 30 meters from river's edge, both screened at 6 meters below land surface, and river stage during high flow, Palisades site, May and June 1990.

below land surface for all herbicides except atrazine, which was detected at 3 m below land surface. Bank-storage water from previous runoff events had not been discharged completely from the aquifer during May 9–10, 1990; therefore, the maximum intrusion of bank-storage water into the aquifer during May 23–24, 1990, represents the accumulation of bank storage in the aquifer from multiple runoff events.

During the high streamflow of May 23–24, 1990, nitrate-nitrogen concentrations of 5.5, 0.70, less than 0.10, and less than 0.10 mg/L were detected in water from wells at 5, 10, 20, and 30 m from the river's edge along section A–A' (Schulmeyer and others, 1995), all screened at a depth of 3 m. Nitrate-nitrogen concentrations in water from most other wells were very small, 0.10 mg/L or less. After the May 1990 runoff, during June 1990, concentrations of nitrate in the minipiezometer samples collected within 1 to 3 m of the river bottom were generally less than 0.10 mg/L. These data support what was previously stated; that is, nitrate typically is not discharged back into the river with bank-storage water.

Discussion

Chemical and hydrologic evidence indicates that herbicides and nitrate were transported into the alluvial aquifer from the Cedar River with bank-storage water at the Palisades site. Alachlor, cyanazine, and metolachlor were detected in ground water only during runoff periods. Therefore, in the absence of flooding, any detection of these chemicals in ground water is an indication of the intrusion of bank-storage water into the alluvial aquifer. The large applications of these herbicides contribute to their detection in the Cedar River and its alluvium.

Herbicide bank storage, defined as the mass of herbicides transported into the adjacent alluvial aquifer during bank storage of river water, is a temporary and reversible process in which herbicides are transported from surface water to ground water. Herbicide bank storage occurs when the hydraulic gradient between the surface water and ground water reverses because of an increase in river stage (fig. 10). Normally, when the river stage increases, the concentrations of herbicides in the river water also increase (fig. 9), but the maximum concentrations of herbicides in the river during runoff can be expected to decrease with time since application. Therefore, herbicide bank storage is event specific; the storage

depends on the hydraulic gradient and the concentrations of agricultural chemicals in the river.

Once herbicides are transported into the alluvial aquifer, the herbicide degradation process is expected to be slow (Klint and others, 1993), especially when compared to what occurs in the soil. For example, atrazine half-life in the top 10 cm of soil in a West Tennessee watershed was reported to be 21.5 days (Klaine and others, 1988). Mullaney and others (1991) found that pesticide residence time in soil was inversely related to soil organic content. A fact sheet prepared by the U.S. Environmental Protection Agency (1991b) gives atrazine half-lives ranging from 60 to 146 days. Nair and Schnoor (1992) reported that atrazine mineralization rates for ring carbon were 140 times slower in anoxic conditions (typically found in many aquifers) than in oxygenated conditions. The aquifer at the Palisades site is mostly anaerobic except near the surface where dissolved-oxygen concentrations can be as large as 13 mg/L (Schulmeyer and others, 1995). Furthermore, it is predominantly a sandy aquifer with low organic carbon content (table 2), and it is characterized by relatively low water temperatures (approximately 10 °C). The half-lives of atrazine and other herbicides at the study site are expected to be in the upper range of those reported by U.S. Environmental Protection Agency (1991b).

The data collected during high flows in March and May indicate that nitrate-nitrogen bank storage is minor compared to herbicide bank storage. Nitrate is much more mobile but is biogenetically more reactive than herbicides (Butcher and others, 1992). Nitrate was generally absent in the alluvial aquifer, probably due to denitrification, except in shallow areas of the aquifer where dissolved oxygen is also present (Schulmeyer and others, 1995). Even if nitrate moves with bank-storage water into the aquifer it generally was not discharged back into the river with the bank-storage water as the same species of nitrogen; the concentrations of nitrate in minipiezometer samples collected beneath the river were generally less than 0.10 mg/L.

Simulation of Bank Storage

A transient, two-dimensional, ground-water flow model was constructed using the U.S. Geological Survey's finite-difference modular flow model (McDonald and Harbaugh, 1988), with an option that

allows model cells that have gone dry to become resaturated (McDonald and others, 1991). The objective of using the model was to quantitatively describe the transient movement of bank-storage water into and out of the alluvial aquifer in response to the rise and fall of the river stage at the Palisades site during March 7–April 17, 1990. To describe this movement, a budget of the water movement between the river and the aquifer is presented. The movement of water into and out of the aquifer was calculated using a computer program (ZONEBUDGET) by Harbaugh (1990). A sensitivity analysis of the calibrated model shows potential variations in the results.

A quantitative description of the movement of bank-storage water helps explain how some agricultural chemicals—those that are conservative and nonreactive with the aquifer material—move between ground water and surface water with the bank-storage water. Because atrazine in an alluvial aquifer is not quickly degraded (Klint and others, 1993) and does not appear to be sorbed to the aquifer material at this site in substantial or appreciable quantities (discussed earlier), the atrazine data were used to trace the movement of bank-storage water and was used for model calibration.

Model Design and Assumptions

The model simulated ground-water flow in a cross section along the line of wells labeled A–A' (fig. 4). Line A–A' is perpendicular to the Cedar River and was along the direction of ground-water flow; in plan view the water-table contours constructed from daily water-level measurements in wells along A–A' and B–B' (fig. 11 and Schulmeyer and others, 1995) made between March 8 and April 5, 1990, were perpendicular to A–A'. The cross-sectional area simulated in the model was 440 m wide and 15 m deep and was represented by a grid with 15 layers, each with 44 cells (fig. 15). The grid-cell dimensions are 10 m in the horizontal direction and 1 m in the vertical direction. The depth of each cell into the plane of the cross section was 1 m.

The model was constructed by assuming the following conditions:

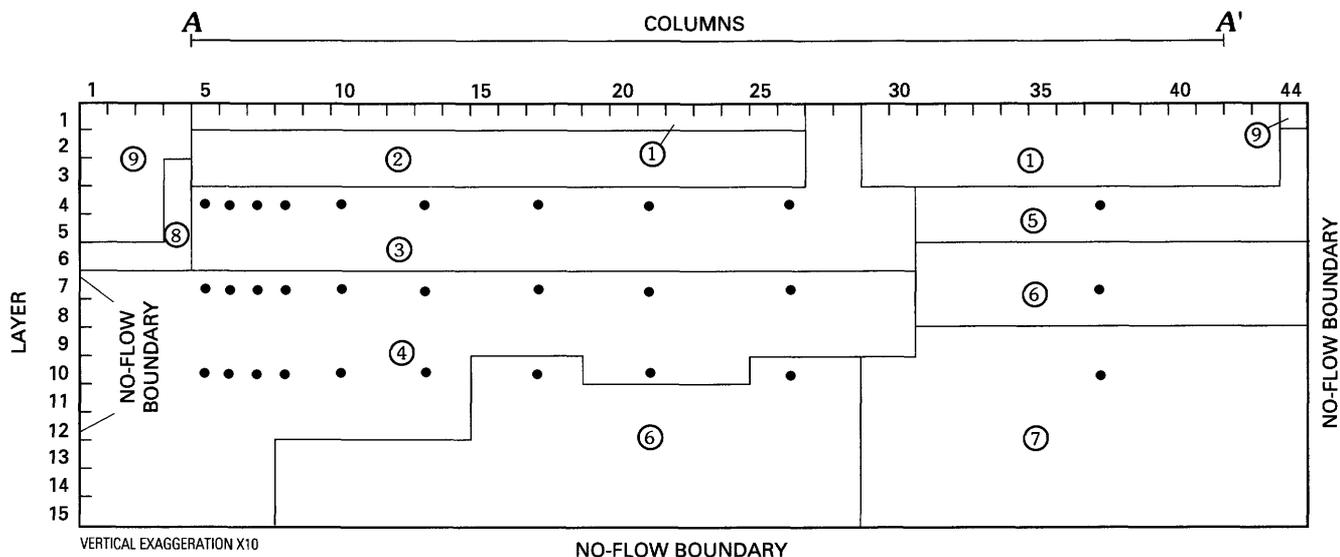
(1) The only area for ground-water discharge is the river, whereas recharge to the aquifer can occur from the river, an ephemeral stream, and precipitation. Evapotranspiration was not considered important during the period modeled because the ground

was frozen for much of the simulated time period and the trees were dormant.

- (2) The ground-water system was assumed to be in steady-state conditions before the runoff occurred; therefore, a steady-state model was used to calculate the starting hydraulic heads for the transient model. Once the river stage began to rise, the ground-water system responded to the new hydrologic conditions; therefore, a transient model was used to simulate the ground-water flow during the runoff. The transient model simulated the movement of ground water during March 7–April 17, 1990. There were 42 stress periods in the model, each representing 1 day.
- (3) Only the primary hydraulic conductivity of the aquifer was considered; macropores from tree roots within the shallow aquifer were not simulated.

The model was constructed using the following boundaries:

- (1) In the steady-state model an estimated recharge of 1.0×10^{-3} m/d was applied to the uppermost active layer of the aquifer in columns 5–44. This recharge is equivalent to 38 cm/yr and represents 60 percent of the annual precipitation in Iowa for 1989 and is about twice the recharge estimated by Hansen and Steinhilber (1977) for a nearby alluvial aquifer in southeast Iowa. Therefore, the estimated recharge would seem to be fairly large, which would reduce the movement of bank-storage water into the aquifer. For the transient simulation, this same recharge rate was applied in columns 5–43; however, a larger recharge was applied in the uppermost active cell in column 44. This larger recharge represented infiltration from an ephemeral stream and was applied only during the transient simulation because the Palisades site received about 19 cm of precipitation during March 1990 and because the stream did not flow during dry periods that characterize steady-state conditions.
- (2) The left-lateral model boundary beneath the river (fig. 15) was assumed to be a ground-water divide and, therefore, was represented as a no-flow boundary; the ground water at this boundary was assumed to be moving vertically upward or downward. This boundary was located approximately in the center of the river.
- (3) The right-lateral model boundary farthest from the river (fig. 15) was assumed to be a no-flow boundary because of the presence of thick deposits (about 15 m) of glacial till in this area. These till deposits,



EXPLANATION

- ⑥ ——— Boundary of hydrogeologic subunit—
 Number refers to subunit: 1, sandy clayey silt; 2, silty clayey fine-grained sand; 3, medium-grained sand; 4, coarse-grained sand; 5, silty clayey medium-grained sand; 6, silty clayey coarse-grained sand; 7, glacial till; 8, general head-dependant boundary and bed sediment (when simulated); 9, inactive
- A ——— A' Trace of section shown in figure 4
- Observation well used in model calibration

Figure 15. Model grid and location of hydrogeologic subunits and observation wells at Palisades site used in simulation of bank storage. Trace of section shown in figure 4.

although permeable, are orders of magnitude less permeable than the alluvial aquifer, and flow from them was assumed to be negligible.

- (4) The basal boundary was assumed to be a no-flow boundary (fig. 15) because of the thick deposits (15 m) of glacial till that underlie the study site.
- (5) A general head-dependent boundary was used to simulate the river stage (fig. 15). This boundary allowed simulated flow into or out of the aquifer where the boundary is located. The simulated hydraulic heads for this boundary were based on the daily mean river stage at the Palisades site between March 7 and April 12, 1990 (Schulmeyer and others, 1995). The measured river stage between April 13 and 17, 1990, increased slightly due to runoff. For this period of time, the simulated hydraulic heads for the river boundary were estimated by extrapolating the river-stage recession for another 5 days. This extrapolation was done so that the model could simulate an unaffected discharge of bank-storage water from the aquifer for a longer

period of time. The hydraulic conductance (product of the hydraulic conductivity and cross-sectional area of flow divided by the length of flow path) was set at 1,000 m²/d for the head-dependent boundary.

The same cells containing the general head-dependent boundaries also were used to simulate the 0.5-m thick bed sediment along the riverbank and bottom (fig. 15). The river bottom is simulated by cells located in layer 6 and columns 1–4, whereas the riverbank is simulated by cells in layers 3–5 in column 4. The presence of a thin layer of finer grained bed-sediment material along the riverbank has been documented in many rivers (Schumm, 1960) and is present at the Palisades site. However, it is not known if this sediment significantly retards the movement of water through the riverbank or if fine-grained sediment on the river bottom restricts the movement of water into the aquifer. Therefore, the model was designed to allow testing the potential effect of the bed sediment. To simulate a 0.5-m thick layer of bed sediment on the river bottom, the hydraulic conductivity of the cells in layer 6,

columns 1 through 4 (fig. 15), was reduced. Because the grid spacing in the horizontal direction is 10 m, it was necessary to calculate an equivalent horizontal hydraulic conductivity for the cells representing the riverbank (layers 3–5, column 4; layer 6, columns 1–4) when simulating the 0.5-m thick layer. To simulate the absence of bed sediment, the hydraulic conductivity of these cells was set sufficiently large so that water movement into the aquifer was limited only by the hydraulic conductivity of the aquifer.

Calibration

Input values for the calibrated model are shown in table 3, and the model was calibrated or compared to the following data:

- (1) The largest hydraulic conductivity estimated for the coarse-grained sand by the slug-test analysis (53 m/d) and calculated diffusivity (70 m/d) were similar to what was used in the model (100 m/d). The difference between 70 and 100 m/d was considered small.
- (2) Between March 8 and April 5, 1990, 745 daily ground-water-level measurements from 27 wells (shown in fig. 15 in columns 5–27) were used in three ways to calibrate the model. First, a general comparison of the measured and model-generated hydraulic heads was made. The mean difference between the measured and calculated heads for the wells located in columns 5 through 27 was 3.2 cm for the calibrated model, with a standard deviation of 4.7 cm. The water-level measurements from the wells shown in column 37 (fig. 15) were used to calibrate the model but were not included in the general comparison of the measured and model-generated heads. They were excluded in this comparison because they do not lie within the principal aquifer adjacent to the river, and due to slow recovery after sampling, their water levels were not in equilibrium with the flow system. The water levels from the deepest well in column 37 never fully recovered between water-quality sample collection on March 20–22 and April 3–5, 1990.

