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**WATER-QUALITY MONITORING AND EVALUATION
OF NONPOINT-SOURCE CONTAMINATION
IN THE BIG SIOUX AQUIFER, SOUTH DAKOTA, 1993**

by

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INTRODUCTION

In 1989, a water quality monitoring program was initiated in the Big Sioux aquifer. The objective of this program was to establish a ground water monitoring network in the Big Sioux aquifer and systematically sample this network, over a period of years, to identify changes in the water quality of the aquifer. A ground water monitoring network has been established and consists of 28 monitoring wells installed at 11 locations throughout the Big Sioux aquifer. The network wells are not located downgradient from any identifiable point source pollution areas and provide for monitoring over much of the aquifer's extent. Network monitoring wells are nested at each site to monitor the water quality vertically within the aquifer. Ground-water samples have been regularly collected and analyzed for organic and inorganic constituents, including nitrate-nitrogen plus nitrite-nitrogen, ammonia-nitrogen, total phosphorus, and selected pesticides. An earlier report (Hammond, 1994) outlines the physical installation of the ground water monitoring network and water-quality results from 1989 through 1992.

Due to record and near-record precipitation received throughout the Big Sioux River drainage basin during the spring and summer of 1993, the Big Sioux River climbed above flood stage and major flooding occurred in many locations. In late May, the Big Sioux River went above flood stage and remained in flood through mid-June (U.S. Department of Commerce, 1994). Every county in the Big Sioux River drainage basin was declared a disaster area as much of the flood water inundated prime agricultural land. Because the Big Sioux aquifer and the Big Sioux River are hydraulically connected, and because of the surficial and unconfined nature of the Big Sioux aquifer, it was extremely important to collect samples from the ground water monitoring network in order to assess the impact of flooding on ground-water quality during 1993.

Acknowledgments

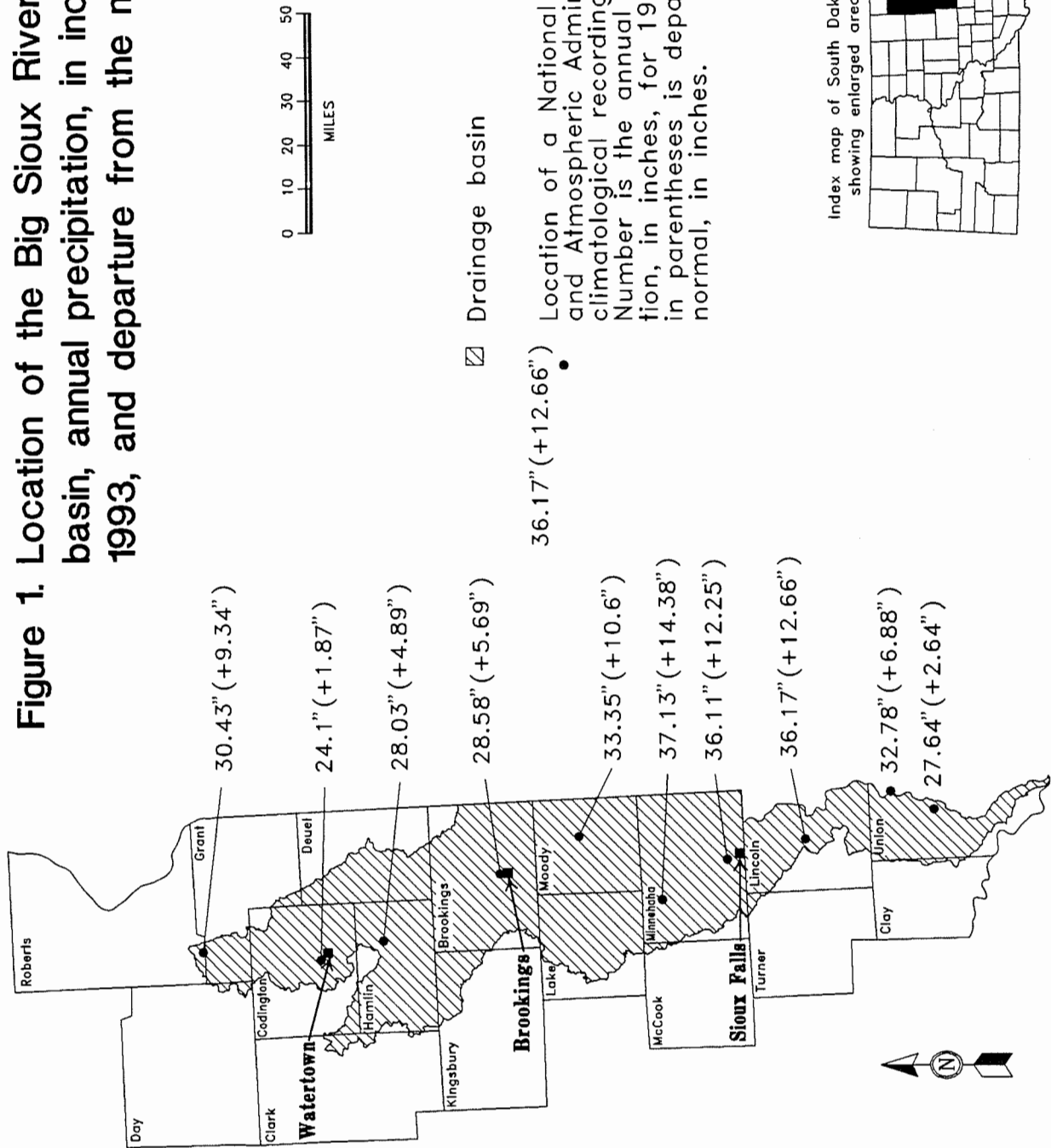
Funding for pesticide analyses during the 1993 sampling period was provided by the South Dakota Department of Agriculture (SDDA), Division of Regulatory Services. The pesticides selected for analysis and the sampling schedule were determined cooperatively by the SDDA and the South Dakota Geological Survey (SDGS), a program within the South Dakota Department of Environment and Natural Resources. The assistance and cooperation of the SDDA were important factors in the success of this project.

Background

The Big Sioux River drainage basin in eastern South Dakota is 6,154 square miles in area (Amundson and others, 1985). The drainage basin extends from Roberts County in the northeast portion of the state to Union County in the southeast corner of the state (fig. 1).

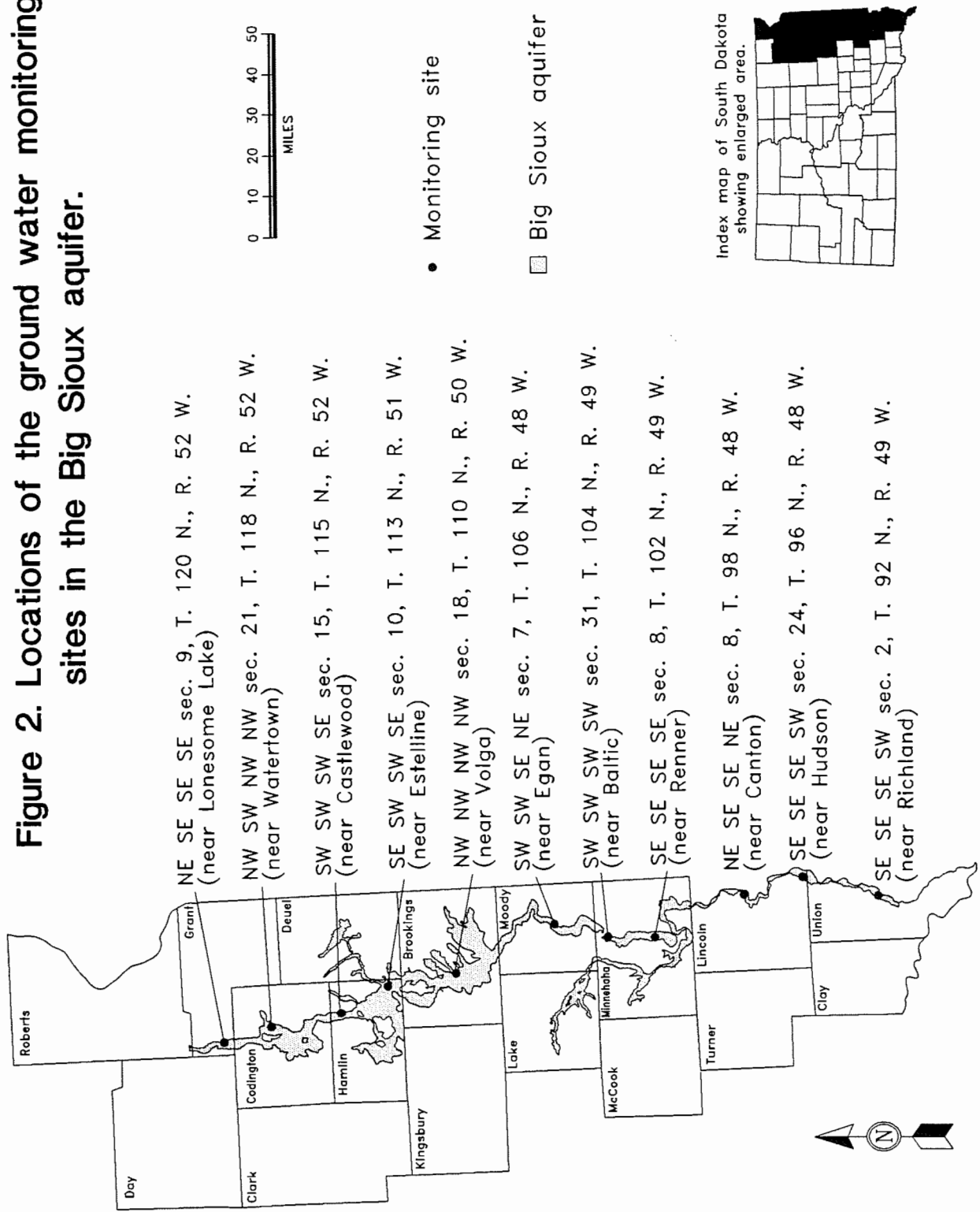
The Big Sioux aquifer (fig. 2) is primarily an unconfined, surficial aquifer composed of sand and gravel (outwash) which underlies approximately 1,300 square miles of the Big Sioux River drainage basin. The Big Sioux aquifer underlies portions of 12 counties and provides approximately one-third of the state's population with water for various uses including municipal, rural-water systems, and irrigation (South Dakota Department of Water and Natural Resources, undated). Because of the surficial nature of the Big Sioux aquifer, it is especially vulnerable to contamination.

Figure 1. Location of the Big Sioux River drainage basin, annual precipitation, in inches, for 1993, and departure from the normal.



Index map of South Dakota showing enlarged area.

Figure 2. Locations of the ground water monitoring sites in the Big Sioux aquifer.



Agriculture is the primary land use in the Big Sioux River drainage basin. Corn, soybeans, and small grains are the major crops. Livestock consist of dairy cattle, beef cattle, and hogs. Feed lots and livestock-holding areas are common throughout the basin. Farmsteads have private wells or utilize rural water distribution systems. Septic systems are quite common in the basin. Also in the Big Sioux River drainage basin are three of South Dakota's largest urban areas: Sioux Falls, Brookings, and Watertown.

Due to the aquifer's vulnerability and growing public concerns about the quality and long-term suitability of water for drinking-water supplies, a ground water monitoring network was established in 1989 to monitor the water quality in the Big Sioux aquifer. Ground water monitoring network installation and water-quality data from 1989 through 1992 are published in a report entitled *Water-quality monitoring and evaluation of nonpoint-source contamination in the Big Sioux aquifer, South Dakota, 1989 through 1992* (Hammond, 1994).

For this report, nitrate-nitrogen plus nitrite-nitrogen will be referred to simply as nitrate. Ammonia-nitrogen will be referred to simply as ammonia.

METHODS AND PROCEDURES

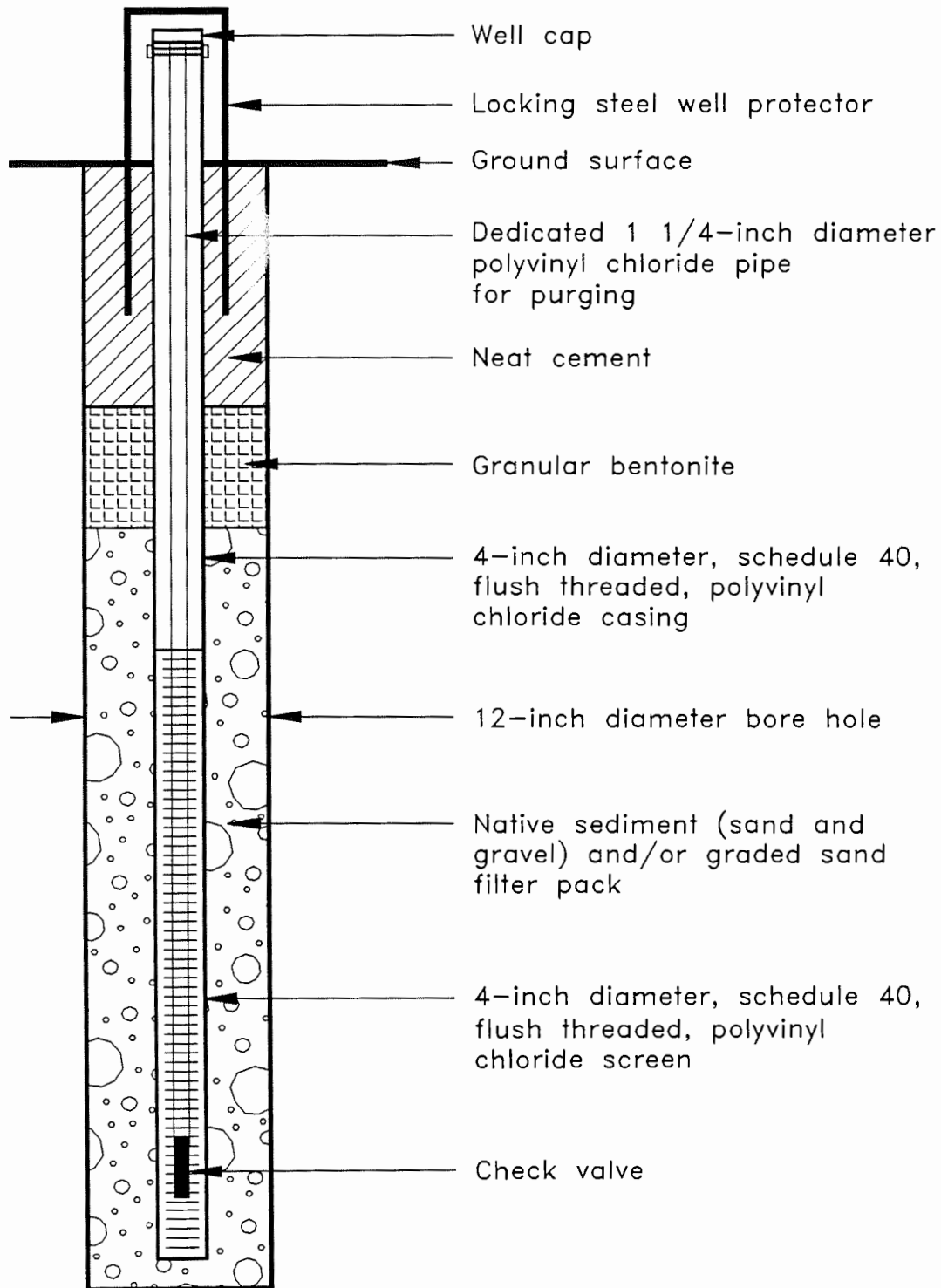
Drilling and Monitoring Well Installation

In addition to the monitoring wells installed in 1989, one monitoring well (well identifier R20-93-30) was drilled for this program during 1993 (app. A). Drilling occurred on July 6, 1993, and was performed using the hollowstem auger drilling method. The monitoring well was constructed using 4-inch diameter, schedule 40, flush threaded, polyvinyl chloride (PVC) casing and screen. The well was added to an existing monitoring site near Lonesome Lake, Grant County, to help examine nitrate concentrations near the water table. Data on the screen length, well depth, and well construction are presented in appendix A. Figure 3 presents a generalized diagram of well construction. Appendix A also contains monitoring well construction diagrams and hydrostratigraphic cross sections for all other ground water monitoring network wells located in the Big Sioux aquifer. The lithologic logs for all the ground water monitoring wells are on file at the SDGS. See Hammond (1994) for a detailed discussion on drilling and monitoring well installation.

Monitoring Well Development

Monitoring well R20-93-30 was developed using a jet pump attached to a dedicated 1¼-inch diameter PVC pipe with a check valve attached to the bottom of the pipe (fig. 3). Fifty well volumes of water were removed from the well during development. Temperature and conductivity of water removed from the well stabilized after 3 consecutive 15-minute readings.

Figure 3. Generalized diagram showing well construction.



Water Sampling

Ground Water

During each sampling event, all but two monitoring wells were purged by pumping with a jet pump attached to a dedicated 1¼-inch diameter PVC pipe with a check valve attached to the bottom. Two shallow monitoring wells (R20-89-38, near Lonesome Lake, Grant County, and R20-89-44, near Castlewood, Hamlin County) were purged using a laboratory cleaned Teflon bailer because there was not enough water in the wells, and the wells could not recharge quickly enough to sustain the jet pump. Before a sample was collected, (1) a minimum of 3 well volumes of water was evacuated from each well and (2) the parameters of pH, temperature, and conductivity must have stabilized for 3 consecutive 15-minute readings.

For organic water quality analyses, each water sample was collected using a laboratory cleaned Teflon bailer attached to a stainless-steel wire and a down-rigger assembly. Latex gloves were worn during sample collection. For inorganic water quality analyses, each water sample was collected from a hose attached to the jet pump. Field measurements, sample preparation, and sample handling followed SDGS protocol (Coker and others, 1988).

All 11 monitoring sites in the Big Sioux aquifer ground water monitoring network (fig. 2, table 1) were sampled. Monitoring well R20-93-30 near Lonesome Lake, Grant County, was installed during July 1993, and was sampled for the first time during August 1993. For this report, general geographic location or monitoring-well name will be used for identification purposes rather than legal locations (table 1).

Surface Water

In an attempt to try to understand elevated nitrate concentrations in ground water at the monitoring site near Lonesome Lake, Grant County, the Big Sioux River was sampled near this monitoring site. See table 2 for the legal location.

Because of the good hydraulic connection between the Big Sioux aquifer and the Big Sioux River, the river was sampled at the ground water monitoring site near Egan, Moody County, in the middle portion of the drainage basin. The Big Sioux River was sampled at this location because (1) the river is easily accessed and (2) pesticides were consistently detected in water collected from the monitoring wells at this location (Hammond, 1994). During late June 1993, after 9½ inches of rain fell in this area, the Big Sioux River rose to just above flood stage. The monitoring wells at this location remained accessible but the river had risen 8 feet and flood water was beginning to encroach upon the monitoring wells.

In addition to the planned surface water sampling just described, major flooding along the southern portion of the Big Sioux River during June 1993 caused the ground water monitoring site near Canton, Lincoln County, to become completely inaccessible. Also, during May, June, and July, major flooding caused the ground water monitoring site near Richland, Union County, to become completely inaccessible. When a ground water monitoring site was inaccessible, surface-water samples were collected near the flooded monitoring site. The number of surface-water samples collected near a flooded ground water monitoring site equaled the number of monitoring wells located at that site.

