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OPEN-FILE REPORT 67-UR

WATER-QUALITY MONITORING AND EVALUATION OF NONPOINT-SOURCE CONTAMINATION IN THE BIG SIOUX AQUIFER, SOUTH DAKOTA, 1989 THROUGH 1992

by

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1994

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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 permanent ground water monitoring network throughout the Big Sioux River drainage basin (fig. 1) and systematically sample this network, over a period of years, to identify changes in the water quality of the aquifer. For this program, a permanent ground water monitoring network, consisting of 27 monitoring wells, was established. 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. Because of the good hydraulic connection between the Big Sioux aquifer and the Big Sioux River, the Big Sioux River has also been sampled for organic and inorganic constituents.

This project is being conducted by the South Dakota Geological Survey (SDGS), a Division of the South Dakota Department of Environment and Natural Resources.

Acknowledgments

Partial funding for the construction of monitoring wells, and the initial collection and analysis of water samples, was provided by the United States Environmental Protection Agency (U.S. EPA) through the Section 319 Nonpoint Source Implementation Fund. Funding for pesticide analyses during the 1992 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 SDGS. The assistance and cooperation of the SDDA were important factors in the success of this project.

Background

The Big Sioux aquifer provides approximately one-third of the state's population with water for various uses including municipal, rural water, and irrigation (South Dakota Department of Water and Natural Resources, undated). Because of the surficial and unconfined nature of the Big Sioux aquifer, it is potentially vulnerable to contamination. Previous ground-water investigations in the Big Sioux aquifer (Barari and others, 1988; Hammond, 1989) have found that several areas contain elevated concentrations of nitrate that are indicative of nonpoint-source contamination. For this report, because the nitrite-nitrogen component is very small, nitrate-nitrogen plus nitrite-nitrogen will be reported simply as nitrate. Also, ammonia-nitrogen will be reported simply as ammonia.

Due to the aquifer's vulnerability and growing public concerns about the quality and long-term suitability of water for drinking-water supplies, a permanent ground water monitoring network was established in 1989 to monitor the water quality in the Big Sioux aquifer. Throughout the basin, from Grant County to Union County, 27 monitoring wells were installed at 11 locations (fig. 2). The permanent monitoring network wells are not located downgradient from any identifiable point source pollution areas and provide for monitoring over much of the aquifer's extent.

Figure 1. Location of the Big Sioux River drainage basin and the average annual precipitation, in inches.

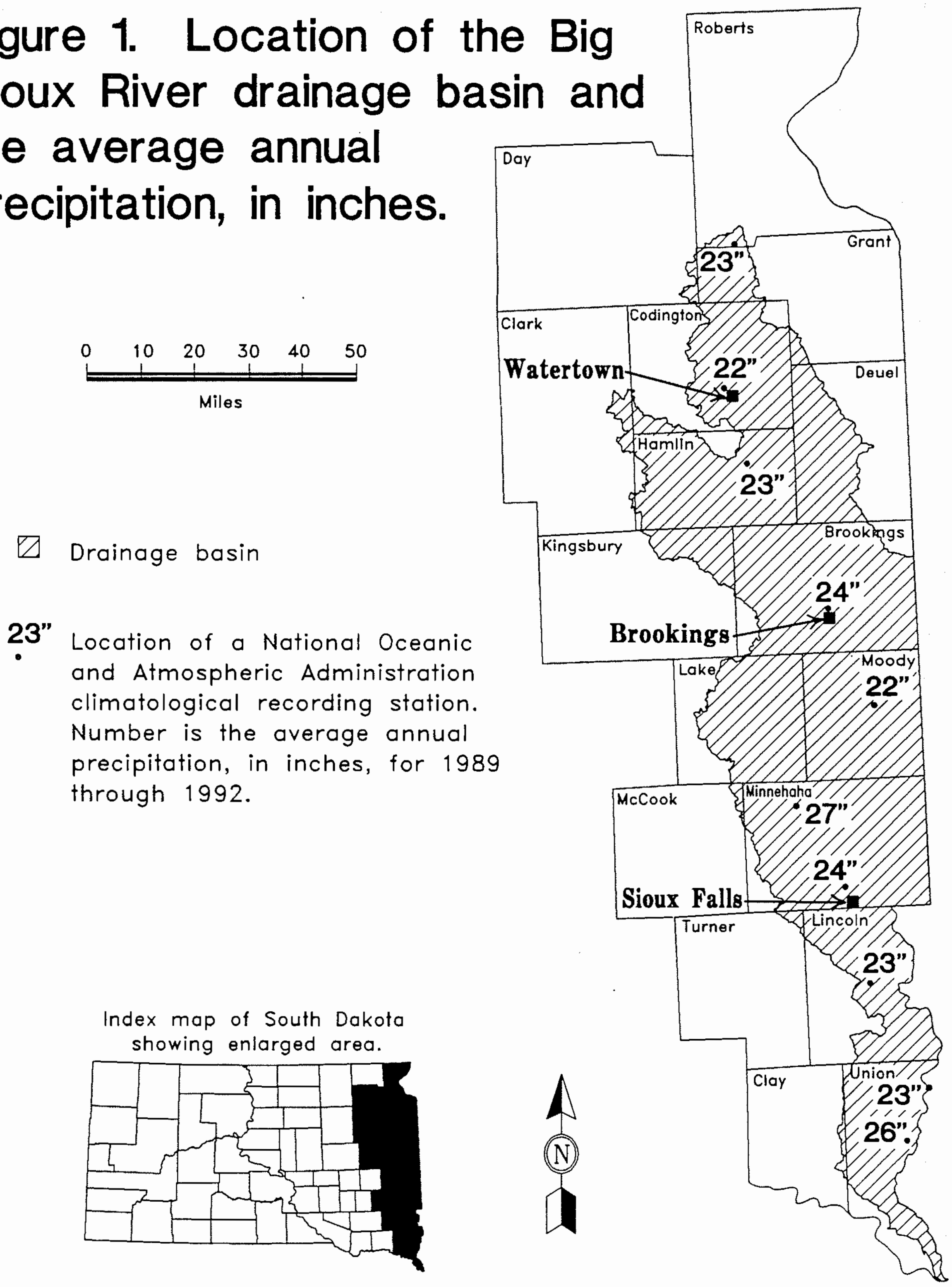
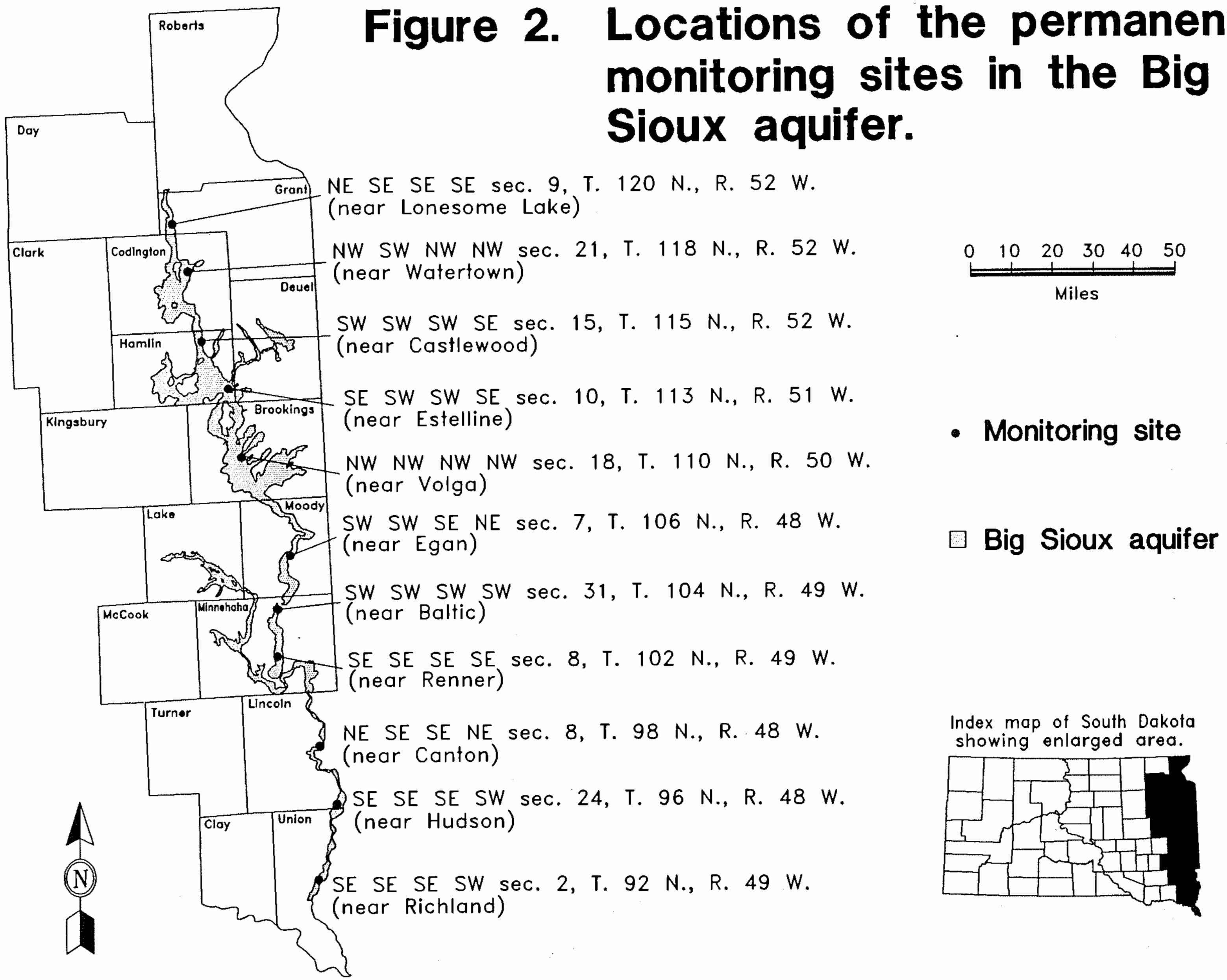


Figure 2. Locations of the permanent monitoring sites in the Big Sioux aquifer.



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 corner of the state to Union County in the southeast portion of the state (fig. 1).

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.

METHODS AND PROCEDURES

Site Selection

The Big Sioux aquifer underlies approximately 1,300 square miles of the Big Sioux River drainage basin and available information was reviewed before choosing permanent monitoring sites. Because nitrate has been found to be stratified within an aquifer (Freeze and Cherry, 1979; Hill, 1982; Ritter and Chirnside, 1984; Pěkný and others, 1989; Rajagopal and Tobin, 1989; Townsend and Marks, 1990), one initial objective was to choose locations throughout the basin where aquifer thickness was sufficient to allow for the placement of monitoring wells at various depths (nested monitoring wells at each site). This would permit the collection of water samples from various depths within the aquifer. During the site selection process, those areas deemed most desirable were areas where the saturated thickness was sufficient to accommodate three nested monitoring wells at each site. However, a saturated thickness that could accommodate only two nested monitoring wells was deemed acceptable if the aquifer was not thick enough. Another consideration in selecting monitoring sites was to achieve a fairly even areal distribution of the sites throughout the aquifer. It was hoped that with an initial even distribution of the sites, a general baseline perspective of the aquifer could be acquired. Then, if necessary, more sites could be added to the network.

With the two criteria for site selection in mind (adequate aquifer thickness to allow for nesting monitoring wells and even areal distribution of sites throughout the aquifer), the SDGS database was searched. Over 7,000 logs (lithologic, water quality, and water level) from within the Big Sioux River drainage basin were examined and 11 sites were chosen for the permanent ground water monitoring network (fig. 2). These sites were then field checked so as to identify specific drilling locations and to be sure that the sites were not downgradient from apparent point source pollution areas.

Drilling and Monitoring Well Installation

Drilling occurred from July 11, 1989, through August 24, 1989, and was performed using the hollowstem auger drilling method. Thirty-one test holes were drilled and 27 were completed as monitoring wells (fig. 2 and app. A). Lithologic logs are on file at the SDGS.

Monitoring wells were constructed using 4-inch diameter, schedule 40, flush threaded, polyvinyl chloride (PVC) casing and screen. Two or three 4-inch diameter monitoring wells are nested at each site to examine the water quality vertically within the aquifer. Data on screen length, well depth, and well construction are presented in appendix A. Figure 3 presents a generalized diagram of well construction.

Before drilling commenced, the drilling rig and all drilling tools were cleaned using high-temperature, high-pressure water. This cleaning included the augers and auger racks, saw horses, split-spoon sampler, shovels, and any other tools used in the drilling process. The water truck was also cleaned. The drilling rig was thoroughly cleaned at each monitoring site while the drilling tools were thoroughly cleaned between each test hole drilled. In short, anything that potentially might come in contact with the aquifer material during the drilling process was thoroughly cleaned. It was imperative that each test hole be as "clean" as possible and that no contaminants were introduced from the drilling or well-installation process.

The PVC casing and screens were shipped from the manufacturer precleaned and individually wrapped. If the protective wrap had been torn, the PVC was completely cleaned again. Clean gloves were worn during the time of well installation and were used whenever the PVC was handled.

After drilling, the casing and screen were lowered to the specified depth within the hollowstem augers (6⅝-inch inside diameter) in order to ensure proper placement of the screen. The augers were then lifted from the hole and native sediment was allowed to collapse around the screen providing a natural filter pack. On several occasions, the aquifer material collapsed to the water-table level covering the screen and casing up to 40 feet above the top of the screen. If the collapsed native material did not cover the screen, a clean, well-sorted, coarse sand was placed around the outside of the screen up to at least 1 foot above the top of the screen. Granular bentonite was then poured into the annular space around the outside of the casing. The remaining upper portion of the annular space was filled with cement grout and finally topped with soil. A locking steel well protector was installed into the cement and secured shut with a padlock.

Well Development

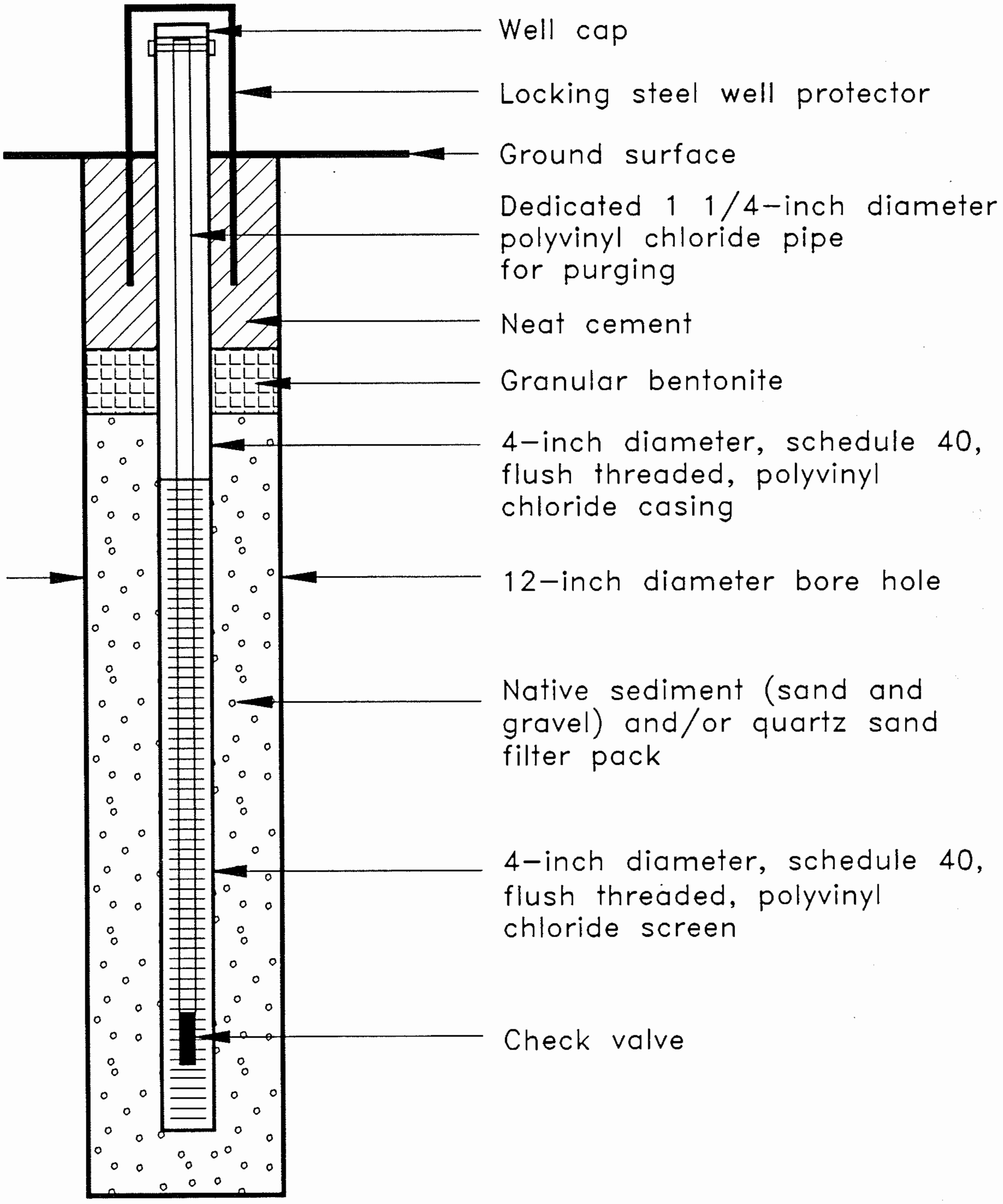
Monitoring wells were developed using: 1) a Teflon bailer, or 2) a jet pump or inertia pump attached to a dedicated 1¼-inch diameter PVC pipe with a check valve attached to the bottom of the pipe (fig. 3). A minimum of 6 well volumes of water was removed from each monitoring well during development and, on the average, 38 to 40 well volumes were removed.