The second way in which the water-level measurements (Schulmeyer and others, 1995) were used to calibrate the model was by comparing the measured vertical hydraulic-head differences from well nests at the Palisades site with those generated by the model. The hydraulic heads measured in the wells at 3 and 9 m deep were associated with layers 4 and 10 of the

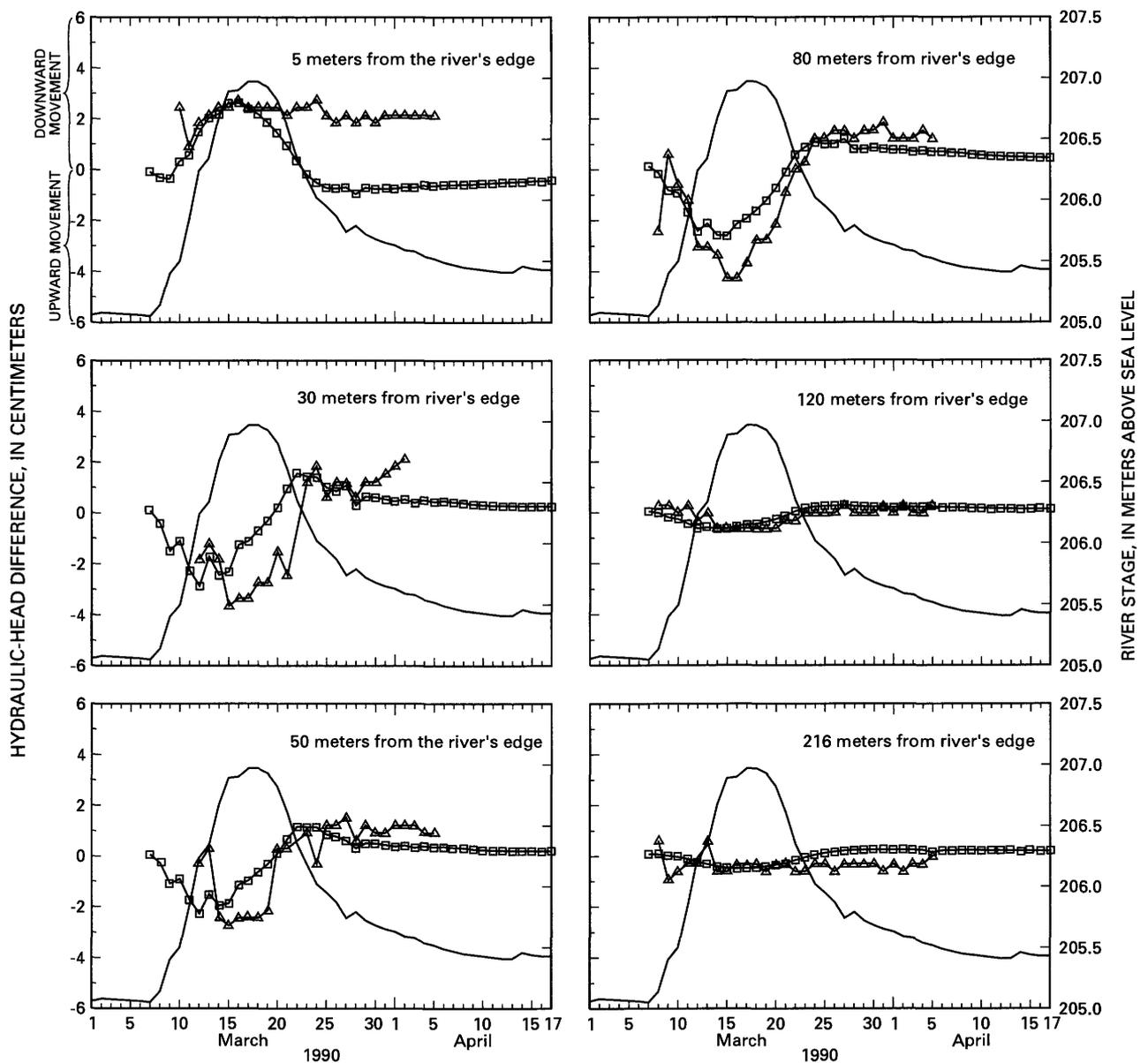
model. The difference in hydraulic head between the wells 3 m and 9 m deep compared to the modeled hydraulic-head difference between layers 4 and 10 is shown in figure 16. Measured and modeled vertical hydraulic-head differences are shown at various distances from the river's edge. A positive, vertical hydraulic-head gradient indicates a downward movement of the ground water.

The third way that the water-level measurements were used in the model calibration was by comparing the measured daily horizontal ground-water hydraulic gradient between the wells 5 and 30 m from the river's edge with the model results (fig. 17). This agreement was important because bank storage occurred within this area and these horizontal gradients strongly affect the movement of bank-storage water.

- (3) By using the measured hydraulic gradients (fig. 17) and assuming a hydraulic conductivity of 100 m/d and a porosity of 25 percent, it was calculated that the bank-storage water would have moved a distance of about 35 m into the aquifer during March 8–22, 1990, at a depth of 6 m from land surface. The model indicates that river water moved about 31 m into the aquifer at the same depth, assuming a hydraulic conductivity of 100 m/d and a porosity of 25 percent and using the model-generated hydraulic gradients shown in figure 17.
- (4) At a depth of 6 m below land surface the water-chemistry data show that bank-storage water moved laterally about 30 m into the aquifer, which agrees with the hydrologic data and the calibrated model discussed in (3). A comparison of specific conductance (fig. 18) and the concentrations of atrazine in water samples collected on February 20–22 and March 20–22, 1990 (fig. 9), shows that bank-storage water moved laterally about 30 m into the aquifer at a depth of 6 m below land surface; in this area, bank-storage water had a smaller specific conductance and larger concentrations of atrazine when compared with the background (or ambient) ground water.
- (5) Between March 20–22 and April 3–5, 1990, the 0.40- $\mu\text{g/L}$ line of equal atrazine concentration occurred about 15 m closer to the river at depths of about 6 m below the land surface (fig. 9). The travel distance during that period was estimated to be 17 m on the basis of measured hydraulic gradients (fig. 17) and assuming a hydraulic conductivity of 100 m/d and a porosity of 25 percent. Using the model-generated hydraulic gradients and assuming

Table 3. Calibrated values and range of values used in the sensitivity analyses of the ground-water flow model

| Model input variable | Calibration values | Range of values used in sensitivity analysis | |
|--|-----------------------|--|-----------------------|
| Confining unit horizontal hydraulic conductivity (meters per day) | | | |
| Glacial till | 1.0×10^{-3} | 1.0×10^{-4} | 1.0×10^{-2} |
| Sandy clayey silt | .01 | .001 | .1 |
| Silty clayey coarse sand | 1.0 | .1 | 10.0 |
| Aquifer horizontal hydraulic conductivity (meters per day) | | | |
| Silty clayey medium sand | 50.0 | 25.0 | 100.0 |
| Silty clayey fine sand | 1.0 | .5 | 2.0 |
| Medium sand | 50.0 | 25.0 | 100.0 |
| Coarse sand | 100.0 | 50.0 | 200.0 |
| Confining unit vertical anisotropy (horizontal hydraulic conductivity/vertical hydraulic conductivity, unitless) | | | |
| Glacial till | 20.0 | 4.0 | 100.0 |
| Sandy clayey silt | 20.0 | 4.0 | 100.0 |
| Silty clayey coarse sand | 20.0 | 4.0 | 100.0 |
| Aquifer vertical anisotropy (horizontal hydraulic conductivity/vertical hydraulic conductivity, unitless) | | | |
| Silty clayey fine sand | 10.0 | 2.0 | 50.0 |
| Medium sand | 10.0 | 2.0 | 50.0 |
| Coarse sand | 10.0 | 2.0 | 50.0 |
| Silty clayey medium sand | 10.0 | 2.0 | 50.0 |
| Recharge (meters per day) | | | |
| Columns 5–43 | 1.04×10^{-3} | $.52 \times 10^{-3}$ | 2.08×10^{-3} |
| Stream-column 44 | .03 | .01 | .09 |
| Aquifer storage coefficient (decimal fraction by volume) | | | |
| Specific yield—clean sand units | .2 | .1 | .3 |
| Specific yield—silty sand units | .05 | .05 | .15 |
| Specific storage | 1.0×10^{-4} | 1.0×10^{-5} | 1.0×10^{-3} |
| Confining unit storage coefficient (decimal fraction by volume) | | | |
| Specific yield | 0.01 | 0.01 | 0.15 |
| Specific storage | 1.0×10^{-3} | 1.0×10^{-4} | 1.0×10^{-2} |
| River-bottom sediment | | | |
| Horizontal and vertical hydraulic conductivity (0.5-meter thick zone) (meters per day) | 5.0 | .5 | 200.0 |
| River-bottom and bank sediment | | | |
| Changed the horizontal and vertical hydraulic conductivity (0.5-meter thick zone) in the river bottom and riverbank at the same time. River bottom /riverbank (meters per day) | 5.0/200.0 | 200.0/0.5 | 200.0/5.0 |



EXPLANATION

- River stage
- ▲▲▲ Measured vertical hydraulic-head difference
- Modeled vertical hydraulic-head difference

Figure 16. Vertical hydraulic-head difference between layers 4 and 10 in model and those measured in wells at Palisade site screened 3 and 9 meters below land surface at selected distances from the Cedar River, March and April 1990.

the same hydraulic conductivity and porosity, it was calculated that water moved about 16 m toward the river during that period.

- (6) The amount of ground-water discharge that directly enters the Cedar River during base-flow conditions was used to help evaluate the model

results. Even though the model only simulates the movement of water between the Cedar River and the alluvial aquifer along a 1-m reach of the river, ground-water discharge to the river computed by the model was compared with what was indirectly measured along a 48-km reach of the Cedar River.

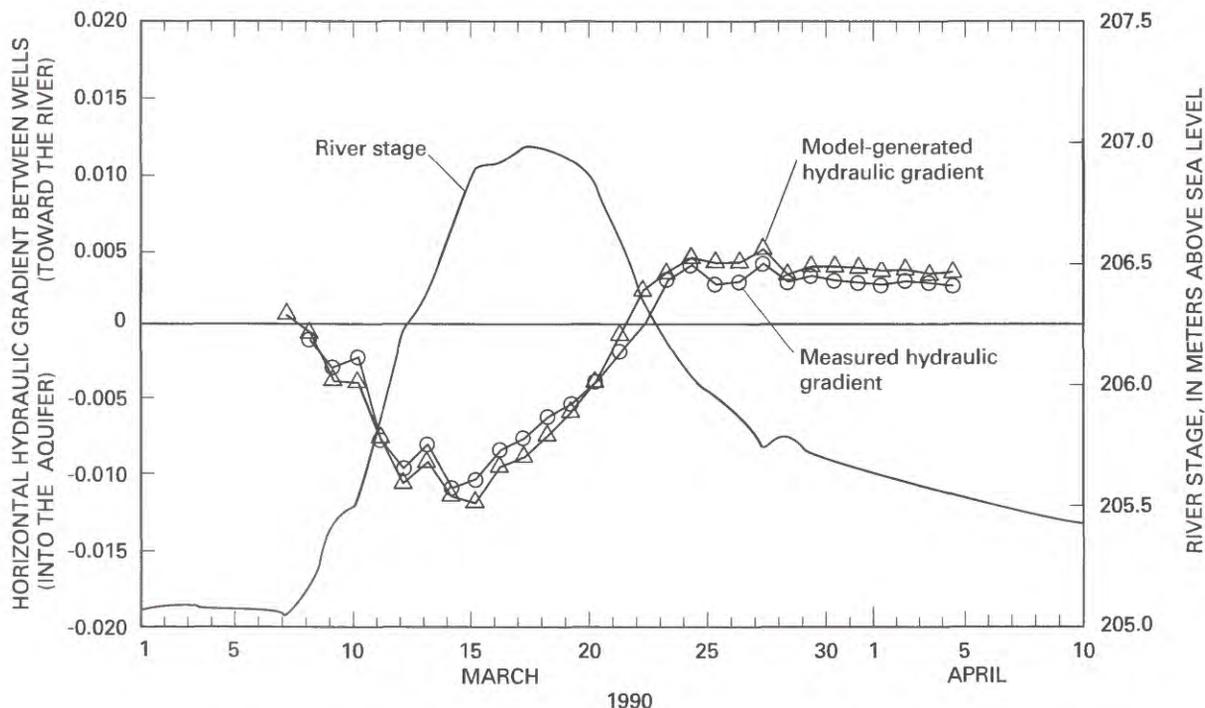


Figure 17. Measured and model-generated horizontal hydraulic gradients, March and April 1990. Horizontal hydraulic gradients are those between two wells 5 and 30 meters from the Cedar River and at a depth of 6 meters below the land surface at Palisades site.

This comparison was used to determine if the modeled ground-water flux was reasonable.

The amount of ground water that directly discharges to the Cedar River during base-flow conditions is consistent with the discharge calculated by the model. During base-flow conditions, on September 20–22, 1989, and October 31 and November 2, 1990, the average ground-water discharge was calculated for a 48-km reach of the Cedar River between Cedar Rapids and Cedar Bluff (fig. 1). To calculate this ground-water discharge, stream discharge was measured for the Cedar River at Cedar Rapids (upstream site) and Cedar Bluff (downstream site), and the difference in these two discharge measurements showed a net increase along the river. Next, the tributary contribution was subtracted, and the remaining discharge was ground-water discharge that directly entered the Cedar River from the alluvial aquifer. Assuming equal ground-water discharge from both sides of the river, it was calculated that the average ground-water discharge from one side of the river was 2.1 and 1.8 ($\text{m}^3/\text{d}/\text{m}$) length of river, for each time period, respectively. In the model, the ground-water discharge to the river had stabilized to about 1.9 ($\text{m}^3/\text{d}/\text{m}$) length of river on April 8, 1990.

Sensitivity Analysis

Selected input parameters to the flow model were varied one at a time from the calibration values to determine how variations in these parameters affect model results. Values used in the sensitivity analysis are shown in table 3, how these changes affected simulated bank storage and hydraulic head is shown in figure 19. The range of values used in the sensitivity analysis does not describe the absolute minima and maxima but is believed to include fairly extreme values.