Table 1. Legal locations of monitoring network wells, well name, and relative depth of well within the Big Sioux aquifer.

Legal Location/Geographic Location	Well Name	Relative depth of well within the aquifer
NE SE SE SE sec. 9, T. 120 N., R. 52 W. (near Lonesome Lake, Grant County)	R20-89-38 R20-93-30 R20-89-37 R20-89-39	shallow shallow intermediate deep
NW SW NW NW sec. 21, T. 118 N., R. 52 W. (near Watertown, Codington County)	R20-89-42 R20-89-40 R20-89-41	shallow intermediate deep
SW SW SW SE sec. 15, T. 115 N., R. 52 W. (near Castlewood, Hamlin County)	R20-89-44 R20-89-43	shallow deep
SE SW SW SE sec. 10, T. 113 N., R. 51 W. (near Estelline, Hamlin County)	R20-89-46 R20-89-45	shallow deep
NW NW NW NW sec. 18, T. 110 N., R. 50 W. (near Volga, Brookings County)	R20-89-48 R20-89-47	shallow deep
SW SW SE NE sec. 7, T. 106 N., R. 48 W. (near Egan, Moody County)	R20-89-50 R20-89-49	shallow deep
SW SW SW SW sec. 31, T. 104 N., R. 49 W. (near Baltic, Minnehaha County)	R20-89-64 R20-89-63 R20-89-62	shallow intermediate deep
SE SE SE SE sec. 8, T. 102 N., R. 49 W. (near Renner, Minnehaha County)	R20-89-55 R20-89-54	shallow deep
NE SE SE NE sec. 8, T. 98 N., R. 48 W. (near Canton, Lincoln County)	R20-89-57 R20-89-56	shallow deep
SE SE SE SW sec. 24, T. 96 N., R. 48 W. (near Hudson, Lincoln County)	R20-89-60 R20-89-59 R20-89-58	shallow intermediate deep
SE SE SE SW sec. 2, T. 92 N., R. 49 W. (near Richland, Union County)	R20-89-65 R20-89-67 R20-89-66	shallow intermediate deep

Table 2. Legal locations of Big Sioux River sampling sites.

Legal Location	Big Sioux River sampling site
SW SE SE SE sec. 8, T. 120 N., R. 52 W.	near Lonesome Lake, Grant County
SW SW SE NE sec. 7, T. 106 N., R. 48 W.	near Egan, Moody County
NE SE SE NE sec. 8, T. 98 N., R. 48 W.	next to R20-89-56 and R20-89-57 near Canton, Lincoln County
NW NW SW SW sec. 16, T. 98 N., R. 48 W.	east of Canton, Lincoln County
NE SW SW SW sec. 36, T. 93 N., R. 49 W.	near Akron, Iowa
SE SE SW SW sec. 30, T. 93 N., R. 48 W.	upstream from Akron, Iowa
SE SW NW NE sec. 28, T. 92 N., R. 49 W.	near Richland, Union County

For example, if there were two nested wells at a flooded ground water monitoring site, then two surface water samples were collected. See table 2 for legal locations of surface water sampling points.

Surface-water samples, during 1993, were collected from the Big Sioux River at the northern reaches of the drainage basin, near the center of the basin, and in the southern portion of the basin. The surface-water samples were collected by cautiously wading out into the river and allowing the flow of the river to fill the filter barrel or the sample bottles, or by lowering a Teflon bailer over the side of a bridge and transferring the sample into either the filter barrel or the sample bottles.

Sampling Frequency and Sample Analysis

Ground Water

INORGANIC PARAMETERS

The entire ground water monitoring network was sampled four times during 1993 for inorganic analysis: May, June, July, and August. One site, near Richland, Union County, was flooded three of the four sampling events (May, June, and July sampling events), and one site, near Canton, Lincoln County, was flooded during the June sampling event. When a ground water monitoring site was inaccessible due to flood water, surface-water samples were collected in the vicinity of the monitoring site.

Ground-water samples from all four sampling events were analyzed for nitrate, ammonia, and total phosphorus. A complete analysis for major cations and anions was performed in July. To more

closely examine fluctuations in nitrate concentrations over time, seven monitoring wells were sampled monthly for nitrate analysis from January through December. The monitoring well installed in July 1993 (R20-93-30), near Lonesome Lake, Grant County, was sampled monthly from August through December.

The SDGS Basic and Analytical Studies Laboratory performed the analyses for major cations and anions. Parameters that were determined are: total alkalinity, phenolphthalein alkalinity, ammonia, bicarbonate, carbonate, calcium, chloride, conductivity, fluoride, iron, hardness, magnesium, manganese, nitrate, pH, potassium, sodium, total dissolved solids, total phosphorus, and sulfate.

PESTICIDES

The ground water monitoring network was sampled four times for pesticide analysis: May, June, July, and August 1993. The newly installed monitoring well, R20-93-30, near Lonesome Lake, Grant County, was not sampled for pesticide analysis due to monetary constraints. One site, near Richland, Union County, was flooded three of the four sampling events (May, June, and July sampling events), and one site, near Canton, Lincoln County, was flooded during the June sampling event. When a ground water monitoring site was inaccessible due to flood water, surface-water samples were collected in the vicinity of the monitoring site.

All ground-water samples were analyzed for the same pesticides as the surface-water samples, thus allowing a direct comparison of ground-water and surface-water quality. Table 3 contains a list of the pesticides that were analyzed using the gas chromatography/mass spectrometry method of analysis. Pesticide analyses using the gas chromatography/mass spectrometry method were performed on all samples by the University of Iowa Hygienic Laboratory at Iowa City, Iowa.

In analyzing water collected from the Big Sioux aquifer, the SDGS used immunoassay test kits for atrazine, alachlor, and 2,4-D analyses. The immunoassay test kits were used as a quantitative procedure for detection of a single pesticide in water. The atrazine and alachlor kits have a detection limit of 0.1 micrograms per liter ($\mu\text{g/L}$). The 2,4-D kit has a detection limit of 1 $\mu\text{g/L}$. The immunoassay method of analysis was performed by the SDGS.

Surface Water

INORGANIC PARAMETERS

In an attempt to try to understand the elevated nitrate concentrations in ground water at the ground water monitoring site near Lonesome Lake, Grant County, the Big Sioux River near the ground water monitoring site was sampled four times for inorganic analysis: May, June, July, and August. Because of the good hydraulic connection between the Big Sioux aquifer and the Big Sioux River, the river was sampled at the ground water monitoring site near Egan, Moody County. At this location, the river was sampled four times for inorganic analysis: May, June, July, and August. Where flood water made access to some ground water monitoring sites impossible, the Big Sioux River was sampled instead. The Big Sioux River near Canton, Lincoln County, was sampled during June and the Big Sioux River near Richland, Union County, was sampled during May, June, and July. The

Table 3. Pesticides analyzed in water samples.

Common Name	Trade Name	U.S. Environmental Protection Agency Maximum Contaminant Level¹	U.S. Environmental Protection Agency Lifetime Health Advisory²
alachlor	Lasso	2	--
atrazine	AAtrex	3	--
bentazon	Basagran	--	20
butylate	Sutan	--	350
carbofuran	Furadan	40	--
chlorpyrifos	Lorsban	--	20
cyanazine	Bladex	--	1
2,4-D	2,4-D	70	--
dicamba	Banvel	--	200
EPTC	Eradicane	--	--
ethoprop	Mocap	--	--
fonofos	Dyfonate	--	10
MCPA	MCPA	--	10
metolachlor	Dual	--	100
metribuzin	Sencor	--	200
pendimethalin	Prowl	--	--
phorate	Thimet	--	--
picloram	Tordon	500	--
terbufos	Counter	--	0.9
2,4,5-TP	Silvex	50	--
trifluralin	Treflan	--	5

¹ Maximum contaminant level (MCL) is presented in micrograms per liter.

² Lifetime health advisory (HA) is presented in micrograms per liter.

The symbol "--" indicates that an MCL or HA is not established for this pesticide.

number of surface-water samples collected near the flooded ground water monitoring site equaled the number of nested monitoring wells located at each site.

During the May, June, and August sampling events, the Big Sioux River was analyzed for nitrate, ammonia, and total phosphorus only. A complete analysis for major cations and anions was performed in July. The SDGS Basic and Analytical Studies Laboratory performed the analyses for major cations and anions. Parameters that were determined are: total alkalinity, phenolphthalein alkalinity, ammonia, bicarbonate, carbonate, calcium, chloride, conductivity, fluoride, iron, hardness, magnesium, manganese, nitrate, pH, potassium, sodium, total dissolved solids, total phosphorus, and sulfate.

PESTICIDES

With one exception, the gas chromatography/mass spectrometry method of analysis and the immunoassay method of analysis were performed on all the river samples collected during all four sampling events. Due to monetary constraints, the Big Sioux River near Lonesome Lake, Grant County, was analyzed using only the immunoassay method of analysis. The Big Sioux River near Egan, Moody County, was sampled four times for pesticide analysis: May, June, July, and August 1993. Because flood waters made access to some ground water monitoring sites impossible, the Big Sioux River near Canton, Lincoln County, was sampled during June and the river near Richland, Union County, was sampled during May, June, and July. Using the gas chromatography/mass spectrometry method of analysis, all river samples were analyzed for the same pesticides (table 3) as the ground-water samples, thus allowing a direct comparison of surface-water and ground-water quality. Pesticide analyses using the gas chromatography/mass spectrometry method were performed by the University of Iowa Hygienic Laboratory at Iowa City, Iowa. The immunoassay method of analysis was performed by the SDGS.

In analyzing water collected from the Big Sioux River, the SDGS used immunoassay test kits for atrazine, alachlor, and 2,4-D analyses. Water samples from all four sampling events were analyzed for these three pesticides using the immunoassay method of analysis.

Laboratory Credentials

The SDGS laboratory is certified under the authority of the U.S. Environmental Protection Agency (U.S. EPA) for analytical methods used to determine the parameters of arsenic, fluoride, nitrate as nitrogen, nitrite as nitrogen, and selenium. In addition, twice yearly, the laboratory participates in the U.S. Geological Survey's Analytical Evaluation Program for other analytical methods used in this study. The SDGS laboratory also has documented and established quality-assurance and quality-control practices.

The University of Iowa Hygienic Laboratory certifications and accreditation are as follows: U.S. EPA Certified Superfund Contract Laboratory, U.S. EPA Certified Drinking Water Laboratory, Principal Safe Drinking Water Act (SDWA) Laboratory for the state of Iowa, American Industrial Hygiene Association (AIHA) Accredited, and Clinical Laboratories Improvement Act (CLIA) Licensed. The Hygienic Laboratory is used by the SDGS because of its reputation and quality-assurance/quality-control practices.

Water-Level Measurements

Water levels in the monitoring wells were measured during each sampling event to the nearest 0.01 foot. Water-level data are on file at the SDGS. Measurements were made using an electronic measuring device that emits an audible sound and a visual indication upon contact with the water. This instrument was thoroughly cleaned between use in each well by rinsing the tape and the probe first with distilled water followed by nano-pure water.

Precipitation Data

For this investigation, the SDGS used monthly total precipitation data collected from recording stations located near each of the ground water monitoring sites (table 4). These data are gathered by the State Climatologist at South Dakota State University and are compiled and published by the National Oceanic and Atmospheric Administration. Monthly precipitation data, annual total, and departure from normal are shown in appendix B for the recording station located near each ground water monitoring site.

GENERAL CLIMATE SUMMARY

Weather summaries for 1993 were acquired from the South Dakota Agricultural Statistics Service and from the South Dakota State Climatologist. This information is on file at the SDGS. Additional climate information can be found in the publication entitled *Natural Disaster Survey Report -- The Great Flood of 1993* (U.S. Department of Commerce 1994).

Generally, the climate of South Dakota is characterized by large seasonal and daily variations in temperature. Winter lows can be -20°F and summer highs can be 100°F . Normally, there is marginal to adequate precipitation during the growing season and minimal winter precipitation (Lawrence and Sando, 1991). Figure 1 shows annual precipitation (in inches) for 1993, and the amount of rainfall above normal for the recording stations located near each ground water monitoring site (table 4).

Excessive rainfall during the summer and fall of 1992 set the stage for flooding in the spring of 1993 along the Big Sioux River. In March 1993, the southern portion of the Big Sioux River drainage basin received nearly $2\frac{1}{2}$ inches of rain. In April, an average of $2\frac{1}{2}$ inches of rain fell within the entire Big Sioux River drainage basin. The rains continued during May with the heaviest amounts falling in the southern portion of the Big Sioux River drainage basin. Nearly 9 inches of rain fell in the southern portion of the drainage basin during May and by the end of May, field conditions in the southeast were considered water-logged and flooding along the Big Sioux River was beginning to occur. During the month of June, nearly 10 inches of rain fell in the middle portion of the Big Sioux River drainage basin and nearly 8 inches of rain fell in the northern portion of the basin. Precipitation occurred every week in July with every part of the state receiving heavy amounts (2 to 4 inches) at sometime during the month. During July, over 9 inches of rain fell in the northern and middle portions of the basin while the southern portion of the basin received nearly 8 inches of rain. During August, nearly 4 inches of rain fell in the southern portion of the drainage basin. September precipitation was moderate with nearly $3\frac{1}{2}$ inches of rain falling in the northern portion of the drainage basin and an average of 2 inches falling throughout the middle and southern portions of the drainage basin. October brought light and scattered precipitation which allowed many areas a chance

Table 4. Nearest climatological recording station for each ground water monitoring site.

Geographic locations of ground water monitoring sites	Nearest National Oceanic and Atmospheric Administration recording station
near Lonesome Lake, Grant County	Summit 1 W
near Watertown, Codington County	Watertown FAA AP
near Castlewood, Hamlin County	Castlewood
near Estelline, Hamlin County	Castlewood
near Volga, Brookings County	Brookings 2 NE
near Egan, Moody County	Flandreau
near Baltic, Minnehaha County	Colton
near Renner, Minnehaha County	Sioux Falls WSFO
near Canton, Lincoln County	Canton 4 WNW
near Hudson, Lincoln County	Hawarden, Ia
near Richland, Union County	Elk Point 13 NE

to dry out. However, snow fell in the Big Sioux River drainage basin during November corresponding to an average of over 1½ inches of additional liquid precipitation.

In the Big Sioux River drainage basin, precipitation for 1993 ranged from 1.87 to 14.38 inches above normal (fig. 1). For example, from March through August, Sioux Falls alone received 30.3 inches, or 2½ feet of rain. The normal annual precipitation for Sioux Falls is 23.86 inches.

RESULTS OF INVESTIGATION

Water Quality

Major Anions and Cations

GROUND WATER

A trilinear diagram is used to display water-quality data in graphical form and allow for visual comparison of individual chemical analyses. Cation and anion compositions of water samples are represented on a trilinear diagram in which major groupings or trends in the data can be identified visually. A trilinear diagram conveniently reveals similarities or differences among water samples because those samples with similar qualities will tend to plot together as groups.

A trilinear diagram (app. C) was constructed for analyses of water samples collected from the Big Sioux aquifer and the Big Sioux River during the July 1993 sampling event. During the July sampling event, water samples were collected from 24 ground water monitoring wells. The trilinear diagram shows that the predominant type of water collected from the Big Sioux aquifer is a calcium-bicarbonate type. This type of water is typical of the glacial materials in the Midwest region of the United States (Freeze and Cherry, 1979). Comparing this trilinear diagram with three trilinear diagrams constructed for analyses of water samples collected from the Big Sioux aquifer during 1989, 1990, and 1992 (Hammond, 1994), it appears that the overall water quality in the Big Sioux aquifer has not changed and continues to be primarily a calcium-bicarbonate type of water.

The water quality in the Big Sioux aquifer is generally good. Total dissolved solids ranged from 250 to 868 milligrams per liter (mg/L). Hardness ranged from 230 to 660 mg/L. Sulfate ranged from 15 to 385 mg/L. Since systematic monitoring began in 1989, general water quality in the Big Sioux aquifer has remained consistent over time. The precipitation increase and flooding which occurred throughout the Big Sioux River drainage basin during 1993 appear to have had no major influence on the general water quality of the Big Sioux aquifer.

SURFACE WATER

During the July sampling event, five water samples were collected from the Big Sioux River. One river sample was collected near Lonesome Lake, Grant County; one river sample was collected near Egan, Moody County; and three river samples were collected near Richland, Union County. A problem arose, however, during the laboratory analysis of the river sample collected near Lonesome Lake, Grant County. The sulfate parameter would not stabilize and the concentration rapidly decreased. As a result, the finalized concentration for this parameter is considered suspect and, therefore, the sample was not included in the preparation of the trilinear diagram.

The trilinear diagram shows that the type of water collected from the Big Sioux River is calcium-bicarbonate and similar to water in the Big Sioux aquifer. When compared with trilinear diagrams in Hammond (1994), the water quality in the Big Sioux River has not changed from 1990 to 1993.

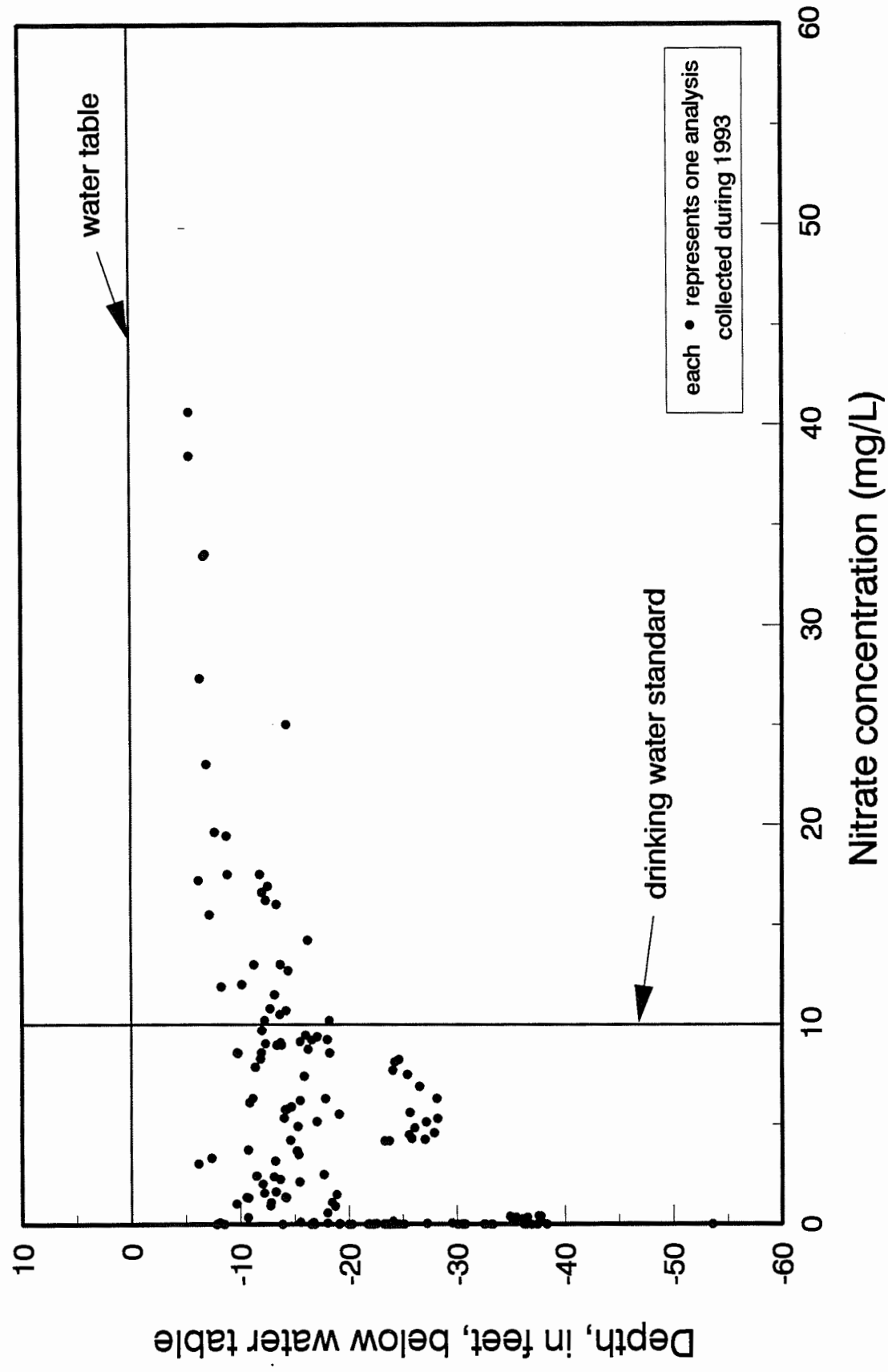
The water quality in the Big Sioux River is generally good. Total dissolved solids ranged from 610 to 650 mg/L. Hardness ranged from 460 to 490 mg/L. Sulfate ranged from 184 to 214 mg/L. Since systematic monitoring began in 1989, general water quality in the Big Sioux river has remained consistent over time. The precipitation increase and flooding which occurred throughout the Big Sioux River drainage basin during 1993 appear to have had no major influence on the general water quality of the Big Sioux River.

