Ground-Water Sampling Methods and Quality-Control Data for the Red River of the North Basin, Minnesota, North Dakota, and South Dakota, 1993-95

By Michael A. Menheer and Mark E. Brigham

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Mounds View, Minnesota
1997

U.S. DEPARTMENT OF THE INTERIOR

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<URL:http://wwwmn.cr.usgs.gov/redn/index.html>

Foreword

The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth resources of the Nation and to provide information that will assist resource managers and policymakers at Federal, State, and local levels in making sound decisions. Assessment of water-quality conditions and trends is an important part of this overall mission.

One of the greatest challenges faced by water-resources scientists is acquiring reliable information that will guide the use and protection of the Nation's water resources. That challenge is being addressed by Federal, State, interstate, and local water-resource agencies and by many academic institutions. These organizations are collecting water-quality data for a host of purposes that include: compliance with permits and water-supply standards; development of remediation plans for specific contamination problems; operational decisions on industrial, wastewater, or water-supply facilities; and research on factors that affect water quality. An additional need for water-quality information is to provide a basis on which regional- and national-level policy decisions can be based. Wise decisions must be based on sound information. As a society we need to know whether certain types of water-quality problems are isolated or ubiquitous, whether there are significant differences in conditions among regions, whether the conditions are changing over time, and why these conditions change from place to place and over time. The information can be used to help determine the efficacy of existing water-quality policies and to help analysts determine the need for and likely consequences of new policies.

To address these needs, the U.S. Congress appropriated funds in 1986 for the USGS to begin a pilot program in seven project areas to develop and refine the National Water-Quality Assessment (NAWQA) Program. In 1991, the USGS began full implementation of the program. The NAWQA Program builds upon an existing base of water-quality studies of the USGS, as well as those of other Federal, State, and local agencies. The objectives of the NAWQA Program are to:

- Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.
- Describe how water quality is changing over time.
- Improve understanding of the primary natural and human factors that affect water-quality conditions.

This information will help support the development and evaluation of management, regulatory, and monitoring decisions by other Federal, State, and local agencies to protect, use, and enhance water resources.

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of 60 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 60 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

National synthesis of data analysis, based on aggregation of comparable information obtained from the study units, is a major component of the program. This effort focuses on selected water-quality topics using nationally consistent information. Comparative studies will explain differences and similarities in observed water-quality conditions among study areas and will identify changes and trends and their causes. The first topics addressed by the national synthesis are pesticides, nutrients, volatile organic compounds, and aquatic biology. Discussions on these and other water-quality topics will be published in periodic summaries of the quality of the Nation's ground and surface water as the information becomes available.

This report is an element of the comprehensive body of information developed as part of the NAWQA Program. The program depends heavily on the advice, cooperation, and information from many Federal, State, interstate, Tribal, and local agencies and the public. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch

Chief Hydrologist

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Conversion Factors, Abbreviations, Acronyms, and Definitions

Multiply	By	To obtain
foot (ft)	0.3048	meter
gallon (gal)	3.785	liter
gallon per minute (gal/min)	.06308	liter per second
degree Fahrenheit (°F)	(°F - 32)/1.8	degree Celsius

Chemical concentrations: Chemical concentrations of substances in water are given in metric units of micrograms per liter (µg/L). Micrograms per liter is a unit expressing the concentration of chemical constituents in solution as mass (micrograms) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter.

Use of trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Abbreviations, Acronyms, and Definitions:

CV—coefficient of variation, the standard deviation divided by mean, multiplied by 100 to express in percent.

DI—deionized water.

DO—dissolved oxygen.

DOC—dissolved organic carbon.

HCl—hydrochloric acid.

HPLC—high performance liquid chromatography.

MDL—method detection limit, the smallest concentration of an analyte which can be accurately detected and quantified by an analytical method.

µg/L—microgram per liter, concentration of an analyte expressed in 1×10^{-6} grams per liter.

µm—micrometer or micron, filter pore size expressed in 1×10^{-6} meter.

µS/cm—microsiemens per centimeter, the specific electrical conductance of water, equivalent to micromhos per centimeter at 25 degrees Celsius.

mg/L—milligram per liter, concentration of an analyte expressed in 1×10^{-3} grams per liter.

MRL—minimum reporting level, the smallest concentration, for a given analyte and method, that is reported by a laboratory.

NAWQA—National Water Quality Assessment Program.

NWQL—National Water Quality Laboratory, a laboratory operated by the U.S. Geological Survey in Arvada, Colorado.

OWQ—Office of Water Quality.

QC—quality control.

QWSU—Water Quality Service Unit, U.S. Geological Survey.

SD—standard deviation.

USGS—U.S. Geological Survey.