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.

Figure 3. Generalized diagram showing well construction.



Two shallow monitoring wells (R20-89-38, near Lonesome Lake, Grant County, and R20-89-44, near Castlewood, Hamlin County) were purged using a Teflon bailer.

Each water sample was collected using a laboratory-cleaned Teflon bailer attached to a steel wire and a down-rigger assembly. Latex gloves were worn during sample collection. Field measurements, sample preparation, and sample handling followed SDGS protocol (Coker and others, 1988).

All 27 monitoring wells in the Big Sioux aquifer permanent ground water monitoring network (fig. 2, table 1) were sampled. For this report, general geographic location or monitoring well name will be used for identification purposes rather than legal locations. See table 1 for assistance.

Surface Water

Because of the good hydraulic connection between the Big Sioux aquifer and the Big Sioux River, the river was also sampled. The river sample was collected at SW SW SE NE sec. 7, T. 106 N., R. 48 W. (near Egan, Moody County). At this location, the river is easily reached and is near the only site where there were consistent pesticide detections in the ground water. The surface water sample was collected by wading out into the river and allowing the flow of the river to fill the filter barrel or the sample bottle.

Sampling Frequency and Sample Analysis

Ground Water

INORGANIC PARAMETERS

For this report, because the nitrite-nitrogen component is very small, nitrate-nitrogen plus nitrite-nitrogen will be reported simply as nitrate. Ammonia-nitrogen will be reported simply as ammonia.

The entire permanent ground water monitoring network has been sampled 13 times for inorganic analysis: September and November 1989; March, April, May, June, and July 1990; May and August 1991; January, May, July, and August 1992. Water samples from all 13 sampling events were analyzed for nitrate, ammonia, and total phosphorus. To more closely examine fluctuations in nitrate concentrations over time, seven monitoring wells were sampled monthly for nitrate analysis. A complete analysis for major cations and anions was performed in September 1989; April 1990; and May 1992. A nearly complete analysis for major cations and anions was performed in May 1991. The SDGS Basic and Analytical Studies Laboratory performed the analyses for major cations and anions. Parameters that were determined are: total alkalinity, ammonia, bicarbonate, carbonate, calcium, chloride, conductivity, fluoride, iron, hardness, magnesium, manganese, nitrate, pH, potassium, sodium, total-dissolved solids, and sulfate.

Table 1. Legal locations of permanent 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 R20-89-37 R20-89-39	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. Pesticides analyzed in water samples.

Common Name	Trade Name
alachlor	Lasso
atrazine	AAtrex
bentazon	Basagran
butylate	Sutan
carbofuran	Furadan
chlorpyrifos	Lorsban
cyanazine	Bladex
2,4-D	2,4-D
dicamba	Banvel
EPTC	Eradicane
ethoprop	Mocap
fonofos	Dyfonate
MCPA	MCPA
metolachlor	Dual
metribuzin	Sencor
pendimethalin	Prowl
phorate	Thimet
picloram	Tordon
terbufos	Counter
2,4,5-TP	Silvex
trifluralin	Treflan

PESTICIDES

The entire permanent ground water monitoring network was sampled five times for pesticide analysis: August 1991; January, May, July, and August 1992. Analyses were performed for pesticides listed on table 2. This list contains the pesticides that are most heavily used in the study area and some additional pesticides that were selected by the SDDA. 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. The immunoassay method of analysis was performed on all samples by the SDGS.

The SDGS purchased immunoassay test kits for atrazine, alachlor, and 2,4-D analysis. Atrazine and alachlor were analyzed during all five sampling events. However, the 2,4-D test kit was not released by the manufacturer until May 1992. Therefore, 2,4-D was analyzed only during the May, July, and August 1992, sampling events. The immunoassay test kits purchased by SDGS can be used as a qualitative (yes/no) test or as a quantitative procedure for detection of a single pesticide in water. The kits purchased by the SDGS have a detection limit of 0.1 micrograms per liter. Analyses using the immunoassay method were compared against the results from the gas chromatography/mass spectrometry method.

Surface Water

INORGANIC PARAMETERS

The Big Sioux River was sampled seven times for inorganic analysis: March and April 1990; August 1991; January, May, July, and August 1992. Water samples from all seven sampling events were analyzed for nitrate, ammonia, and total phosphorus. A complete analysis for major cations and anions was performed in April 1990 and May 1992. The SDGS Basic and Analytical Studies Laboratory performed the analyses for major cations and anions. Parameters that were determined are: total alkalinity, ammonia, bicarbonate, carbonate, calcium, chloride, conductivity, fluoride, iron, hardness, magnesium, manganese, nitrate, pH, potassium, sodium, total-dissolved solids, and sulfate.

PESTICIDES

The Big Sioux River was sampled five times for pesticide analysis: August 1991; January, May, July, and August 1992. River samples were analyzed for the same pesticides as the ground-water samples (table 2), thus allowing a direct comparison of surface-water and ground-water quality. The gas chromatography/mass spectrometry method of analysis was performed on river samples collected during January, May, July, and August 1992. The immunoassay method of analysis was performed on all river samples. 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.

The SDGS purchased immunoassay test kits for atrazine, alachlor, and 2,4-D analysis. Atrazine and alachlor were analyzed during all five sampling events. However, the 2,4-D test kit was not released by the manufacturer until May 1992. Therefore, as with the ground-water samples, 2,4-D was analyzed only during the May, July, and August 1992, sampling events.

Laboratory Credentials

The SDGS laboratory is certified by the U.S. EPA for analytical methods used for the parameters of arsenic, fluoride, mercury, nitrate plus nitrite as nitrogen, nitrite 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 has been used previously by the SDGS because of its reputation and quality-assurance/quality-control practices. Chain-of-custody forms were used for all pesticide samples.

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 with distilled water and then nano-pure water.

Precipitation Data

For this investigation, the SDGS used monthly total precipitation data collected from recording stations located near each of the monitoring well sites (table 3). These data are gathered by the State Climatologist at South Dakota State University and compiled and published by the National Oceanic and Atmospheric Administration.

HYDROGEOLOGIC SETTING

General Geology

The surficial geology of the eastern half of South Dakota is derived primarily from glaciation. The result of this glaciation was the deposition of material referred to as glacial drift composed of till and outwash. Till consists of a heterogeneous mixture of boulders, gravel, sand, clay, and silt. The till matrix is composed predominantly of clay and silt. Outwash consists primarily of sand and gravel that has been washed, sorted, and deposited by flowing meltwater. Varying amounts of less permeable materials (silt and clay) may be dispersed throughout the outwash matrix. These sand and gravel deposits (outwash) are often important aquifers.

Big Sioux Aquifer

Outwash deposits along the Big Sioux River and its tributaries comprise the Big Sioux aquifer. The Big Sioux aquifer (fig. 2) is primarily an unconfined, surficial aquifer composed of sand and

Table 3. Locations of nearest climatological recording stations.

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

gravel (outwash) and covers an area of approximately 1,300 square miles and underlies portions of 12 counties. The predominant grain size of the aquifer material ranges from fine sand to very coarse gravel. The outwash ranges in thickness from a few feet to more than 100 feet. Ground-water recharge is thought to be primarily from downward percolation of precipitation or, in some areas, excess irrigation. Surface water, such as the Big Sioux River, may also infiltrate into the aquifer when surface-water elevations are higher than adjacent ground water elevations.

GENERAL CLIMATE SUMMARY

Weather summaries and crop information (1989 through 1992) were acquired from the South Dakota Agricultural Statistics Service. This information is on file at the SDGS.

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 illustrates average precipitation (in inches), for the years 1989 through 1992, for the recording stations located near each monitoring well site (table 3).

During 1989, weather was drier than normal for South Dakota. Soil moisture conditions varied, but subsoil moisture was considered down for the season. During the growing season, timely rains occurred during the first week of May and the second and third weeks of September, however, 90 percent of the subsoil moisture was reported as short or critically short as of November 5.

During 1990, weather conditions over the state of South Dakota were generally favorable, although drought conditions continued in the northwest and north-central portions of the state. Throughout the state, dry conditions prevailed in April and May. Heavy rains occurred in mid-May and continued through June, causing some low-land flooding. Dry conditions occurred late in the year and by mid-November 59 percent of the state was either short or critically short of stock water supplies.

In 1991, South Dakota experienced unusually wet conditions in the spring followed by dry to drought-like conditions in the summer. In the northeast and southwest portions of the state, heavy rains in May caused flash flooding. Very dry conditions followed the heavy rainfall and drought conditions were reported in the southeast and northwest portions of the state.

In 1992, South Dakota had very unusual weather for the crop year. A dry spring was followed by a very wet and cool summer and fall.

RESULTS OF INVESTIGATION

Aquifer Description

At the permanent monitoring network drill sites, the outwash material ranges in composition from fine sand to very coarse gravel and varies in thickness from 50 feet (near Lonesome Lake, Grant County) to 17 feet (near Castlewood, Hamlin County). The Big Sioux aquifer (saturated outwash) ranges in thickness from approximately 34 feet (near Richland, Union County) to approximately 10 feet (near Canton, Lincoln County). Near Sioux Falls, bedrock (Sioux Quartzite) crops out at, or is found very near, the ground surface. Here the aquifer is relatively thin or absent.

At 4 of the 11 monitoring sites, outwash directly underlies the soil profile. At the other seven monitoring sites, clay, or silt and clay, directly underlies the soil profile and directly overlies the outwash. This overlying layer of clay, or silt and clay, is generally less permeable than the outwash and ranges in thickness from 1 to 2 feet (near Castlewood, Hamlin County) to 13 feet (near Richland, Union County). See appendix A for monitoring well construction and hydrostratigraphic cross sections for each monitoring location.

Water Quality

Major Anions and Cations

Trilinear diagrams (app. B) are 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 graph in which major groupings or trends in the data can be identified visually. These diagrams conveniently reveal similarities or differences among water samples because those samples with similar qualities will tend to plot together as groups.

Trilinear diagrams were constructed for analyses of water samples collected from the Big Sioux aquifer and the Big Sioux River during the September 1989, April 1990, and May 1992, sampling events. These diagrams are used in this study to: 1) identify the dominant ions in the water, and 2) to show any changes or fluctuations in general water quality over time. The trilinear diagrams show 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 the three trilinear diagrams (app. B), it appears that generally the water quality in the Big Sioux aquifer has not changed from 1989 to 1992 and continues to be primarily a calcium-bicarbonate type of water. The trilinear diagrams show that the type of water collected from the Big Sioux River is also calcium-bicarbonate, and generally, the water quality in the Big Sioux River had not changed from 1990 to 1992.

The water quality in the Big Sioux aquifer is generally good. Total-dissolved solids ranged from 314 to 844 milligrams per liter (mg/L) in 1989, and in 1992 from 343 to 955 mg/L. Hardness, in 1989, ranged from 239 to 685 mg/L, and in 1992 ranged from 287 to 710 mg/L. Sulfate ranged from 30 to 298 mg/L in 1989, and from 38 to 371 mg/L in 1992. There were slight increases in concentrations of some of the parameters, but generally the increases were small and the overall water quality in the aquifer remained consistent over time.

Nitrate

Nitrate, the most common contaminant identified in ground water, generally originates from nitrogen sources on the land surface, in the soil zone, or in shallow subsoil zones where nitrogen-rich wastes are buried (Freeze and Cherry, 1979). Through the process of ammonification, organic nitrogen is converted to ammonia. Taking this conversion one step further, through the process of nitrification, the ammonia is converted to nitrate. Normally, the ammonification and nitrification processes take place in the soil zone where organic matter and oxygen are abundant.

In South Dakota, nitrogen accounts for approximately 60 percent of the actual nutrients applied to agricultural land (this information is based on data acquired from the South Dakota Agricultural Statistics Service). Generally, when nitrogen is delivered to the soil as ammonia or ammonium ion, it is retained in the soil profile better than when the nitrogen is delivered as nitrate. This is because the ammonium ion is positively charged and tends to be adsorbed to the negatively charged silicate minerals in the soil. The nitrate ion, however, is a negatively charged ion and tends to be repelled from the mineral-grain surfaces and, consequently, moves freely with downward percolating water

(Chapelle, 1993). Therefore, nitrate is soluble, very mobile, and readily leaches into the shallow ground water. Also, shallow ground water tends to be aerobic (oxygen is present) near the water-table surface and nitrate accumulates here in solution. In deeper portions of the ground water, anaerobic conditions (oxygen is not present) are more common and because of denitrification, nitrate concentrations decrease. Nitrate stratification in the ground water is therefore primarily dependent on the delivery of nitrate to the water-table surface and the presence or absence of oxygen (Chapelle, 1993).