Nitrate

GROUND WATER

In the Big Sioux aquifer, it is common to find nitrate stratified within the aquifer (Hammond, 1994). When plotting nitrate concentration (app. D) versus depth below the water table, the nitrate stratification is obvious (fig. 4). For reference, the national interim primary drinking water standard for public water systems is 10 mg/L for nitrate (U.S. Environmental Protection Agency, 1985). Figure

Figure 4. Nitrate concentration versus depth below water table.



4 shows that nitrate concentrations greater than 10 mg/L are generally found within 20 feet of the water table. Throughout the Big Sioux aquifer ground water monitoring network, the highest concentrations of nitrate are found in the monitoring wells screened at, near, or through the water table, showing a vertical stratification of nitrate in the ground water.

One of the 11 monitoring sites (shallow monitoring wells R20-89-38 and R20-93-30 near Lonesome Lake, Grant County) had nitrate concentrations consistently above the national interim primary drinking water standard of 10 mg/L for public water systems. Shallow monitoring wells R20-89-42 near Watertown, Codington County; R20-89-64 near Baltic, Minnehaha County; R20-89-57 near Canton, Lincoln County, R20-89-60 near Hudson, Lincoln County, and R20-89-65 near Richland, Union County, and an intermediate-depth well, R20-89-63 near Baltic, Minnehaha County, had many occurrences of nitrate concentrations greater than 5 mg/L. Although the concentration of nitrate used to indicate the influence of human activities has yet to be clearly defined, Madison and Brunett (1984) suggest that nitrate concentrations greater than 3 mg/L may be the result of human sources. Because there are no known point sources of contamination near any of the ground water monitoring network sites, the data suggest nonpoint-source pollution is a factor in nitrate contamination in some places within the Big Sioux aquifer.

To more closely examine fluctuations in nitrate concentrations over time, the 8 wells just described, located at 6 of the 11 ground water monitoring sites, were sampled monthly in 1993 for nitrate analysis. Sample collection usually occurred during the last week of the month. To help understand trends in nitrate concentrations and to identify correlations between nitrate concentration and other hydrogeologic conditions, the following information was also examined from each of the six monitoring sites: lithology, thickness of the unsaturated zone, monthly depth to water, and monthly precipitation.

When comparing nitrate concentrations with (1) lithology, (2) thickness of the unsaturated zone, and (3) monthly depth to water, no direct correlations could be made; nitrate concentrations varied independently of these factors. Also, the highest nitrate concentrations were not observed at the same time throughout the aquifer. Some sites exhibited yearly high nitrate concentrations at the same time other sites exhibited yearly low nitrate concentrations. The highest nitrate concentrations were observed in January, March, April, August, or October. The lowest concentrations were observed in January, March, July, or August. This indicates that there is no seasonal control on nitrate concentrations in the Big Sioux aquifer as a whole.

When examining all the hydrogeologic data collected from these six monitoring sites, a correlation was found between nitrate concentration and monthly precipitation. Based on data collected from the eight wells, a statistical cross correlation was performed between nitrate concentration and monthly precipitation. Statistically, the best correlation between nitrate concentration and monthly precipitation was observed at a 2- to 4-month lag. What this means is that the highest nitrate concentrations were generally observed approximately 2 to 4 months after high monthly precipitation. While the data do not show a very high correlation between nitrate concentration and monthly precipitation, it does appear, statistically, that some of the variability in the nitrate concentrations observed throughout the Big Sioux aquifer can be explained by the influence of precipitation. This is to be expected because precipitation is a driving force which influences the downward movement and leaching of nitrate from the unsaturated zone into the ground water. Specific rain events were not identified for this investigation and, therefore, direct correlations between nitrate and specific rain events cannot be determined.

It is important to remember that for this investigation only general hydrogeologic conditions were examined when trying to determine trends in nitrate concentrations found in water collected from the Big Sioux aquifer. There are many other variables which influence the behavior of nitrate in the environment. The next logical step in understanding nitrate behavior in the subsurface would include an examination of the unsaturated zone and an examination of agricultural activities near each site.

Lonesome Lake, Grant County, Ground Water Monitoring Site

The monitoring site near Lonesome Lake, Grant County, consistently had nitrate concentrations above 10 mg/L. Because of the elevated nitrate concentrations found in water collected from a shallow monitoring well at this site (R20-89-38), an additional shallow monitoring well (R20-93-30) was installed during 1993 to help monitor nitrate concentrations near the water table. At this site, monitoring well R20-89-38 has a screened interval from 11 to 21 feet below land surface, with the bottom of the screen located approximately 7 feet below the water table (app. A). Monitoring well R20-93-30 has a screened interval from 16.5 to 26.5 feet, with the bottom of the screen located approximately 12.5 feet below the water table (app. A).

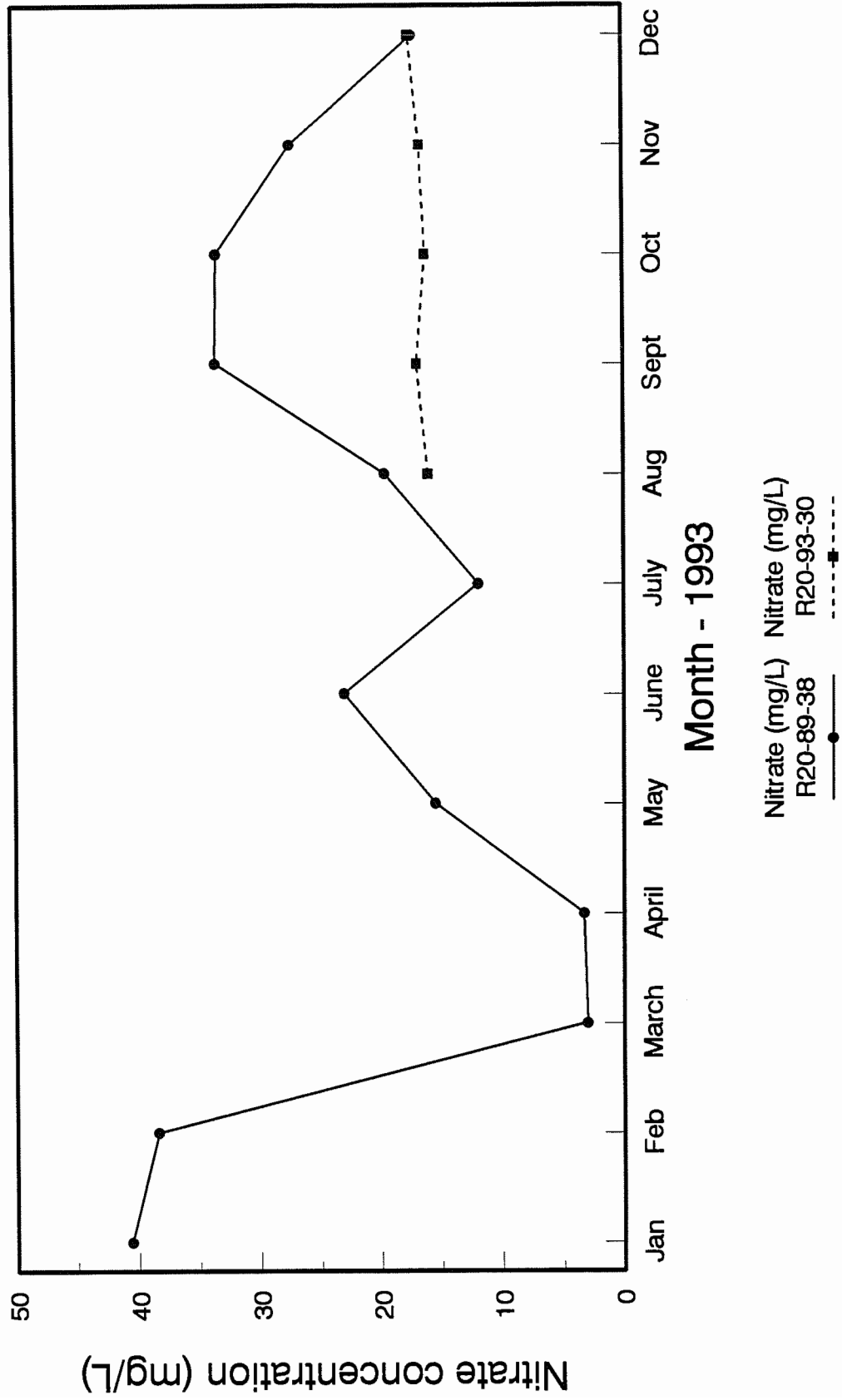
Monitoring well R20-89-38, the more shallow of the two monitoring wells (app. A), had nitrate concentrations ranging from 3.03 mg/L on March 30, 1993, to 40.6 mg/L on January 27, 1993 (app. D). Monitoring well R20-93-30, the deeper of the two monitoring wells, had nitrate concentrations ranging from 16.0 mg/L on August 30, 1993 to 17.5 mg/L on December 30, 1993 (app. D). In almost every sampling event, ground-water samples were collected during the last week of the month. When plotting nitrate concentration over time (fig. 5), water collected from monitoring well R20-89-38 showed the greatest fluctuation in nitrate concentration while water collected from monitoring well R20-93-30 showed more consistent nitrate concentrations. These data suggest that at this site, while nitrate stratification occurs within the upper 20 feet of the water table, the upper portion of this zone (within approximately 7 to 10 feet of the water table) is highly responsive to processes controlling nitrification.

SURFACE WATER

In the Big Sioux River, nitrate concentrations ranged from 0.09 to 4.66 mg/L (app. E). These concentrations are higher than concentrations previously observed in the Big Sioux River (Hammond, 1994) and may be attributed to increased surface-water runoff caused by the abnormally high precipitation. In water samples collected from the Big Sioux River, the highest concentrations of nitrate were found in flood water collected near Richland, Union County.

In an attempt to try to understand the elevated nitrate concentrations in ground water near the Lonesome Lake, Grant County, monitoring site, the Big Sioux River was sampled near this monitoring site (see table 2 for location). Nitrate concentrations in the Big Sioux River at this location were low and ranged from 0.09 to 0.97 mg/L.

Figure 5. Nitrate fluctuation at the ground water monitoring site near Lonesome Lake, Grant County.



Ammonia

GROUND WATER

Ammonia concentrations in shallow ground waters are normally very low because of the rapid conversion process of ammonia to nitrate and because ammonia is absorbed readily onto soil particles. However, in deeper portions of the aquifer, anaerobic conditions are common and because of denitrification, nitrate is converted to ammonia. For these reasons, ammonia concentrations are used to examine nitrate stratification in an aquifer.

In the Big Sioux aquifer, ammonia concentrations ranged from less than 0.05 to 1.29 mg/L in 1993 (app. D). These concentrations are similar to ammonia concentrations determined in previous years for the Big Sioux aquifer (Hammond, 1994). Due to denitrification, higher ammonia concentrations are generally found in the deeper portions of the aquifer where nitrate concentrations are low. The U.S. EPA has not established any drinking-water regulations or health advisories for ammonia concentrations in ground water. The ammonia concentrations are, however, indicative of nitrate stratification in the Big Sioux aquifer.

SURFACE WATER

In the Big Sioux River, ammonia concentrations ranged from less than 0.05 to 0.23 mg/L in 1993 (app. E). Generally, in small streams, ammonia concentrations are less than 3 mg/L to as low as 0.5 mg/L, and are as low as 0.1 mg/L in uncontaminated reaches of a stream (McCutcheon and others, 1993).

Phosphorous

GROUND WATER

The major sources of phosphorus are soil-applied fertilizers and waste water. Phosphoric acid (phosphorus) accounts for approximately 30 percent of actual nutrients applied to agricultural land in South Dakota (this information is based on data acquired from the South Dakota Agricultural Statistics Service). Usually, phosphorus contamination is considered together with nitrogen contamination; however, phosphorus is less important than nitrogen because of its low solubility in ground water and limited mobility due to its tendency to adsorb on soils (Domenico and Schwartz, 1990). For this investigation, total phosphorus concentrations were examined to see if they could be used as an indicator of contamination from fertilizer. Phosphorus does not present a significant health risk, but it can accelerate the growth of certain blue-green algae that are toxic to livestock (Krider, 1988). The U.S. EPA has not established any drinking-water regulations or health advisories for phosphorus concentrations in ground water.

In the Big Sioux aquifer, total phosphorus concentrations were low in 1993, ranging from less than 0.010 to 0.333 mg/L (app. D). Generally, in treated drinking water, phosphorus concentrations of 4 mg/L are found (Drinking Water Health Effects Task Force, 1989). Based on the low total phosphorus concentrations found in the Big Sioux aquifer, it is concluded that total phosphorus concentrations alone were not indicative of contamination from soil-applied fertilizer.

SURFACE WATER

In the Big Sioux River, total phosphorus concentrations range from 0.061 to 0.300 mg/L (app. E). In streams, phosphorous is generally present in low concentrations, 0.1 mg/L or less, while polluted segments of a stream may contain phosphorous concentrations of 1 mg/L or more (McCutcheon and others, 1993). Generally, natural background concentrations of total phosphorous in rivers is about 0.025 mg/L (McCutcheon and others, 1993). Total phosphorus concentrations detected in the Big Sioux River during 1993 were slightly higher than total phosphorus concentrations determined in previous years for the Big Sioux River (Hammond, 1994). This increase may have been caused by an increase in surface-water runoff due to the abnormally high amounts of precipitation during 1993.

Pesticides

GROUND WATER

Gas Chromatography/Mass Spectrometry Method of Analysis

Using the gas chromatography/mass spectrometry method of analysis, pesticides were detected, at one time or another, in 8 of 27 monitoring wells (table 5). Four of the 11 shallow monitoring wells showed the presence of a pesticide at one time or another. None of the five intermediate depth monitoring wells showed the presence of a pesticide. Four of the 11 deep monitoring wells showed the presence of a pesticide at one time or another. Seven shallow monitoring wells, five intermediate depth monitoring wells, and seven deep monitoring wells, showed no pesticide.

Using the gas chromatography/mass spectrometry method of analysis, the following pesticides were detected in water collected from the Big Sioux aquifer: atrazine, cyanazine, dicamba, metolachlor, bentazon, alachlor, and 2,4-D. These pesticides were detected in some of the monitoring wells at one time or another; however, no aquifer-wide trends were observed and pesticides were not found to be stratified within the aquifer. Figure 6 shows that atrazine was detected most frequently, followed by cyanazine. Atrazine was the only pesticide detected during all four sampling events (fig. 7).

Three wells had pesticide detections during all four sampling events; R20-89-38 near Lonesome Lake, Grant County; R20-89-50 near Egan, Moody County; and R20-89-54, near Renner, Minnehaha County (table 5). Table 5 also shows that during the June sampling event, monitoring well R20-89-54 near Renner, Minnehaha County, had an atrazine concentration of 4.2 $\mu\text{g/L}$. This concentration is above the maximum contaminant level (MCL) of 3 $\mu\text{g/L}$. Four ground-water samples had a cyanazine concentration above the lifetime health advisory (HA) of 1 $\mu\text{g/L}$. All other pesticide concentrations were below their MCLs and HAs established by the U.S. EPA (Office of Drinking Water, 1993).

In addition to the pesticides listed above, two major metabolites (degradation products) of atrazine were also detected in water collected from the Big Sioux aquifer. These metabolites are desethyl atrazine and desisopropyl atrazine. Desethyl atrazine was detected in three monitoring wells and desisopropyl atrazine was detected in two monitoring wells (table 5). If the atrazine metabolite concentrations are added to the atrazine concentration to determine total atrazine residue

Table 5. Concentrations of detected pesticides, in micrograms per liter, as determined by gas chromatography/mass spectrometry.