VOC—volatile organic compounds.

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Abstract

Ground-water-quality samples were collected for the intensive data-collection phase of the Red River of the North Basin study unit, one of 60 study units of the National Water Quality Assessment (NAWQA) Program throughout the United States. The sampling protocols used were designed for the NAWQA Program. The protocols include sampling equipment, cleaning procedures, sample-collection methods, and quality-control plans to monitor the accuracy of the data collected. One of the goals of the NAWQA Program was to collect data using similar methods to build a nationally consistent water-quality data base.

Quality-control data demonstrated that most constituents measured for this study yielded reproducible data, with low to undetectable contamination from the sampling and analytical procedures. Several constituents were occasionally or frequently detected in blank samples at levels similar to low-concentration ground-water-quality samples. For example, iron was detected in 75 percent of the blank samples, with a maximum concentration of 27 µg/L, indicating that iron contamination may interfere with its determination at low levels in ground waters. Copper, aluminum, and dissolved organic carbon concentrations in blank samples overlap those determined in ground-water-quality samples, thereby precluding quantitative reporting of those constituents. Most pesticide data are reproducible, with minimal bias. Some pesticides had low but consistent recoveries; these data may be useful if spike and surrogate data are carefully considered. Data for some pesticides measured in this study should not be quantitatively reported or used, because they may underestimate the concentrations of those pesticides in ground waters.

Introduction

The USGS began full implementation of the NAWQA Program in 1991. The goal of this program is to collect reliable and nationally consistent information on the status of and trends in the quality of the Nation's water resources, and to provide scientifically valid explanations of these conditions and trends (Cohen and others, 1988, p. 1147). Much of the data collected will come from 60 hydrologic regions called study units. The part of the Red River of the North drainage basin in the United States (hereinafter referred to as the Red River Basin) is one of these 60 study units. An intensive ground-water data collection phase for the Red River Basin study unit began in 1993 and continued through 1995. Figure 1 shows the location of the study unit and of the wells sampled. Data from the study units will be compiled in a national data base. National synthesis teams will review and make larger-scale assessments and interpretations of the data.

Purpose and Scope

The purpose of this report is to describe the ground-water sampling protocols, sampling equipment, field data-collection techniques, and quality-control data used during the intensive data-collection phase of the Red River Basin NAWQA study. This report describes (1) methods used to prepare wells for sampling, (2) equipment used, (3) sample collection procedures, (4) shipping and storage of the samples, (5) equipment cleaning procedures, (6) and types of quality-control samples collected, with a summary of the quality-control data.

Acknowledgments

Special appreciation is given to the numerous property owners in the Red River Basin study unit for allowing observation wells to be installed on their property or water-quality samples to be collected from their wells, and to Tim Cowdery, U.S. Geological Survey, for his guidance in the collection of the field samples.