The results of the sensitivity analysis (fig. 19) show that the accumulation and release of bank storage is most sensitive to aquifer storage, hydraulic conductivity, and recharge. However, changes made in these parameters caused the hydraulic heads to be significantly different from the calibrated model and what was measured onsite (fig. 19). The top five layers of the model were allowed to convert between confined and unconfined conditions depending on the location of the water table; therefore, the storage coefficient alternated between specific storage (confined conditions) and specific yield (unconfined conditions) in

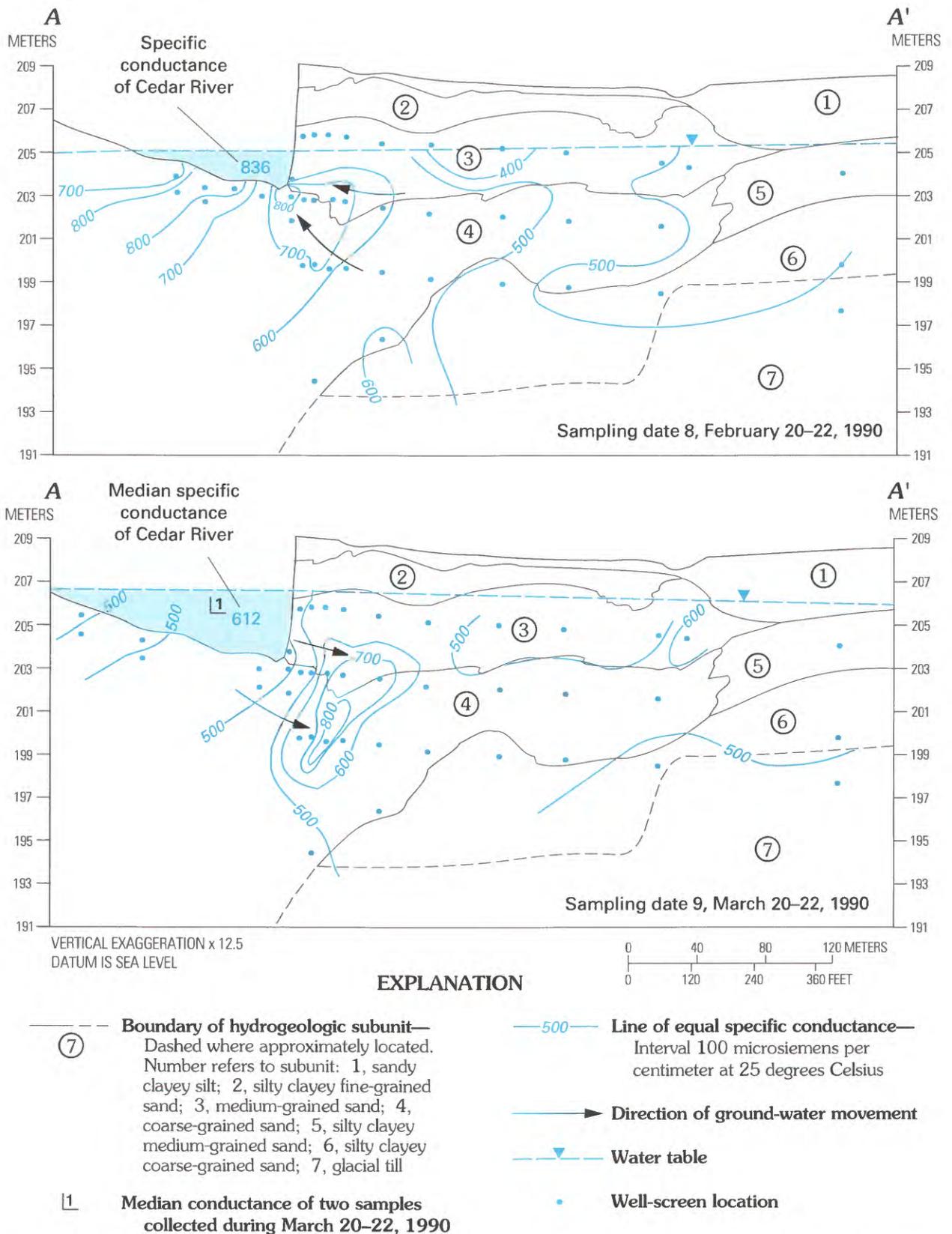


Figure 18. Distribution of specific conductance in water samples from the alluvial aquifer and Cedar River at Palisades site, February and March 1990. Trace of section shown in figure 4.

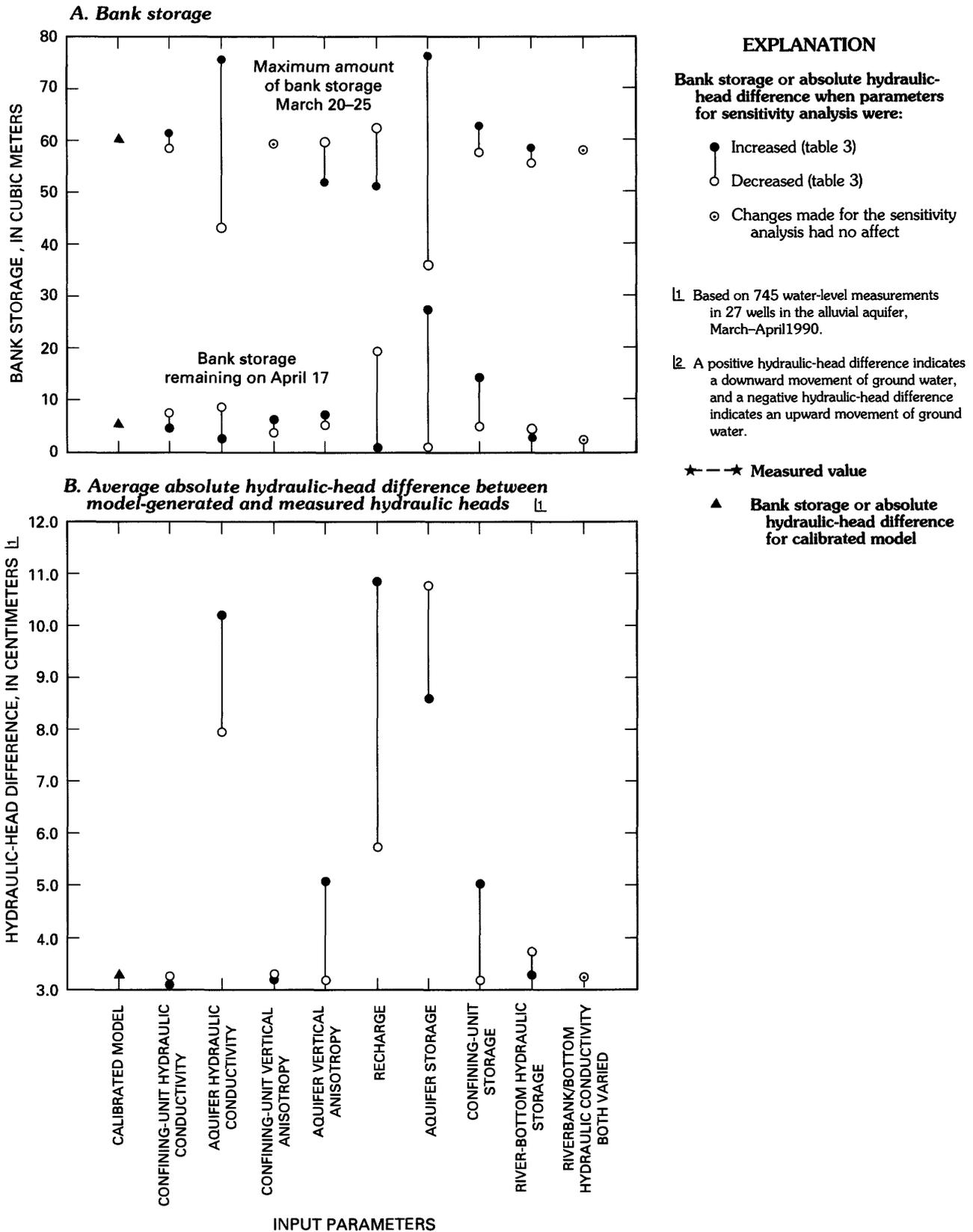


Figure 19. Results of model sensitivity-analysis testing of bank storage and hydraulic-head differences for selected wells at Palisades site.

these upper layers. Any unit completely saturated was assigned a specific-storage value.

The amount of bank storage that is simulated and the time that it takes for that amount to be returned to the river can vary independently. For example, when the hydraulic conductivity of the aquifer was increased, the simulated bank storage increased, but the simulated amount of bank-storage water remaining in the aquifer on April 17 (fig. 19) was similar to the amount when the hydraulic conductivity was reduced. Changes in the aquifer storage coefficient caused the largest change in simulated bank-storage water in the sensitivity analysis. Increasing the storage coefficient caused a large increase and slow release of the simulated bank-storage water. When the simulated recharge from precipitation and from the ephemeral stream (column 44) was increased, the residence time of the bank-storage water was decreased substantially (fig. 19). In fact, the model indicated that when recharge was increased all of the bank-storage water was released from the aquifer by April 10. Intuitively, this makes sense because if recharge were increased, hydraulic-head gradients toward the river should increase, which would result in the flushing out of bank-storage water.

Changes in the other parameters did not significantly affect the simulated accumulation and release of bank-storage water from what was calculated by the calibrated model. However, even when bank storage was not affected by varying the input parameters, simulated hydraulic heads can be somewhat different from what was measured onsite (fig. 19). Increasing and decreasing the aquifer vertical anisotropy resulted in simulated hydraulic heads that were substantially different from what was measured onsite. The hydraulic characteristics of the confining units do not substantially affect bank storage or the hydraulic heads within the modeled alluvial aquifer.

The vertical hydraulic conductivity of the river bottom (in an area 0.5 m thick) can be 50 percent less than the vertical hydraulic conductivity of the underlying aquifer and still not appreciably affect the movement of water between the aquifer and river (fig. 19). Increasing the river-bottom hydraulic conductivity resulted in little change in the accumulation and release of bank-storage water.

If the hydraulic conductivity is reduced along the riverbank to simulate fine-grained bed sediment, the vertical gradients in the cells adjacent to the river's edge (column 5) are reversed from what was measured

onsite (fig. 19). Scouring of the river may remove fine-grained sediment at the river bottom but not along the riverbank. To test this possibility, the riverbank hydraulic conductivity, in a zone that is 0.5 m thick, was decreased from 200 to 0.5 m/d and to 5.0 m/d in two different simulations, and the river-bottom hydraulic conductivity was increased from 5.0 to 200 m/d. These changes caused the vertical hydraulic-head differences between layers 4 and 10 in column 5 to be reversed from what was measured onsite and what was simulated in the calibrated model (fig. 19). The calibrated model and the measured vertical hydraulic-head differences in the wells 5 m from the edge of the river indicate that ground water was moving through the riverbank and downward into the aquifer (fig. 19). Macropores from roots (fig. 13) in the sediment may have allowed greater movement of water between the river and the aquifer along the riverbank even though there is some less-permeable bed sediment along the riverbank. These macropores would occur within the upper part of the alluvial aquifer but are not simulated in the model.

Results and Discussion

On the basis of model results, bank-storage water moving through the river bottom accounts for 70 percent of the total bank-storage water, whereas the remaining 30 percent moves through the riverbank (fig. 20). Differences in the hydraulic conductivity do not explain the large amount of bank-storage water that moves through the river bottom. In fact, the vertical hydraulic conductivity for water moving through the river bottom is much less than the horizontal hydraulic conductivity for water moving through the riverbank; the vertical hydraulic conductivity is 5 m/d for the river-bottom sediment and 10 m/d for the coarse-grained sand, whereas the horizontal hydraulic conductivity is 200 m/d for the riverbank sediment and 50 m/d for the medium-grained sand. A maximum of about 0.25 m³/d moved through a square meter of the simulated river bottom when the hydraulic gradient reversed (from the river to the aquifer) between March 8 and March 20, 1990. During the same simulated period a maximum of about 1.0 m³/d (four times as much water) moved through a 1-m² area of the riverbank. The comparison of the simulated ground-water flux between the river bottom and bank indicates that the flux of bank-storage water through the riverbank is large (per unit area), but the total amount of area along

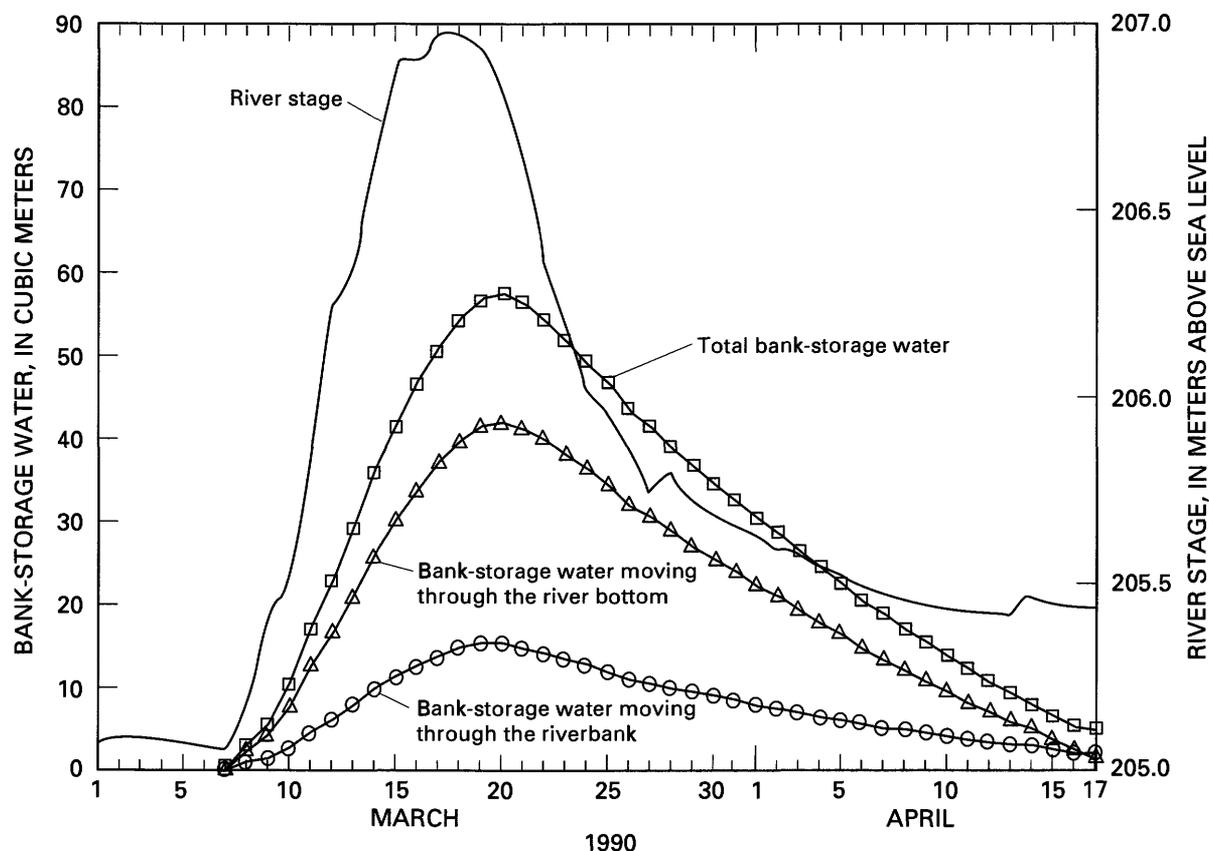


Figure 20. Model-simulated accumulation and release of bank-storage water through the riverbank and river bottom in a section of the alluvial aquifer at Palisades site that is 1 meter wide, and measured stage of Cedar River, March and April 1990.

the simulated riverbank is at least an order of magnitude less than what is on the river bottom.

The model indicates that bank-storage water that enters the aquifer through the river bottom or bank probably leaves the aquifer through the same location. Because the chemical and hydrologic data show that bank-storage water occurs within 30 m from the river's edge at a depth of 6 m, a budget of the simulated ground-water movement within this area can help determine a potential imbalance of the movement of bank-storage water between the river bottom and the riverbank. For example, it was hypothesized that bank-storage water can enter the aquifer through the river bottom but leave through the riverbank. When the simulated hydraulic gradient is from the river to the aquifer, 5.9 m³ of ground water moves in a circuitous path from the coarse-grained sand that lies beneath the river bottom to the medium-grained sand that lies adjacent to the riverbank (fig. 15). When the simulated hydraulic gradient reverses (is from the aquifer to the river), the net ground-water movement

back into the coarse-grained sand, from the medium-grained sand, is also 5.9 m³. Because the simulated volume of ground water moving between these two areas is equal, the simulated bank-storage water entering from the river bottom or bank probably leaves from the same location.