Well/River Identifier	1993			
	May 17 - 19 May 24 - 27	June 21 - 23 June 28 - 30	July 19 - 21 July 26 - 28	August 23 - 25 August 30 - 31, September 1
R20-89-38	atrazine 0.34	atrazine 0.29, desethyl atrazine 0.15	atrazine 0.23	atrazine 0.17, desethyl atrazine 0.12
R20-89-37	--	--	--	--
R20-89-39	--	--	--	--
R20-89-42	--	--	atrazine 0.11	--
R20-89-40	--	--	--	--
R20-89-41	--	--	--	--
R20-89-44	--	--	--	--
R20-89-43	--	--	atrazine 0.34	--
R20-89-46	--	--	--	--
R20-89-45	--	--	--	--
R20-89-48	--	--	--	--
R20-89-47	--	--	atrazine 0.15	--
R20-89-50	atrazine 0.16	atrazine 0.18	atrazine 0.24	atrazine 0.26
R20-89-49	atrazine 0.11	--	atrazine 0.12	atrazine 0.11
R20-89-64	--	--	--	--
R20-89-63	--	--	--	--
R20-89-62	--	--	--	--
R20-89-55	--	atrazine 1.3, cyanazine 2.7, metolachlor 0.21, alachlor 0.13, dicamba 1.2, desethyl atrazine 0.15	atrazine 0.51, cyanazine 0.24, dicamba 0.41, bentazon 0.23	atrazine 1.3, cyanazine 0.61, dicamba 0.23, desethyl atrazine 0.16, desisopropyl atrazine 0.19
R20-89-54	atrazine 0.14	atrazine 4.2, cyanazine 8.8, metolachlor 0.66, alachlor 0.37, dicamba 1.3, desethyl atrazine 0.54	atrazine 2.5, cyanazine 1.2, metolachlor 0.29, dicamba 0.68, bentazon 0.39, desethyl atrazine 0.28	atrazine 2.7, cyanazine 1.5, 2,4-D 0.22, desethyl atrazine 0.35, dicamba 0.73, bentazon 0.32, desisopropyl atrazine 0.24
R20-89-57	--	NS	--	--
R20-89-56	--	NS	--	--
R20-89-60	--	--	--	--
R20-89-59	--	--	--	--
R20-89-58	--	--	--	--
R20-89-65	NS	NS	NS	--
R20-89-67	NS	NS	NS	--
R20-89-66	NS	NS	NS	--
Big Sioux River near Egan, Moody County	--	atrazine 3.0, cyanazine 4.5, metolachlor 1.1, alachlor 0.88, dicamba 1.6, desethyl atrazine 0.42	atrazine 1.5, desethyl atrazine 0.22, cyanazine 0.52, dicamba 0.37, bentazon 0.72	atrazine 0.19, bentazon 0.25
Big Sioux River upstream from Akron, Iowa	atrazine 0.25, cyanazine 0.20, metolachlor 1.3, alachlor 0.96	atrazine 4.2, cyanazine 3.6, metolachlor 1.3, alachlor 0.48, dicamba 1.9, desethyl atrazine 0.32	atrazine 1.4, cyanazine 0.58, metolachlor 0.25, dicamba 0.23, bentazon 0.34, desethyl atrazine 0.20	
Big Sioux River near Akron, Iowa	atrazine 0.27, cyanazine 0.24, metolachlor 1.4, alachlor 1.0, EPTC 0.11	atrazine 3.1, cyanazine 2.1, metolachlor 1.7, alachlor 0.48, dicamba 2.0, desethyl atrazine 0.35	atrazine 1.4, cyanazine 0.58, metolachlor 0.24, dicamba 0.22, bentazon 0.33, desethyl atrazine 0.23	
Big Sioux River near Richland, Union County	atrazine 0.28, cyanazine 0.26, metolachlor 1.4, alachlor 1.1, EPTC 0.12	atrazine 3.7, cyanazine 2.3, metolachlor 1.9, alachlor 0.53, dicamba 2.2, desethyl atrazine 0.45	atrazine 1.4, cyanazine 0.58, metolachlor 0.26, dicamba 0.21, bentazon 0.40, desethyl atrazine 0.23	
Big Sioux River next to R20-89-56 & R20-89-57 near Canton, Lincoln County		atrazine 3.0, cyanazine 3.6, metolachlor 0.85, alachlor 0.39, dicamba 1.8, desethyl atrazine 0.39		
Big Sioux River east of Canton, Lincoln County		atrazine 3.0, cyanazine 3.6, metolachlor 0.81, alachlor 0.39, dicamba 1.9, desethyl atrazine 0.37		

The symbol "--" indicates a sample was collected and no pesticides were detected.

NS - Not sampled due to flooding.

Figure 6. Pesticides detected in the Big Sioux aquifer.

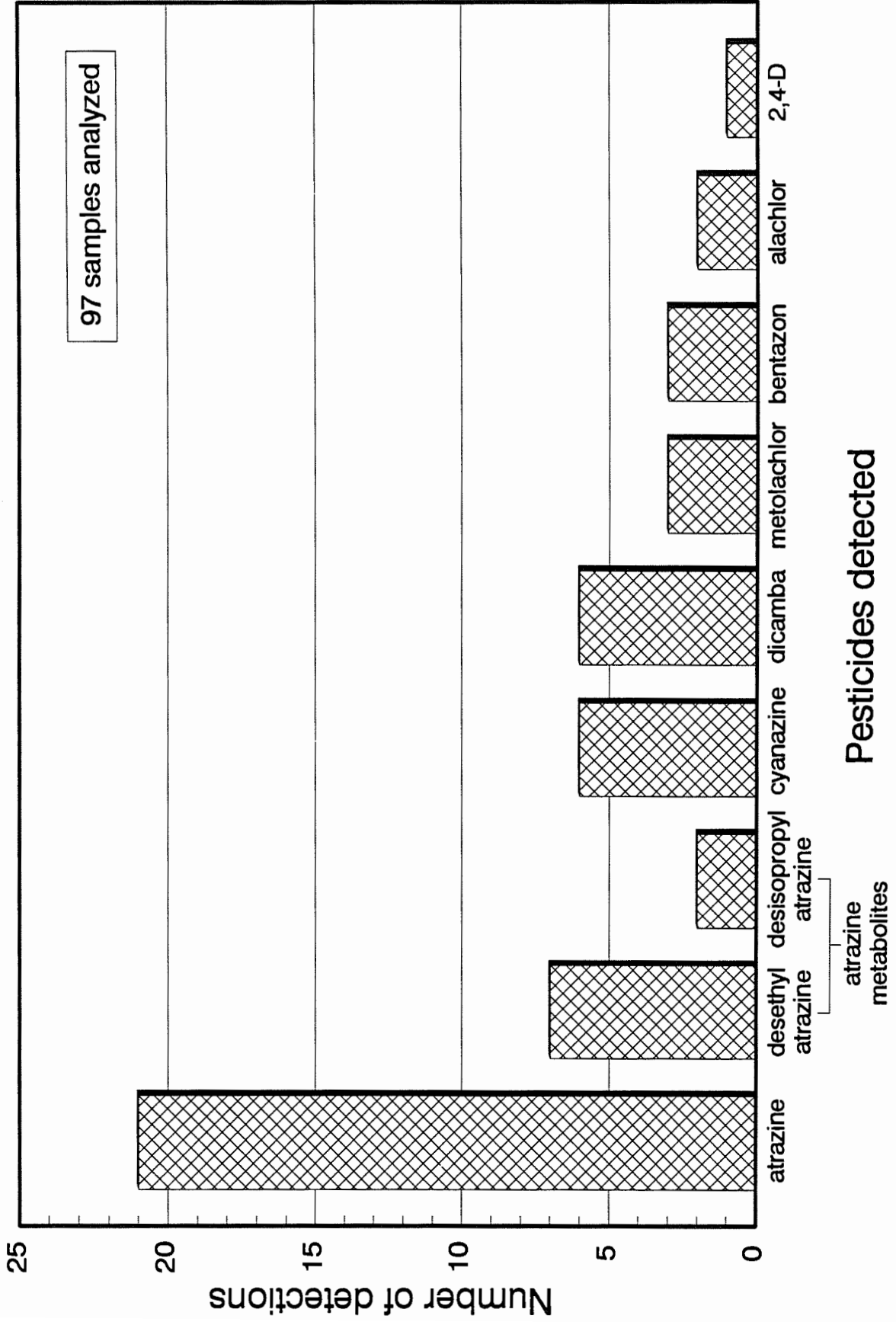
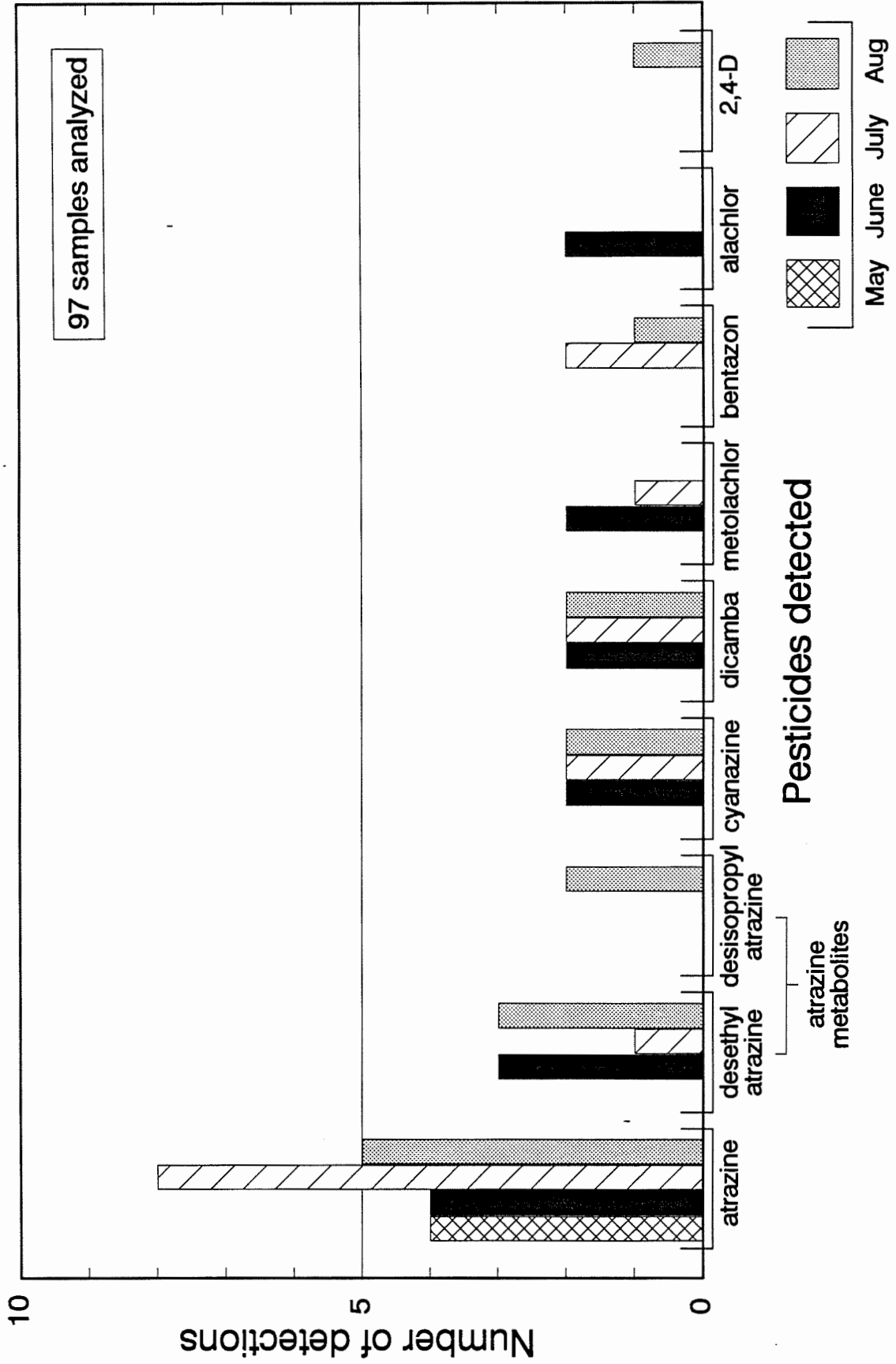


Figure 7. Pesticides detected in the Big Sioux aquifer, by sampling event.



concentration, then during the August sampling event, monitoring well R20-89-54 near Renner, Minnehaha County, would have had a total atrazine residue concentration above the atrazine MCL of 3 $\mu\text{g/L}$. Desethyl atrazine was detected during the June, July, and August sampling events while desisopropyl atrazine was detected only during the August sampling event (fig. 7 and table 5).

Data collected previously (1989 through 1992) from the Big Sioux aquifer (Hammond, 1994) show that out of 135 ground-water samples collected, 13 samples (10 percent) had detectable levels of atrazine, and that atrazine ranged in concentration from 0.11 to 0.85 $\mu\text{g/L}$ with an average of 0.40 $\mu\text{g/L}$. During 1993, data show that of the 97 ground-water samples collected for pesticide analysis, 21 samples (22 percent) had detectable levels of atrazine, and that atrazine ranged in concentration from 0.11 to 4.2 $\mu\text{g/L}$ with an average of 0.74 $\mu\text{g/L}$. This comparison shows that atrazine was detected more frequently in ground-water samples collected during 1993 than in previous years, and not only were there more atrazine detections, the atrazine concentrations were generally higher than in previous years. This may be due to an increase in precipitation which flushed atrazine from the unsaturated zone into the ground water. However, there are many factors which predetermine pesticide behavior within the subsurface, therefore it is not possible to explain pesticide behavior or detections based solely on precipitation. The processes which influence the transport and fate of organic compounds (pesticides) in the subsurface are extremely complex and beyond the scope of this investigation.

Immunoassay Method of Analysis

Using the immunoassay method of analysis, the following pesticides were detected at one time or another in water collected in 1993 from the Big Sioux aquifer: atrazine was detected in 14 of the 28 monitoring wells, alachlor was detected in 11 of the 28 monitoring wells, and 2,4-D was detected in 2 of the 28 monitoring wells (table 6). These three pesticides were the only pesticides analyzed using the immunoassay method. Four ground-water samples had atrazine detections above the MCL of 3 $\mu\text{g/L}$. Two ground-water samples had alachlor detections at or above the MCL of 2 $\mu\text{g/L}$. Concentrations of 2,4-D did not exceed the MCL of 70 $\mu\text{g/L}$.

SURFACE WATER

Gas Chromatography/Mass Spectrometry Method of Analysis

Using the gas chromatography/mass spectrometry method of analysis, the following pesticides were detected in water collected from the Big Sioux River (table 5): atrazine, cyanazine, metolachlor, dicamba, alachlor, bentazon, and EPTC. Figure 8 shows that in 1993, atrazine was the pesticide most frequently detected followed by cyanazine. Also, atrazine was the only pesticide detected during all four sampling events (fig. 9). Table 5 shows that six Big Sioux River samples had an atrazine concentration at or above the MCL of 3 $\mu\text{g/L}$ established by the U.S. EPA (Office of Drinking Water, 1993). These six samples were all collected during the June sampling event. Six surface-water samples had a cyanazine concentration above the lifetime HA of 1 $\mu\text{g/L}$ established by the U.S. EPA. These six samples were also collected during the June sampling event. All other pesticide concentrations were below the MCLs and HAs established by the U.S. EPA (Office of Drinking Water, 1993). In addition to the pesticides listed above, desethyl atrazine, a major metabolite of atrazine, was also detected in water collected from the Big Sioux River. Desethyl atrazine was

Table 6. Concentrations of detected pesticides, in micrograms per liter, as determined by immunoassay.

Well/River Identifier	1993			
	May 17 - 19	June 21 - 23	July 19 - 21	August 23 - 25
	May 24 - 27	June 28 - 29	July 26 - 28	August 30 - 31, Sept. 1
R20-89-38	atrazine 0.7	atrazine 0.4	atrazine 0.4	atrazine 0.4
R20-89-37	--	--	--	--
R20-89-39	--	--	--	--
R20-93-30	Well not installed	Well not installed	Well not installed	--
R20-89-42	atrazine 0.1	atrazine 0.1	alachlor 0.1	atrazine 0.3, alachlor 0.1
R20-89-40	--	--	--	--
R20-89-41	--	--	--	--
R20-89-44	--	--	--	--
R20-89-43	--	--	--	--
R20-89-46	--	--	--	--
R20-89-45	--	--	atrazine 0.1, alachlor 0.1	--
R20-89-48	--	alachlor 0.1	atrazine 0.3, alachlor 0.2	atrazine 0.3, alachlor 0.1
R20-89-47	--	--	alachlor 0.1	--
R20-89-50	atrazine 0.6, alachlor 0.4	atrazine 0.4, alachlor 0.2	atrazine 0.4, alachlor 0.2	atrazine 0.5, alachlor 0.3
R20-89-49	atrazine 0.3, alachlor 0.4	atrazine 0.2, alachlor 0.2	atrazine 0.6, alachlor 0.4	atrazine 0.4, alachlor 0.4
R20-89-64	--	--	atrazine 0.1	atrazine 0.1
R20-89-63	--	--	--	--
R20-89-62	--	--	atrazine 0.1	--
R20-89-55	--	atrazine 3.8, alachlor 2.0, 2,4-D 1.0	atrazine 2.5, alachlor 0.9	atrazine 1.2, alachlor 0.4
R20-89-54	atrazine 0.4, alachlor 0.3	atrazine 4.4, alachlor 2.3, 2,4-D 1.0	atrazine 3.7, alachlor 1.4	atrazine 3.2, alachlor 1.4
R20-89-57	atrazine 0.3	NS	atrazine 0.2, alachlor 0.2	atrazine 0.3, alachlor 0.1
R20-89-56	--	NS	alachlor 0.2	atrazine 0.1, alachlor 0.1
R20-89-60	--	atrazine 0.2, alachlor 0.1	atrazine 0.1	atrazine 0.1
R20-89-59	--	--	--	--
R20-89-58	--	--	--	--
R20-89-65	NS	NS	NS	atrazine 0.1
R20-89-67	NS	NS	NS	--
R20-89-66	NS	NS	NS	--
Big Sioux River near Egan, Moody County	atrazine 0.3, alachlor 0.5, 2,4-D 1.0	atrazine 2.8, alachlor 3.0, 2,4-D 1.7	atrazine 3.2, alachlor 1.1	atrazine 0.6, alachlor 0.4
Big Sioux River near Lonesome Lake, Grant County	--	atrazine 0.5, alachlor 0.3, 2,4-D 7.5	atrazine 1.5, alachlor 0.9	atrazine 0.1, alachlor 0.1
Big Sioux River near Akron, Iowa	atrazine 0.8, alachlor 3.2, 2,4-D 1.0	atrazine 5.0, alachlor 2.9	atrazine 1.8, alachlor 0.7	
Big Sioux River upstream from Akron, Iowa	atrazine 0.7, alachlor 3.2	atrazine 3.6, alachlor 2.9	atrazine 1.9, alachlor 0.7	
Big Sioux River near Richland, Union County	atrazine 0.8, alachlor 3.5	atrazine 5.0, alachlor 2.7	atrazine 1.9, alachlor 0.7	
Big Sioux River next to R20-89-56 & R20-89-57 near Canton, Lincoln County		atrazine 3.3, alachlor 3.2		
Big Sioux River east of Canton, Lincoln County		atrazine 3.6, alachlor 3.2, 2,4-D 1.0		

The symbol "--" indicates a sample was collected and no pesticides were detected.

NS - Not sampled due to flooding

Figure 8. Pesticides detected in the Big Sioux River.