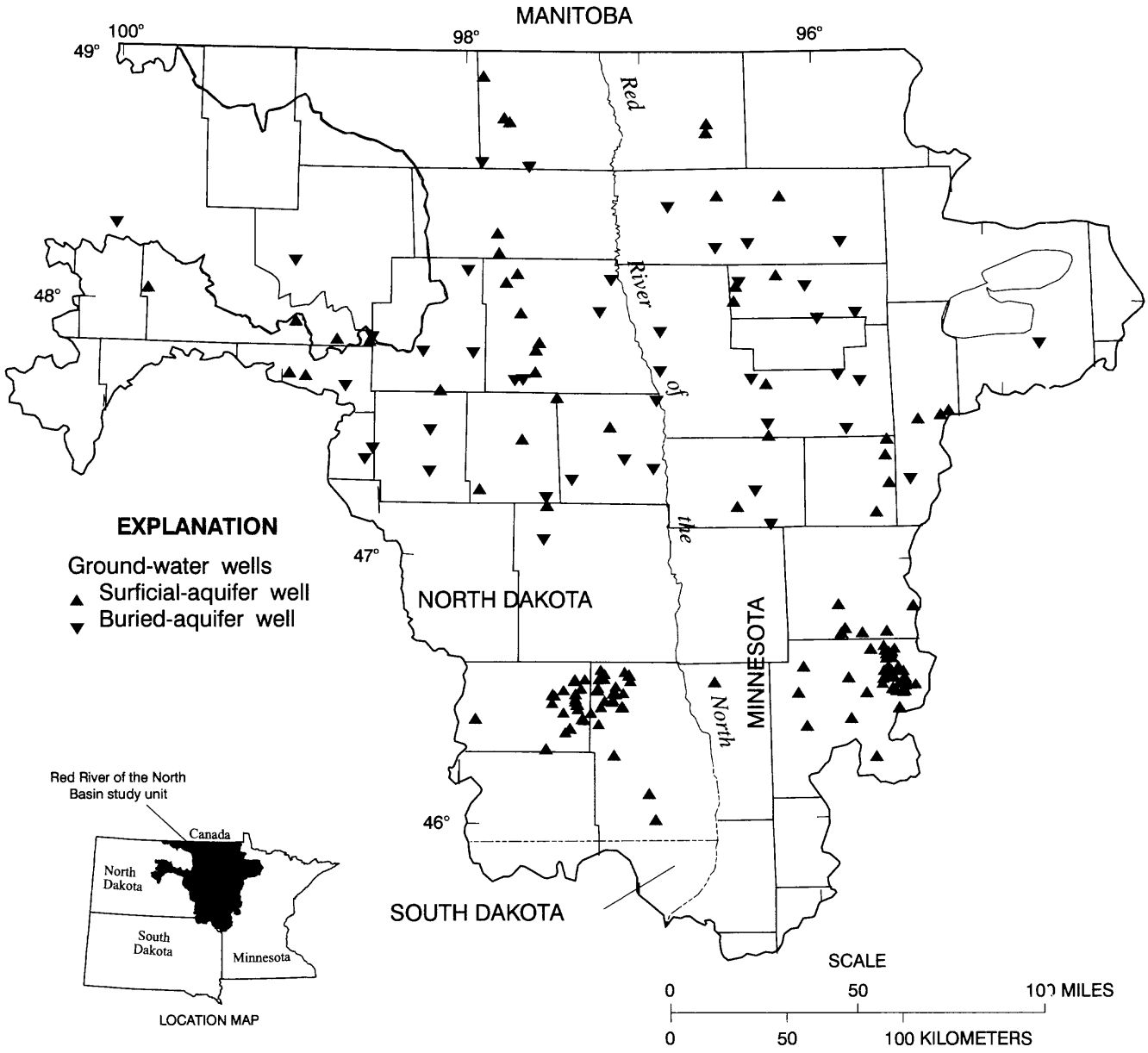

Figure 1. Location of Red River of the North Basin study unit and ground-water sampling sites.

Well Description and Development

Ground-water sampling for the NAWQA Program was designed to investigate study areas at several different spatial scales. A large-scale study-unit survey was done to provide an overview of the water quality. Wells included in this study were selected from pre-existing wells screened in surficial and buried aquifers. Pre-existing wells were privately owned domestic wells, farm wells used for livestock and irrigation, and small-business wells.

On a more geographically limited scale, a land-use study was done to consider the effects of human activities on the quality of the ground water. Wells selected included pre-existing, privately owned wells and observation wells drilled for this study.

The pre-existing wells were chosen from wells which met the following criteria:

(1) The depth and type of well screen, or open interval, was known.

(2) The casing material and well diameter were known.

(3) The stratigraphy of the bore hole, usually recorded on a well log, was known to determine if the well was screened in a surficial or buried aquifer.

(4) The water, at the sampling point, was untreated.

A small-scale study was done to monitor changes in water quality along defined flowpaths to determine land-use effects (Stoner and Lorenz, 1995). Two flowpaths through surficial aquifers (located in the land-use study area) were investigated. All wells for the flowpath study were drilled by study-unit personnel.

Seventy-five wells were drilled for this study using a hollow-stem rotary hydraulic auger drill rig. Drill cuttings from the bore holes were described and collected for archival. Cores were collected in polycarbonate tubing at several sites. The drilling equipment was cleaned between each site using a steam cleaner or a commercial self-car-wash facility to minimize the possibility of cross contamination between well sites. Observation-well construction for this study is shown schematically in figure 2. The well casing used was flush-threaded 2-inch inside-diameter (ID), polyvinyl chloride (PVC). Two types of screens were used. The majority were 5-ft-long, flush-threaded, machine-slotted (0.010 slot), PVC screens. Sand-packed PVC screens were used for nine wells finished in silty-sand aquifers. Washed medium to coarse sand was used to backfill the hole around the well screen. Bentonite grout was pumped into the annular space above the sand pack. A 6.5-inch ID diameter, 7-ft-long protective steel casing was placed around the PVC casing at the land surface to protect the well. This protection pipe was cemented in place to divert surface drainage away from the well. An aluminum locking cap was installed on the top of the pipe.

Wells installed for this study were developed. Well development refers to any of several techniques used to remove particles and sediment from the bottom of the well, the well screen, and the formation immediately surrounding the well screen. Wells were developed to remove excess fine-grained particles from the screen and well for the following reasons:

(1) Analytes could adsorb to sediment in the water, making it difficult to obtain a sample that is representative of the ground water;

(2) Particles could fully or partially clog the well screen, preventing a good hydraulic connection between the well and the surrounding formation. (This is important because it allows the water in the surrounding formation to enter the well from the whole or most of the screened interval, not a restricted area); and

(3) Fine-grained particles will wear out sampling pumps and clog filters used to collect samples.