The model also indicates that the ground-water flux (both into and out of the aquifer) through the river bottom will decrease toward the ground-water divide. If the ground-water flow to a river is symmetrical on both sides of the river, then the ground-water divide would be located in the center of the river; asymmetrical ground-water flow would move the divide away from the center of the river. The simulated ground-water flux through the river bottom decreased along the 40 m of river bottom with distance from the riverbank (fig. 21). The simulated ground-water flux through the river bottom to the aquifer reached a maximum on March 11, 1990. On this particular day, 48 percent of the flux through the river bottom occurred within 10 m of the river's edge, and 71 percent of

the flux moved through the river bottom within 20 m of the river's edge. The fluxes continued to decrease toward the center of the river. The simulated ground-water flux, both to the river and to the aquifer, was always largest in the cell adjacent to the riverbank (fig. 21).

Onsite measurements of the vertical and horizontal hydraulic gradients of the alluvial aquifer under transient conditions were useful for calibrating the model. Matching the hydraulic heads measured onsite with those generated by a model commonly is used for model calibration. However, it is possible to obtain a fair match of the hydraulic heads and yet the vertical gradients (which generally are small) may be in error, which could result in erroneous simulation of the vertical direction of ground-water movement.

Simulated bank storage is very sensitive to vertical recharge to the top of the aquifer. Therefore, conceptually, an alluvial aquifer that has limited vertical recharge from precipitation, runoff from upland areas,

and flooding of rivers and tributary streams has the greatest potential for bank storage.

The model shows that discharge of bank-storage water from the aquifer to the river can greatly increase the amount of ground-water discharge to the river during base flow. The model shows that the ground-water discharge to the river during base flow increased almost five times after high flow and bank storage; discharge to the river increased from 0.42 (m³/d)/m on March 7, 1990, to 1.9 (m³/d)/m on April 8, 1990. These model results indicate that bank storage is an important source of recharge to the alluvial aquifer and that during early base-flow conditions much of the ground-water discharge may be from bank storage. During extended base-flow conditions, after the depletion of bank storage, the ground water discharged to the river can originate from other sources, including bedrock, recharge from past flooding of the Cedar River, recharge from ephemeral and perennial streams draining the upland areas, and precipitation falling on the flood plain. Recharge from ephemeral and peren-

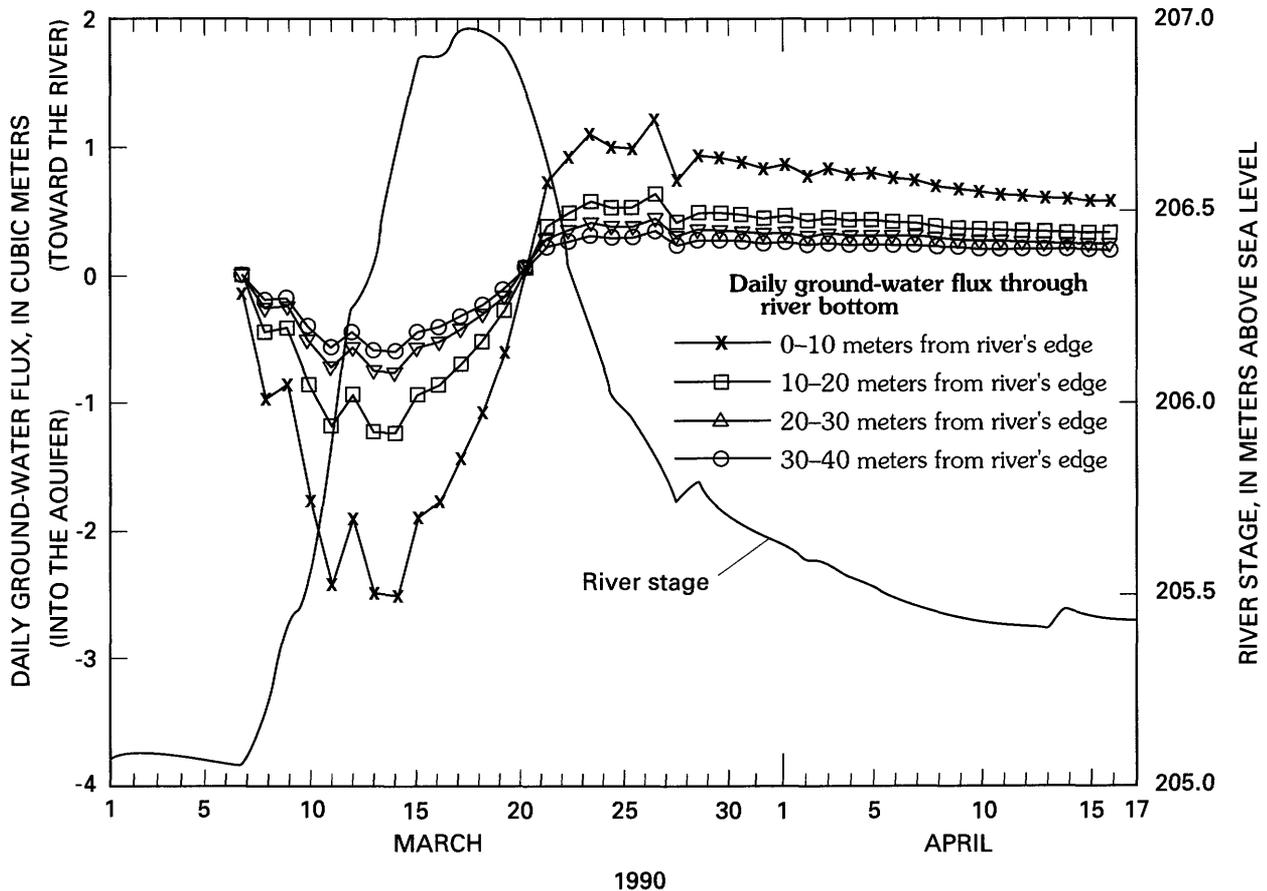


Figure 21. Model-simulated daily ground-water flux through river bottom at selected distances from Cedar River in response to change in river stage, March and April 1990.

nial streams may be a very significant source of recharge to the aquifer and is probably the least studied.

MOVEMENT OF AGRICULTURAL CHEMICALS INTO GROUND WATER FROM FLOODING

When discharge of the Cedar River or tributary streams flowing across the flood plain of the Cedar River exceeds channel capacity, excess surface water flows over the surface of the flood plain. Ground-water recharge can occur in areas inundated by the floodwater, and this recharge water can carry dissolved herbicides to the alluvial aquifer.

June 1990 Data

The small concentrations of herbicides in the ground water adjacent to the Cedar River indicate that bank storage was very minor during flooding in June 1990 (fig. 8). Cyanazine and metolachlor were not detected in samples collected on June 26, 1990, in any wells that were within 30 m of the river's edge. Furthermore, the concentrations of atrazine, deethylatrazine, and deisopropylatrazine did not increase substantially and in many cases decreased from the June 4, 1990, sampling. The river stage increased more than 3 m during this flood (compared to 2 m in March 1990), and yet apparently the ground-water hydraulic gradient remained primarily toward the river; large amounts of vertical recharge from the flooding and the rapid rise in river stage limited the amount of bank storage that occurred.

The chemical data (Schulmeyer and others, 1995) indicate that large concentrations of herbicides were introduced vertically to the top of the alluvial aquifer at two locations as the result of the flooding in June 1990 (fig. 22). Water from two wells showed a substantial increase in the concentrations of the herbicides on June 27, 1990. The concentrations of atrazine, cyanazine, deethylatrazine, deisopropylatrazine, and metolachlor in water from an observation well 216 m from the river and at a depth of 3 m were 7.6, 0.43, 1.3, 0.23, and 2.7 $\mu\text{g/L}$, respectively. The concentration of alachlor was less than the detection level of 0.05 $\mu\text{g/L}$. The concentrations of atrazine, deethylatrazine, deisopropylatrazine, and metolachlor in water from an observation well 80 m from the river and at a

depth of 3 m were 1.5, 0.41, 0.13, and 0.45 $\mu\text{g/L}$, respectively.

The large concentrations of herbicides in ground water were detected downgradient of shallow depressions that hold water and function as recharge areas for the ground-water system. Upgradient of the wells 216 m from the river's edge is a pond. The bottom of this pond lies within 0.5 m of the medium-grained sand. Therefore, pond water could easily move vertically into the underlying alluvial aquifer. The base map used in figure 4 shows a small depression upgradient of well 1-80.

Floodwater enters the pond from the Cedar River and an ephemeral stream. However, the ephemeral stream is likely to be the primary source of herbicides in the pond. For example, the concentration of atrazine was 62 $\mu\text{g/L}$ in a water sample collected from the stream on May 19, 1990, and atrazine concentrations of 67, 12, 48, and 40 $\mu\text{g/L}$ were detected in water from the pond on May 16, 19, 25, and 29, 1990, respectively. These concentrations are much larger than any water sample collected from the Cedar River during the entire study period. With time, the pond water percolated into the subsurface, transporting large concentrations of herbicides into the ground water.

April 1991 Data

During March 2-April 3, 1991, the ground-water hydraulic gradient was once again predominately toward the river during the flooding in March 1991 (fig. 8), and therefore bank storage of herbicides did not occur. Furthermore during March 2-April 3, 1991, concentrations of atrazine and deethylatrazine in water from an observation well (1-12-4), which is at a depth of 4 m and at that time was 2 m from the river's edge, were consistently larger than those detected in the river (Schulmeyer and others, 1995). Atrazine and deethylatrazine in ground water were emplaced at an earlier time.

Discussion

The herbicide data collected between June 1990 and February 1991 (Schulmeyer and others, 1995) show the movement of large concentrations of herbicides that were introduced during flooding in June 1990. On June 27, 1990, large concentrations of atrazine, cyanazine, deethylatrazine, deisopropylatra-

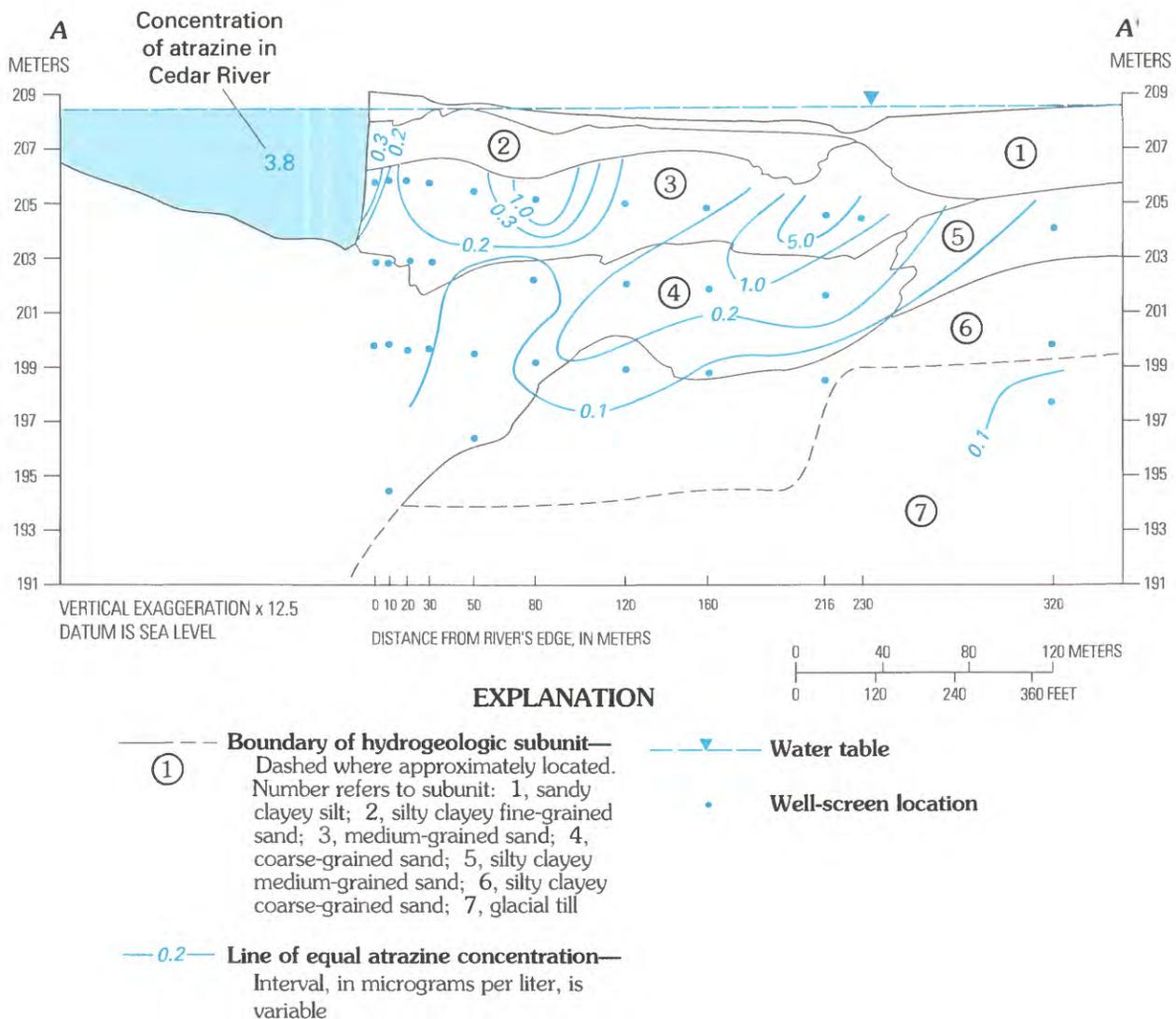


Figure 22. Distribution of atrazine in the alluvial aquifer on the basis of atrazine concentrations in ground-water samples collected at Palisades site, June 26–27, 1990. Trace of section shown in figure 4.

zine, and metolachlor (8.0, 0.50, 1.4, 0.23, and 2.7 µg/L, respectively) were detected in water from an observation well 216 m from the river's edge and 3 m below land surface. At the same location on July 25, 1990, a field duplicate sample had even larger concentrations of atrazine, cyanazine, deethylatrazine, deisopropylatrazine, and metolachlor (20, 1.4, 3.2, 1.0, and 5.9 µg/L, respectively). These two samples merely indicate that during June and July 1990 large concentrations of herbicides and metabolites were introduced into the aquifer but that the concentration plume was not accurately defined. On February 5, 1991, concentrations of the same compounds detected in water from the observation well 10 m from the river's edge and 9 m deep were 18, 1.3, 1.4, 0.40, and 7.0 µg/L,

respectively. These large concentrations were verified by results from adjacent wells (fig. 23). Between June 1990 and February 1991 the hydraulic gradient was predominately toward the river. Because there are no known source(s) of herbicide to the ground water at the study site other than those that have been discussed previously, it can be assumed that the large concentrations detected on February 5, 1991, at 10 m from the river's edge originated during June and July 1990, 216 m from the river's edge (figs. 22 and 23). The distance of travel was 206 m in 193 to 223 days (assuming the date of origin between June 27 and July 25, 1990), giving a horizontal mean velocity of approximately 0.9 to 1.1 m/d.