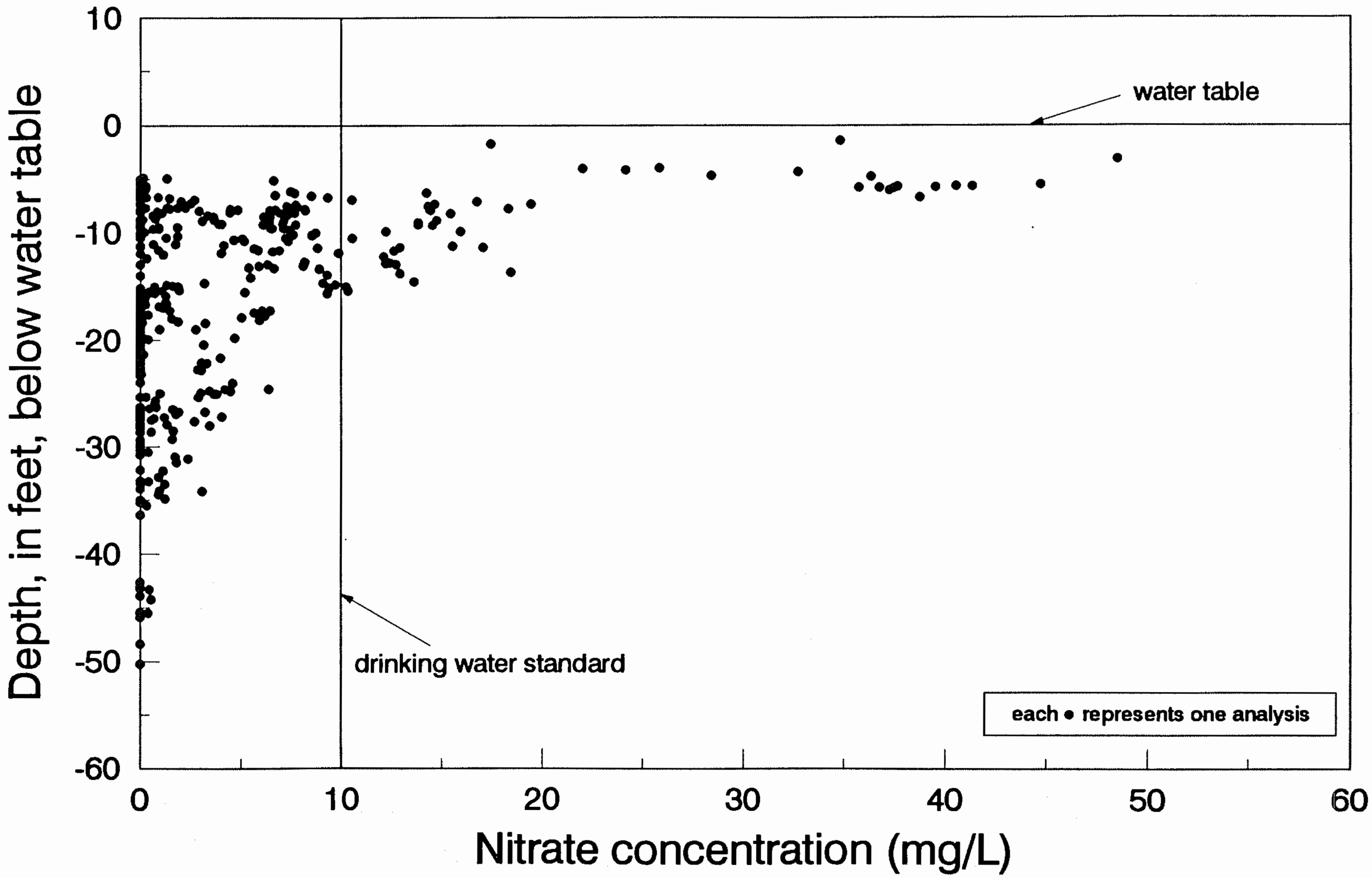
Nitrate is transported from the root zone to ground water by downward moving water in the vadose (unsaturated) zone (Bouwer, 1989). The downward moving water, or deep-percolation flow, may be generated in pulses with each rainfall or irrigation event. According to Bouwer (1989), half of the nitrogen applied as fertilizer to a crop is used by the crop, one-fourth is denitrified, and the other one-fourth moves as nitrate down to the water table. This statement should be considered only as a "rule of thumb." When looking at the actual disposition of nitrogen, it is important to consider numerous factors such as: amount and timing of fertilizer application, precipitation amounts, irrigation practices, and agronomic practices.

When water from the vadose zone reaches the ground water, the vadose-zone water tends to stay at the top of the water table. This stratification occurs where the density (total dissolved salt content) of the water in the vadose zone does not exceed the density of the water in the aquifer (Bouwer, 1989). In humid areas, where the total dissolved salt content of the vadose-zone water is low, stratification of nitrate in the aquifer might be expected. In relatively dry climates, where water from irrigated lands percolates downward, the salt content of the vadose-zone water can be elevated. If this salt-enriched water reaches an aquifer with a lower salt content, the salt-rich water will tend to "sink" deeper into the aquifer causing a more complete mixing with the original ground water (Bouwer, 1989).

In the Big Sioux aquifer, it is common to find nitrate stratified within the aquifer. When plotting the nitrate concentration (app. C) versus depth below the water table (fig. 4), the nitrate stratification is obvious. 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 4 shows that nitrate concentrations greater than 10 mg/L are generally found within 15 feet of the water table. Throughout the Big Sioux permanent ground water monitoring network, the highest concentrations of nitrate are found in the shallow monitoring wells screened at, near, or through the water table showing a vertical stratification of nitrate in the ground water.

Two of the 11 monitoring sites (shallow monitoring wells R20-89-38 near Lonesome Lake, Grant County, and R20-89-64 near Baltic, Minnehaha 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; R20-89-57 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 between 5 and 10 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 permanent ground water monitoring

Figure 4. Nitrate concentration versus depth below water table



network sites, the data suggest nonpoint-source pollution is a factor in nitrate contamination in some places within the Big Sioux aquifer.

Further examination of ground water for the monitoring site near Lonesome Lake, Grant County, shows fluctuating nitrate concentrations over time (fig. 5). At this site, nitrate concentrations ranged from a low of 14.2 mg/L on August 12, 1991, to a high of 48.5 mg/L on August 24, 1992.

When precipitation data are added to figure 5, a correlation begins to appear between precipitation and nitrate concentrations. The data suggest that during a period of increased precipitation, a dilution event causes a temporary decrease in nitrate concentration followed by an increase in nitrate concentration. For this investigation, precipitation data were recorded on a monthly basis and do not take into account specific rain events. Therefore, data were not collected from this site frequently enough to make any direct correlations between nitrate concentration and precipitation. Ground-water samples must be collected at least monthly, if not more frequently, and correlated with monthly or daily precipitation data in order to attempt to explain the conditions at the Lonesome Lake site.

In the Big Sioux River, nitrate concentrations ranged from less than 0.04 to 1.83 mg/L. These concentrations are low and indicate that nitrate contamination is not a concern in the Big Sioux River at this location.

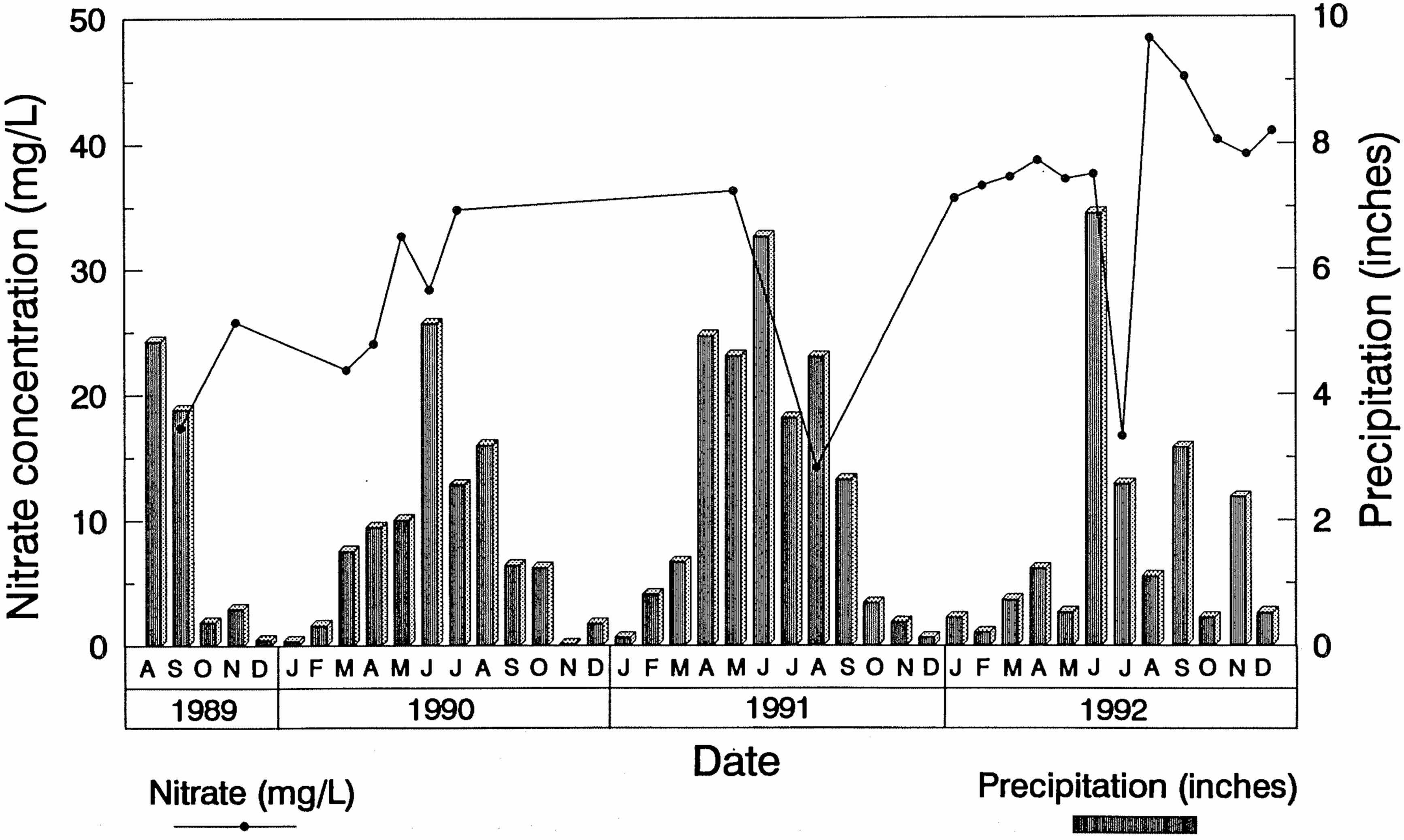
Ammonia

Most fertilizer nitrogen is applied as ammonium or in forms that are rapidly converted to ammonium (Blackmer, 1988). When nitrogen fertilizers are applied to soils, the nitrification process begins, and within 2 to 3 weeks most of the ammonium is converted to nitrate (Blackmer, 1988). The nitrification process may, however, be slower in the fall when soils are too cold for rapid microbial activity. In this case, fertilizers are nitrified the following spring when soil temperatures increase. As stated previously, because ammonium is a cation (positively charged ion), it is attracted to soil particles and is not readily leached from soils to the ground water. Therefore, because of the rapid conversion process (nitrification) of ammonium to nitrate and because ammonium is adsorbed readily onto soil particles, ammonium is unlikely to be found in shallow ground water. However, in deeper portions of the aquifer, anaerobic conditions are more common and because of denitrification, nitrate is converted to ammonia.

In the Big Sioux aquifer, ammonia concentrations range from less than 0.05 mg/L to 1.78 mg/L (app. C). The higher ammonia concentrations are generally found in the deeper portions of the aquifer where nitrate concentrations are low. Where ammonia concentrations are low, in the upper portions of the aquifer, nitrate concentrations are elevated. Based on these numbers, ammonia contamination is not a problem in water collected from the Big Sioux aquifer.

In the Big Sioux River, ammonia concentrations range from less the 0.05 to 0.09 mg/L. For reference, downstream of waste-water discharges, ammonia concentrations may approach 5 mg/L while concentrations of ammonia in untreated sewage may exceed 30 mg/L (McCutcheon and others, 1993). Generally, in small streams ammonia concentrations are less than 3 mg/L to as low as 0.5

Figure 5. Nitrate fluctuation with time and precipitation for the monitoring site near Lonesome Lake, Grant County (monitoring well R20-89-38).



mg/L, and are as low as 0.1 mg/L in uncontaminated reaches of a stream (McCutcheon and others, 1993). Ammonia concentrations greater than 0.5 mg/L tend to cause significant ammonia toxicity to fish and other organisms (McCutcheon and others, 1993). Based on these numbers, ammonia contamination is not a problem in water collected from the Big Sioux River.

Phosphorous

The major sources of phosphorus are soil-applied fertilizers and waste water. In South Dakota, phosphoric acid (phosphorus) accounts for approximately 30 percent of actual nutrients applied to agricultural land (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 solids (Domenico and Schwartz, 1990). Consequently, phosphorus is seldom found in the ground water. However, in areas of coarse-grained soils, soluble forms of phosphorus will leach into the ground water (Krider, 1988) and can be used to indicate contamination from soil-applied fertilizers. Phosphorus does not present a significant human health risk, but it can accelerate the growth of certain blue-green algae that are toxic to livestock (Krider, 1988).

In the Big Sioux aquifer, total-phosphorus concentrations are low, ranging from less than 0.010 to 0.398 mg/L. In treated drinking water, phosphorous concentrations of 4 mg/L are found (Drinking Water Health Effects Task Force, 1989), and 6 mg/L represents weak domestic sewage (U.S. Environmental Protection Agency, 1976). Based on these numbers, phosphorus contamination is not a problem in water collected from the Big Sioux aquifer.

In the Big Sioux River, total-phosphorus concentrations range from 0.030 to 0.186 mg/L. 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). Based on these numbers, phosphorus contamination is not a problem in water collected from the Big Sioux River.

Pesticides

Some pesticides are more mobile or more persistent than others in the soil profile and for these reasons it is important to set a sampling schedule that takes these factors, as well as farming practices and precipitation, into consideration. When monitoring ground water for pesticides, the most useful information will be acquired if water samples are collected at least seasonally and if the pesticides used in the basin are targeted for analysis. For this project a list was compiled, from data supplied by the South Dakota Department of Agriculture, which identified the pesticides used in the counties where the SDGS has a Big Sioux aquifer permanent monitoring network site. This list showed that the most commonly used pesticides in those counties are: 2,4-D, Atrazine, Banvel, Basagran, Bladex, Eradicane, Lasso, MCPA, Oust, Sencor, Tordon, and Treflan. According to county extension agents, the most heavily used and consistently used pesticides in the area of the monitoring network are:

2,4-D, Banvel, Eradicane, Lasso (southern corn counties primarily), MCPA (northern wheat counties primarily), and Treflan. Oust and Basagran were reportedly not heavily used in the study area and Tordon was reportedly used primarily on noncrop areas (pastures and ditches) at low rates. Most of the heavily used chemicals are applied just before or just after planting in the spring or when the crop is beginning to emerge from the soil in late spring or early summer.

Using the gas chromatography/mass spectrometry method of analysis, pesticides were detected in 11 of the 27 monitoring wells and in the surface-water sample collected from the Big Sioux River (table 4). Eight of the 11 shallow monitoring wells showed the presence of a pesticide at one time or another. One of the five intermediate monitoring wells, and 2 of the 11 deep monitoring wells showed the presence of a pesticide at one time or another. Three shallow monitoring wells, four intermediate monitoring wells, and nine deep monitoring wells, showed no pesticide.

Using the gas chromatography/mass spectrometry method of analysis, the following pesticides have been detected in water collected from the Big Sioux aquifer: atrazine, 2,4-D, trifluralin (Treflan), cyanazine (Bladex), bentazon (Basagran), EPTC (Eradicane), and picloram (Tordon). These pesticides were detected in some of the monitoring wells at one time or another; however, no aquifer-wide trends can be determined from these data. Figure 6 shows that atrazine was detected most frequently, followed by Bladex. At the permanent monitoring site near Egan, Moody County, atrazine and Bladex have consistently been detected (table 4) . All pesticide concentrations were below the maximum contaminant level (MCL) and health advisories established by the U.S. EPA (Office of Drinking Water, 1993).

Using the gas chromatography/mass spectrometry method of analysis, the following pesticides have been detected in water collected from the Big Sioux River near the town of Egan, Moody County: atrazine, 2,4-D, bentazon (Basagran), cyanazine (Bladex), and EPTC (Eradicane). The Big Sioux River was sampled four times during 1992 and pesticides were detected during each sampling event (table 4). Figure 7 shows that atrazine and Bladex were the pesticides most frequently detected. All pesticide concentrations were below the MCLs and health advisories established by the U.S. EPA (Office of Drinking Water, 1993).

Using the immunoassay method of analysis, the following pesticides were detected at one time or another: atrazine was detected in 25 of the 27 monitoring wells, alachlor was detected in 18 of the 27 monitoring wells, and 2,4-D was detected in 1 of the 27 monitoring wells (table 5). The pesticide 2,4-D was not analyzed for during the August 1991, or January 1992, sampling events because the test kits had not yet been made available. The May 1992, sampling event was the first time immunoassay analyses were performed for 2,4-D.