The wells were developed by pumping with a hand pump and/or a gas powered centrifugal pump. When the water being pumped from the well began to clear, some native water was poured back into the well. This was done to suspend particles in the water so they could be pumped from the well. A hand pump was often used to begin pumping the well. A hand pump was used because it would pump sediment-laden water without clogging or being damaged. The hand pump was used until the water visibly began to clear or the well was pumped dry.

If the well pumped dry it was allowed to refill with water and was pumped again. While pumping, native water from the well was collected in a bucket and was poured back into the well. This was done to reduce the time needed for the well to recharge with water. If the water level was less than 25 ft below land surface, and the well produced enough water, a motorized centrifugal pump was used to pump the well for a longer period of time, 0.5-1.5 hours. During pumping, a visual description of the water clarity, flow rate, and volume of water pumped was recorded. Flow rate was measured using a graduated water bucket and a stop watch. Water-levels were measured before and after the well was pumped to determine water-level recovery. Water-level recovery was an indicator of production-zone permeability and an adequately developed well. It was necessary to redevelop some wells that had not been pumped for 8 to 12 months before samples were collected.

Sampling Methods

The sampling equipment (fig. 3a and 3b) and procedures used in the Red River Basin study were based on the ground-water sampling protocols of the NAWQA Program (Lapham and others, 1995; and Koterba and others, 1995). A list of the equipment used for sampling is contained in the Supplemental Information section at the end of this report.

Sample Collection and Processing

The sampling equipment was designed to minimize contact between atmospheric, ambient conditions, and the sample water. The samples were collected in one of two vehicles equipped specifically for this study (fig. 4). One vehicle was used only occasionally for flowpath-