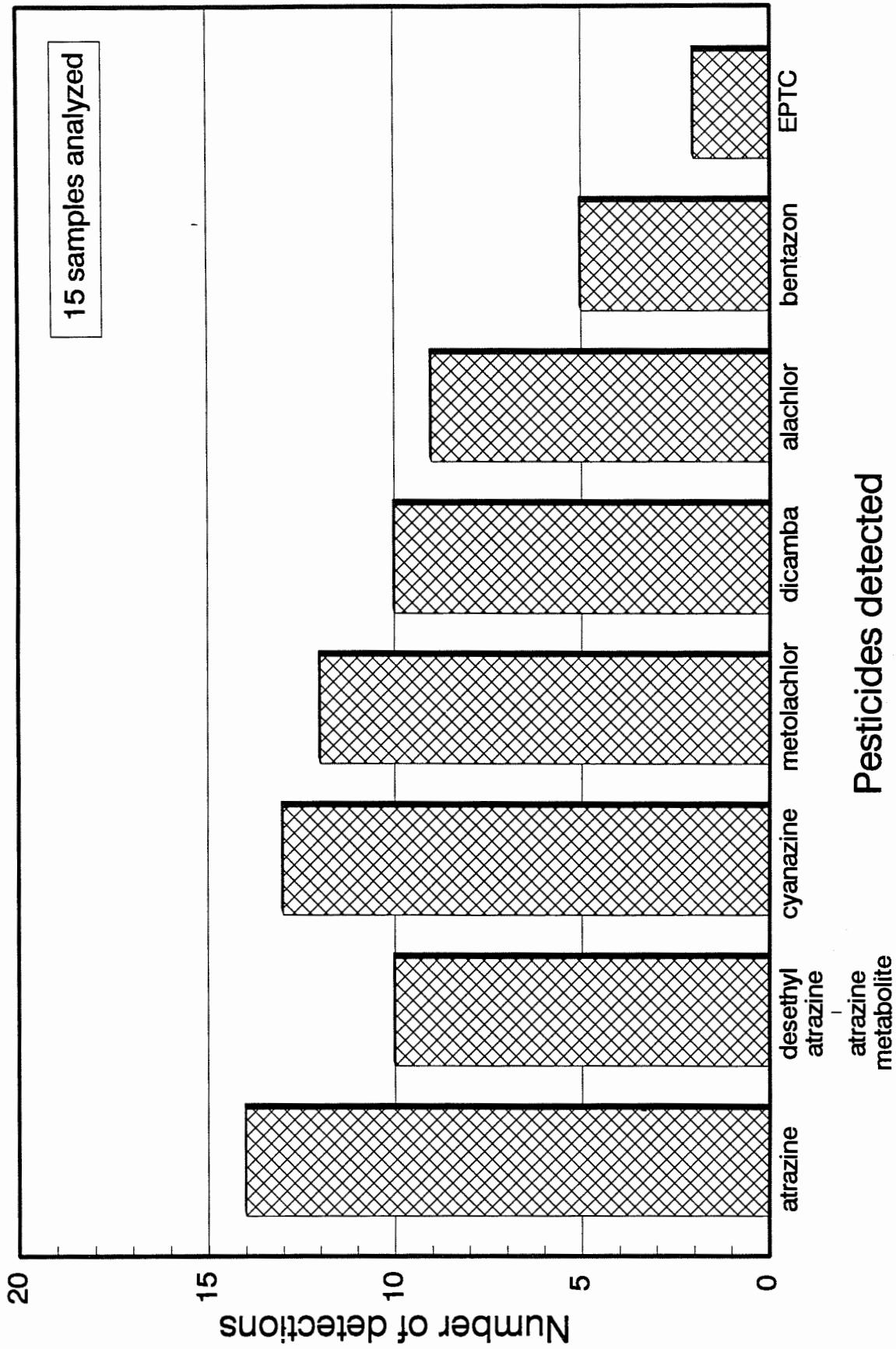
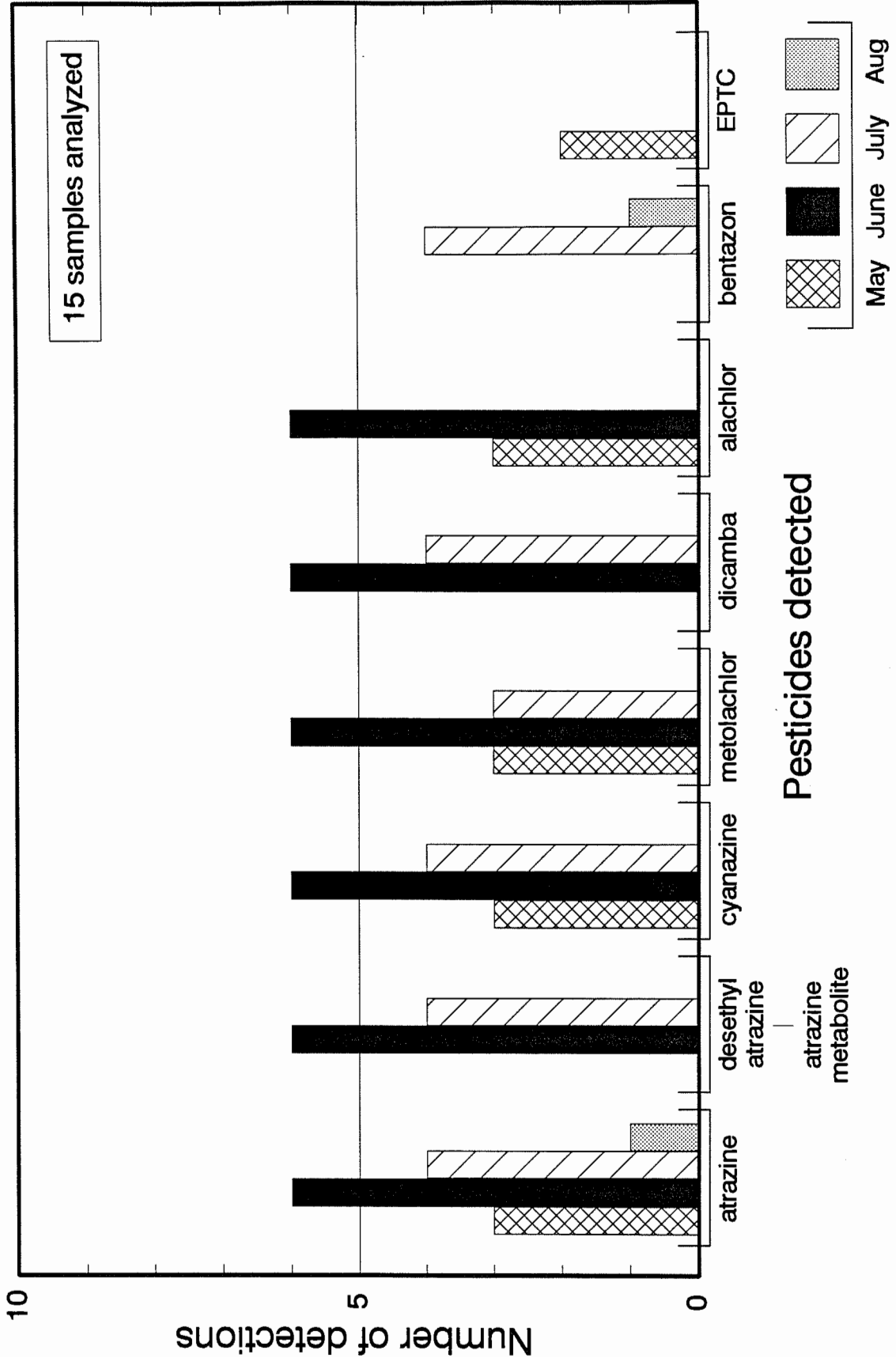


Figure 9. Pesticides detected in the Big Sioux River, by sampling event.



detected in 10 of the 15 surface-water samples. This metabolite was detected during the June and July sampling events (fig. 9 and table 5).

Data collected previously (1989 through 1992) from the Big Sioux River (Hammond, 1994) show that out of four surface-water samples collected, two samples (50 percent) had detectable levels of atrazine at 0.15 $\mu\text{g/L}$ and 0.56 $\mu\text{g/L}$, respectively. During 1993, of the 15 surface-water samples collected for pesticide analysis, 14 samples (93 percent) had detectable levels of atrazine. Atrazine concentrations ranged from 0.19 to 4.2 $\mu\text{g/L}$ with an average atrazine concentration of 1.91 $\mu\text{g/L}$. Comparison of the data shows that atrazine was detected more frequently in surface-water samples collected during 1993 than in previous years and not only were there more atrazine detections, the atrazine concentrations were generally higher than in previous years. This may be due to the increase in surface-water runoff from agricultural areas. However, there are many factors which predetermine pesticide behavior, therefore it is not possible to explain pesticide behavior or detections based solely on precipitation.

Immunoassay Method of Analysis

Using the immunoassay method of analysis, the following pesticides were detected at one time or another in water collected in 1993 from the Big Sioux River: atrazine was detected in 18 of the 19 surface-water samples, alachlor was detected in 18 of the 19 surface-water samples, and 2,4-D was detected in 5 of the 19 surface-water samples (table 6). These three pesticides were the only pesticides analyzed using the immunoassay method. Six surface-water samples had atrazine detections above the MCL of 3 $\mu\text{g/L}$. Nine surface-water samples had detections above the alachlor MCL of 2 $\mu\text{g/L}$. Concentrations of 2,4-D did not exceed the MCL of 70 $\mu\text{g/L}$.

GAS CHROMATOGRAPHY/MASS SPECTROMETRY AND IMMUNOASSAY COMPARISON

For the pesticide atrazine, there appears to be a fairly good correlation between results provided by the immunoassay method of analysis and the gas chromatography/mass spectrometry method of analysis. Based on data collected from the Big Sioux aquifer and the Big Sioux River from 1991 through 1993, out of 257 immunoassay analyses performed, 109 samples had an atrazine concentration equal to or greater than 0.1 $\mu\text{g/L}$ (the assay detection limit). Out of 251 samples collected for gas chromatography/mass spectrometry analysis, 50 samples had an atrazine concentration equal to or greater than 0.1 $\mu\text{g/L}$ (the laboratory detection limit). A total of 45 samples had both an immunoassay and a gas chromatography/mass spectrometry detection of atrazine. Based on these 45 samples, the data show that the immunoassay method of analysis will generally indicate a higher concentration than the gas chromatography/mass spectrometry method of analysis. For example, it was observed that an atrazine concentration of 0.3 $\mu\text{g/L}$ using the immunoassay method of analysis will correspond to an atrazine concentration just above the detection limit (0.1 $\mu\text{g/L}$) using the gas chromatography/mass spectrometry method of analysis. This might be expected as the atrazine assay can also detect atrazine metabolites and related triazines while the gas chromatography/mass spectrometry method detects only atrazine. For this reason, immunoassay results could be higher than gas chromatography/mass spectrometry results because the immunoassay method includes the metabolites and other related triazines in the calculation for atrazine.

Based on data for the pesticide alachlor, there is not a good correlation between results provided by the immunoassay method of analysis and the gas chromatography/mass spectrometry method of analysis. On many occasions, alachlor detections were noted with the immunoassay method while the gas chromatography/mass spectrometry method did not detect alachlor. For example, based on data collected from the Big Sioux aquifer and the Big Sioux River from 1991 through 1993, out of 257 immunoassay analyses performed, 70 samples had an alachlor concentration equal to or greater than 0.1 $\mu\text{g/L}$ (the assay detection limit). Out of 251 samples collected for gas chromatography/mass spectrometry analysis, only 11 samples had an alachlor concentration equal to or greater than 0.1 $\mu\text{g/L}$ (the laboratory detection limit). The alachlor assay detects a major alachlor soil metabolite, ethanesulfonate, which is not detected by standard gas chromatography methods and consequently, the alachlor detections using the immunoassay method are probably caused by cross-reaction with the soil metabolite (Carol Townsend, Ohmicron Corporation, personal communication, 1992; Macomber and others, 1992).

For the pesticide 2,4-D, there is an insufficient amount of data to make any correlation between results provided by the immunoassay method of analysis and the gas chromatography/mass spectrometry method of analysis. Based on data collected from the Big Sioux aquifer and the Big Sioux River from 1992 and 1993, out of 257 immunoassay analyses performed, only 11 samples had a 2,4-D concentration equal to or greater than 1 $\mu\text{g/L}$ (the assay detection limit). Out of 251 samples collected for gas chromatography/mass spectrometry analysis, only 4 samples had a 2,4-D concentration equal to or greater than 0.2 $\mu\text{g/L}$ (the laboratory detection limit). Only one sample had both an immunoassay and a gas chromatography/mass spectrometry detection of 2,4-D.

SUMMARY

In 1993, the Upper Midwest experienced the most devastating flood in modern United States history. Within the Missouri River drainage basin, record flood stages surpassed old record stages by more than 6 feet in some cases (U.S. Department of Commerce, 1994). In South Dakota the Big Sioux River, which drains into the Missouri River, went above flood stage in late May and remained in flood through mid-June. Every county in the Big Sioux River drainage basin was declared a disaster area as much of the flood water inundated prime agricultural land.

A ground water monitoring network, established in 1989 to monitor the water quality in the Big Sioux aquifer, was sampled during the months of May, June, July, and August 1993. Because of the good hydraulic connection between the Big Sioux aquifer and the Big Sioux River, the river was also sampled. Where monitoring sites were inaccessible due to flooding, the Big Sioux River was sampled at locations near the monitoring site. The emphasis of this water-quality investigation has been on nitrates and pesticides.

The ground water monitoring network consists of 28 monitoring wells installed at 11 locations in the Big Sioux aquifer and provides for monitoring over much of the aquifer's extent. Network monitoring wells are nested at each site to monitor the water quality vertically within the aquifer.

Major Anions and Cations

The water quality in the Big Sioux aquifer is generally good and is of the calcium-bicarbonate type. Since 1989, the general water quality in the Big Sioux aquifer has not changed. There were slight increases in concentrations of some parameters, but the increases were generally small and the overall water quality in the aquifer remained consistent over time. The increased precipitation and flooding within the Big Sioux River drainage basin in 1993 did not affect the general inorganic water quality in the Big Sioux aquifer.

The water quality in the Big Sioux River is generally good and is of the calcium-bicarbonate type. Since 1990, the general water quality in the Big Sioux River has not changed. The increased precipitation and flooding within the Big Sioux River drainage basin in 1993 did not affect the general inorganic water quality of the Big Sioux River.

Nitrate

Nitrate concentrations greater than 5 mg/L were detected in 8 of the 28 Big Sioux aquifer monitoring network wells at six sites in 1993. Of these eight monitoring wells, the highest concentrations of nitrate are found in the monitoring wells screened at, near, or through the water table, demonstrating a vertical stratification of nitrate in the ground water. Two monitoring wells, located near Lonesome Lake, Grant County, consistently had nitrate concentrations above the primary drinking water standard of 10 mg/L for public water systems. Based on available data, it is concluded that the elevated concentrations of nitrate are symptomatic of nonpoint-source contamination. Also, it appears that the nitrate concentrations are influenced in part by the high precipitation during the summer months. However, it is important to remember that in addition to precipitation there are many variables which influence the availability, transport, and fate of nitrates in the subsurface.

During 1993, in the Big Sioux River, nitrate concentrations were generally low and ranged from less than 0.09 to 4.66 mg/L. These concentrations are higher than concentrations found previously in the Big Sioux River and may be attributed to increased surface-water runoff caused by the abnormally high precipitation.

Ammonia

During 1993, in the Big Sioux aquifer, ammonia concentrations ranged from less than 0.05 to 1.29 mg/L with the higher ammonia concentrations found in the deeper portions of the aquifer where nitrate concentrations are low. The increased precipitation and flooding within the Big Sioux River drainage basin did not affect the ammonia concentrations in the Big Sioux aquifer.

During 1993, in the Big Sioux River, ammonia concentrations ranged from less than 0.05 to 0.23 mg/L. The increased precipitation and flooding within the Big Sioux River drainage basin did not affect ammonia concentrations in the Big Sioux River.

Phosphorous

During 1993, in the Big Sioux aquifer, phosphorus concentrations ranged from less than 0.010 to 0.333 mg/L. The increased precipitation and flooding within the Big Sioux River drainage basin did not affect total phosphorus concentrations in the Big Sioux aquifer.

During 1993, in the Big Sioux River, phosphorus concentrations ranged from 0.015 to 0.300 mg/L. The increased precipitation and flooding within the Big Sioux River drainage basin did not affect total phosphorus concentrations in the Big Sioux River.

Pesticides

During 1993, in the Big Sioux aquifer, pesticide analyses using the gas chromatography/mass spectrometry method detected atrazine, cyanazine, dicamba, metolachlor, bentazon, alachlor, and 2,4-D. In addition to these pesticides, desethyl atrazine and desisopropyl atrazine, two major metabolites of atrazine, were also detected. Pesticides were detected in some of the monitoring wells at one time or another, however no specific aquifer-wide trends were observed and pesticides were not found to be stratified within the aquifer.

Atrazine was the pesticide most frequently detected in water collected from the Big Sioux aquifer. Using the gas chromatography/mass spectrometry method, one ground-water sample was found to have an atrazine concentration of 4.2 $\mu\text{g/L}$. This concentration is above the MCL of 3 $\mu\text{g/L}$ established by the U.S. EPA. Also, using the gas chromatography/mass spectrometry method, four ground-water samples had a cyanazine concentration above the lifetime HA of 1 $\mu\text{g/L}$. All other pesticide concentrations were below their MCLs and HAs established by the U.S. EPA (Office of Drinking Water, 1993).

During 1993, not only was atrazine detected more frequently than in previous years, but atrazine was also detected at higher concentrations than in previous years. This observation may be due to an increase in precipitation which flushed atrazine from the unsaturated zone into the ground water. However, there are many factors which predetermine pesticide behavior within the subsurface, therefore it is not possible to explain pesticide behavior or detections based solely on precipitation.

The immunoassay method of analysis was also used in this investigation and detected atrazine, alachlor, and 2,4-D in water collected from the Big Sioux aquifer. These three pesticides were the only pesticides analyzed using the immunoassay method. Four ground water samples had atrazine detections above the MCL of 3 $\mu\text{g/L}$. Two ground-water samples had alachlor detections at or above the MCL of 2 $\mu\text{g/L}$. Concentrations of 2,4-D did not exceed the MCL of 70 $\mu\text{g/L}$.

In the Big Sioux River, pesticide analyses using the gas chromatography/mass spectrometry method detected, at one time or another, concentrations of atrazine, cyanazine, metolachlor, dicamba, alachlor, bentazon, and EPTC. In addition to these pesticides, desethyl atrazine, a major metabolite of atrazine, was also detected in water collected from the Big Sioux River. Fifteen samples were collected from the Big Sioux River and 14 samples contained at least one pesticide. Atrazine was the most frequently detected pesticide in the Big Sioux River followed by cyanazine. Of the 15 surface water samples collected for pesticide analysis, 14 had detectable levels of atrazine and six had an atrazine concentration at or above the MCL of 3 $\mu\text{g/L}$ established by the U.S. EPA. These six samples

were collected during the June sampling event. Six surface-water samples had a cyanazine concentration above the lifetime HA of $1 \mu\text{g/L}$ established by the U.S. EPA. These six samples were also collected during the June sampling event. All other pesticide concentrations were below MCLs and HAs established by the U.S. EPA. The increase in the number of atrazine detections and the increase in atrazine concentrations in water collected from the Big Sioux River may be influenced by the increased surface water runoff over agricultural areas due to the increased precipitation and flooding within the Big Sioux River drainage basin. However, there are many factors which predetermine pesticide behavior, therefore it is not possible to explain pesticide behavior or detections based solely on precipitation.

The immunoassay method of analysis was also used in this investigation and detected atrazine, alachlor, and 2,4-D in water collected from the Big Sioux River. These pesticides were the only pesticides analyzed for using the immunoassay method. Atrazine was the most frequently detected pesticide and six river samples had an atrazine concentration above the MCL of $3 \mu\text{g/L}$. Five of these samples were collected during the June sampling event and one sample was collected during the July sampling event. Nine surface-water samples had detections above the alachlor MCL of $2 \mu\text{g/L}$. Concentrations of 2,4-D did not exceed the MCL of $70 \mu\text{g/L}$.