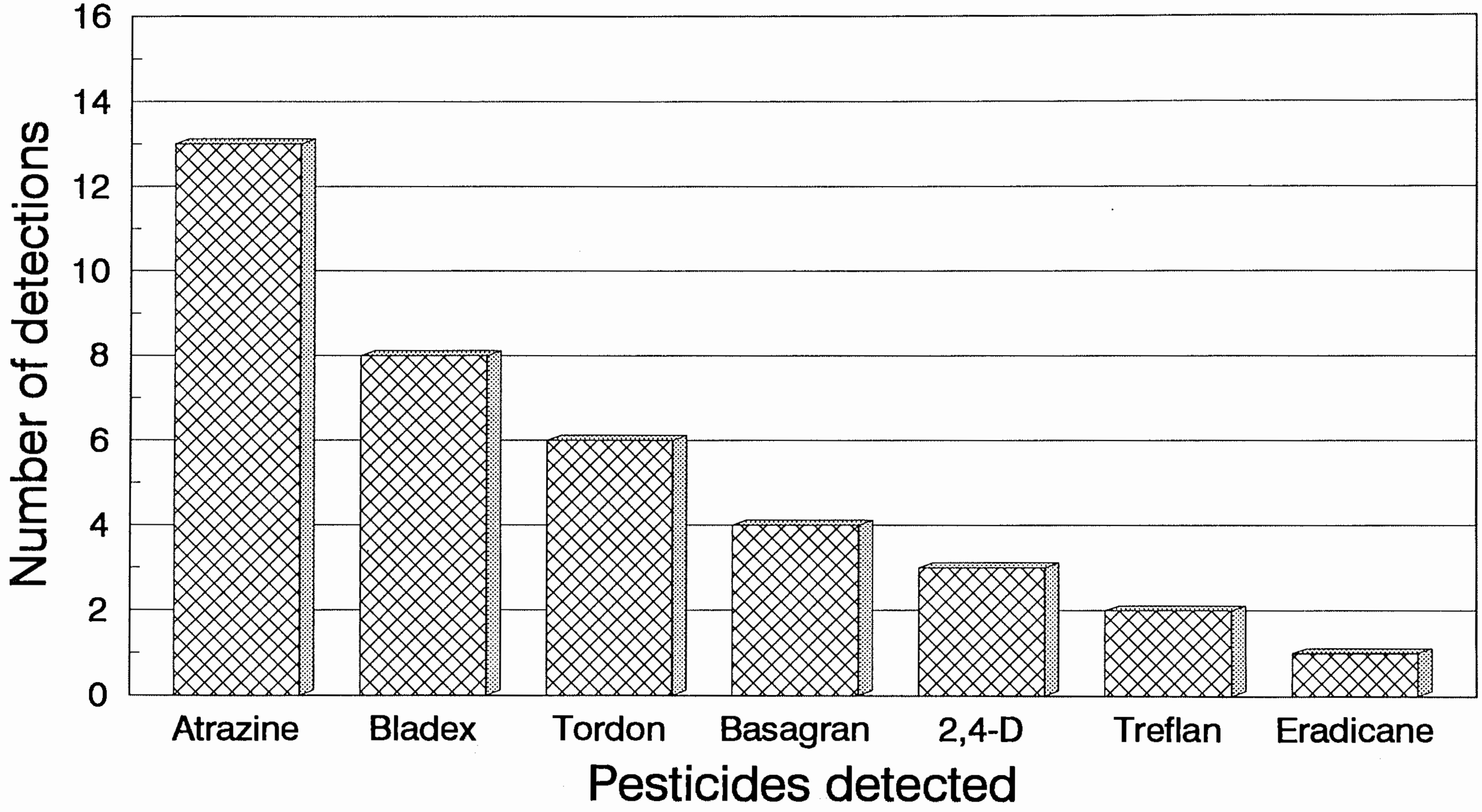
Based on limited data for the pesticide atrazine, there appears to be a good correlation between results provided by the immunoassay method of analysis and the gas chromatography/mass spectrometry method of analysis. However, on several occasions there were detections using the immunoassay method when detections were not reported with the gas chromatography/mass spectrometry method. This was especially noticeable with the immunoassay analysis for alachlor.

Table 4. Concentrations of detected pesticides, in micrograms per liter, as determined by gas chromatography/mass spectrometry.

Monitoring Point *	1991	1992			
	August 5 - 7 August 12 - 14	January 7 - 9 January 13 - 14, 16 January 21 - 23	May 11 - 13 May 18 - 20	July 20 - 22 July 27 - 29	August 17 - 19 August 24 - 26
R20-89-38	--	--	Eradicane 0.11	atrazine 0.13	--
R20-89-37	--	--	--	--	--
R20-89-39	--	--	--	--	--
R20-89-42	--	--	--	--	--
R20-89-40	Treflan 0.59	Treflan 0.29	--	--	--
R20-89-41	--	--	--	--	--
R20-89-44	--	--	--	atrazine 0.14	--
R20-89-43	--	--	--	--	--
R20-89-46	atrazine 0.12, Bladex 0.15	--	--	--	--
R20-89-45	--	--	--	--	--
R20-89-48	--	--	--	Tordon 9.6	Tordon 64
R20-89-47	atrazine 0.36, Bladex 0.50	--	--	--	--
R20-89-50	Basagran 0.31, atrazine 0.59, Bladex 0.19	--	2,4-D 0.32, atrazine 0.11	atrazine 0.72, Bladex 0.32	atrazine 0.71, Bladex 0.30
R20-89-49	Basagran 0.48, atrazine 0.85, Bladex 0.79	Basagran 0.45, atrazine 0.66, Bladex 0.60	Basagran 0.47, atrazine 0.55, Bladex 0.50	2,4-D 0.23, atrazine 0.15	atrazine 0.15
Big Sioux River	No pesticide analysis	2,4-D 0.24	Bladex 0.11, Eradicane 0.14	atrazine 0.56, Basagran 0.35, Bladex 0.39	atrazine 0.15
R20-89-64	--	--	Tordon 0.26	--	--
R20-89-63	--	--	--	--	--
R20-89-62	--	--	--	--	--
R20-89-55	--	--	Tordon 0.75	Tordon 0.54	Tordon 0.39
R20-89-54	--	--	--	--	--
R20-89-57	--	--	--	--	2,4-D 0.22
R20-89-56	--	--	--	--	--
R20-89-60	--	--	--	--	--
R20-89-59	--	--	--	--	--
R20-89-58	--	--	--	--	--
R20-89-65	--	--	--	--	--
R20-89-67	--	--	--	--	--
R20-89-66	--	--	--	--	--

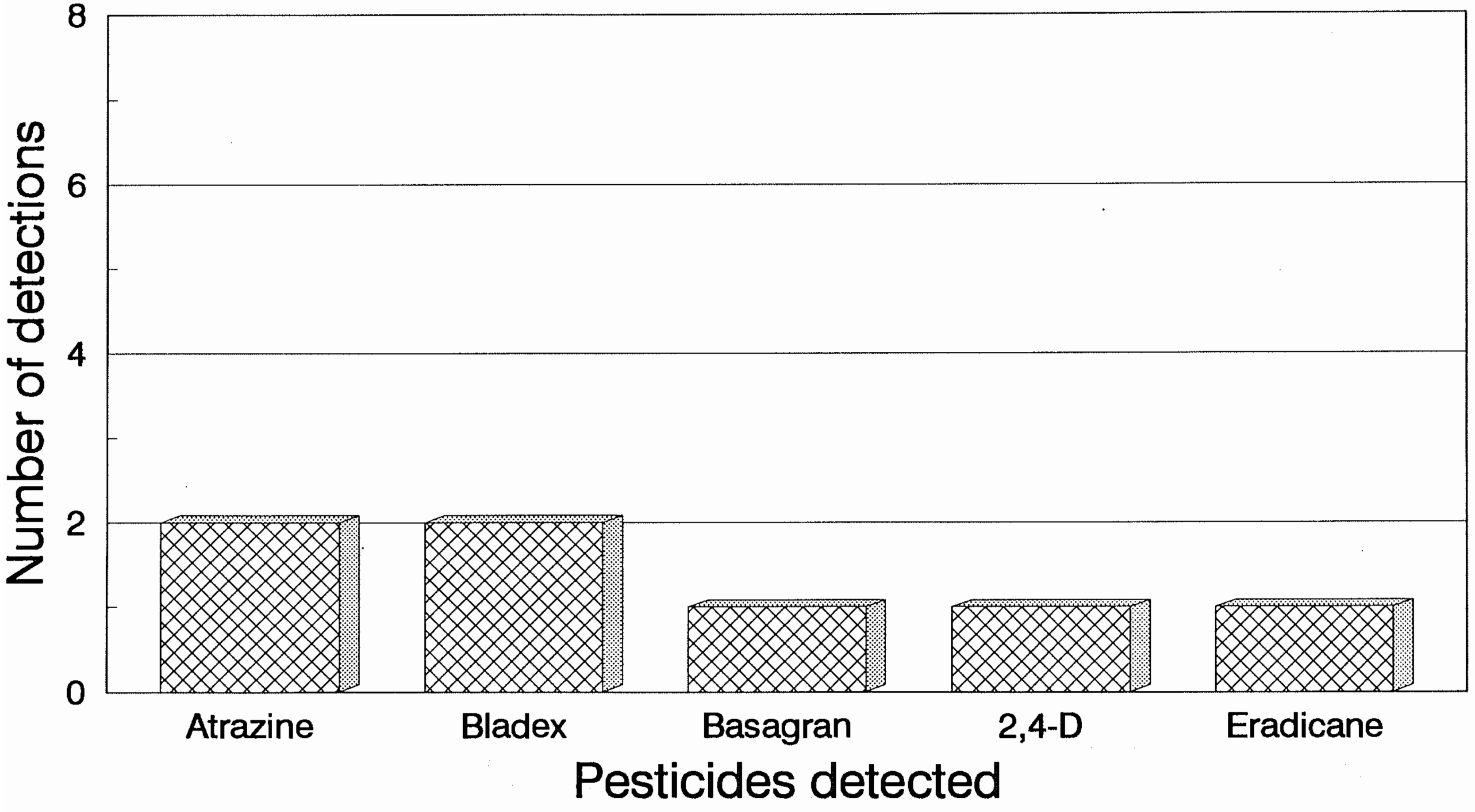
* Monitoring points are grouped and arranged as presented in table 1.

Figure 6. Pesticides detected in the Big Sioux aquifer



135 samples analyzed

Figure 7. Pesticides detected in the Big Sioux River



4 samples analyzed

Table 5. Concentrations of detected pesticides, in micrograms per liter, as determined by immunoassay.

Monitoring Point *	1991	1992			
	August 5 - 7 August 12 - 14	January 7 - 9 January 13 - 14, 16 January 21 - 23	May 11 - 13 May 18 - 20	July 20 - 22 July 27 - 29	August 17 - 19 August 24 - 26
R20-89-38	–	atrazine 0.4	–	atrazine 0.34	atrazine 0.1
R20-89-37	–	atrazine 0.3	–	–	alachlor 0.1
R20-89-39	–	atrazine 0.3	–	–	–
R20-89-42	–	–	–	–	atrazine 0.1, alachlor 0.1
R20-89-40	–	atrazine 0.1	–	–	–
R20-89-41	–	–	–	–	alachlor 0.1
R20-89-44	–	atrazine 0.3	–	atrazine 0.34	atrazine 0.2, alachlor 0.1
R20-89-43	–	atrazine 0.4	–	–	atrazine 0.2, alachlor 0.1
R20-89-46	–	atrazine 0.4	–	–	alachlor 0.1
R20-89-45	–	atrazine 0.4	atrazine 0.1	atrazine 0.1	alachlor 0.1
R20-89-48	–	atrazine 0.1	–	–	alachlor 0.1
R20-89-47	–	atrazine 0.3	–	–	alachlor 0.2
R20-89-50	atrazine 0.6, alachlor 0.6	atrazine 0.3, alachlor 0.2	atrazine 0.4, alachlor 0.21	atrazine 1.0, alachlor 0.6	atrazine 1.2, alachlor 0.8
R20-89-49	atrazine 0.9, alachlor 0.9	atrazine 1.1, alachlor 0.6	atrazine 1, alachlor 0.71	atrazine 0.3, alachlor 0.5, 2,4-D 1	atrazine 0.4, alachlor 0.5
Big Sioux River	–	atrazine 0.2, alachlor 0.4	atrazine 0.4, alachlor 0.41 2,4-D 1	atrazine 0.8, alachlor 0.6, 2,4-D 1	atrazine 0.5, alachlor 0.4 2,4-D 1
R20-89-64	atrazine 0.1	–	–	atrazine 0.1	–
R20-89-63	atrazine 0.1	atrazine 0.1	alachlor 0.1	alachlor 0.1	atrazine 0.1
R20-89-62	atrazine 0.1	–	–	atrazine 0.1	–
R20-89-55	atrazine 0.2, alachlor 0.1	–	–	–	atrazine 0.1
R20-89-54	alachlor 0.1	atrazine 0.2	–	–	–
R20-89-57	atrazine 0.2	–	–	atrazine 0.2	atrazine 0.3
R20-89-56	atrazine 0.3, alachlor 0.4	–	alachlor 0.14	alachlor 0.2	alachlor 0.2
R20-89-60	atrazine 0.1	atrazine 0.1	–	–	–
R20-89-59	atrazine 0.1	–	–	–	–
R20-89-58	atrazine 0.3	–	–	–	–
R20-89-65	alachlor 1.0	–	–	–	–
R20-89-67	atrazine 0.1	atrazine 0.1	alachlor 0.1	–	–
R20-89-66	alachlor 1.7	–	–	atrazine 0.1	–

* Monitoring points are grouped and arranged as presented in table 1.

Alachlor detections were noted with the immunoassay method while the gas chromatography/mass spectrometry method did not detect alachlor. Upon consultation with the manufacturer of the immunoassay test kit, it was learned that a major alachlor soil metabolite (degradation product), ethanesulfonate, is not detected by standard gas chromatography methods, but is detected by some immunoassay kits (Carol Townsend, Ohmicron Corporation, personal communication, 1992; Macomber and others, 1992). Ohmicron's alachlor assay does detect this metabolite. Consequently, when comparing between the immunoassay method and the gas chromatography/mass spectrometry method, results show alachlor was detected by immunoassay but was not detected by standard gas chromatography/mass spectrometry. Because the immunoassay positive response to alachlor cannot be confirmed by gas chromatography/mass spectrometry, it can be concluded that a detection of alachlor, using the immunoassay method, was most likely caused by cross-reaction with the alachlor soil metabolite, ethanesulfonate.

The fact that the monitoring sites are not located downgradient from any identifiable point sources of contamination and the fact that pesticides have been detected in ground water and surface water suggest that nonpoint-source pollution is occurring in the Big Sioux aquifer and the Big Sioux River. However, further long term monitoring is necessary to determine any trends in the detection and concentrations of the pesticides.

SUMMARY

The Big Sioux aquifer provides approximately one-third of South Dakota's population with water for municipal, rural water, irrigation, and other uses. Because of the surficial and unconfined nature of the Big Sioux aquifer, it is potentially vulnerable to contamination. Previous ground-water investigations in the Big Sioux aquifer have found that several areas contain elevated concentrations of nitrate that are indicative of nonpoint-source contamination. Due to the aquifer's vulnerability and growing public concerns about the quality and long-term suitability of water for drinking-water supplies, a permanent monitoring network was established in 1989 to monitor the water quality in the Big Sioux aquifer. Since then, water quality has been studied with an emphasis on nitrates and pesticides.

The permanent monitoring network consists of 27 monitoring wells installed at 11 locations in the Big Sioux aquifer. The network monitoring 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.

Major Anions and Cations

The water quality in the Big Sioux aquifer is generally good. Trilinear diagrams show that the type of ground water collected from the Big Sioux aquifer is calcium-bicarbonate. Comparing three trilinear diagrams, it appears that from 1989 to 1992, generally the 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 water quality in the Big Sioux River, near Egan, Moody County, is generally good. Trilinear diagrams show that the type of water collected from the Big Sioux River is calcium-bicarbonate. Comparing two trilinear diagrams, it appears that from 1990 to 1992, generally the water quality in the Big Sioux River has not changed.

Nitrate

Nitrate concentrations greater than 5 mg/L have been detected in 9 of the 27 Big Sioux aquifer permanent monitoring network wells. Of these nine monitoring wells, the highest concentrations of nitrate are found in the shallow monitoring wells screened at, near, or through the water table, indicating a vertical stratification of nitrate in the ground water. Two of the nine monitoring wells consistently had nitrate concentrations above the primary drinking water standard of 10 mg/L for public water systems. Nitrate fluctuations at one site appear to be driven by precipitation events. However, there are gaps in the data and in order for this interpretation to be examined further, more data must be collected, at least monthly, from this site. Based on available data, it is concluded that the elevated concentrations of nitrate are symptomatic of nonpoint-source contamination.