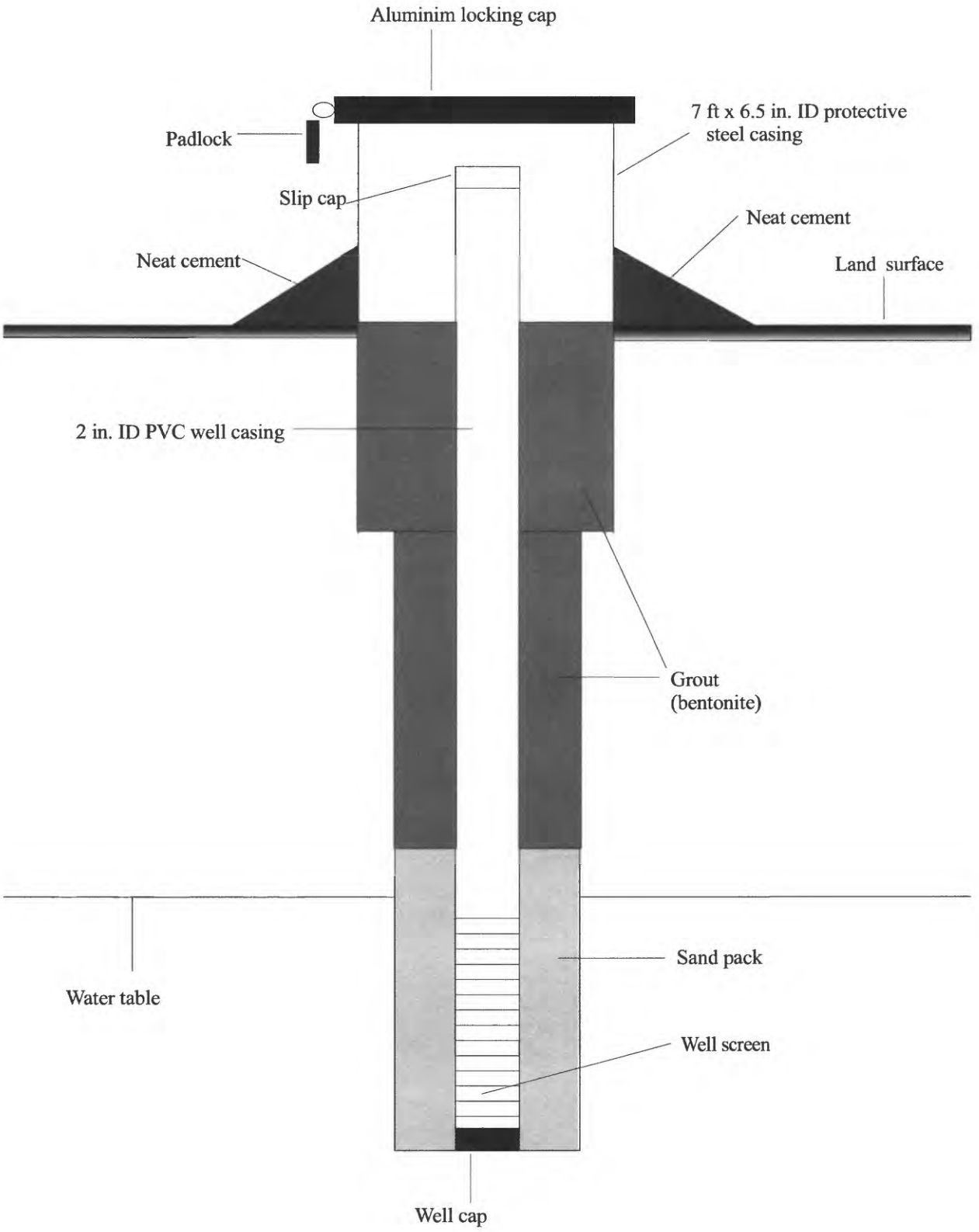

Figure 2. Observation well construction.

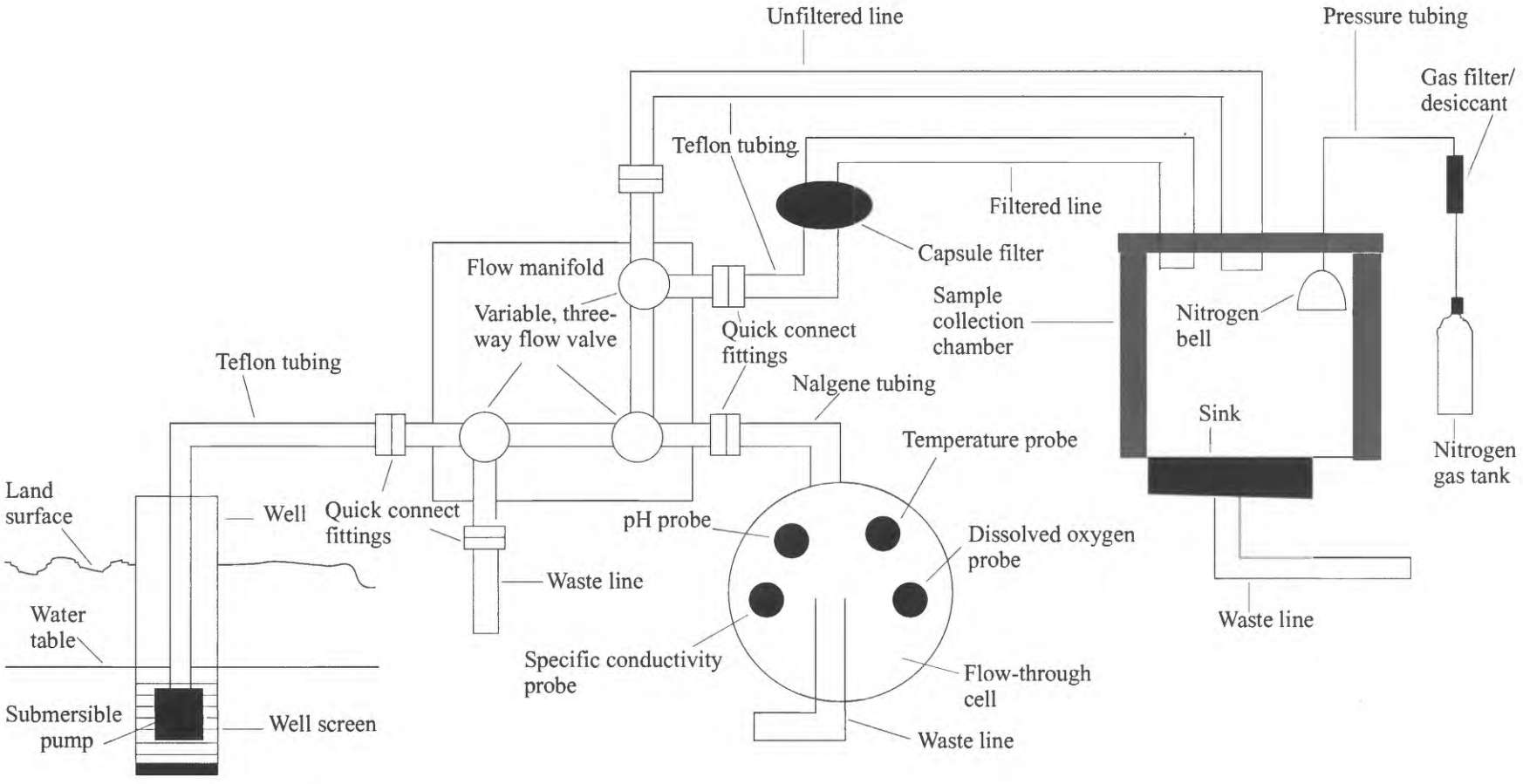

Figure 3a. Schematic of ground-water sampling equipment.