When comparing results from the immunoassay method of analysis and the gas chromatography/mass spectrometry method of analysis for the pesticide atrazine, there appears to be a fairly good correlation between results provided by the two methods. As a general "rule of thumb," it appears that an atrazine concentration of $0.3 \mu\text{g/L}$ using the immunoassay method of analysis will correspond to an atrazine concentration just above the detection limit ($0.1 \mu\text{g/L}$) using the gas chromatography/mass spectrometry method of analysis. Based on data for the pesticide alachlor, there is not a good correlation between results provided by the immunoassay method of analysis and the gas chromatography/mass spectrometry method of analysis. For the pesticide 2,4-D, there is an insufficient amount of data to make any correlation between results provided by the immunoassay method of analysis and the gas chromatography/mass spectrometry method of analysis.

In conclusion, based on available data, it is determined that the detections of pesticides, whether in the river or the aquifer, are symptomatic of nonpoint-source contamination. Also during 1993, the increase in the number of atrazine detections and the increase in atrazine concentrations in ground water and surface water appear to have been influenced in part by the unusually high precipitation and surface-water runoff during the summer months. However, it is important to remember that in addition to precipitation there are many variables which influence the transport and fate of pesticides in the environment.

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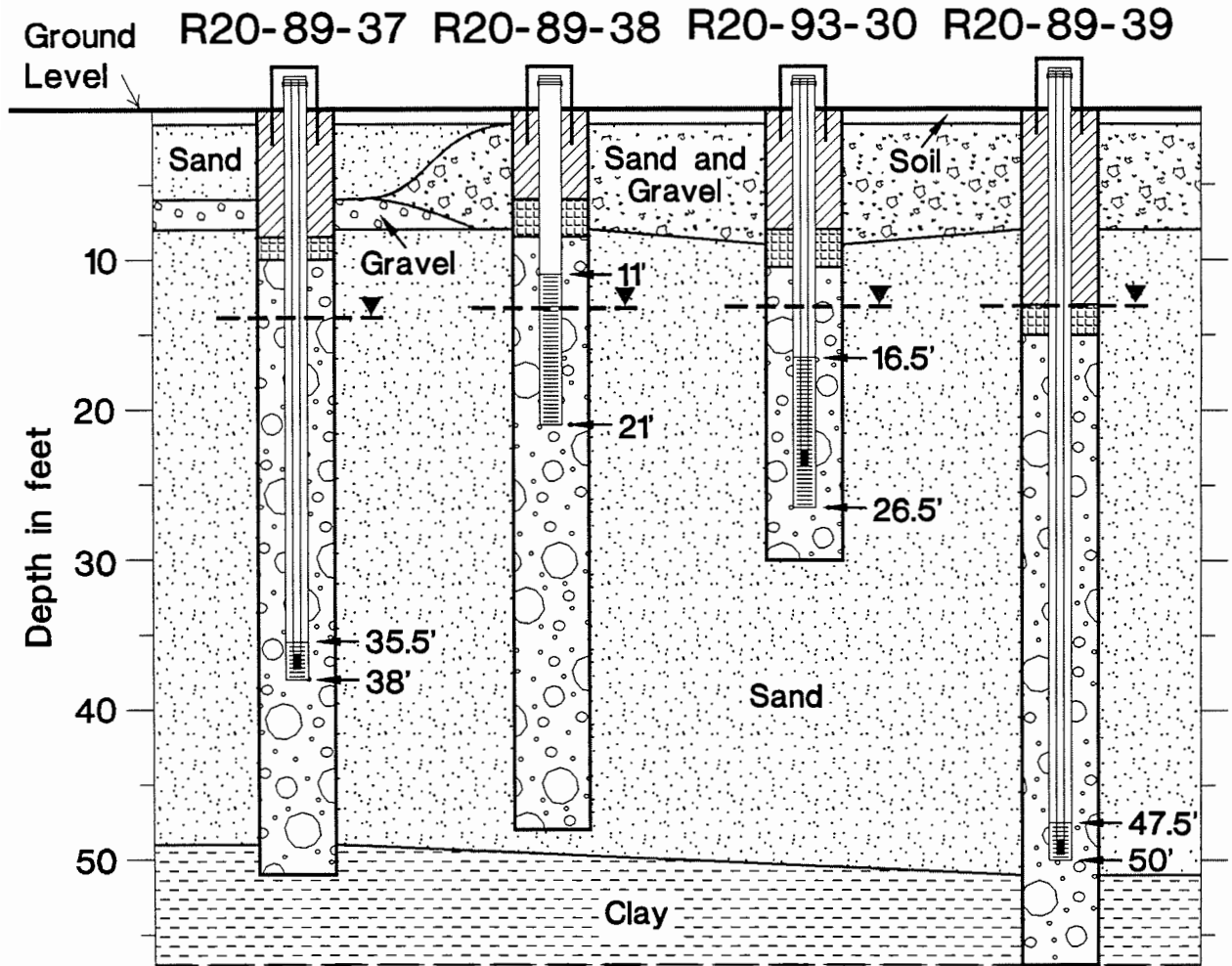
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APPENDIX A

Monitoring well construction diagrams and hydrostratigraphic cross sections
for ground water monitoring network wells located in the Big Sioux aquifer

**NE SE SE SE sec. 9, T. 120 N., R. 52 W.
(near Lonesome Lake, Grant County)**

N ← → S



Neat cement



Granular bentonite



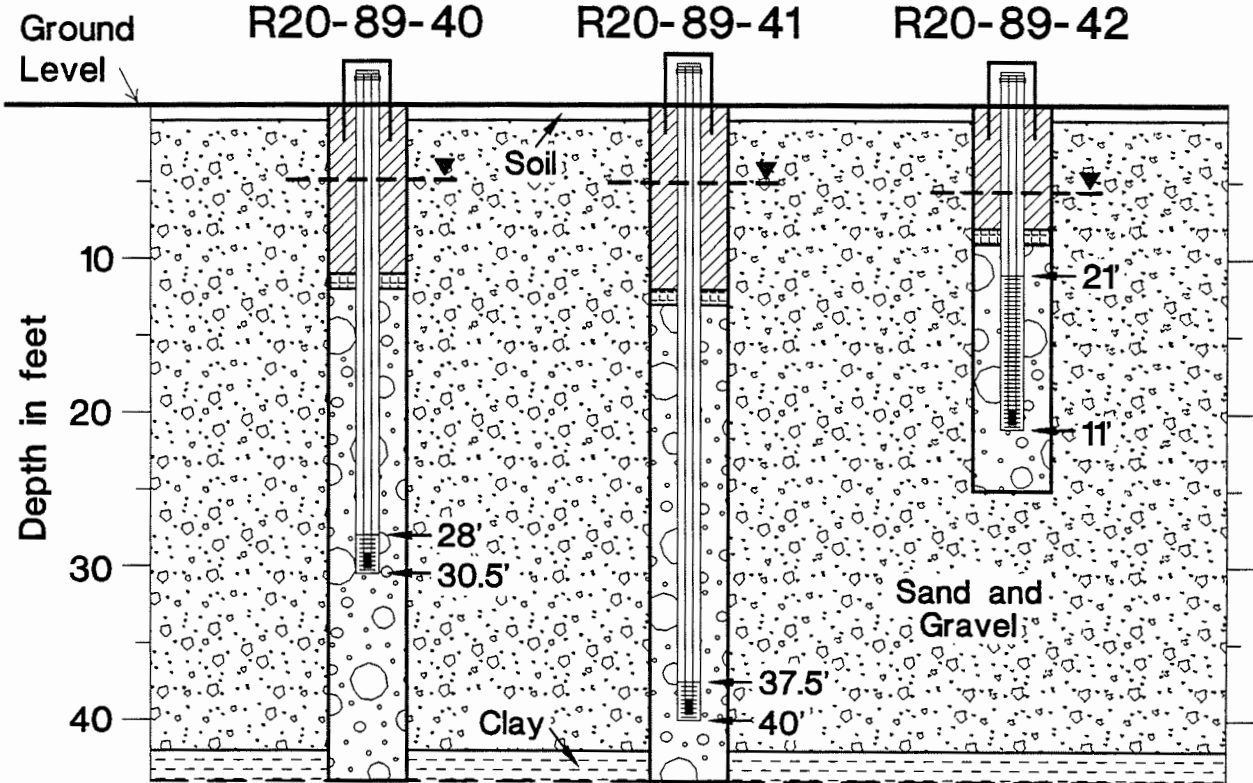
Native sediment (sand/gravel) and/or graded sand filter pack







Water level in the Big Sioux aquifer on August 30, 1993

**NW SW NW NW sec. 21, T. 118 N., R. 52 W.
(near Watertown, Codington County)**

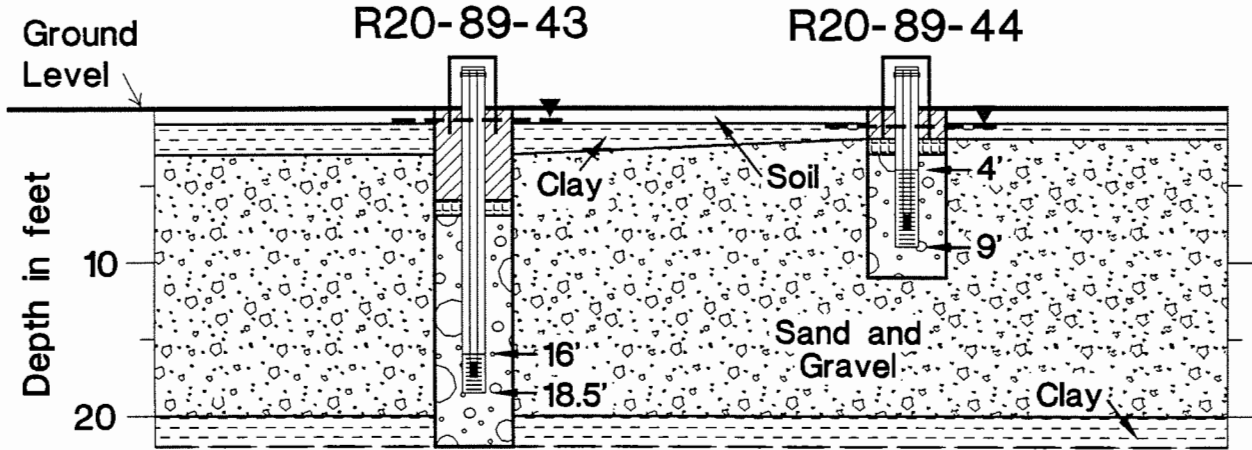
N ← → S



-  Neat cement
-  Granular bentonite
-  Native sediment (sand/gravel) and/or graded sand filter pack
-  Water level in the Big Sioux aquifer on August 31, 1993

**SW SW SW SE sec. 15, T. 115 N., R. 52 W.
(near Castlewood, Hamlin County)**

W ← → E



Neat cement



Granular bentonite



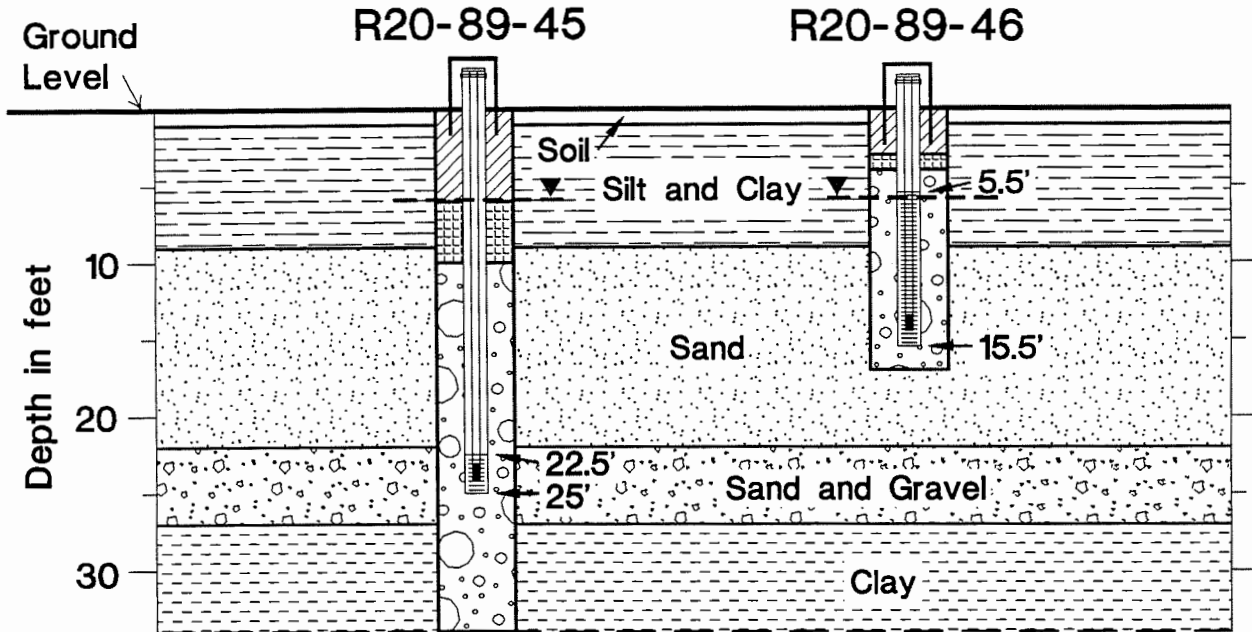
Native sediment (sand/gravel) and/or graded sand filter pack







Water level in the Big Sioux aquifer on August 31, 1993

**SE SW SW SE sec. 10, T. 113 N., R. 51 W.
(near Estelline, Hamlin County)**

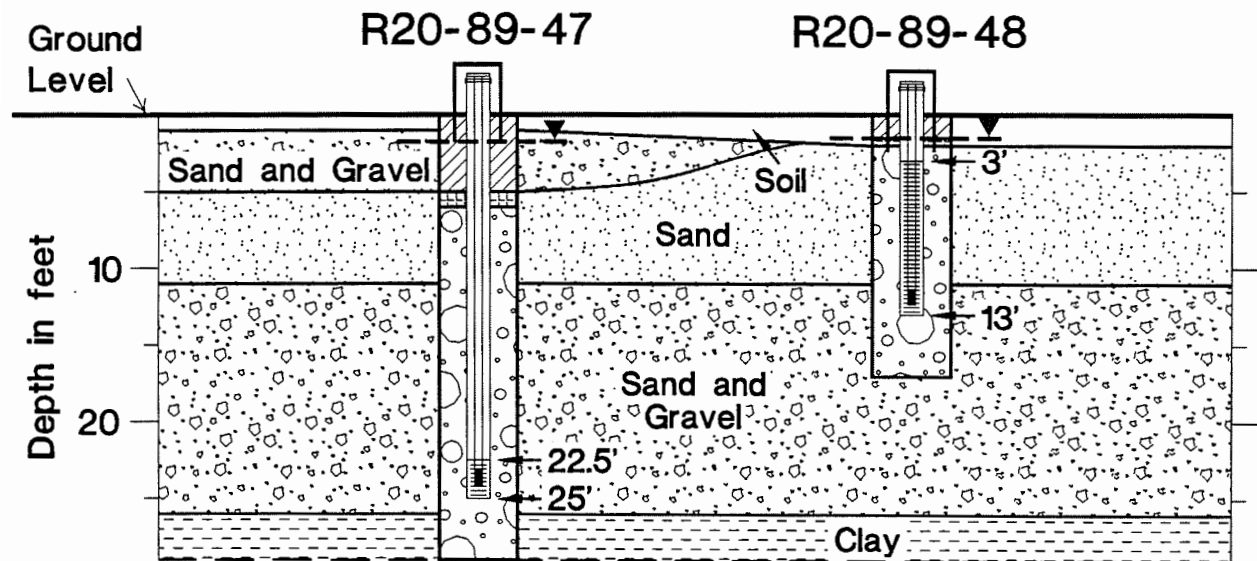
W ← → E



-  Neat cement
-  Granular bentonite
-  Native sediment (sand/gravel) and/or graded sand filter pack
-  Water level in the Big Sioux aquifer on August 31, 1993

NW NW NW NW sec. 18, T. 110 N., R. 50 W. (near Volga, Brookings County)

W ← → E



Neat cement



Granular bentonite



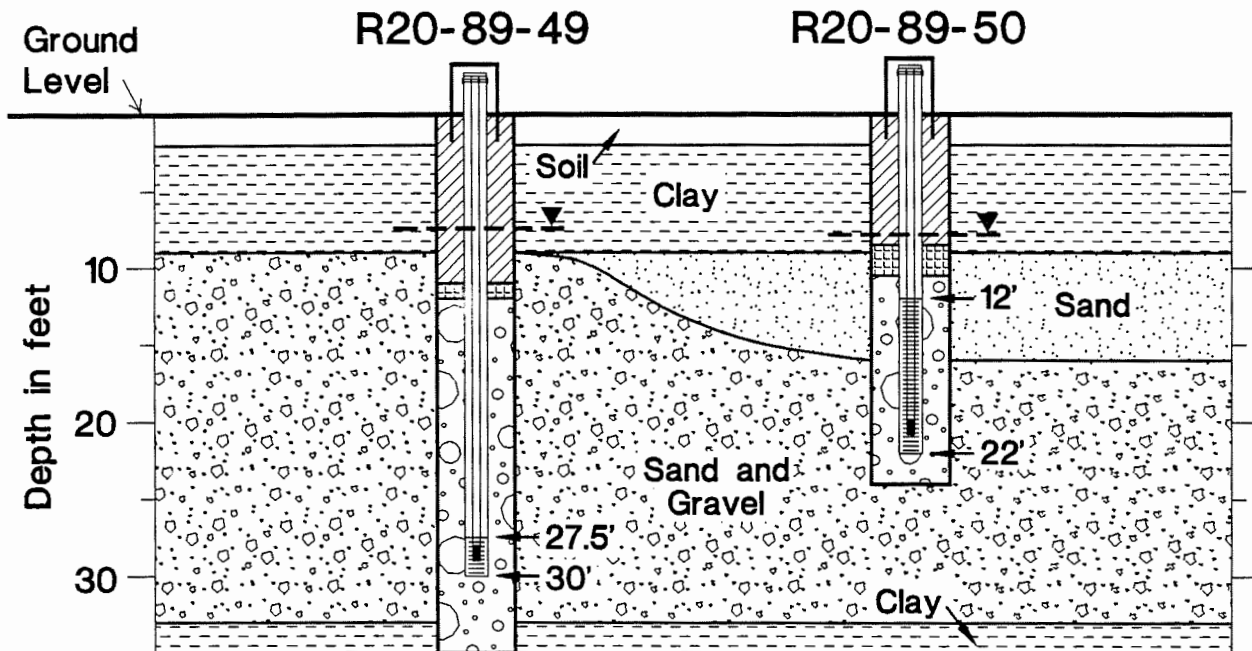
Native sediment (sand/gravel) and/or graded sand filter pack