In the Big Sioux River, near Egan, Moody County, nitrate concentrations were low and ranged from less than 0.04 to 1.83 mg/L. These concentrations indicate that nitrate contamination is not a problem in the Big Sioux River at this location.

Ammonia

In the Big Sioux aquifer, ammonia concentrations range from less than 0.005 mg/L to 1.78 mg/L. The higher ammonia concentrations are generally found in the deeper portions of the aquifer where nitrate concentrations are low. Where ammonia concentrations are low in the upper portions of the aquifer, nitrate concentrations are elevated. Because ammonium is adsorbed readily onto soil particles, ammonium is unlikely to be found in shallow ground water. However, in deeper portions of the aquifer, anaerobic conditions are more common and because of denitrification, nitrate is converted to ammonia. For this investigation, ammonia contamination was not found to be a problem in water collected from the Big Sioux aquifer.

In the Big Sioux River, near Egan, Moody County, ammonia concentrations ranged from less than 0.05 to 0.09 mg/L. These concentrations are low and indicate that ammonia contamination in the Big Sioux River, at this location, is not a problem.

Phosphorous

Phosphorus has a low solubility in ground water and limited mobility due to its tendency to adsorb onto soils. As a result, phosphorus is seldom found at high concentrations in ground water.

In the Big Sioux aquifer, phosphorus concentrations are low, ranging from less than 0.010 to 0.398 mg/L. These low concentrations indicate that phosphorus contamination is not a problem in water collected from the Big Sioux aquifer.

In the Big Sioux River, near Egan, Moody County, phosphorus concentrations ranged from 0.030 to 0.186 mg/L. These concentrations are low and indicate that phosphorus contamination is not a problem in the Big Sioux River at this location.

Pesticides

In the Big Sioux aquifer, pesticide analyses using the gas chromatography/mass spectrometry method detected atrazine, 2,4-D, trifluralin (Treflan), cyanazine (Bladex), bentazon (Basagran), EPTC (Eradicane), and picloram (Tordon). Pesticides were detected in some of the monitoring wells at one time or another, but no specific aquifer-wide trends can be determined. However, at one site, cyanazine (Bladex) and atrazine have consistently been detected. The immunoassay method of analysis has also been used in this investigation and has detected atrazine, alachlor, and 2,4-D. These three pesticides were the only pesticides analyzed for using the immunoassay method. All pesticide concentrations in the ground water, regardless of analytical technique, were below MCLs and health advisories established by the U.S. EPA.

In the Big Sioux River, near Egan, Moody County, pesticide analyses using the gas chromatography/mass spectrometry method detected, at one time or another, concentrations of atrazine, cyanazine (Bladex), bentazon (Basagran), 2,4-D, and EPTC (Eradicane). Four samples were collected from the river, and each sample contained at least one pesticide. The immunoassay method of analysis has also been used in this investigation and consistently detected atrazine, alachlor, and 2,4-D. These pesticides were the only pesticides analyzed for using the immunoassay method. All pesticide concentrations in the river, regardless of analytical technique, were below MCLs and health advisories established by the U.S. EPA. Based on available data, it is concluded that the detections of pesticides, whether in the river or the aquifer, are symptomatic of nonpoint-source contamination.

Information and interpretations generated as a result of this investigation of the Big Sioux aquifer may be applied to similar aquifers in the state and can be used in formulation of land use management decisions, wellhead protection ordinances, and achieving a comprehensive ground water protection program for these aquifers.

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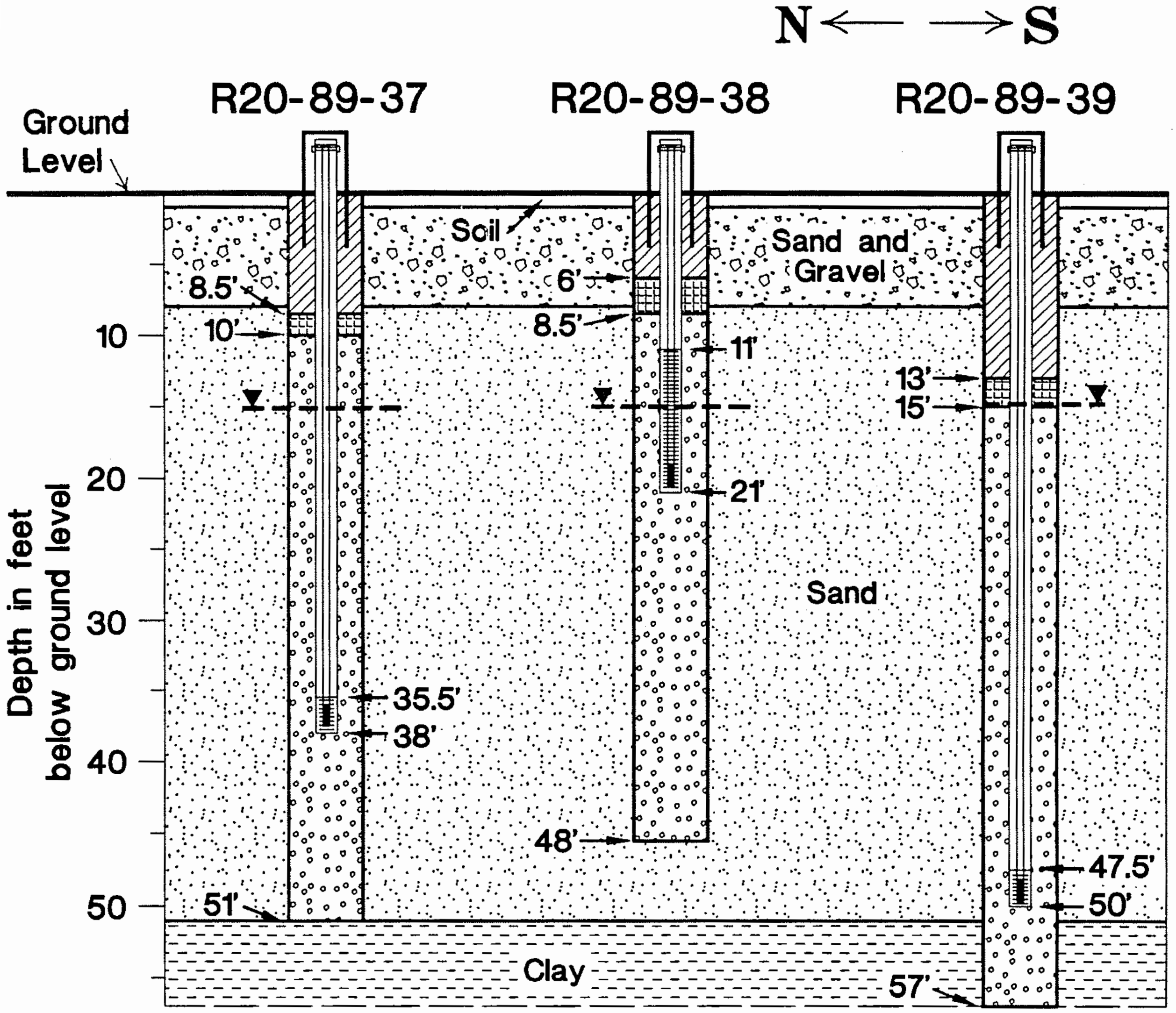
APPENDIX A

Monitoring well construction diagrams and hydrostratigraphic cross sections
for permanent 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)



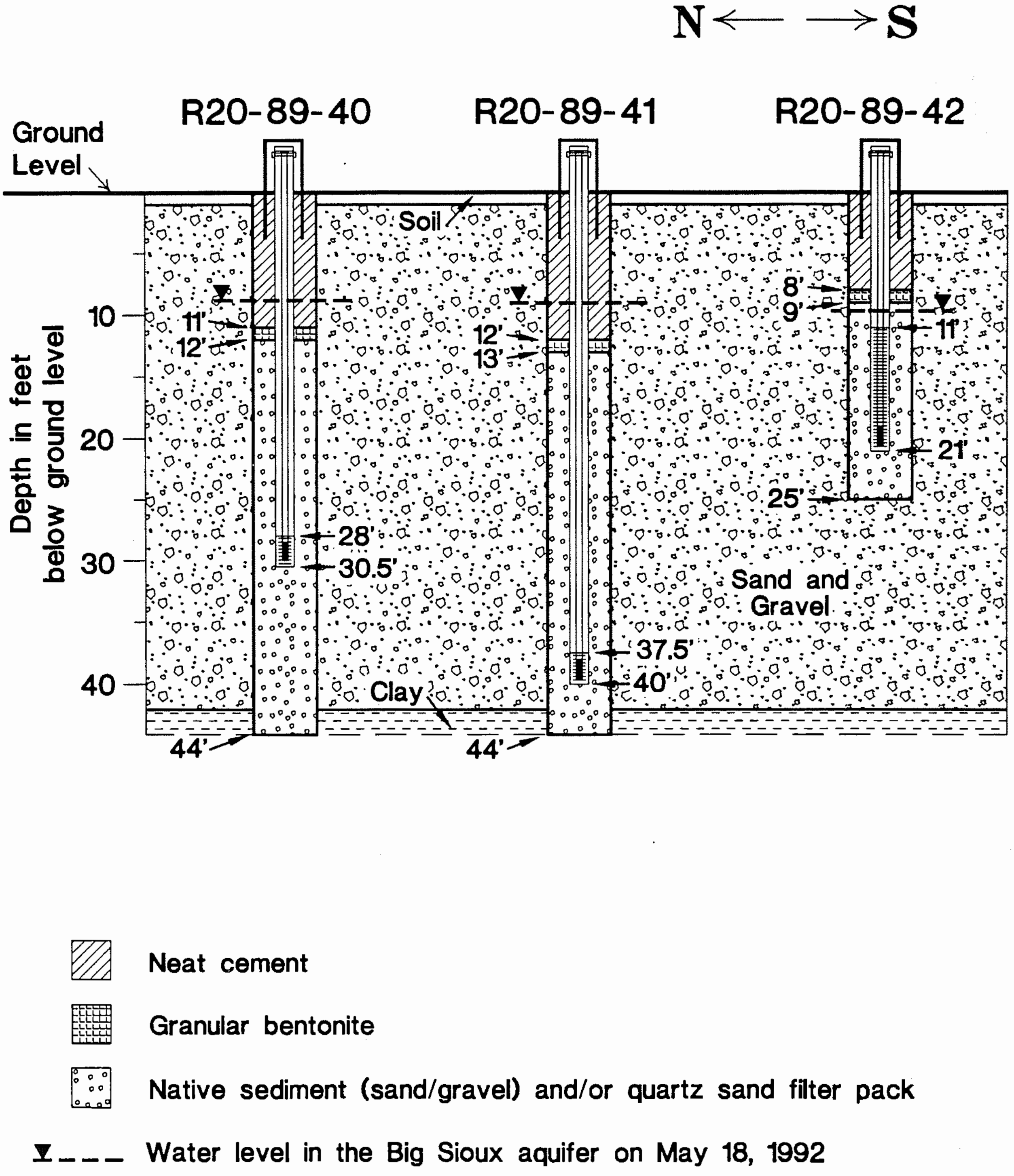
▨ Neat cement

▦ Granular bentonite

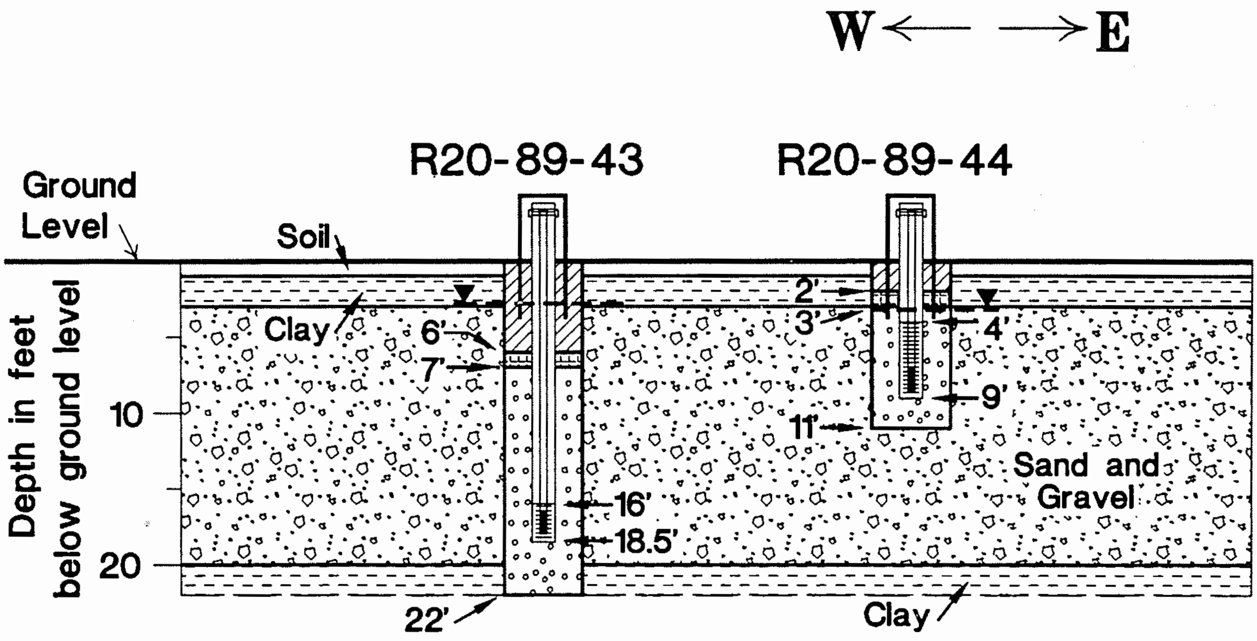
⁘ Native sediment (sand/gravel) and/or quartz sand filter pack