Herbicide movement in the subsurface is governed by many factors. These factors include soil properties (for example, physical-chemical composition, temperature, moisture content, and biological and biochemical properties) and herbicide properties (for example, solubility, adsorbability, octanol-water partition coefficient, ionization coefficient, and stability) (Helling and Gish, 1986). The presence of atrazine in ground water is widespread, which indicates that atrazine is mobile in soil and aquifer material (Pionke and Glotfelty, 1990). Wehtje and others (1984) observed that “direct downward leaching is largely responsible for low level atrazine contamination detected in groundwater...,” whereas in another study, atrazine did not infiltrate below 20 cm during a 238-day study period (Klaine

and others, 1988). Atrazine movement in the subsurface likely depends on site conditions. The conditions at the Palisades site generally are favorable for atrazine movement because of the presence of: (1) coarse-to medium-grained sand materials, (2) small organic content, (3) small clay content, and (4) a dynamic ground-water system. Retardation factors of atrazine movement at the site were slight, ranging from 1.0073 to 1.0180, on the basis of an equation reported by Schwarzenbach and others (1983). The retardation factor is based on the organic-carbon content of the aquifer material; the value of 1.0 indicates no retardation. The results of this study confirm the presence of large herbicide concentrations in ground water from an alluvial aquifer. The source of the

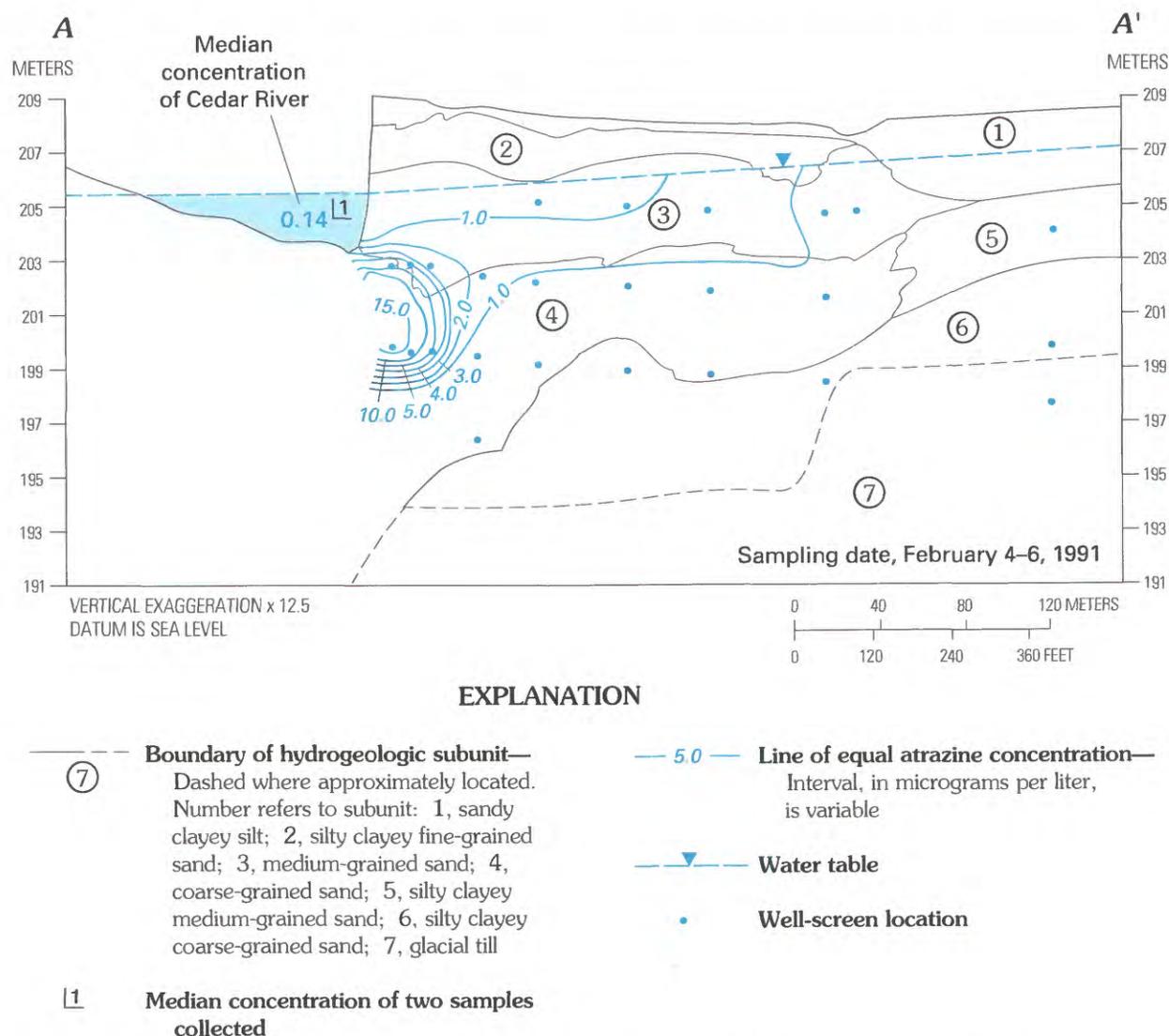


Figure 23. Distribution of atrazine in the alluvial aquifer on the basis of atrazine concentrations in ground-water samples collected at Palisades site, February 4–6, 1991.

herbicide can be either the river through bank storage and flooding or runoff from upland areas carried by ephemeral streams.

MOVEMENT OF AGRICULTURAL CHEMICALS FROM GROUND WATER TO SURFACE WATER DURING BASE-FLOW CONDITIONS

Two seepage investigations were conducted in 1989 and 1990 during base-flow conditions in the Cedar River to quantify the movement of agricultural chemicals from alluvial ground water to surface water. The period of time after the inflection point on the recession curve of a streamflow hydrograph is defined as base flow (Linsley and others, 1975). During this time, ground water is the only source of water in streams (Linsley and others, 1975), and no overland

flow is present in the river discharge. During the two seepage investigations, the discharge of agricultural chemicals was determined at four Cedar River sampling sites and at 27 tributary sampling sites along a 117-km reach of the Cedar River between Cedar Rapids and Conesville (fig. 24). The discharge of agricultural chemicals was determined by measuring the streamflow and the concentrations of agricultural chemicals. Ground-water samples were collected using the minipiezometer at a depth of less than 3 m beneath the river bottom at locations shown in figure 24. Discharge and water-quality data for the seepage investigations are given in Schulmeyer and others (1995). The tributaries that were measured have drainage areas larger than 5 km², and their cumulative drainage areas account for about 75 percent of the total drainage area between Cedar Rapids and Conesville, Iowa. The total amount of agricultural chemicals discharged from tributaries can be determined using the

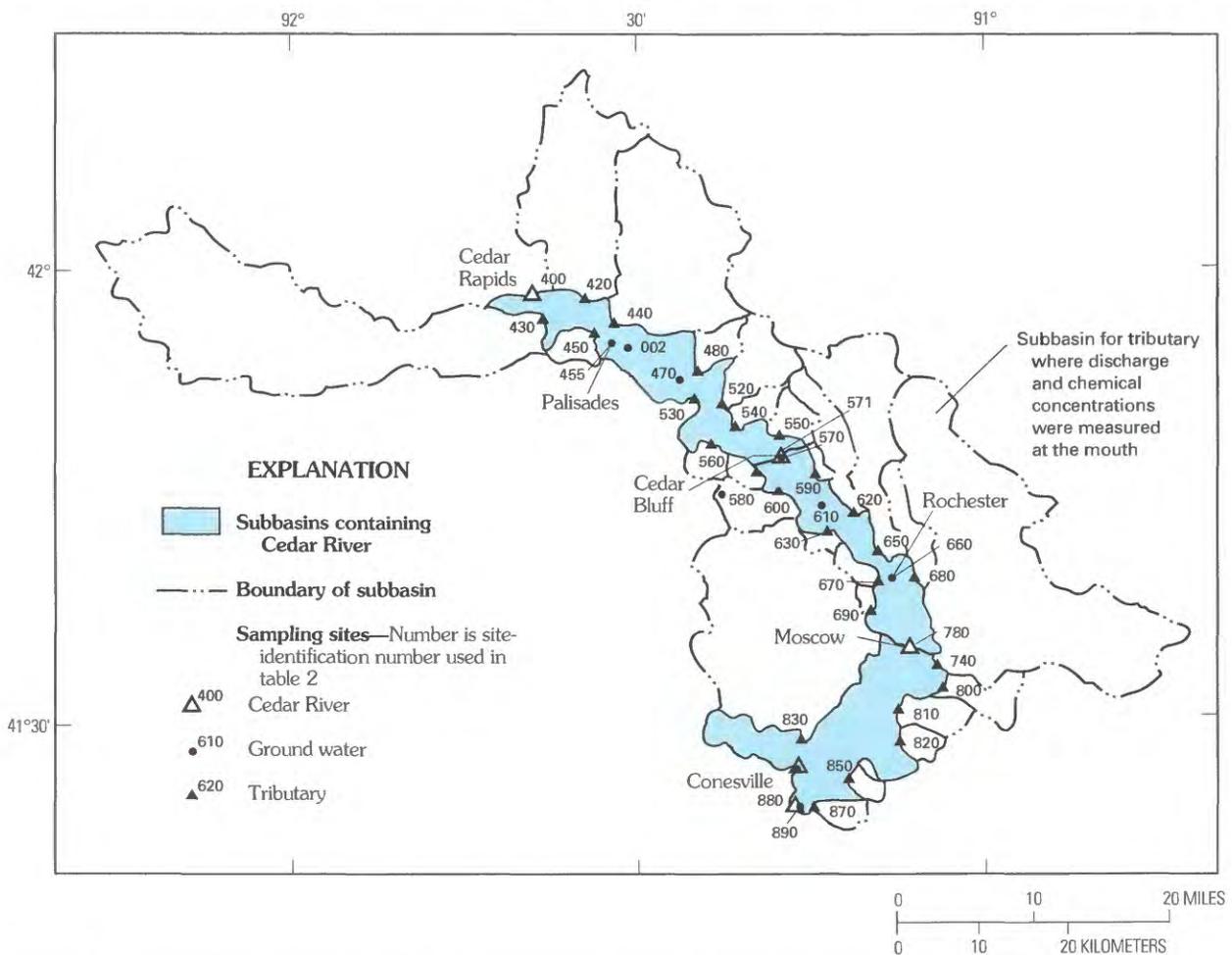


Figure 24. Drainage subbasins of the Cedar River where streamflow discharge and chemical concentrations were determined.

concentrations from the water-quality samples and the discharge measurements. Data from the Cedar River sampling sites define changes in agricultural chemical discharge along the river.

Atrazine, deethylatrazine, deisopropylatrazine, and metolachlor concentrations can be considered conservative in the time it takes to move between Cedar Rapids and Conesville in the Cedar River because the traveltime between these two sites is about 2 days and the half-life of atrazine in surface water has been reported to be more than 65 days (DeNoyelles and others, 1982). To confirm this hypothesis, the sample collected at site 400 on September 20, 1989, at 10:10 a.m. and October 31, 1990, at 9:30 a.m. was split. One-half of each sample was processed immediately, and the other half was placed in a sealed jar and returned to the river for a period of 2 days. The split sample was retrieved 2 days later and processed identically to the other sample. The split samples were dated September 20, 1989, at 10:08 a.m. and on October 31, 1990, at 10:00 a.m. For the samples collected during 1990, the concentrations of nitrate decreased in the sample that was placed in the river for 2 days; the decrease in nitrate concentration was less than 1.0 mg/L. The concentrations of atrazine, deethylatrazine, deisopropylatrazine, and metolachlor were analytically the same for all sample pairs and therefore indicate that these compounds degrade slowly in the river. According to Dr. James Sinclair (U.S. Environmental Protection Agency, oral commun., 1990), this is a standard procedure for determining degradation rates of chemicals in rivers. The results of this onsite test have been substantiated in other studies (Pereira and Rostad, 1990). Photolytic degradation of atrazine within the main-stem river channel of the Cedar River is considered insignificant; only about 1 percent of the atrazine is expected to degrade in the main-stem river as it moves between Cedar Rapids and Conesville (Goldberg and others, 1991).

Hydrologic Conditions

The seepage investigation of September 20–22, 1989 (fig. 25), was conducted during early base-flow conditions about 9 days after storm runoff had occurred. The seepage investigation of October 31 through November 2, 1990 (fig. 26), was conducted about 60 days after a major flood during extended base-flow conditions. The daily mean discharge of the Cedar River at Cedar Rapids and Conesville and the

time frame of the seepage investigations are shown in figures 25 and 26. Even though the 1990 seepage investigation was made during extended base-flow conditions, the river discharge of the Cedar River was about 2.5 times larger than the discharge measured during the 1989 seepage investigation. In 1990, the ground-water discharge from the adjacent alluvial aquifer was larger probably due to flooding and subsequent aquifer recharge that occurred about 60 days earlier and due to substantially less-than-normal rainfall in 1989.

Results of Water-Quality Analyses

The concentrations of agricultural chemicals (atrazine, deethylatrazine, deisopropylatrazine, metolachlor, and nitrate) from paired samples using EDI (equal-discharge increment from 10 vertical sections) and DI (depth integrated at a single vertical section) sampling techniques in the Cedar River were not significantly different, and therefore, the results of the chemical analysis from both methods are considered equally valid. The EDI sampling technique is a better method for sampling the river when the concentrations of chemicals in the river are not uniformly distributed throughout a cross section of the river. However, when the constituents of interest are uniformly distributed throughout the river, then the EDI and DI sampling techniques will yield similar results. When the Cedar River was sampled during the seepage investigations in 1989 and 1990, two samples generally were collected within about 1 hour of each other at the same location using the EDI and DI sampling techniques. A total of 22 sample pairs were collected during the seepage investigations of 1989 and 1990. The Wilcoxon signed-ranks test (Iman and Conover, 1983) showed that there were no significant ($p > 0.05$) differences in the concentrations of agricultural chemicals between the sample pairs.