Water level in the Big Sioux aquifer on August 31, 1993

**SW SW SE NE sec. 7, T. 106 N., R. 48 W.
(near Egan, Moody County)**

SW ← → NE



Neat cement



Granular bentonite



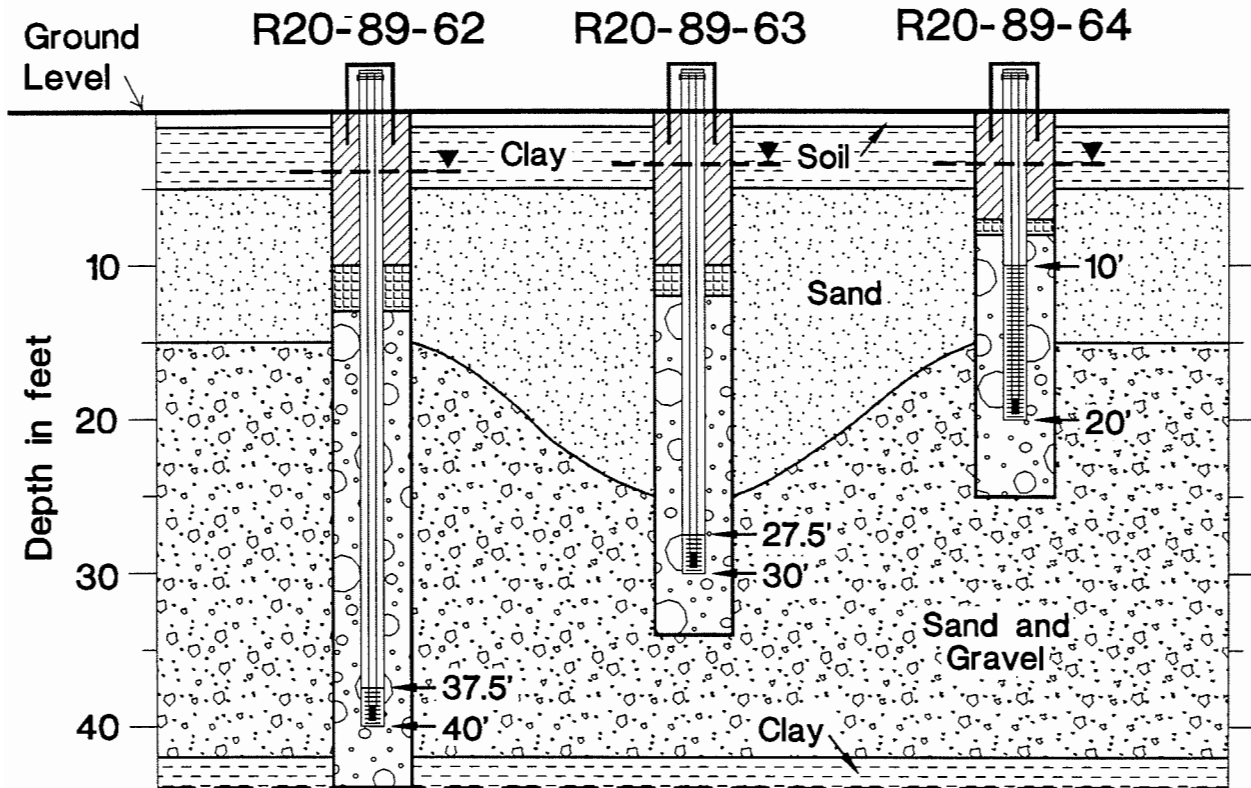
Native sediment (sand/gravel) and/or graded sand filter pack







Water level in the Big Sioux aquifer on September 1, 1993

SW SW SW SW sec. 31, T. 104 N., R. 49 W. (near Baltic, Minnehaha County)

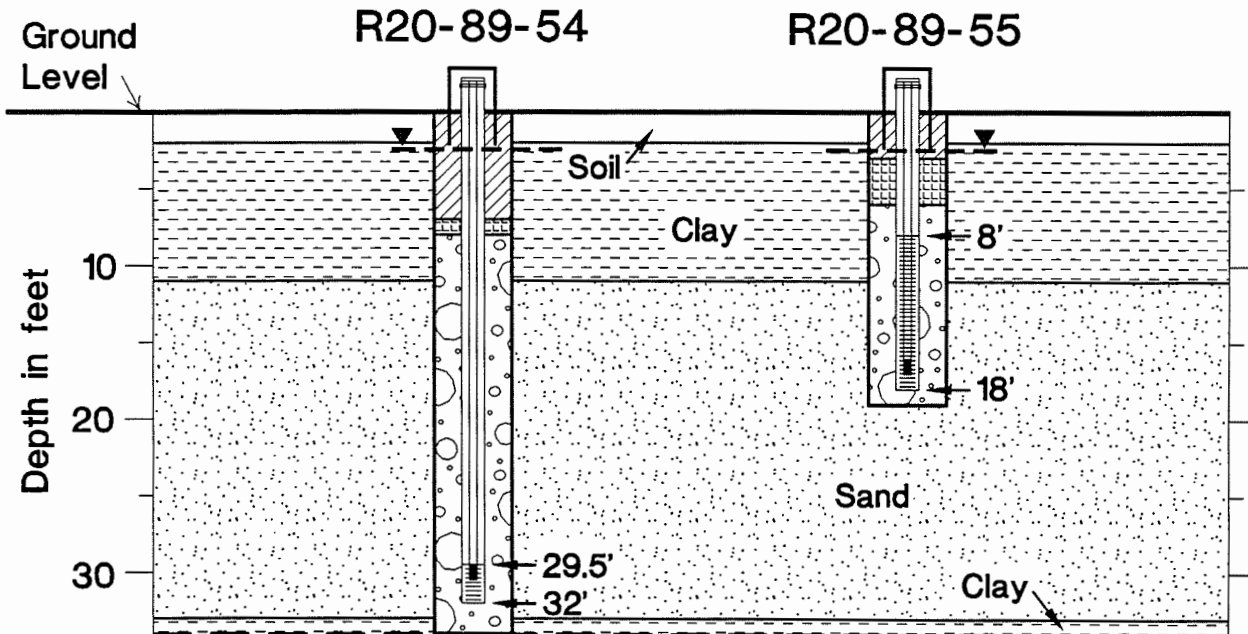
W ← → E







-  Neat cement
-  Granular bentonite
-  Native sediment (sand/gravel) and/or graded sand filter pack
-  Water level in the Big Sioux aquifer on August 24, 1993

**SE SE SE SE sec. 8, T. 102 N., R. 49 W.
(near Renner, Minnehaha County)**

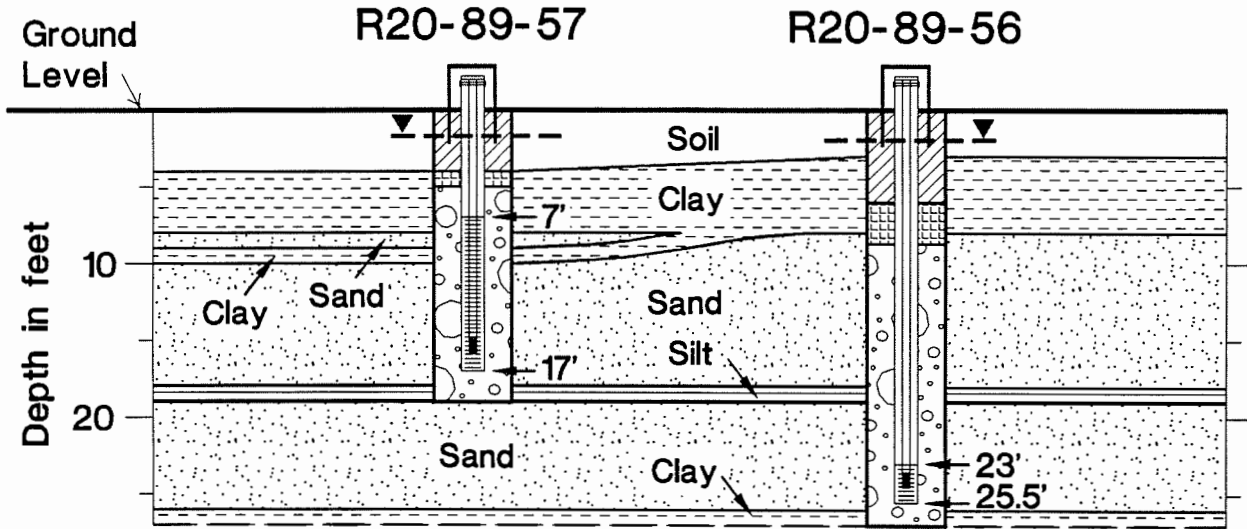
W ← → E



-  Neat cement
-  Granular bentonite
-  Native sediment (sand/gravel) and/or graded sand filter pack
-  Water level in the Big Sioux aquifer on August 24, 1993

**NE SE SE NE sec. 8, T. 98 N., R. 48 W.
(near Canton, Lincoln County)**

W ← → E



Neat cement



Granular bentonite



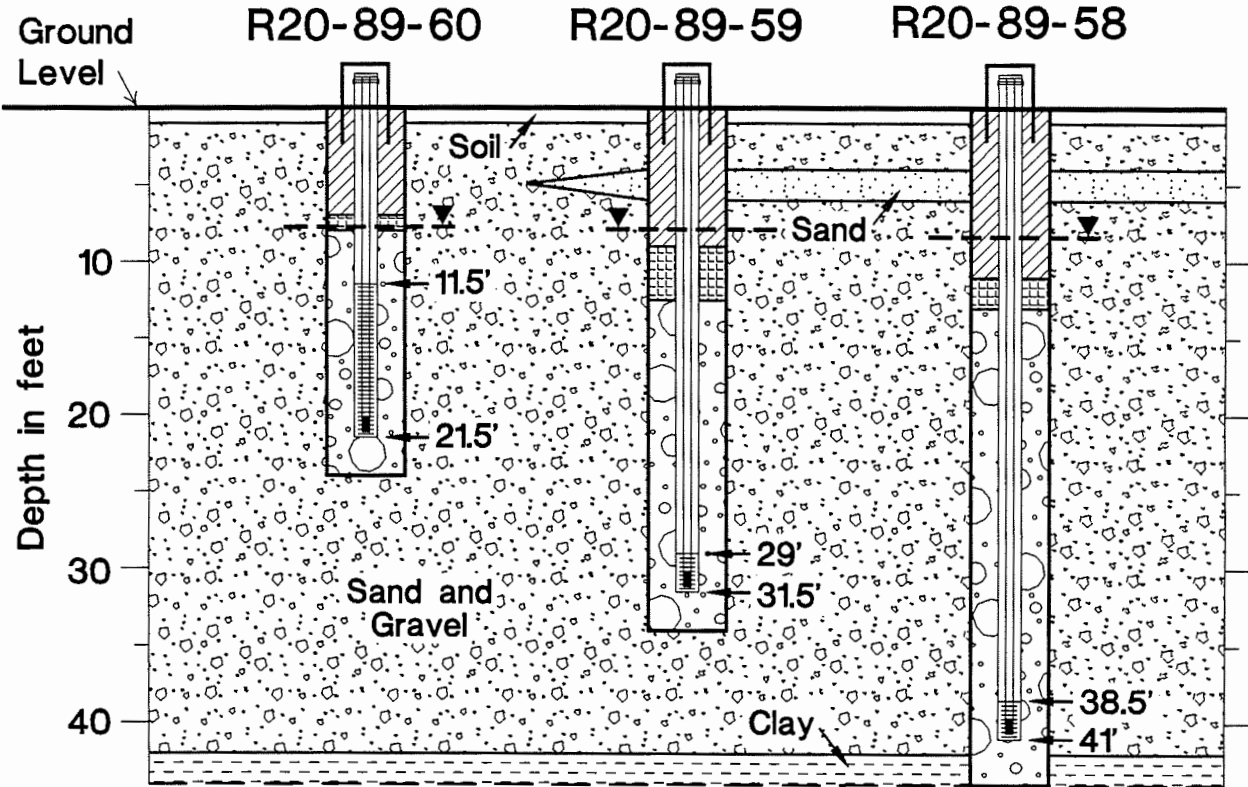
Native sediment (sand/gravel) and/or graded sand filter pack



Water level in the Big Sioux aquifer on August 25, 1993

**SE SE SE SW sec. 24, T. 96 N., R. 48 W.
(near Hudson, Lincoln County)**

W ← → E



Neat cement



Granular bentonite



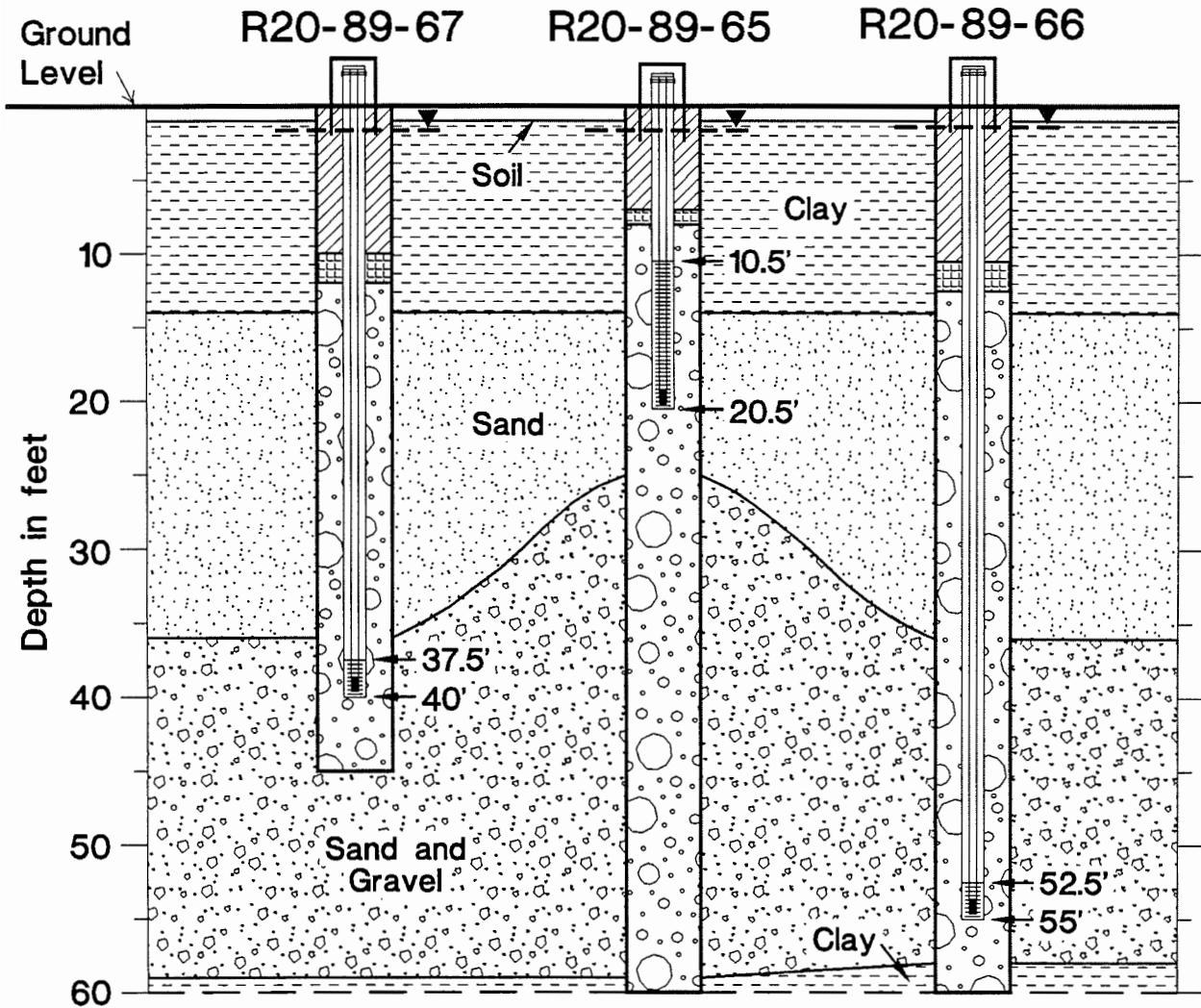
Native sediment (sand/gravel) and/or graded sand filter pack



Water level in the Big Sioux aquifer on August 23, 1993

**SE SE SE SW sec. 2, T. 92 N., R. 49 W.
(near Richland, Union County)**

W ← → E



Appendix B. Precipitation and departure from normal, in inches, for climatological recording stations, 1993

STATION	January		February		March		April		May		June	
	Precip.	Departure	Precip.	Departure	Precip.	Departure	Precip.	Departure	Precip.	Departure	Precip.	Departure
Summit	0.97	0.54	0.36	-0.09	1.05	-0.26	2.06	0.03	3.10	0.08	6.89	3.58
Watertown	0.32	-0.22	0.34	-0.24	0.58	-0.83	2.01	-0.17	2.33	-0.70	5.53	2.00
Castlewood	0.76	0.16	0.56	-0.06	0.80	-0.58	2.22	0.19	3.31	0.25	7.65	3.73
Brookings	0.41	0.09	0.37	-0.05	0.79	-0.45	1.96	-0.11	4.32	1.39	8.69	4.35
Flandreau	0.66	0.30	0.49	0.02	2.48	1.19	1.53	-0.66	3.13	0.23	9.57	5.82
Colton	0.50	0.14	0.97	0.50	2.11	0.82	2.11	-0.08	6.11	3.21	9.29	5.54
Sioux Falls airport	0.70	0.19	0.81	0.17	2.04	0.40	2.61	0.09	8.26	5.23	6.43	3.03
Canton	0.48	0.09	0.46	-0.09	2.02	0.56	1.63	-0.76	8.84	5.97	8.32	4.62
Hawarden, la.	0.57	0.12	1.09	0.17	2.49	1.04	3.80	1.49	4.63	1.17	4.15	0.04
Elk Point	0.20	-0.24	0.99	0.19	1.82	0.28	3.18	0.91	4.13	0.69	3.05	-1.17