▼ – – – Water level in the Big Sioux aquifer on May 19, 1992

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



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



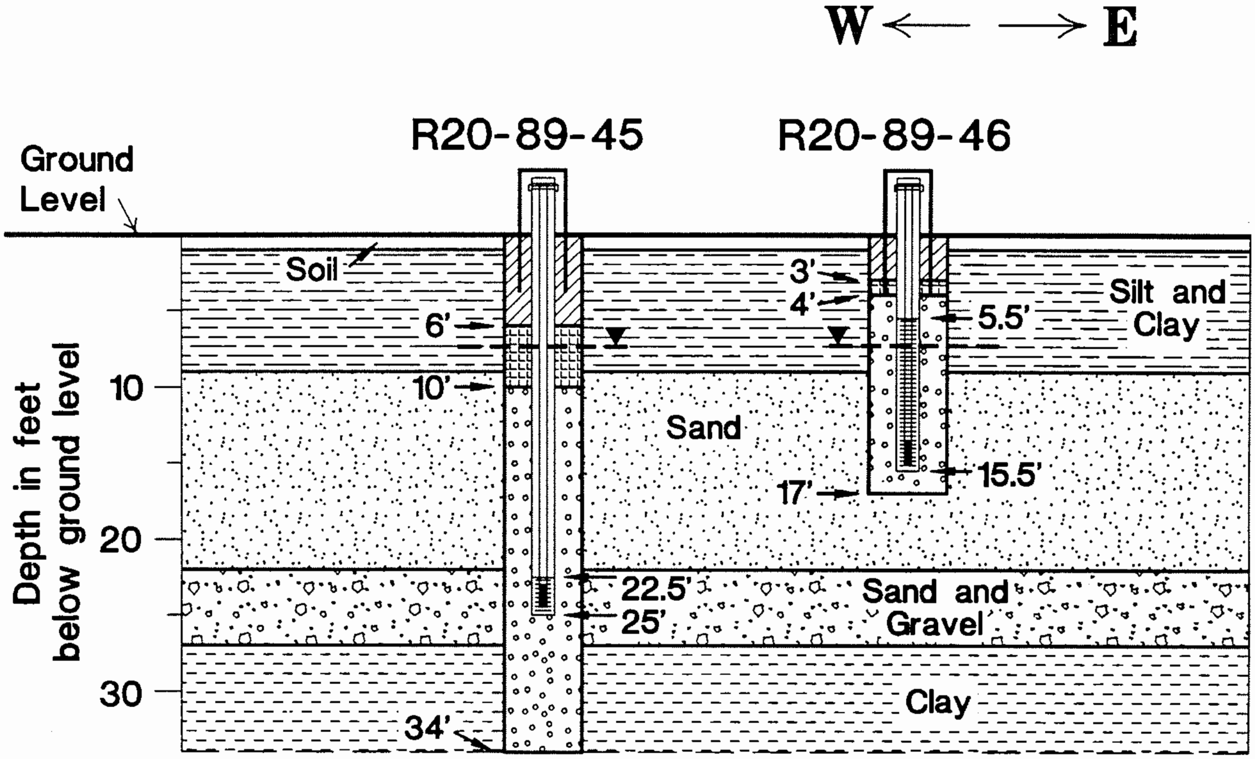
▨ Neat cement

▦ Granular bentonite

⁘ Native sediment (sand/gravel) and/or quartz sand filter pack

▼ – – – Water level in the Big Sioux aquifer on May 20, 1992

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



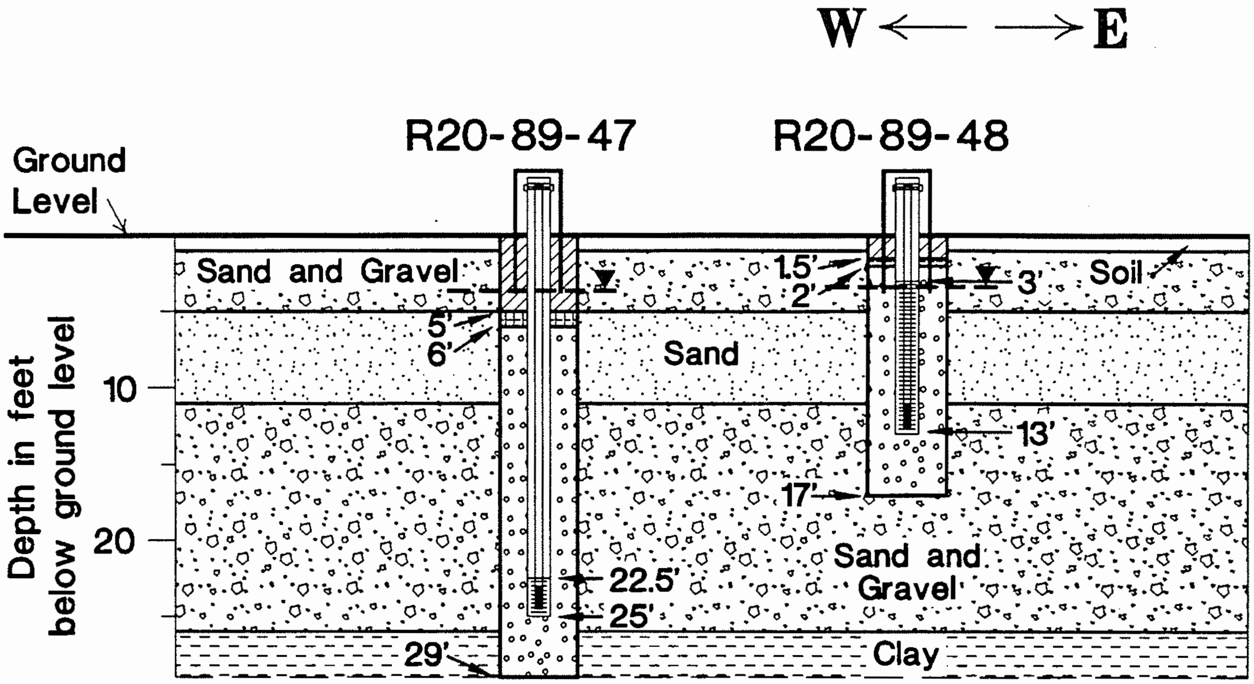
▨ Neat cement

▦ Granular bentonite

⁙ Native sediment (sand/gravel) and/or quartz sand filter pack

▼ – – – Water level in the Big Sioux aquifer on May 20, 1992

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



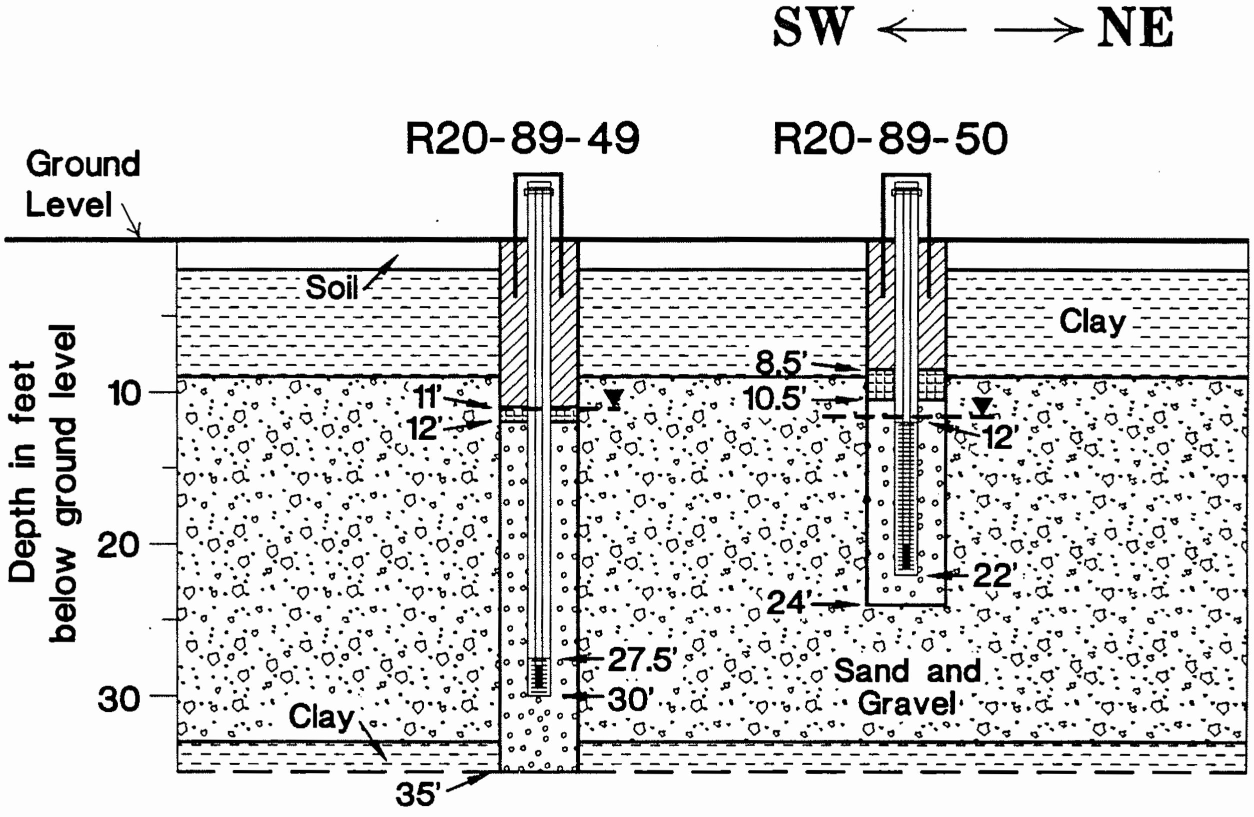
▨ Neat cement

▦ Granular bentonite

⁘ Native sediment (sand/gravel) and/or quartz sand filter pack

▼– – – Water level in the Big Sioux aquifer on May 19, 1992

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



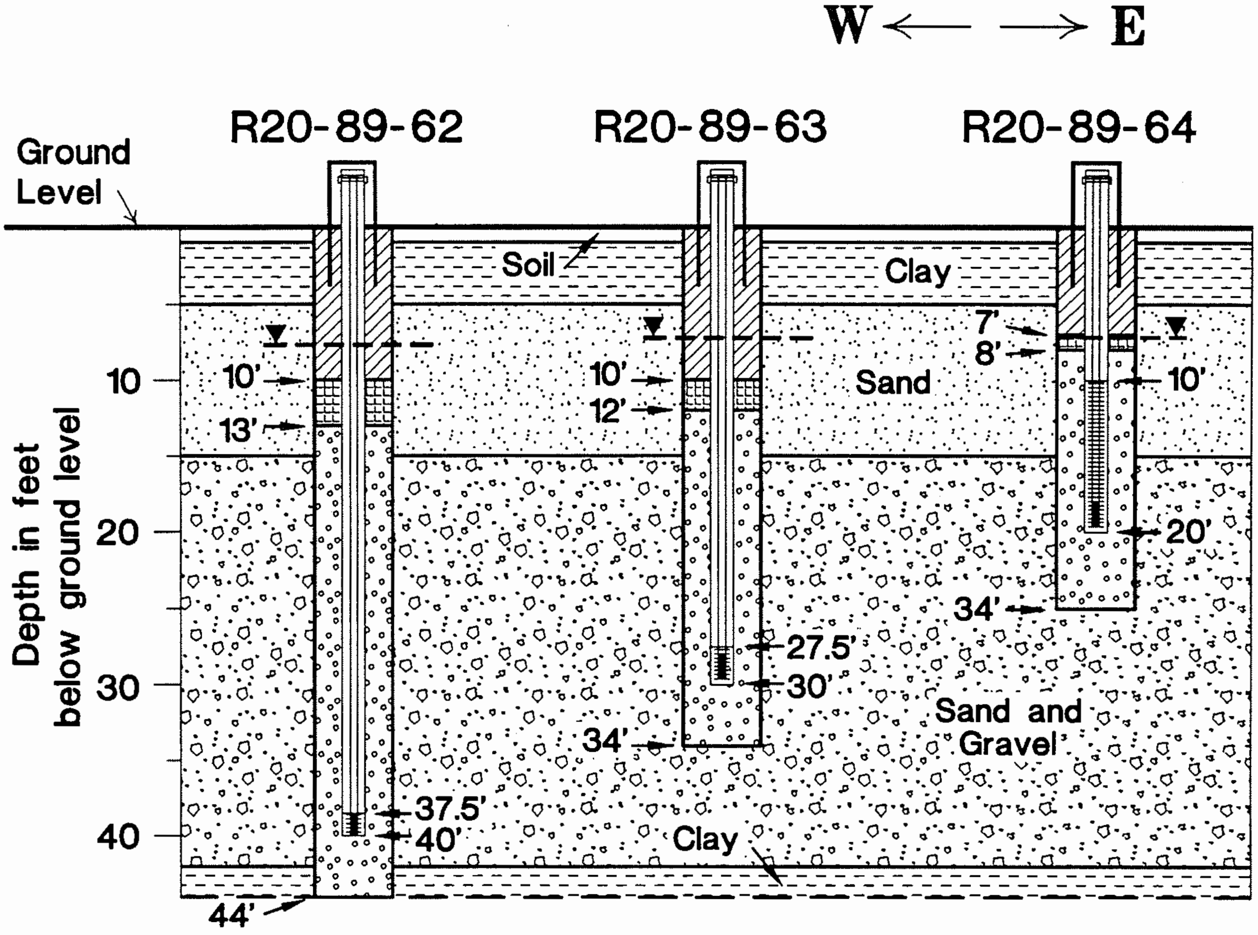
▨ Neat cement

▦ Granular bentonite

⁘ Native sediment (sand/gravel) and/or quartz sand filter pack

▼ - - - Water level in the Big Sioux aquifer on May 13, 1992

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



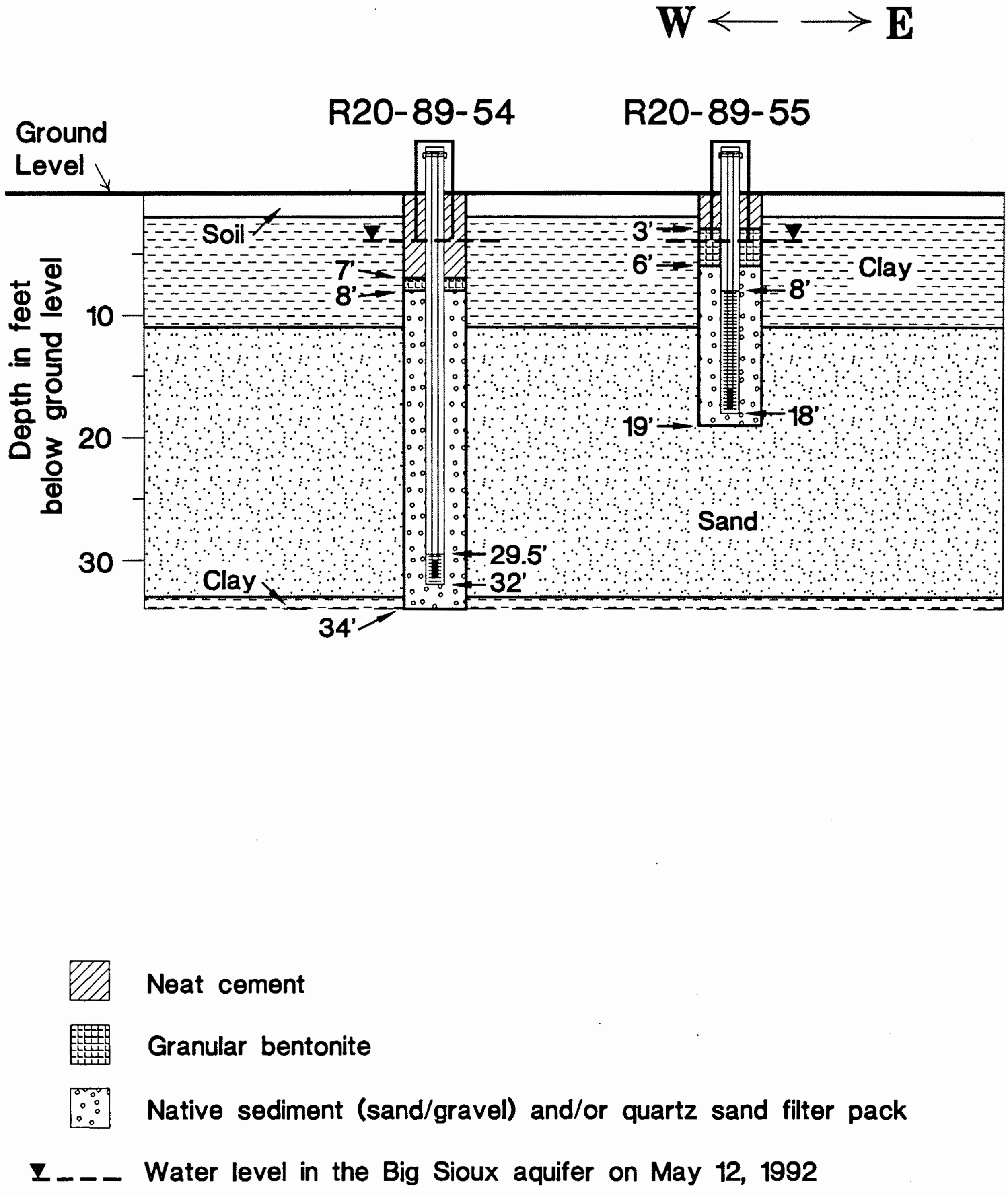
▨ Neat cement

▦ Granular bentonite

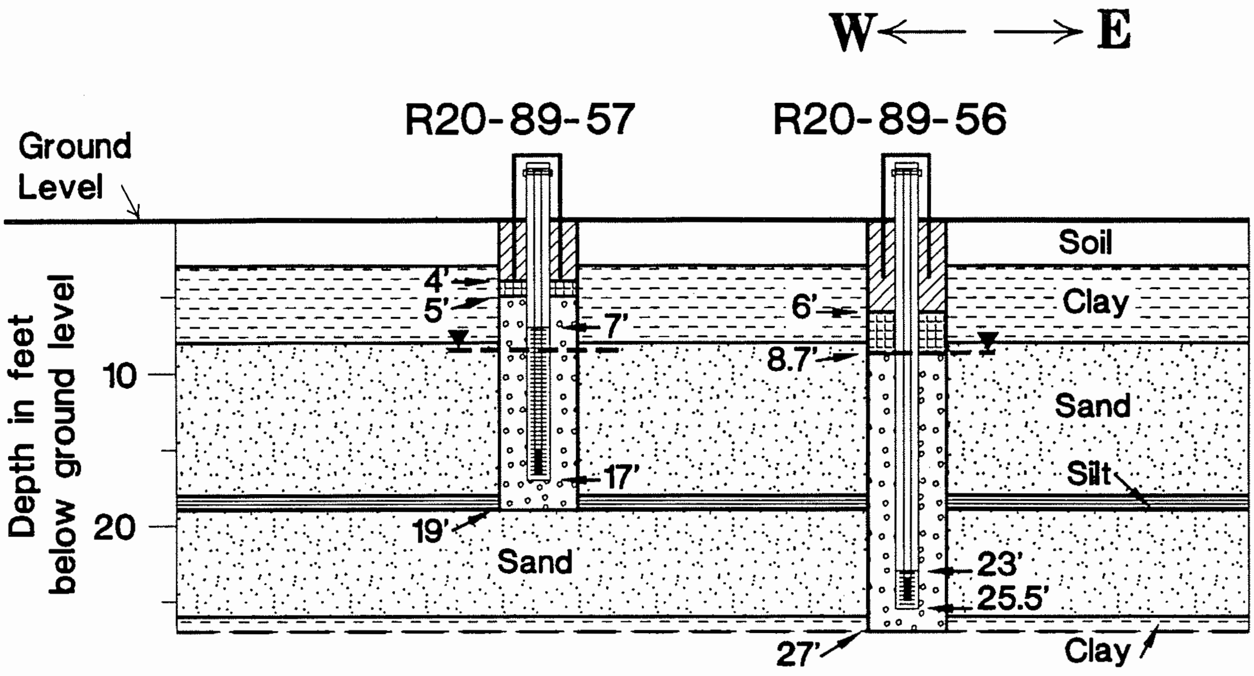
⁘ Native sediment (sand/gravel) and/or quartz sand filter pack