During the 1989 and 1990 seepage investigations, the tributaries generally contributed to the dilution of atrazine, deethylatrazine, and metolachlor in the Cedar River because the median concentrations of these chemicals are larger in the Cedar River than in the tributaries (fig. 27). During the 1989 seepage investigation, this dilution was more significant because the difference in the median concentrations in the Cedar River and the tributaries was larger than during 1990. Deisopropylatrazine was not detected in the tributaries

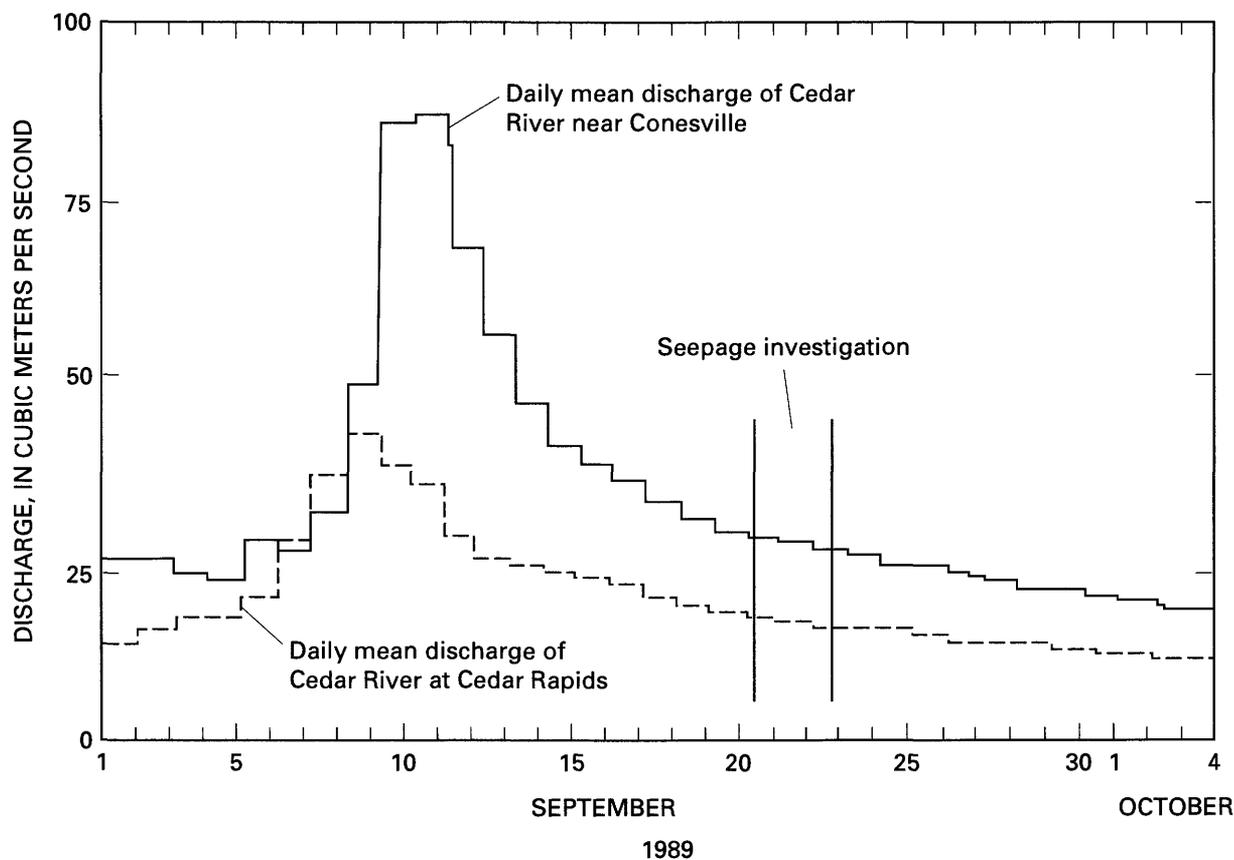


Figure 25. Relation of seepage investigation to daily mean discharge of Cedar River at Cedar Rapids (upstream) and near Conesville (downstream), September 1 through October 4, 1989.

or in the Cedar River during the 1989 seepage investigation but was detected during the 1990 seepage investigation.

The concentrations of atrazine, deethylatrazine, deisopropylatrazine, and metolachlor in ground-water samples collected using a minipiezometer beneath the riverbed were larger and more variable in 1990 than during the 1989 seepage investigation (fig. 28). Furthermore, at the Palisades site the largest concentrations of atrazine detected in a minipiezometer sample during this study were collected during the seepage investigation in October 1990 (fig. 29). A total of 37 minipiezometer samples were collected from three sites located in the Cedar River (002, 660, 890, shown in fig. 24) during the 1989 and 1990 seepage investigations. All samples were collected within 3 m beneath the river bottom, and most were collected about 1 m beneath the river bottom. Hydraulic gradients at these sites were toward the river and were determined by comparing ground-water hydraulic head with the river stage.

Water Budget Analysis

The median discharge of agricultural chemicals, with the exception of nitrate, in the Cedar River increased from the Cedar Rapids to the Conesville sampling sites during both seepage investigations. The median discharges of selected chemicals at four Cedar River sampling sites during the 1989 and 1990 seepage investigations are shown in figures 30 and 31. A statistically significant ($p < 0.05$) change in the discharge of the herbicides (according to the Mann-Whitney nonparametric test) is indicated in figures 30 and 31 when the letter designations at one sampling site do not have letters common with another site. At each of these sites, two or three discharge measurements were made, and as many as six water-quality samples were collected. The river discharge of herbicides was calculated for each water-quality sample using the most recent discharge measurement made for that site.

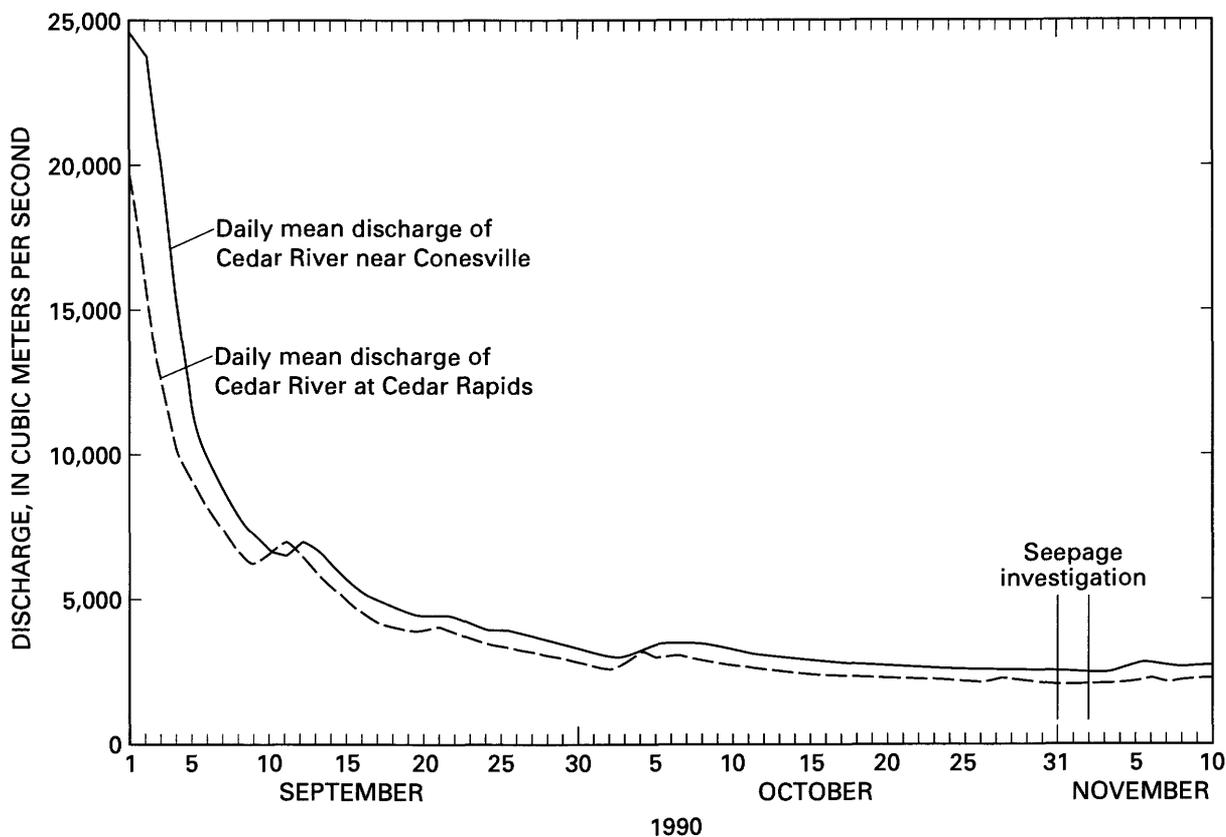


Figure 26. Relation of seepage investigation to daily mean discharge of Cedar River at Cedar Rapids and near Conesville, September 1 through November 10, 1990.

Ground-water discharge from the alluvial aquifer adjacent to the Cedar River is the principal source of atrazine, deethylatrazine, deisopropylatrazine, and metolachlor in the Cedar River during base-flow conditions. Budget calculations indicate that about 40 percent or less of the increase in atrazine, deethylatrazine, deisopropylatrazine, and metolachlor discharge measured between the Cedar Rapids and Conesville sampling sites during the 1989 and 1990 seepage investigations can be attributed to tributary input (fig. 32). The remaining 60 percent or more of the agricultural chemicals enter the Cedar River along the river channel and are shown in figure 32 by the open bars. Ground water that directly enters the Cedar River is the source of these chemicals because the discharge of these chemicals increases substantially with the ground-water discharge from the alluvial aquifer, and these chemicals were not found on the bed sediment (table 2) but were detected in the alluvial ground water adjacent to the river (figs. 7 and 28).

Discharge from field-drainage tile does not alter the budget calculations presented in this report

because this discharge is aggregated by tributary streams; field-drainage tiles commonly do not discharge directly into the Cedar River. The combined drainage area of the tributaries accounted for about 75 percent of the total drainage basin. These tributaries would aggregate all the discharge from field-drainage tiles within each subbasin, and yet these tributaries only contribute about 40 percent or less of the increased discharge of atrazine, deethylatrazine, deisopropylatrazine, and metolachlor measured between the Cedar Rapids and Conesville sampling sites. The remaining 25 percent of the basin lies primarily within the Cedar River flood plain, which contains less drainage tile than the rest of the basin because it is difficult to construct drainage-tile outlets on the flood plain (Iowa State University, 1987). Furthermore, in some cases, field-drainage tile is unnecessary because of the sandy soils (Schemerhorn and Highland, 1975; Schemerhorn, 1983; Dankert, 1989). The effect of discharge from field-drainage tile on the water quality of the tributaries may be significant but was not investigated.

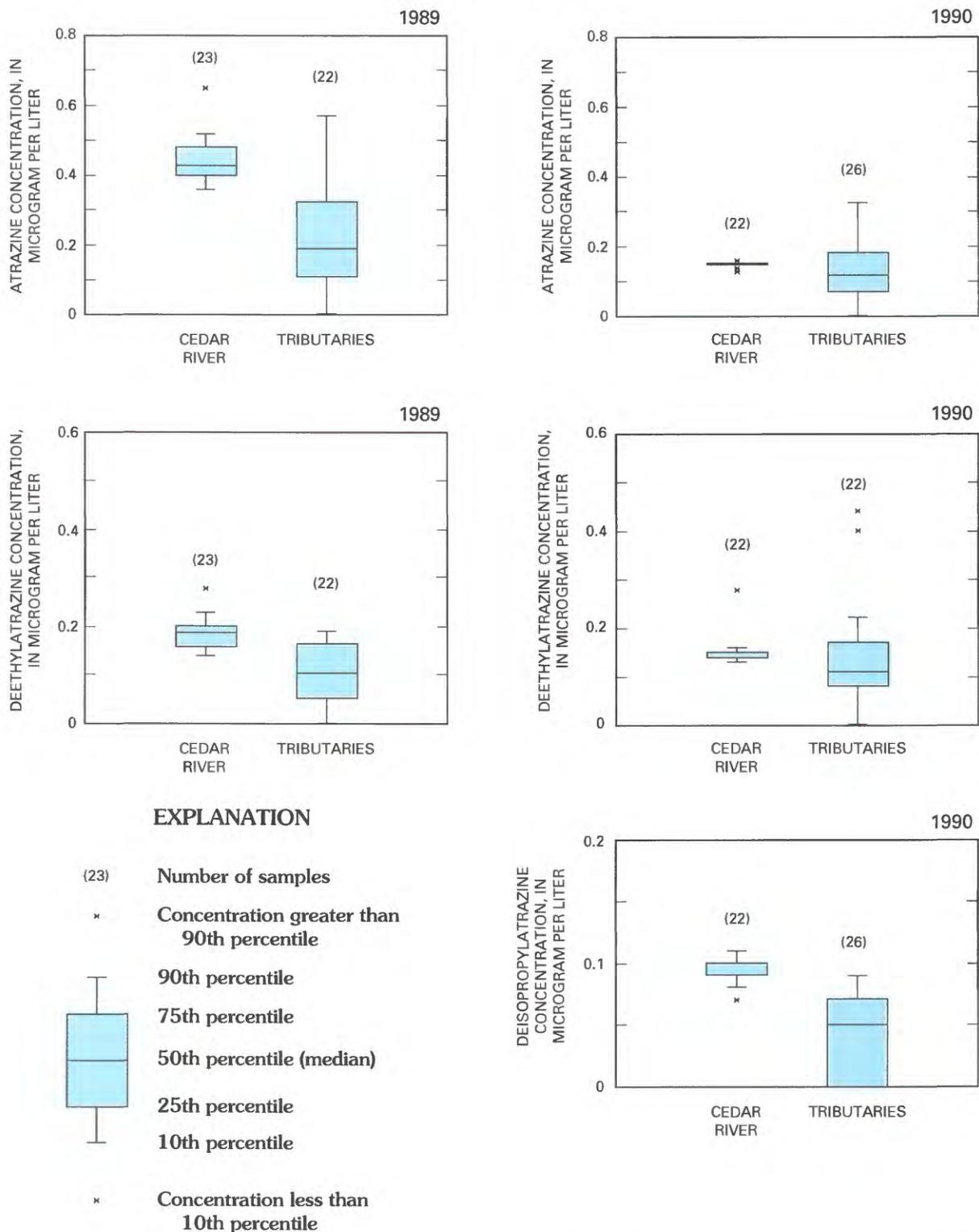


Figure 27. Statistical summary of concentrations of selected herbicides, degradation products, and nitrate in water samples collected from Cedar River and its tributaries during seepage investigations in 1989 and 1990.