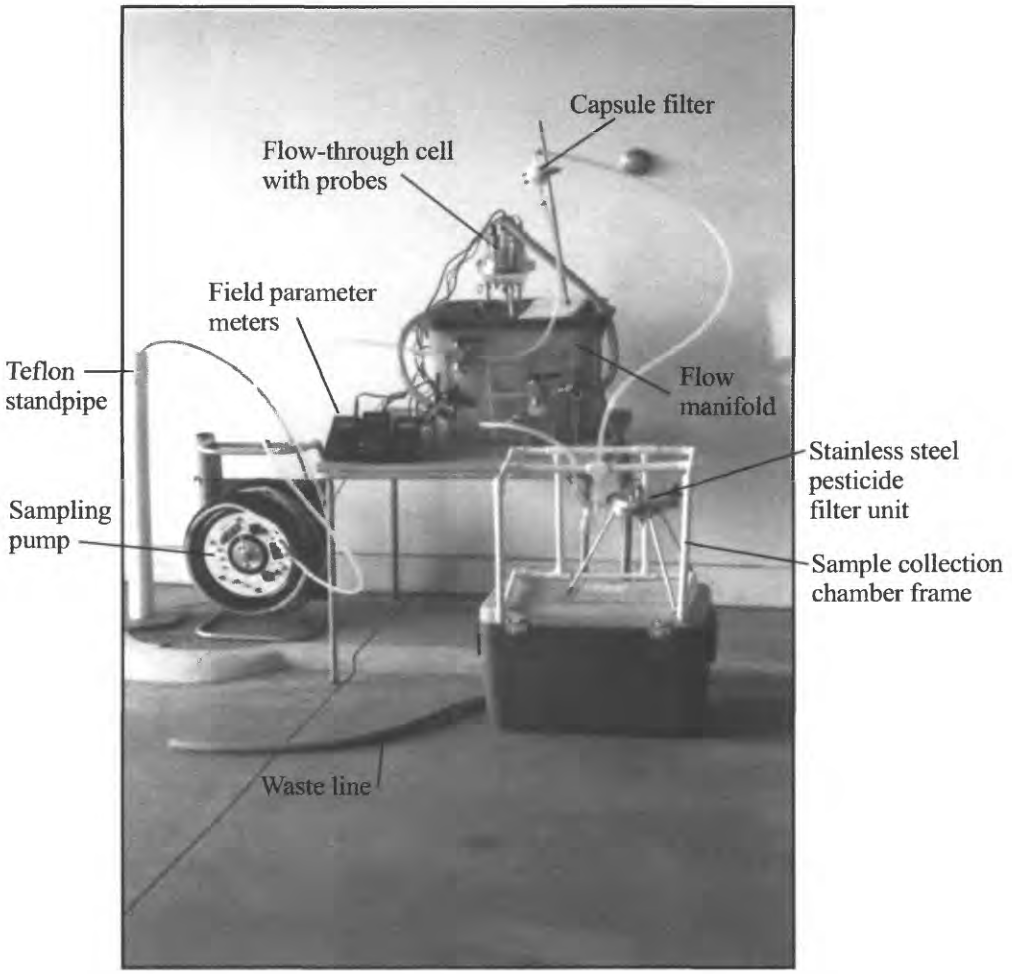

Figure 3b. Photograph of ground-water sampling equipment.

study sampling, for analysis of nutrients, major ions, dissolved organic carbon, tritium, and stable isotopes (deuterium and oxygen-18).

The submersible-sampling pumps used were, Keck model SP-87, Grundfos Redi-Flow II pumps, or the pump present in privately owned pre-existing wells. The Keck pump was used for most of the 1993-95 intensive-sampling period. The Keck and Grundfos Redi-Flow II pumps were equipped with a variable flow rate control. The Keck pump was powered by a deep-cycle marine battery. The Grundfos pump was powered by a 120/240 volt 20 ampere gas-powered generator. The generator was transported in a trailer and was operated 30 to 40 feet downwind of the sampling site to avoid contamination from the exhaust.

Privately owned wells were sampled from an outside tap to ensure that the water did not pass through a water softener, or other water-treatment procedures. If a sample was collected after a pressure tank, the pressure-tank volume was included in the volume of water to be purged before sampling the well. A disposable, plastic threaded adapter was used to connect the tap to the Teflon tubing that was connected to the flow manifold.