▼– – – Water level in the Big Sioux aquifer on May 13, 1992

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



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



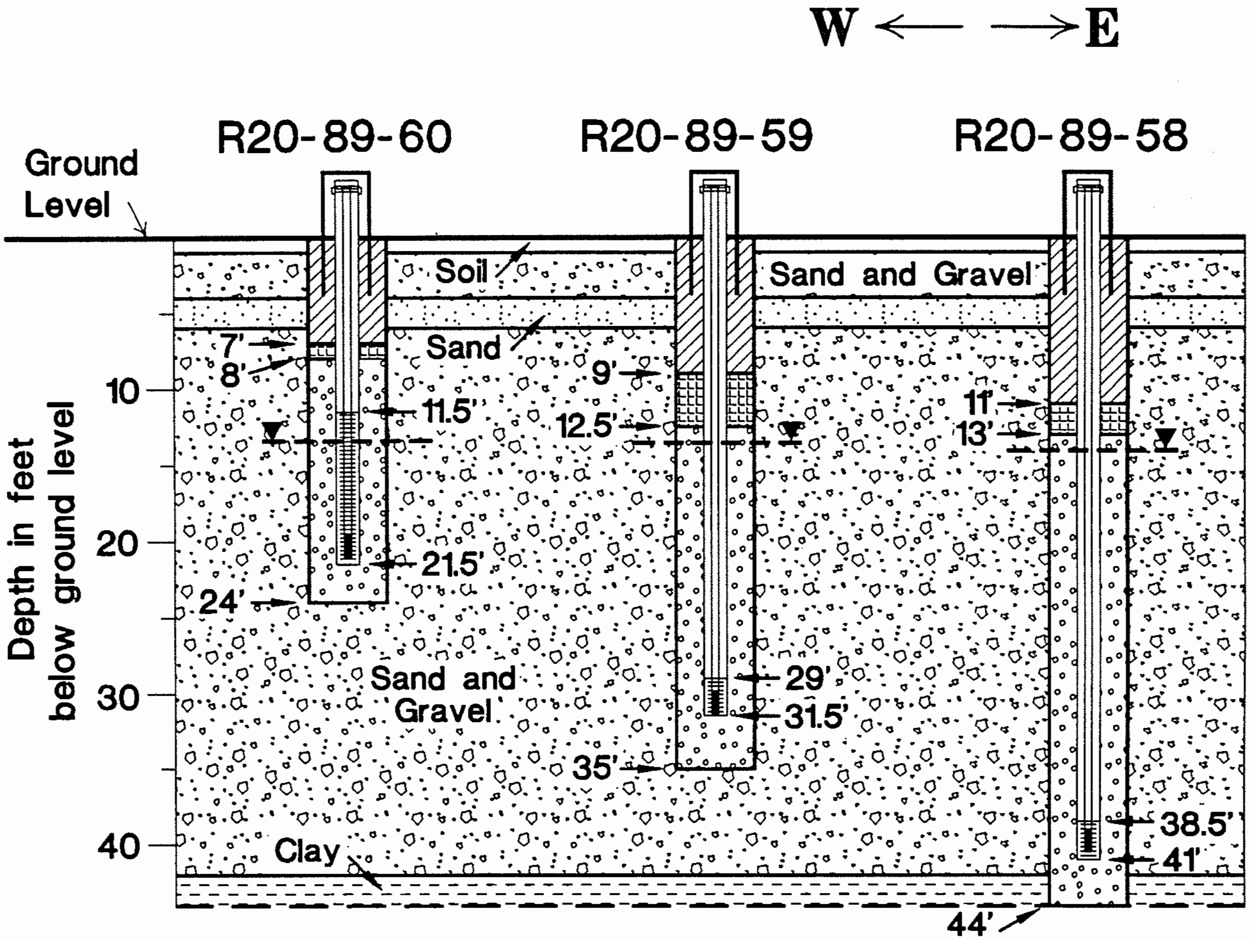
▨ Neat cement

▦ Granular bentonite

⁘ Native sediment (sand/gravel) and/or quartz sand filter pack

▼ - - - Water level in the Big Sioux aquifer on May 12, 1992

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



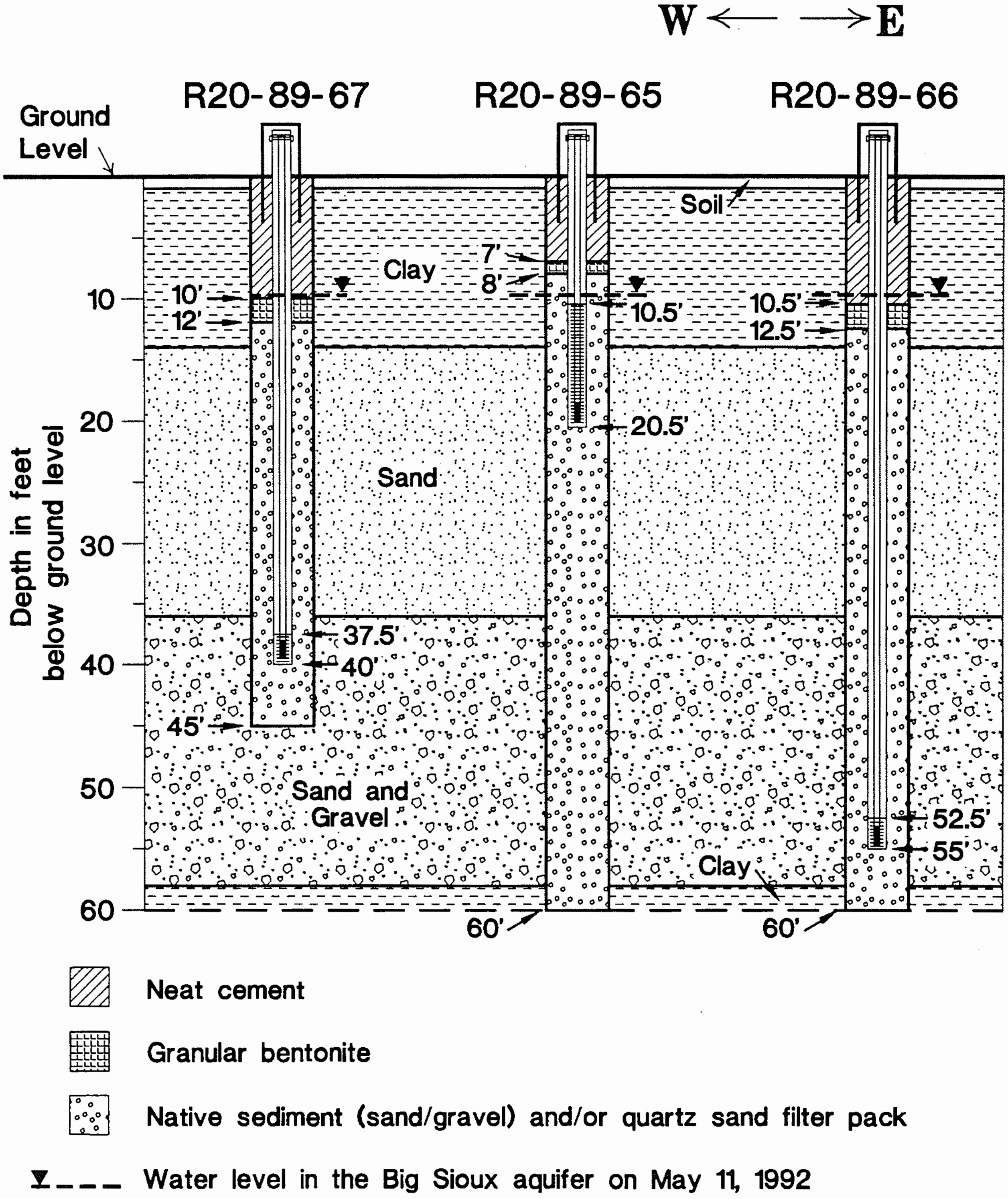
▨ Neat cement

▦ Granular bentonite

⁘ Native sediment (sand/gravel) and/or quartz sand filter pack

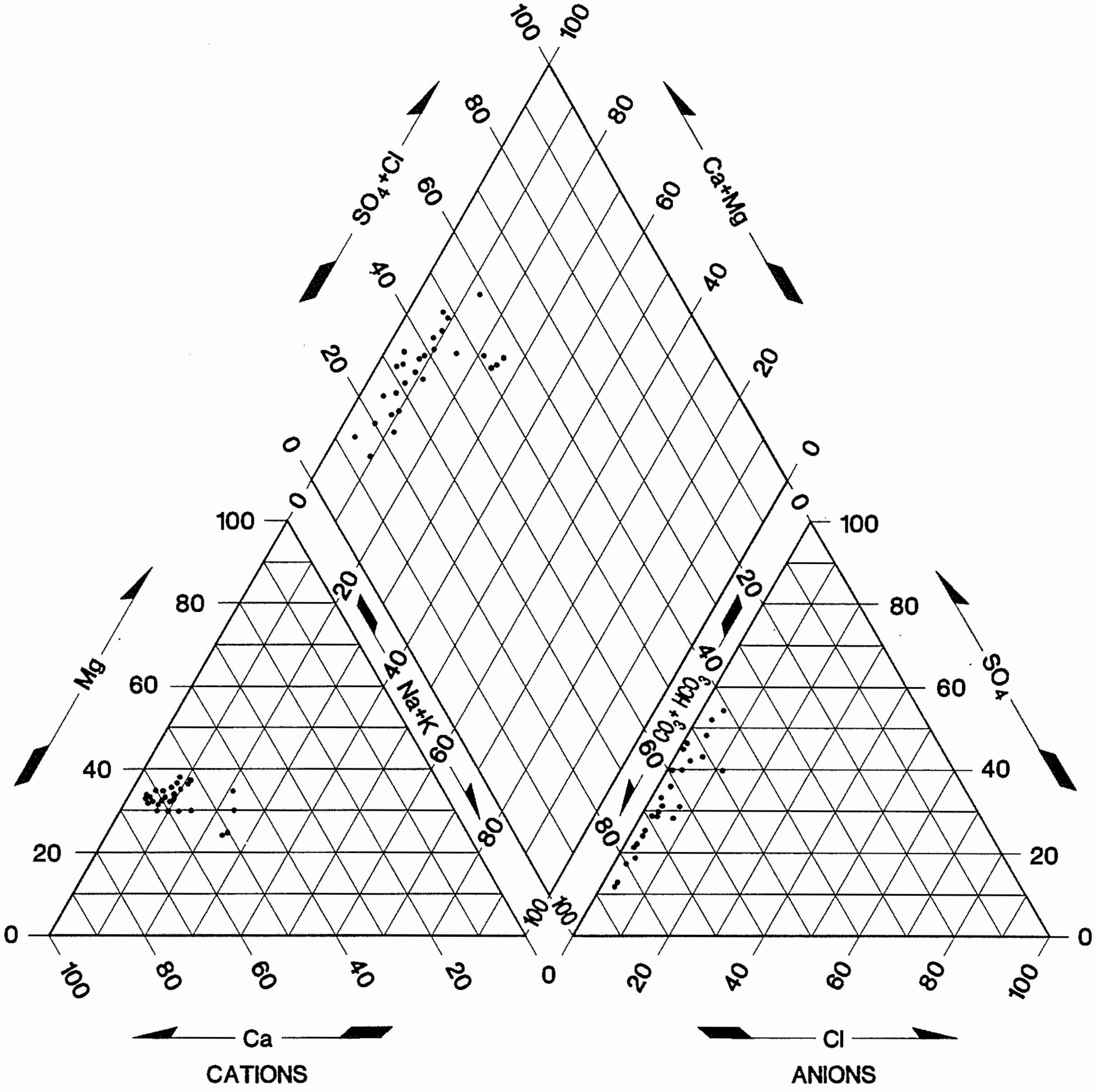
▼--- Water level in the Big Sioux aquifer on May 11, 1992