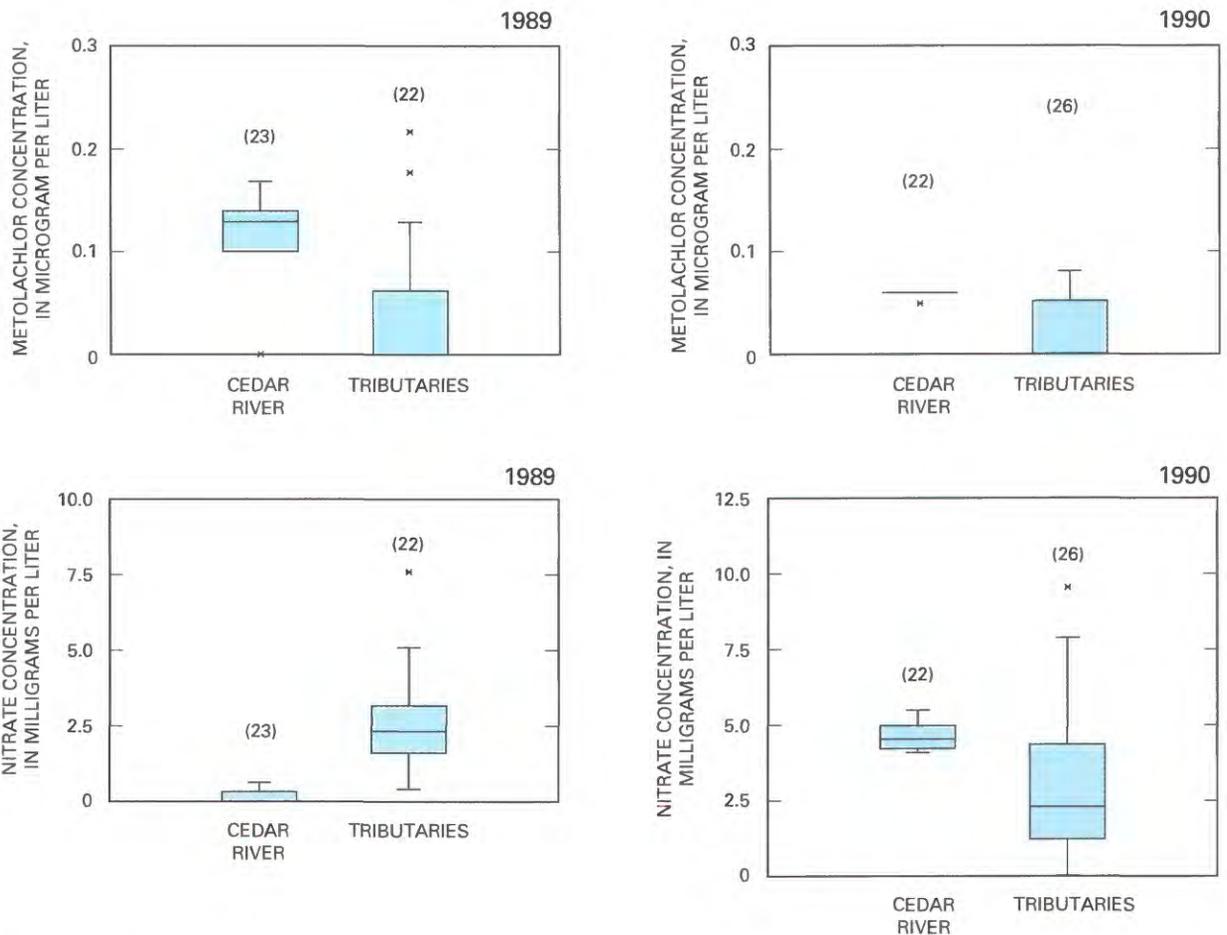


Figure 27. Statistical summary of concentrations of selected herbicides, degradation products, and nitrate in water samples collected from Cedar River and its tributaries during seepage investigations in 1989 and 1990—Continued.

Relation Between Ground Water and Surface-Water Quality

Ground water that directly enters the Cedar River from the alluvial aquifer is the primary source of atrazine, deethylatrazine, deisopropylatrazine, and metolachlor in the river during base-flow conditions. However, what is the source of these chemicals in the alluvial aquifer?

At the Palisades site, the discharge of atrazine and deethylatrazine from the alluvial aquifer to the river during base flow originated from two discernible sources. Bank storage was an important source during early base-flow conditions. The concentrations of these chemicals released from bank storage decreased rather quickly with time until bank storage was depleted. This change in concentration with time results from the unique distribution of these chemicals in the bank-storage water. This distribution for atrazine is apparent in figure 9 (March 20–22, 1990,

sampling), which shows that the concentrations decrease with distance from the river in the bank-storage water. The initial bank-storage water carried smaller concentrations than the water that last entered the alluvial aquifer. This distribution in bank-storage water was documented during other periods of runoff and would be expected because the concentrations of atrazine and deethylatrazine in the river generally increase with river discharge (Squillace and Engberg, 1988; Schulmeyer, 1991; Squillace and Thurman, 1992). However, the maximum concentrations in the river during runoff will decrease with time since the application in the spring (Wauchope, 1978; Frank and others, 1982; Glotfelty and others, 1984; Goolsby and others, 1991; Squillace and Thurman, 1992).

During extended base flow, the discharge of atrazine and deethylatrazine from the alluvial aquifer at the Palisades site continues, but these chemicals originate from ground-water recharge from areas distant from the river. Bank storage occurs within a small vol-

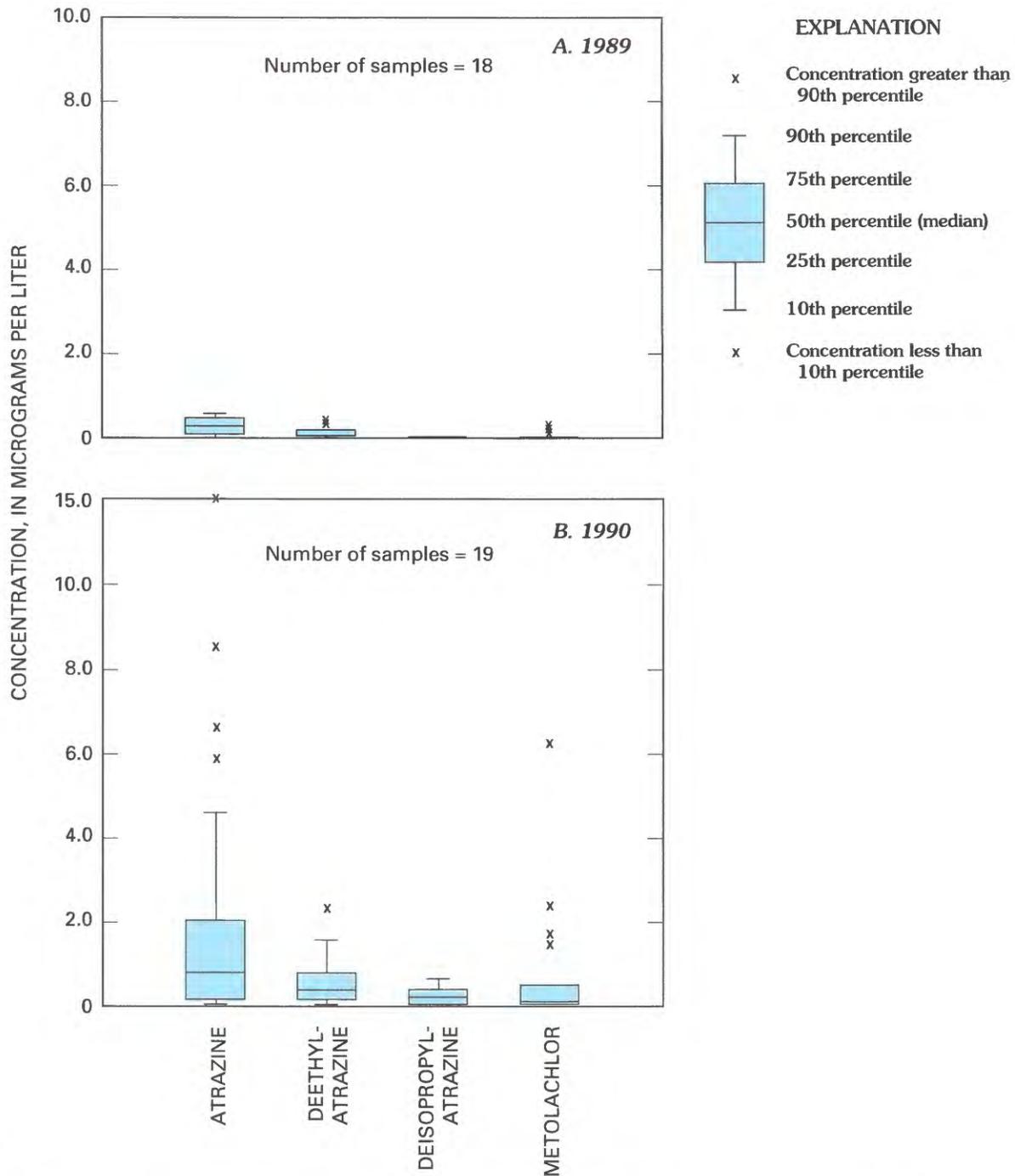


Figure 28. Statistical summary of concentrations of atrazine, deethylatrazine, deisopropylatrazine, and metolachlor in ground-water samples collected with a minipiezometer beneath the riverbed of the Cedar River in (A) 1989 and (B) 1990 at locations 002, 660, and 890 (fig. 24).

ume of the alluvial aquifer, and consequently there is a limited supply of bank-storage water. The concentrations of agricultural chemicals at the Palisades site generally were more uniform in the aquifer after the depletion of bank-storage water (fig. 9) and, therefore, will provide a more stable source of pesticides to the

river during extended base flow when compared to bank-storage water.

In the river, the change in concentrations of atrazine and deethylatrazine through time also seems to indicate a change in the source of these chemicals from early to extended base-flow conditions and may

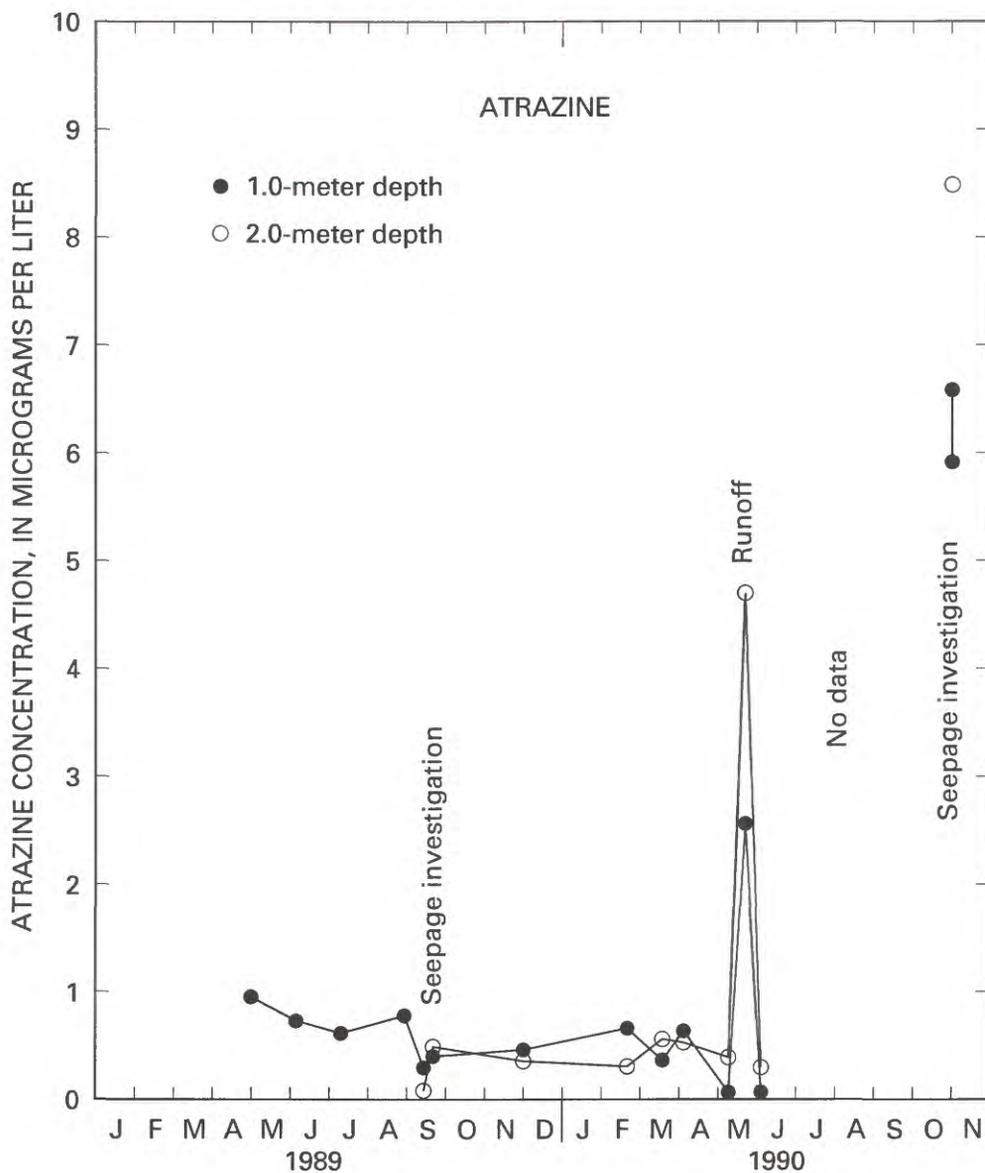


Figure 29. Atrazine concentrations in ground-water samples collected at Palisades site at a depth of 1.0 and 2.0 meters beneath riverbed, April 1989 through October 1990.

correlate with the two sources at the Palisades site. During early base-flow conditions, the concentrations of these chemicals in the river are larger and decrease with time. During extended base-flow conditions more stable, but smaller concentrations are present in the river. For example, between September 20–22 and September 28, 1989, the mean concentration of atrazine decreased from 0.44 to 0.25 µg/L, or 0.03 µg/L per day (Schulmeyer and others, 1995). The source of the chemicals in the ground-water discharge to the river was probably bank storage. Between September 28 and October 2 the mean concentration

of atrazine decreased slightly from 0.25 to 0.22 µg/L, or about 0.01 µg/L per day. At this time, the source of the herbicides in the ground-water discharge to the river entered the alluvial aquifer with ground-water recharge at some distance from the river and was not bank-storage water. The persistence of these chemicals in the river during extended base-flow conditions was verified in October 1990. On October 15, the river had been in base-flow conditions for about 1 month, and the median concentrations of atrazine and deethylatrazine were both 0.15 µg/L. On October 31, 16 days later, the river discharge and the median concentra-

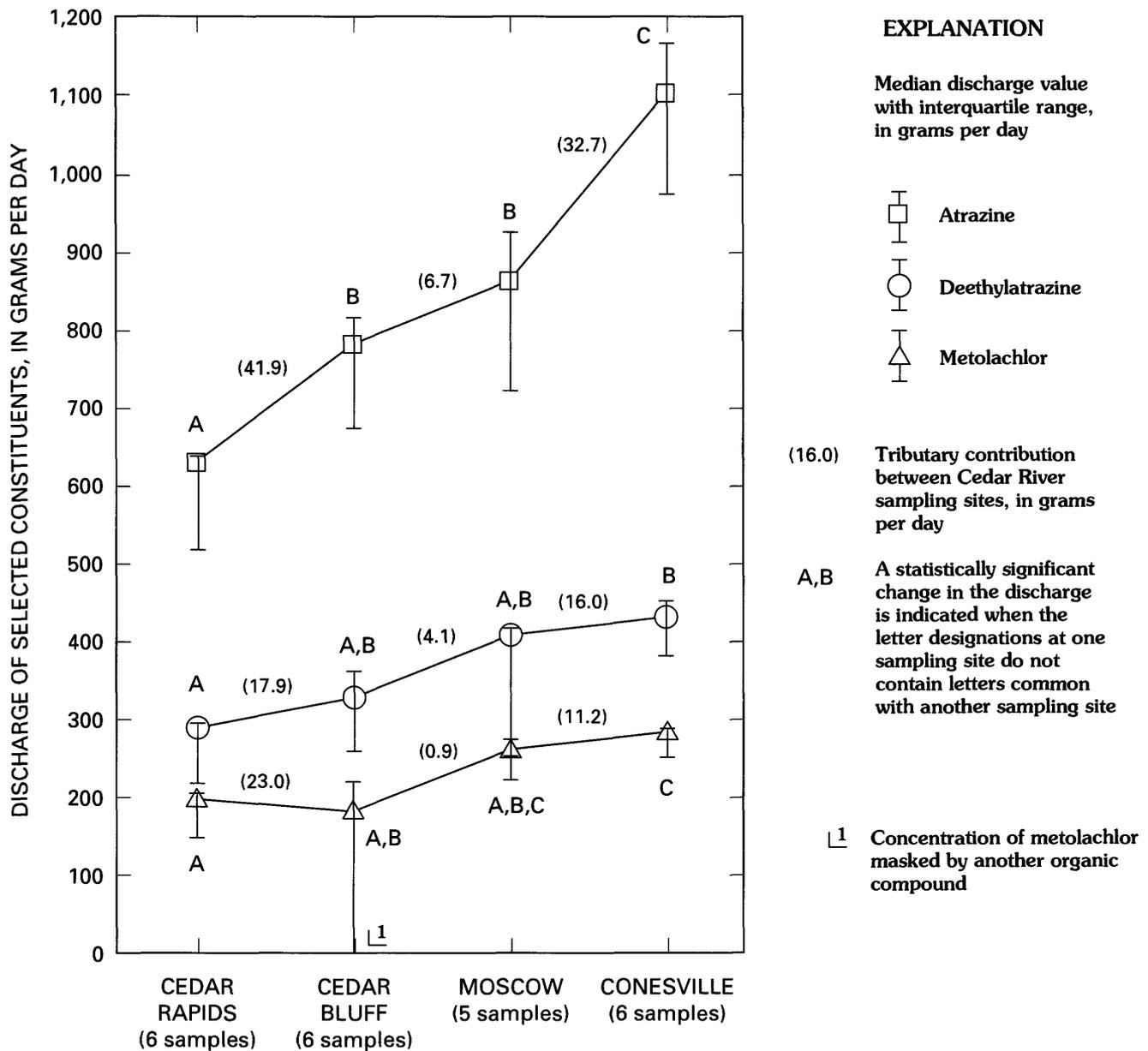


Figure 30. Statistical summary of discharge of atrazine, deethylatrazine, and metolachlor at four sampling sites on the Cedar River, September 20–22, 1989.

tions of atrazine and deethylatrazine were essentially unchanged.