Prior to sampling a well, a static water level was measured, if possible. In some wells, it was not possible to measure water levels because of submersible pumps in the well casing. The water level reported by the driller on the well log was recorded. Then aluminum foil or the plastic bag covering the pump was removed and the pump was lowered into the well 1 to 2 ft below the water level. The tubing from the pump was connected to the flow manifold and the flow of water was directed through the flow manifold to a waste line. A stop watch and a graduated bucket were used to determine the flow rate. The volume of water in the well was determined, based on the water-level measurement,

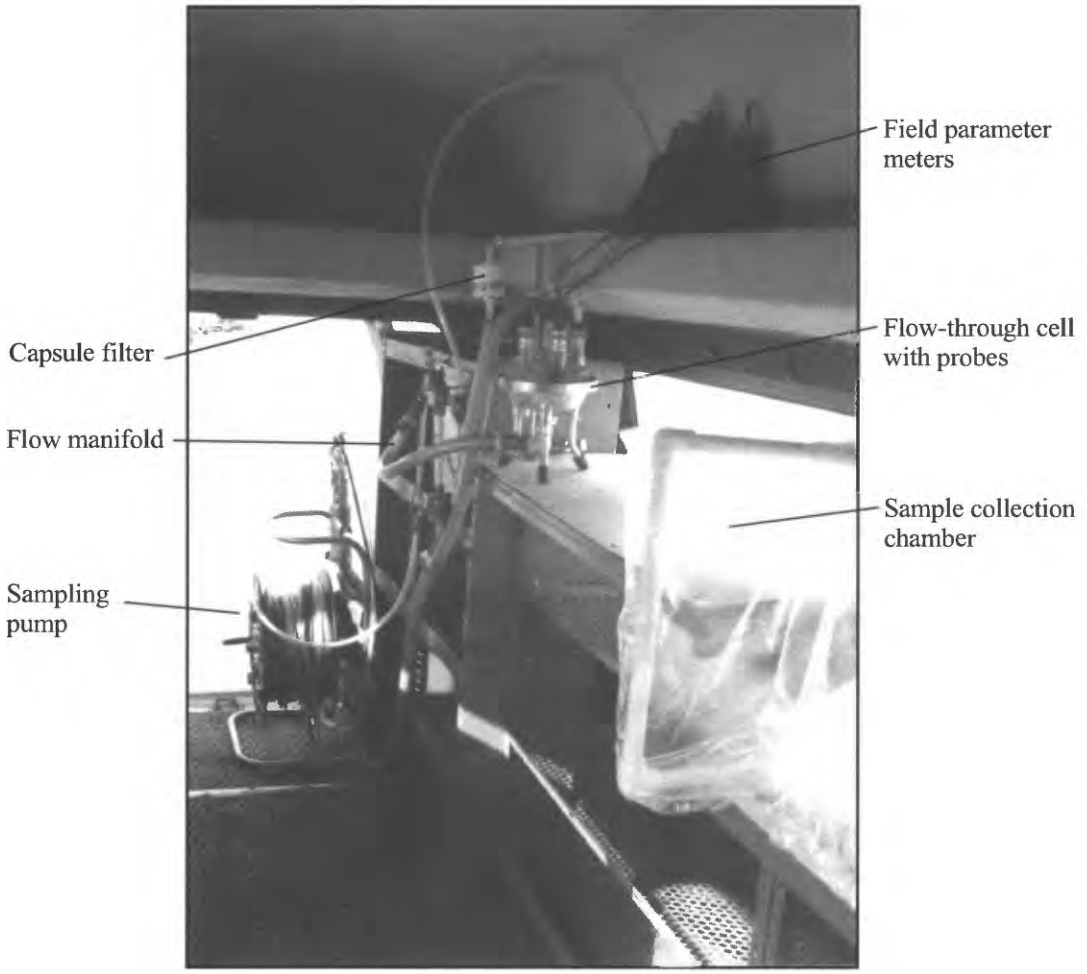

Figure 4. Photograph of interior of vehicle with ground-water sampling equipment.

the well diameter, and the depth of the well. The time needed to purge three well volumes of water was calculated using the flow rate and the volume of water in the well. A standard field form (fig. 5) was used to record the field data.

Initially the pump was set to a high flow rate to quickly purge the well. The flow rate was reduced after the calculated purge volume had been pumped prior to field parameter measurements. The field parameter measurements included air and water temperature, pH, specific conductance, DO, alkalinity, and barometric pressure.