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



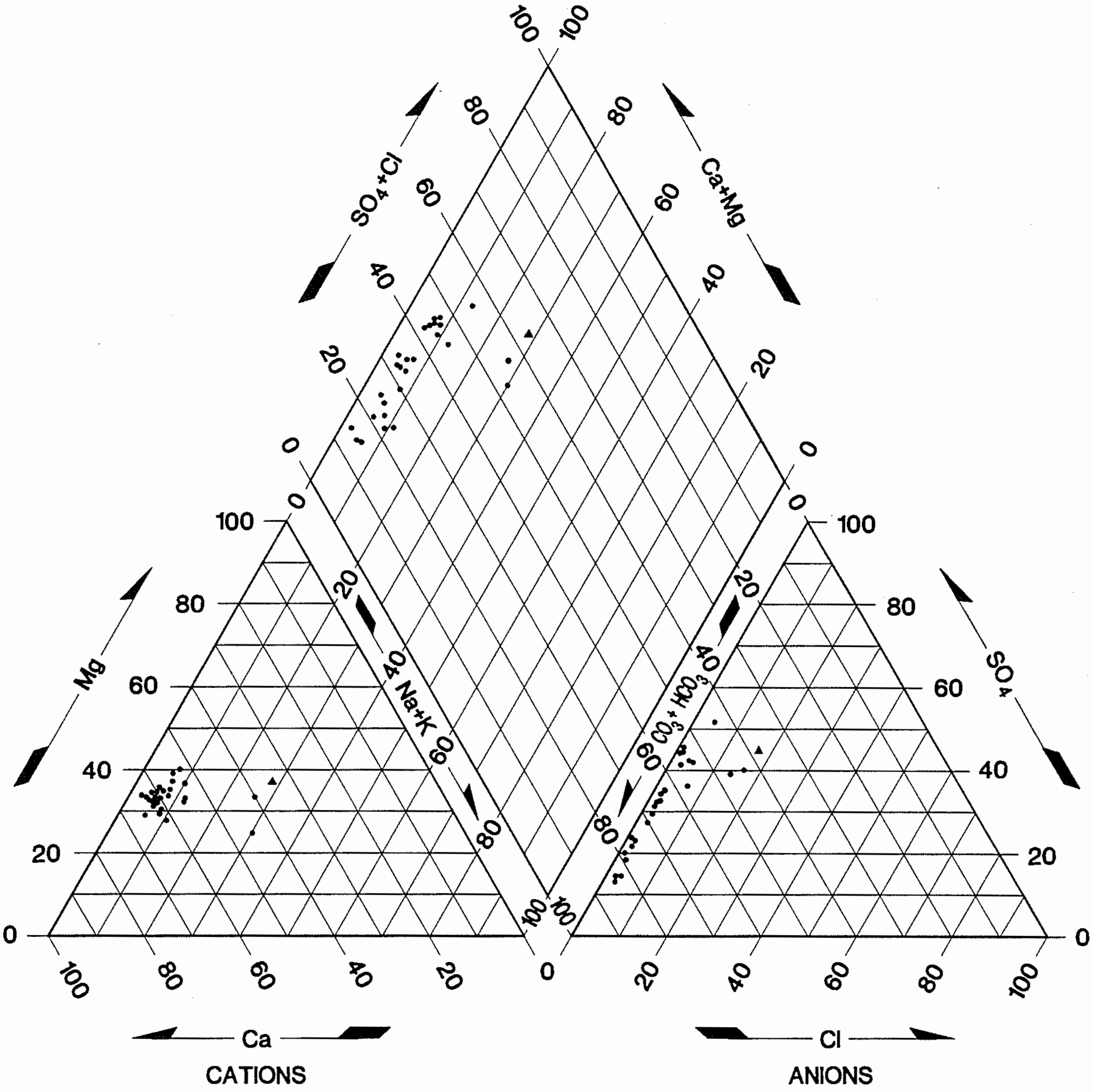
APPENDIX B

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



· Big Sioux aquifer monitoring well data

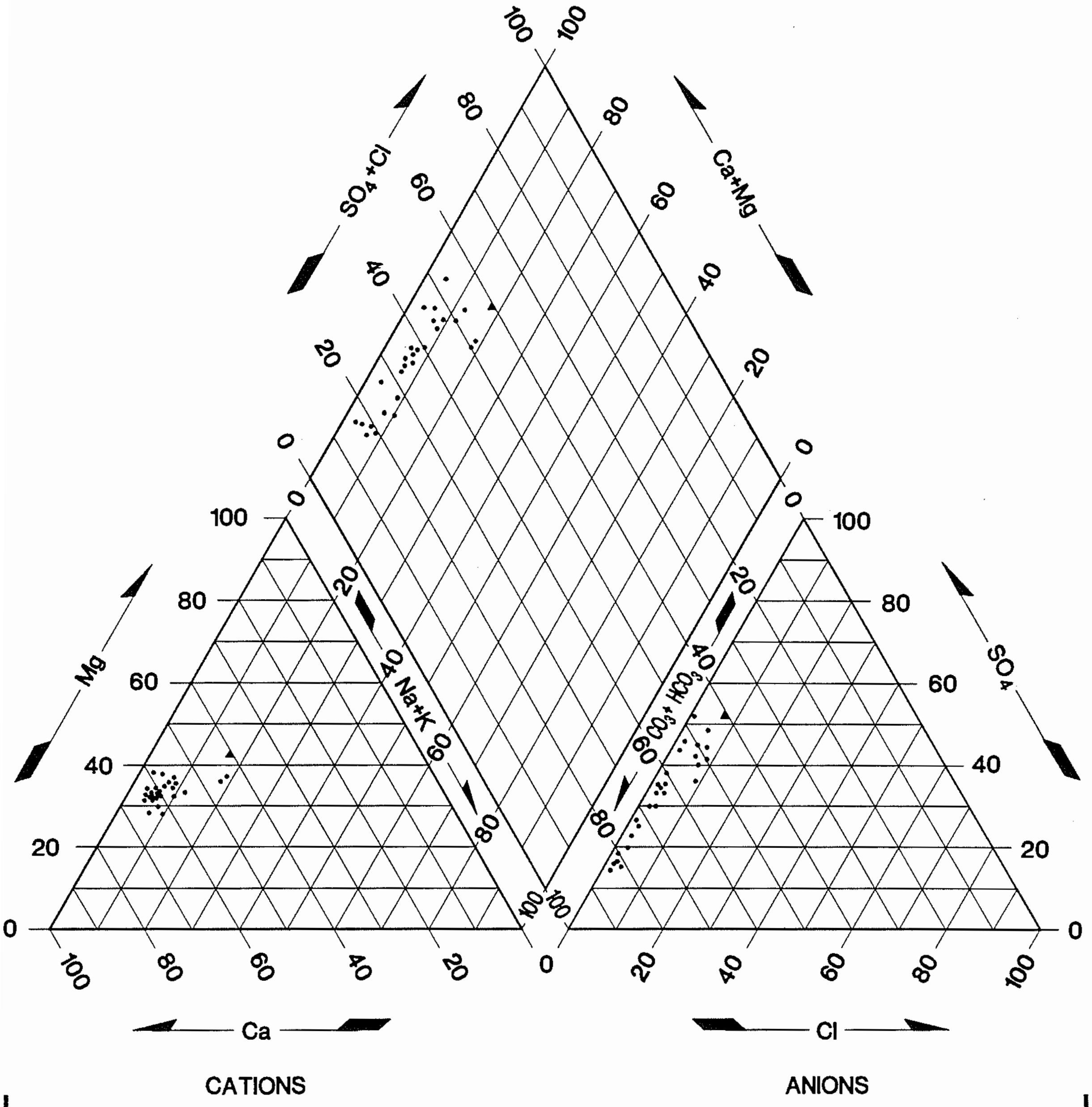
September 1989



• Big Sioux aquifer monitoring well data

▲ Big Sioux River data

April 1990



· Big Sioux aquifer monitoring well data

▲ Big Sioux River data

May 1992

APPENDIX C

Nitrate, ammonia, and total phosphorus concentrations
in the Big Sioux aquifer permanent monitoring network wells
and in the Big Sioux River

NOTE: All concentrations are in milligrams per liter (mg/L)

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
09/12/89	17.4	0.82	--	09/12/89	<0.04	0.65	--	09/11/89	0.07	1.20	--
11/07/89	25.8	0.83	0.023	11/07/89	<0.04	0.57	0.029	11/06/89	<0.04	1.14	0.030
03/12/90	22.0	0.83	0.042	03/12/90	<0.04	0.61	0.052	03/12/90	0.41	0.56	0.131
04/23/90	24.1	0.81	0.018	04/23/90	<0.04	0.61	0.058	04/23/90	<0.04	1.34	0.294
05/14/90	32.7	0.67	0.016	05/14/90	<0.04	0.59	0.047	05/14/90	1.20	<0.05	0.019
06/27/90	28.4	--	0.018	06/27/90	<0.04	--	0.056	06/27/90	<0.04	--	0.284
07/17/90	34.8	0.49	0.030	07/16/90	<0.04	1.24	0.281	07/16/90	<0.04	0.57	0.067
05/15/91	36.3	0.20	0.015	05/15/91	<0.04	0.57	0.062	05/15/91	<0.04	1.29	0.245
08/12/91	14.2	<0.05	0.013	08/12/91	0.04	0.59	0.062	08/12/91	0.30	0.77	0.037
01/14/92	35.7	<0.05	<0.010	01/14/92	<0.04	0.57	0.032	01/14/92	<0.04	1.20	0.273
02/26/92	36.7	--	--	--	--	--	--	--	--	--	--
03/31/92	37.4	--	--	--	--	--	--	--	--	--	--
04/28/92	38.7	--	--	--	--	--	--	--	--	--	--
05/19/92	37.2	<0.05	<0.010	05/19/92	<0.04	0.59	0.063	05/19/92	<0.04	1.26	0.279
06/30/92	37.6	--	--	--	--	--	--	--	--	--	--
07/27/92	16.7	<0.05	0.012	07/27/92	<0.04	0.58	0.092	07/27/92	<0.04	1.23	0.272
08/24/92	48.5	<0.05	0.033	08/24/92	<0.04	0.58	0.027	08/24/92	<0.04	1.22	0.169
09/29/92	44.7	--	--	--	--	--	--	--	--	--	--
10/28/92	40.5	--	--	--	--	--	--	--	--	--	--
11/24/92	39.5	--	--	--	--	--	--	--	--	--	--
12/28/92	41.3	--	--	--	--	--	--	--	--	--	--

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
09/13/89	2.90	<0.05	--	09/13/89	1.85	<0.05	--	09/12/89	0.53	0.12	--
11/06/89	1.83	<0.05	0.023	11/06/89	1.53	<0.05	0.032	11/06/89	1.17	<0.05	0.036
03/13/90	10.5	<0.05	0.025	03/13/90	1.43	<0.05	0.035	03/13/90	1.60	<0.05	0.038
04/24/90	9.29	<0.05	0.023	04/24/90	1.11	<0.05	0.037	04/24/90	0.77	0.07	0.038
05/15/90	8.48	<0.05	0.025	05/15/90	0.91	<0.05	0.022	05/15/90	0.74	<0.05	0.033
06/26/90	7.64	--	0.025	06/26/90	1.28	--	0.031	06/26/90	0.72	--	0.039
07/17/90	7.45	<0.05	0.031	07/17/90	1.22	<0.05	0.039	07/17/90	0.73	<0.05	0.045
05/15/91	6.59	<0.05	0.250	05/15/91	0.78	<0.05	0.037	05/15/91	6.33	<0.05	0.038
08/13/91	3.16	<0.05	0.021	08/13/91	0.96	<0.05	0.070	08/13/91	3.04	<0.05	0.028
01/08/92	3.99	<0.05	0.030	01/07/92	3.28	<0.05	0.043	01/08/92	1.78	0.06	0.037
02/26/92	5.82	--	--	--	--	--	--	--	--	--	--
03/31/92	8.79	--	--	--	--	--	--	--	--	--	--
04/28/92	12.9	--	--	--	--	--	--	--	--	--	--
05/18/92	17.0	<0.05	0.020	05/18/92	3.96	<0.05	0.037	05/18/92	1.71	<0.05	0.037
06/30/92	18.4	--	--	--	--	--	--	--	--	--	--
07/28/92	13.6	<0.05	0.022	07/28/92	4.45	<0.05	0.038	07/28/92	0.94	0.05	0.034
08/25/92	12.9	<0.05	0.071	08/25/92	4.56	<0.05	0.096	08/25/92	0.89	0.06	0.073
09/29/92	9.26	--	--	--	--	--	--	--	--	--	--
10/28/92	8.88	--	--	--	--	--	--	--	--	--	--
11/24/92	8.07	--	--	--	--	--	--	--	--	--	--
12/28/92	8.14	--	--	--	--	--	--	--	--	--	--

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
09/13/89	0.14	<0.05	--	09/13/89	0.69	<0.05	--
11/13/89	<0.04	<0.05	0.037	11/13/89	1.12	<0.05	0.021
03/13/90	1.31	<0.05	0.036	03/13/90	1.30	<0.05	0.023
04/24/90	<0.04	0.08	0.040	04/24/90	1.84	<0.05	0.023
05/15/90	<0.04	<0.05	0.033	05/15/90	1.58	<0.05	0.016
06/26/90	0.24	--	0.042	06/26/90	1.24	--	0.018
07/17/90	0.08	0.05	0.050	07/17/90	1.90	<0.05	0.024
05/15/91	0.09	<0.05	0.047	05/15/91	1.06	<0.05	0.023
08/13/91	0.28	0.06	0.049	08/13/91	0.70	<0.05	<0.010
01/14/92	0.27	<0.05	0.040	01/14/92	0.37	<0.05	0.013
05/20/92	0.06	<0.05	0.046	05/20/92	0.17	<0.05	0.016
07/28/92	<0.04	<0.05	0.047	07/28/92	0.24	<0.05	0.015
08/25/92	<0.04	<0.05	0.053	08/25/92	0.75	<0.05	0.057

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
09/19/89	0.26	<0.05	--	09/18/89	<0.04	0.11	--
11/13/89	0.29	<0.05	0.023	11/13/89	<0.04	0.14	0.016
03/13/90	0.16	<0.05	0.016	03/13/90	0.06	0.08	0.062
04/24/90	0.04	<0.05	0.029	04/24/90	<0.04	0.15	0.014
05/15/90	0.04	<0.05	0.015	05/15/90	<0.04	0.13	0.019
06/26/90	0.19	--	0.017	06/26/90	<0.04	--	0.015
07/18/90	0.11	<0.05	0.020	07/18/90	<0.04	0.11	0.026
05/20/91	1.82	<0.05	0.018	05/20/91	<0.04	0.13	0.013
08/13/91	3.06	<0.05	0.022	08/13/91	0.09	0.13	0.020
01/13/92	1.45	<0.05	0.015	01/13/92	<0.04	0.12	0.015
05/20/92	0.96	<0.05	0.010	05/20/92	<0.04	0.14	<0.010
07/29/92	1.82	<0.05	0.015	07/29/92	<0.04	0.13	0.012
08/26/92	7.09	<0.05	0.032	08/26/92	<0.04	0.13	<0.010

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
09/19/89	1.31	<0.05	--	09/19/89	<0.04	0.15	--
11/15/89	0.88	0.05	0.020	11/15/89	0.05	0.13	0.054
03/14/90	1.07	<0.05	0.242	03/14/90	0.17	<0.05	0.015
04/18/90	0.83	<0.05	0.033	04/18/90	<0.04	0.18	0.095
05/16/90	0.60	0.05	0.034	05/16/90	<0.04	0.18	0.098
06/26/90	0.63	--	0.015	06/26/90	<0.04	--	0.109
07/18/90	0.90	<0.05	0.013	07/18/90	<0.04	0.21	0.090
05/20/91	1.26	0.18	0.011	05/20/91	<0.04	0.24	0.096
08/14/91	0.89	<0.05	0.016	08/14/91	0.15	0.06	0.021
01/13/92	0.73	<0.05	0.017	01/13/92	<0.04	0.18	0.108
05/19/92	0.62	<0.05	<0.010	05/19/92	<0.04	0.18	0.100
07/29/92	0.88	<0.05	0.012	07/29/92	<0.04	0.18	0.108
08/26/92	1.13	<0.05	0.052	08/26/92	<0.04	0.19	0.112

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
08/30/89	7.30	0.08	--	08/30/89	0.37	0.30	--	08/30/89	0.38	0.21	--
11/02/89	4.82	0.09	0.028	11/02/89	<0.04	0.44	0.079	11/02/89	<0.04	0.34	<0.010
03/19/90	3.60	0.08	0.131	03/19/90	0.50	<0.05	0.266	03/19/90	0.44	0.05	<0.010
04/16/90	3.33	0.08	0.035	04/16/90	<0.04	0.43	0.032	04/16/90	<0.04	0.38	0.024
05/21/90	4.01	0.05	0.032	05/21/90	<0.04	0.40	0.030	05/21/90	<0.04	0.40	0.023
06/20/90	4.12	--	0.031	06/20/90	<0.04	--	0.027	06/20/90	<0.04	--	<0.010
07/24/90	4.63	0.05	0.035	07/24/90	<0.04	0.50	0.028	07/24/90	<0.04	0.45	0.034
05/06/91	3.88	<0.05	0.033	05/06/91	<0.04	0.48	0.019	05/06/91	<0.04	0.44	0.022
08/05/91	6.51	<0.05	0.032	08/05/91	0.23	0.26	0.041	08/05/91	0.53	<0.05	0.011
01/16/92	6.11	<0.05	0.032	01/16/92	<0.04	0.47	0.023	01/16/92	<0.04	0.43	0.018
02/25/92	7.19	--	--	--	--	--	--	--	--	--	--
03/30/92	5.61	--	--	--	--	--	--	--	--	--	--
04/27/92	6.87	--	--	--	--	--	--	--	--	--	--
05/11/92	7.32	<0.05	0.034	05/11/92	<0.04	0.48	0.028	05/11/92	<0.04	0.39	0.014
06/29/92	6.30	--	--	--	--	--	--	--	--	--	--
07/20/92	5.16	<0.05	0.074	07/20/92	<0.04	0.46	0.093	07/20/92	<0.04	0.44	0.055
08/17/92	5.45	<0.05	0.010	08/17/92	<0.04	0.47	0.073	08/17/92	<0.04	0.41	0.022
09/28/92	5.04	--	--	--	--	--	--	--	--	--	--
10/26/92	5.36	--	--	--	--	--	--	--	--	--	--
11/23/92	5.86	--	--	--	--	--	--	--	--	--	--
12/29/92	6.55	--	--	--	--	--	--	--	--	--	--