Therefore, the river data indicate that bank storage was the primary source of agricultural chemicals in the ground-water discharge to the Cedar River during the 1989 seepage investigation, whereas during the 1990 seepage investigation, the chemicals entered the aquifer by other pathways (recharge from the upland areas, tributary streams, herbicide application to the land surface, flooding of the Cedar River, and possibly others).

Agricultural chemicals that were identified as originating from the alluvial aquifer (atrazine, deethylatrazine, deisopropylatrazine, and metolachlor) were detected in ground water using a minipiezometer

within a few meters beneath the riverbeds; however, the concentrations in this ground water can vary considerably (fig. 28), even during a single seepage investigation. A direct comparison of the concentrations in the ground water with the concentrations in surface water is not possible because of the variation in the concentrations and the small data set. For example, figure 28 shows a statistical summary of the concentrations of atrazine, deethylatrazine, deisopropylatrazine, and metolachlor in ground-water samples collected during the 1989 and 1990 seepage investigations at sampling sites 002, 660, and 890 (fig. 24). During the 1990 seepage investigation, seven additional ground-water samples were collected from four additional sites. When these additional sample con-

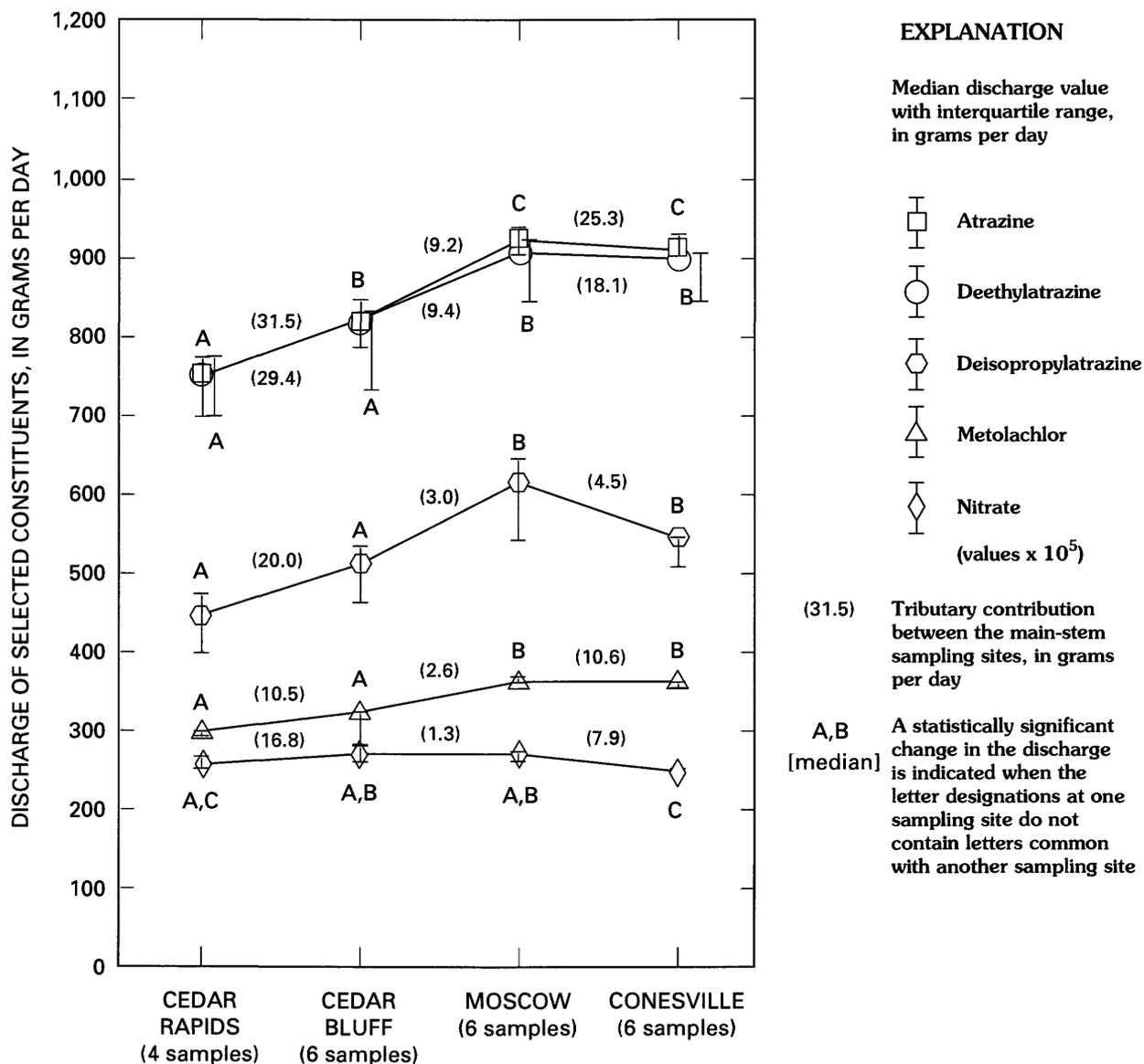


Figure 31. Statistical summary of discharge of atrazine, deethylatrazine, deisopropylatrazine, metolachlor, and nitrate at four sampling sites on the Cedar River, October 31 through November 2, 1990.

concentrations are included in the data set, the median concentrations of atrazine during the 1990 seepage investigation decrease by 0.35 $\mu\text{g/L}$ (from 0.73 to 0.38 $\mu\text{g/L}$).

Flooding and overland runoff that occurred prior to the 1990 seepage investigation probably introduced the large concentrations of agricultural chemicals detected in ground-water samples collected with the minipiezometer at three sampling sites (fig. 28). Figure 29 shows that the concentrations of atrazine substantially increased twice between May 1989 and November 1990 at the Palisades site. The concentrations peaked in May 1990 during runoff and can be explained by bank storage. However the largest

concentrations were detected during extended base-flow conditions at the time of the 1990 seepage investigation, October to November 1990.

SUMMARY AND CONCLUSIONS

The agricultural chemicals alachlor, atrazine, cyanazine, deethylatrazine, deisopropylatrazine, and metolachlor move between ground water and surface water in the alluvial aquifer and in the Cedar River Basin, Iowa. Nitrate generally was absent in the alluvial aquifer during the study period (May 1989 through July 1991), probably due to denitrification,

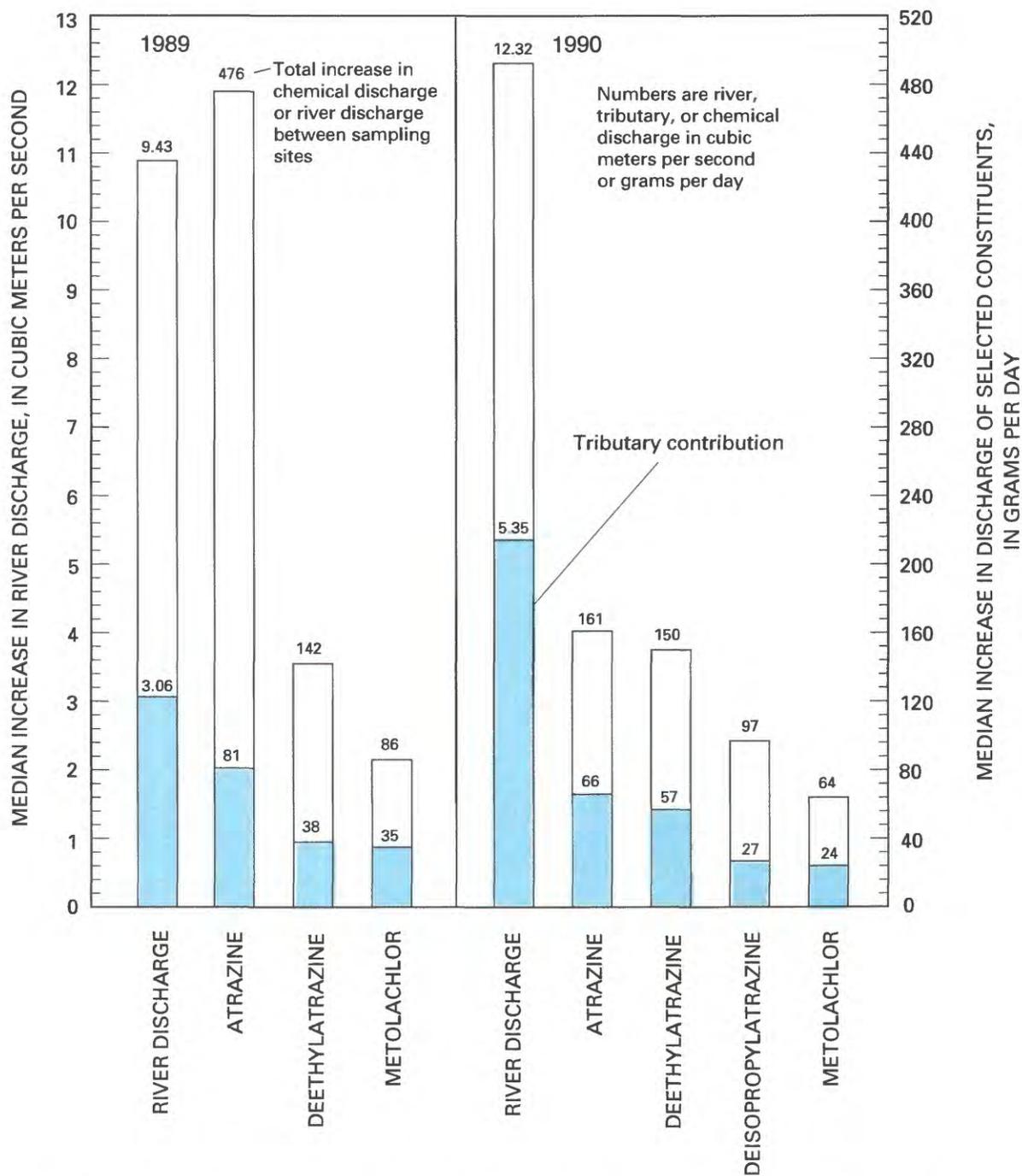


Figure 32. Increase in median river discharge and statistically significant increases in the median discharge of atrazine, deethylatrazine, deisopropylatrazine, and metolachlor measured between Cedar Rapids and Conesville, Iowa, 1989 and 1990.

except in shallow zones of the aquifer where dissolved oxygen also is present. The movement of nitrate between the surface-water and ground-water environments with bank-storage water and with recharge from flooding was minor when compared to other agricultural chemicals.

Ground-water discharge from the alluvial aquifer adjacent to the Cedar River was the principal source of alachlor, atrazine, cyanazine, deethylatrazine, deisopropylatrazine, and metolachlor in the river during base-flow conditions. This discharge exceeded the

combined tributary discharge along a 117-km reach of the Cedar River during two seepage investigations.

Bank storage is probably an important source of the agricultural chemicals in the ground-water discharge from the alluvial aquifer but becomes depleted with time after surface runoff. The largest concentrations of these chemicals in bank-storage water during 1990 at the Palisades site (about 10 km southeast of Cedar Rapids, Iowa) were: alachlor, 2.1 µg/L; atrazine, 4.7 µg/L; cyanazine, 3.2 µg/L; deethylatrazine, 0.54 µg/L; deisopropylatrazine, 0.33 µg/L; and metolachlor, 2.2 µg/L. A ground-water flow model of conditions during runoff between March and April 1990 showed that bank-storage water moving through the river bottom accounted for 70 percent of the total bank-storage water, while the remaining 30 percent moved through the riverbank. Ground-water flow through the river bottom decreased substantially with distance from the riverbank toward the center of the river. Herbicides such as alachlor, cyanazine, and metolachlor were undetectable in ground water during base-flow conditions. Any detection of them in ground water at the Palisades site would be a strong indication of a new episode of river-water intrusion into the aquifer. The intrusion of river water can originate from bank storage or from flooding of the Cedar River or ephemeral streams.

During the high-flow period of March 20–22, 1990, the concentrations of alachlor, atrazine, and metolachlor were largest at the 6-m depth and were detected at 20, 50, and 10 m from the river, respectively. During the high-flow period of May 1990, herbicide bank storage was evident at 20, 50, 10, and 20 m for alachlor, atrazine, cyanazine, and metolachlor, respectively; the principal pathway of herbicide movement was between 3 and 6 m below land surface. It is possible that all these constituents moved 50 m or more from the river during these two high flows, but the smaller concentrations in the river and laboratory detection levels preclude identification of all constituents throughout the bank-storage water.

During periods of extended base flow, chemicals that were discharged from the alluvial aquifer probably entered the aquifer with ground-water recharge at some distance from the river. Flooding at the Palisades site was one important pathway by which agricultural chemicals entered the alluvial aquifer with ground-water recharge. The concentrations at one observation well after flooding were: alachlor, 0.06 µg/L; atrazine, 18 µg/L; cyanazine, 1.3 µg/L; deethylatrazine,

1.4 µg/L; deisopropylatrazine, 0.40 µg/L; and metolachlor, 7.0 µg/L.

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