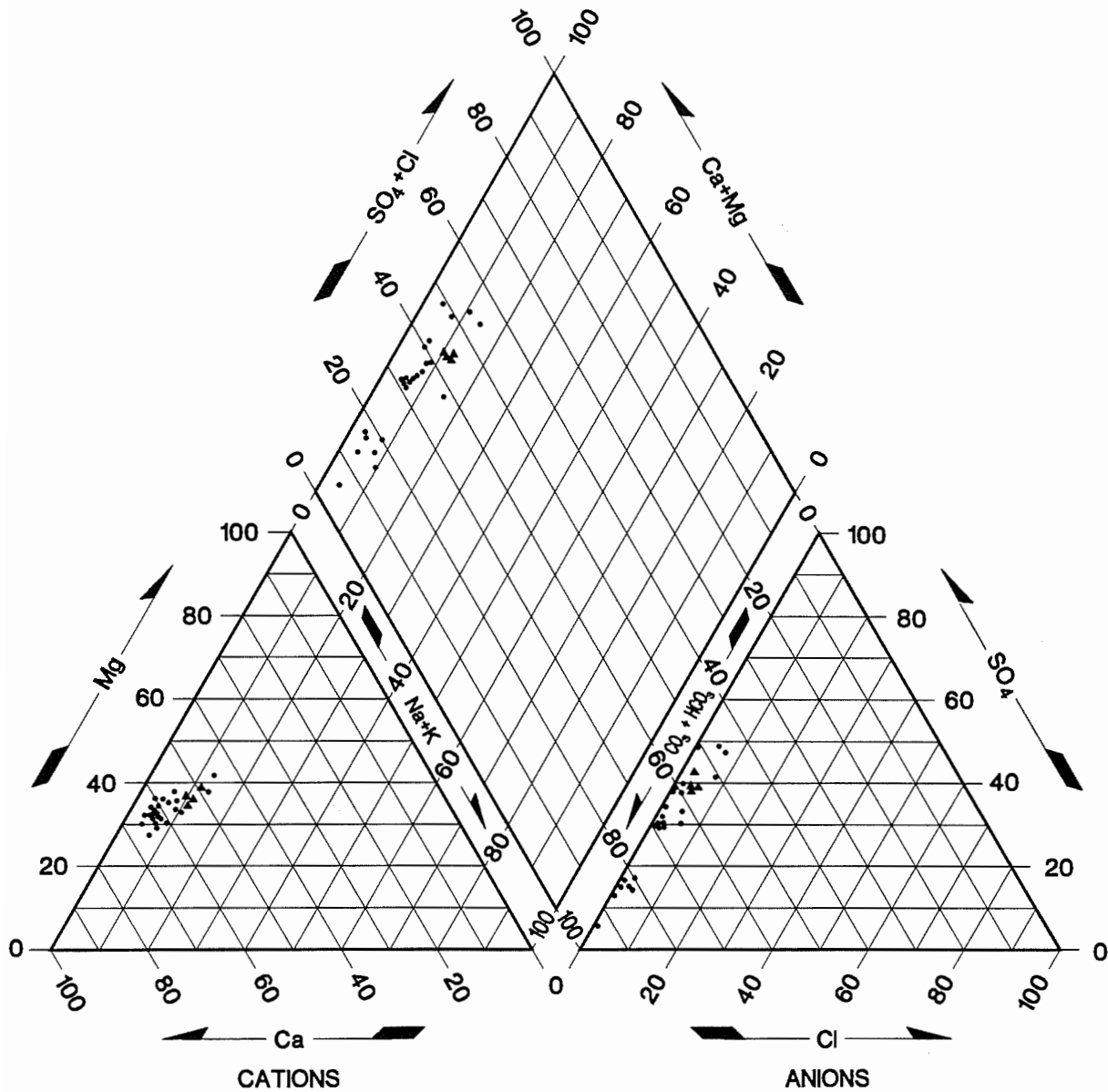
STATION	July		August		September		October		November		December		ANNUAL	
	Precip.	Departure	Precip.	Departure	Precip.	Departure	Precip.	Departure	Precip.	Departure	Precip.	Departure	Precip.	Departure
Summit	9.29	6.09	1.50	-1.32	2.49	0.50	0.75	-0.75	1.20	0.51	0.77	0.43	30.43	9.34
Watertown	5.01	1.96	2.42	-0.30	3.36	1.39	0.07	-1.80	1.58	0.73	0.55	0.05	24.10	1.87
Castlewood	5.25	1.95	1.69	-0.99	2.44	0.10	0.25	-1.53	2.37	1.51	0.73	0.16	28.03	4.89
Brookings	5.18	1.86	2.27	-0.54	2.12	-0.52	0.28	-1.38	1.70	0.89	0.49	0.16	28.58	5.69
Flandreau	9.36	6.20	1.56	-1.20	2.44	-0.29	0.03	-1.83	1.73	0.89	0.37	-0.07	33.35	10.60
Colton	8.69	5.53	2.60	-0.16	2.60	-0.13	0.28	-1.58	1.52	0.68	0.35	-0.09	37.13	14.38
Sioux Falls airport	7.86	5.18	3.10	0.25	1.88	-1.14	0.62	-1.16	1.50	0.41	0.30	-0.40	36.11	12.25
Canton	7.78	4.76	3.47	0.39	1.93	-0.71	0.38	-1.39	0.70	-0.28	0.16	-0.50	36.17	12.66
Hawarden, la.	7.10	3.62	3.63	0.06	1.81	-0.94	1.10	-0.61	1.73	0.81	0.68	-0.09	32.78	6.88
Elk Point	5.14	1.76	3.77	0.84	1.60	-1.04	1.53	-0.18	1.60	0.63	0.63	-0.03	27.64	2.64

NOTE: Because the Colton and Elk Point stations are relatively new and departure from normal values have not yet been established for these stations, departure values for Flandreau were used for the Colton station and departure values for Centerville were used for the Elk Point station.

These suggestions were made by Al Bender, State Climatologist (personal communication, July 1993).

APPENDIX C

Trilinear diagram of major cations and anions in water collected from the Big Sioux aquifer and the Big Sioux River



- Big Sioux aquifer monitoring well data
- ▲ Big Sioux River data

July 1993

Appendix D. Nitrate, ammonia, and total phosphorus concentrations in the Big Sioux aquifer ground water monitoring network wells
 (All concentrations are in milligrams per liter.)

NE SE SE SE sec. 9, T. 120 N., R. 52 W.
 (near Lonesome Lake, Grant County)

WELL NAME: R20-89-38					WELL NAME: R20-89-37					WELL NAME: R20-89-39				
Date	Nitrate	Ammonia	Total Phosphorus		Date	Nitrate	Ammonia	Total Phosphorus		Date	Nitrate	Ammonia	Total Phosphorus	
01/27/93	40.6	--	--		--	--	--	--		--	--	--	--	
02/19/93	38.4	--	--		--	--	--	--		--	--	--	--	
03/30/93	3.03	--	--		--	--	--	--		--	--	--	--	
04/27/93	3.31	--	--		--	--	--	--		--	--	--	--	
05/24/93	15.5	<0.05	0.016		05/24/93	0.12	0.50	0.079		05/24/93	<0.04	1.29	0.283	
06/21/93	23.0	<0.05	0.013		06/21/93	0.04	0.59	0.018		06/21/93	<0.04	1.26	0.263	
07/19/93	11.9	<0.05	0.011		07/19/93	<0.04	0.54	0.098		07/19/93	<0.04	1.22	0.271	
08/30/93	19.6	<0.05	0.017		08/30/93	0.15	0.56	0.095		08/30/93	<0.04	1.24	0.253	
09/28/93	33.5	--	--		--	--	--	--		--	--	--	--	
10/27/93	33.4	--	--		--	--	--	--		--	--	--	--	
11/30/93	27.3	--	--		--	--	--	--		--	--	--	--	
12/30/93	17.2	--	--		--	--	--	--		--	--	--	--	

NE SE SE SE sec. 9, T. 120 N., R. 52 W.
(near Lonesome Lake, Grant County)

WELL NAME: R20-93-30

Date	Nitrate	Ammonia	Total Phosphorus
08/30/93	16.0	<0.05	0.043
09/28/93	16.9	--	--
10/27/93	16.2	--	--
11/30/93	16.6	--	--
12/30/93	17.5	--	--

NW SW NW NW sec. 21, T. 118 N., R. 52 W.
 (near Watertown, Codington County)

WELL NAME: R20-89-42					WELL NAME: R20-89-40					WELL NAME: R20-89-41				
Date	Nitrate	Ammonia	Total Phosphorus		Date	Nitrate	Ammonia	Total Phosphorus		Date	Nitrate	Ammonia	Total Phosphorus	
01/27/93	9.04	--	--		--	--	--	--		--	--	--	--	
02/19/93	9.70	--	--		--	--	--	--		--	--	--	--	
03/30/93	10.7	--	--		--	--	--	--		--	--	--	--	
04/27/93	8.76	--	--		--	--	--	--		--	--	--	--	
05/25/93	9.14	<0.05	0.022		05/25/93	5.61	<0.05	0.048		05/25/93	0.34	0.08	0.046	
06/22/93	9.46	<0.05	0.020		06/22/93	4.83	<0.05	0.039		06/22/93	0.35	0.07	0.036	
07/20/93	5.15	<0.05	0.028		07/20/93	5.12	<0.05	0.042		07/20/93	0.35	0.09	0.037	
08/31/93	3.49	<0.05	0.021		08/31/93	4.49	<0.05	0.040		08/31/93	0.39	0.08	0.039	
09/28/93	3.68	--	--		--	--	--	--		--	--	--	--	
10/27/93	4.20	--	--		--	--	--	--		--	--	--	--	
11/30/93	5.32	--	--		--	--	--	--		--	--	--	--	
12/30/93	9.09	--	--		--	--	--	--		--	--	--	--	

SW SW SW SE sec. 15, T. 115 N., R. 52 W.
 (near Castlewood, Hamlin County)

WELL NAME: R20-89-44				WELL NAME: R20-89-43			
Date	Nitrate	Ammonia	Total Phosphorus	Date	Nitrate	Ammonia	Total Phosphorus
05/19/93	0.06	<0.05	0.051	05/19/93	0.07	<0.05	0.023
06/22/93	0.08	<0.05	0.055	06/22/93	0.57	<0.05	0.017
07/20/93	<0.04	<0.05	0.057	07/20/93	1.10	<0.05	0.025
08/31/93	<0.04	<0.05	0.054	08/31/93	2.50	<0.05	0.015

**SE SW SW SE sec. 10, T. 113 N., R. 51 W.
(near Estelline, Hamlin County)**

WELL NAME: R20-89-46				WELL NAME: R20-89-45			
Date	Nitrate	Ammonia	Total Phosphorus	Date	Nitrate	Ammonia	Total Phosphorus
05/19/93	1.35	<0.05	0.026	05/19/93	<0.04	0.13	0.023
06/22/93	1.09	<0.05	0.020	06/22/93	<0.04	0.13	0.023
07/20/93	1.33	<0.05	0.017	07/20/93	<0.04	0.12	0.015
08/31/93	1.02	<0.05	0.019	08/31/93	<0.04	0.13	0.012

NW NW NW NW sec. 18, T. 110 N., R. 50 W.
 (near Volga, Brookings County)

WELL NAME: R20-89-48				WELL NAME: R20-89-47			
Date	Nitrate	Ammonia	Total Phosphorus	Date	Nitrate	Ammonia	Total Phosphorus
05/19/93	2.02	<0.05	0.019	05/19/93	<0.04	0.17	0.100
06/22/93	1.62	<0.05	0.014	06/22/93	<0.04	0.17	0.108
07/20/93	1.56	<0.05	0.012	07/20/93	<0.04	0.17	0.107
08/31/93	2.42	<0.05	0.015	08/31/93	<0.04	0.17	0.112

**SW SW SE NE sec. 7, T. 106 N., R. 48 W.
(near Egan, Moody County)**

WELL NAME: R20-89-50				WELL NAME: R20-89-49			
Date	Nitrate	Ammonia	Total Phosphorus	Date	Nitrate	Ammonia	Total Phosphorus
05/26/93	<0.04	0.68	0.146	05/26/93	<0.04	0.79	0.182
06/23/93	<0.04	0.61	0.150	06/23/93	<0.04	0.83	0.184
07/21/93	0.09	0.39	0.148	07/21/93	<0.04	0.83	0.178
09/01/93	1.34	0.31	0.142	09/01/93	0.04	0.75	0.157

**SW SW SW SW sec. 31, T. 104 N., R. 49 W.
(near Baltic, Minnehaha County)**

WELL NAME: R20-89-64					WELL NAME: R20-89-63					WELL NAME: R20-89-62				
Date	Nitrate	Ammonia	Total Phosphorus		Date	Nitrate	Ammonia	Total Phosphorus		Date	Nitrate	Ammonia	Total Phosphorus	
01/27/93	8.97	--	--		01/27/93	4.18	--	--		--	--	--	--	
02/19/93	8.96	--	--		02/19/93	4.17	--	--		--	--	--	--	
03/30/93	7.41	--	--		03/30/93	4.29	--	--		--	--	--	--	
04/28/93	9.39	--	--		04/28/93	4.25	--	--		--	--	--	--	
05/18/93	9.24	<0.05	0.065		05/18/93	4.58	<0.05	0.065		05/18/93	0.42	<0.05	0.051	
06/29/93	8.59	<0.05	0.067		06/29/93	5.30	<0.05	0.067		06/29/93	0.21	<0.05	0.042	
07/27/93	10.2	<0.05	0.054		07/27/93	6.31	<0.05	0.064		07/27/93	0.41	<0.05	0.041	
08/24/93	9.21	<0.05	0.018		08/24/93	6.91	0.17	0.018		08/24/93	0.27	<0.05	0.020	
09/29/93	6.20	--	--		09/29/93	7.51	--	--		--	--	--	--	
10/27/93	5.89	--	--		10/27/93	8.25	--	--		--	--	--	--	
11/30/93	5.77	--	--		11/30/93	8.12	--	--		--	--	--	--	
12/29/93	5.75	--	--		12/29/93	7.72	--	--		--	--	--	--	

SE SE SE SE sec. 8, T. 102 N., R. 49 W.
 (near Renner, Minnehaha County)

WELL NAME: R20-89-55				WELL NAME: R20-89-54			
Date	Nitrate	Ammonia	Total Phosphorus	Date	Nitrate	Ammonia	Total Phosphorus
05/18/93	<0.04	0.44	0.196	05/18/93	<0.04	0.58	0.333
06/29/93	0.04	0.37	0.077	06/29/93	<0.04	0.45	0.058
07/27/93	<0.04	0.34	0.036	07/27/93	<0.04	0.54	0.086
08/24/93	0.11	0.42	0.095	08/24/93	0.07	0.56	0.154

NE SE SE NE sec. 8, T. 98 N., R. 48 W.
(near Canton, Lincoln County)

WELL NAME: R20-89-57						WELL NAME: R20-89-56					
Date	Nitrate	Ammonia	Phosphorus	Total Phosphorus		Date	Nitrate	Ammonia	Phosphorus	Total Phosphorus	
01/28/93	19.4	--	--	--		--	--	--	--	--	
02/18/93	17.5	--	--	--		--	--	--	--	--	
03/29/93	Flooded					--	--	--	--	--	
04/28/93	25.0	--	--	--		--	--	--	--	--	
05/17/93	14.2	<0.05	0.144			05/17/93	<0.04	0.48	0.199		
06/28/93	Flooded					06/28/93	Flooded				
07/26/93	0.90	<0.05	0.137			07/26/93	0.04	0.48	0.204		
08/25/93	4.90	<0.05	0.141			08/25/93	<0.04	0.50	0.182		
09/29/93	0.94	--	--	--		--	--	--	--	--	
10/27/93	3.74	--	--	--		--	--	--	--	--	
11/29/93	12.0	--	--	--		--	--	--	--	--	
12/28/93	13.0	--	--	--		--	--	--	--	--	

SE SE SE SW sec. 24, T. 96 N., R. 48 W.
 (near Hudson, Lincoln County)

WELL NAME: R20-89-60					WELL NAME: R20-89-59					WELL NAME: R20-89-58				
Date	Nitrate	Ammonia	Total Phosphorus		Date	Nitrate	Ammonia	Total Phosphorus		Date	Nitrate	Ammonia	Total Phosphorus	
01/28/93	8.56	--	--		--	--	--	--		--	--	--	--	
02/18/93	8.58	--	--		--	--	--	--		--	--	--	--	
03/29/93	0.34	--	--		--	--	--	--		--	--	--	--	
04/28/93	7.86	--	--		--	--	--	--		--	--	--	--	
05/17/93	8.28	<0.05	<0.010		05/17/93	<0.04	<0.05	0.020		05/17/93	<0.04	<0.05	0.027	
06/28/93	10.5	<0.05	<0.010		06/28/93	<0.04	<0.05	0.021		06/28/93	<0.04	<0.05	0.031	
07/26/93	12.7	<0.05	<0.010		07/26/93	<0.04	<0.05	0.022		07/26/93	<0.04	<0.05	0.029	
08/23/93	13.0	<0.05	<0.010		08/23/93	<0.04	<0.05	0.010		08/23/93	<0.04	<0.05	0.017	
09/30/93	11.5	--	--		--	--	--	--		--	--	--	--	
10/28/93	10.8	--	--		--	--	--	--		--	--	--	--	
11/29/93	10.2	--	--		--	--	--	--		--	--	--	--	
12/29/93	8.60	--	--		--	--	--	--		--	--	--	--	

SE SE SE SW sec. 2, T. 92 N., R. 49 W.
 (near Richland, Union County)

WELL NAME: R20-89-65					WELL NAME: R20-89-67					WELL NAME: R20-89-66				
Date	Nitrate	Ammonia	Total Phosphorus		Date	Nitrate	Ammonia	Total Phosphorus		Date	Nitrate	Ammonia	Total Phosphorus	
01/28/93	6.31	--	--		--	--	--	--		--	--	--	--	
02/18/93	6.09	--	--		--	--	--	--		--	--	--	--	
03/29/93	5.52	--	--		--	--	--	--		--	--	--	--	
04/28/93	6.31	--	--		--	--	--	--		--	--	--	--	
05/27/93	Flooded				05/27/93	Flooded				05/27/93	Flooded			
06/28/93	Flooded				06/28/93	Flooded				06/28/93	Flooded			
07/26/93	Flooded				07/26/93	Flooded				07/26/93	Flooded			
08/23/93	1.49	<0.05	0.030		08/23/93	<0.04	0.50	0.021		08/23/93	<0.04	0.42	0.012	
09/30/93	2.11	--	--		--	--	--	--		--	--	--	--	
10/28/93	2.25	--	--		--	--	--	--		--	--	--	--	
11/29/93	2.38	--	--		--	--	--	--		--	--	--	--	
12/28/93	3.17	--	--		--	--	--	--		--	--	--	--	

Appendix E. Nitrate, ammonia, and total phosphorus concentrations in the Big Sioux River

(All concentrations are in milligrams per liter.)

SW SE SE SE sec. 8, T. 120 N., R. 52 W.
(near Lonesome Lake, Grant County)

Date	Nitrate	Ammonia	Total
			Phosphorus
05/25/93	0.47	<0.05	0.061
06/21/93	0.59	0.09	0.281
07/19/93	0.09	<0.05	0.164
08/30/93	0.97	0.23	0.146

SW SW SE NE sec. 7, T. 106 N., R. 48 W.
(near Egan, Moody County)

Big Sioux River			
Date	Nitrate	Ammonia	Total
			Phosphorus
05/26/93	0.39	<0.05	0.086
06/23/93	0.60	0.05	0.160
07/21/93	0.39	0.10	0.300
09/01/93	0.67	<0.05	0.200

NE SE SE NE sec. 8, T. 98 N., R. 48 W. (next to R20-89-56 and R20-89-57 near Canton, Lincoln County)		NW NW SW SW sec.16, T. 98 N., R. 48 W. (east of Canton, Lincoln County)	
Big Sioux River		Big Sioux River	
Date	Nitrate	Ammonia	Total Phosphorus
06/28/93	0.81	0.05	0.196
Date	Nitrate	Ammonia	Total Phosphorus
06/28/93	0.70	0.07	0.201

NE SW SW SW sec. 36, T. 93 N., R. 49 W. (near Akron, Iowa)				SE SE SW SW sec. 30, T. 93 N., R. 48 W. (upstream from Akron, Iowa)				SE SW NW NE sec. 28, T. 92 N., R. 49 (near Richland, Union County)			
Big Sioux River				Big Sioux River				Big Sioux River			
Date	Nitrate	Ammonia	Total Phosphorus	Date	Nitrate	Ammonia	Total Phosphorus	Date	Nitrate	Ammonia	Total Phosphorus
05/27/93	4.19	0.08	0.130	05/27/93	4.13	0.07	0.125	05/27/93	4.07	0.07	0.123
06/28/93	2.29	0.07	0.187	06/28/93	2.60	0.09	0.219	06/28/93	2.30	0.12	0.204
07/26/93	4.55	0.08	0.232	07/26/93	4.66	0.05	0.230	07/26/93	4.56	0.07	0.222