A Hydrolab Scout II fitted with a flow-through cell was used to measure the field parameters during the 1993 field season. A Geotech flow-through cell with an Orion model 250A pH meter, equipped with either a silver/silver chloride (Ag/AgCl) electrode or a Ross combination electrode; an Orion model 124 conductivity meter; and a dissolved oxygen meter were used during the 1994 and 1995 field seasons. The temperature probe on the pH meter was used to measure the water temperature.

The meters were calibrated with fresh conductivity standards and pH buffers daily before sampling and the calibrations were checked at the end of each day. The calibrations were recorded in a log book kept for each meter and on the field form for the first site sampled each day. Field parameter meters and standards were not stored in the sampling vehicles when not on a sampling trip, because excessive heat or cold could damage the meters or affect the values of the standards.

When monitoring field parameters, the flow rate was adjusted to 1 gal/min to reduce turbidity, and flow was diverted from the waste line to the flow-through cell.

Water entered the flow-through cell at the bottom and flowed out at the top. The flow-through cell was made of clear polycarbonate plastic for visual inspection of the probes during sampling. Field parameter readings were recorded every several minutes. The water level and flow rate were recorded with each set of readings. When three consecutive readings met the following criteria the well was considered purged and the water representative of the aquifer. The field parameter criteria were:

for pH,	readings within 0.1 standard unit
for specific conductance,	if conductance was less than 100 µS/cm, readings within 5 µS/cm; if 100-1,000 µS/cm, readings within 10 µS/cm; if greater than 1,000 µS/cm, readings within 50
for dissolved oxygen,	readings within 0.3 mg/L
for water temperature,	readings within 0.2°C

The flow rate was adjusted to 0.4-0.6 gal/min before beginning to collect samples. The well was pumped at this rate until all of the samples had been collected and a final set of field parameters had been recorded.

The DO meter was considered accurate to 0.2 mg/L. In cases where this low concentration was reached, the water was checked for a hydrogen sulfide gas (rotten egg) smell. If hydrogen sulfide was detected, the DO probe was removed from the flow-through cell to prevent fouling.

Sample water with 0.2 mg/L or less DO was considered anoxic and the samples were collected using the following reduced-oxygen sampling-environment protocols. Nitrogen gas was used to displace the oxygen in the sample bottle, which could chemically alter the low-oxygen sample water. The nitrogen gas was passed through drierite (calcium sulfate), a desiccant, to remove any moisture from the gas, then through corrugated Teflon tubing into the sample collection chamber. The uncapped sample bottles were held inverted, the tubing was placed into the bottle near the bottom, and the nitrogen gas was pumped into the bottles for 10-20 seconds. The bottle was considered to be filled with nitrogen gas. The inverted bottle was quickly capped. The samples were collected while the bottle was held under a rigid polycarbonate bell with nitrogen gas continuously pumped into the bell to displace any air.

The sample collection order, analytical laboratory schedules, and related information for the ground-water-quality samples are summarized in table 1. Note that for some schedules more than one bottle is collected. QC replicate and triplicate samples were collected in the same order. QC blank sample order is summarized in table 2. The capsule filter was changed between collection of ground-water-quality and QC samples.

Most samples were collected in a sample-collection chamber, which was covered with a clear plastic bag. The sample-collection chamber and the sample-preservation chambers were frames made out of 0.5 inch ID PVC pipes and elbows fastened with nylon screws. Powder-free latex gloves were worn while sampling. Additional information on NAWQA sample collection protocols, are described in Koterba and others (1995).

Sample collection protocols for VOC, radon, tritium (H^3), and stable isotopes ($Oxygen^{18}/Oxygen^{16}$ and deuterium/protium, H^2/H^1) are briefly discussed below because of their special collection requirements.

The VOC sample was collected first to avoid overpurging the well and thereby collecting a nonrepresentative sample. The VOC sample was collected unfiltered and in triplicate.

A 40-mL clear glass sample vial was held with the Teflon tubing near the bottom of the vial. The vial was not rinsed. The vial was slowly lowered as it filled with sample water. Care was taken to avoid creating air bubbles while collecting the sample as aeration of the water can affect the VOC concentration, due to volatilization. The vial was allowed to overfill creating an inverted meniscus at the top of the vial. The vial was capped, inverted, and tapped to check for air bubbles. If any air bubbles were found, the vial was discarded and a new sample was collected. The VOC samples were chilled with ice.

The radon sample was collected outside of the sample collection chamber from a special assembly using a syringe (fig. 6). The assembly was fitted with a flow valve used to constrict the flow of water against a septum through which a needle was inserted to collect the sample. The septum on the radon assembly was held so that it pointed downward to prevent any air bubbles from accumulating. The flow valve was partially closed so pressure was exerted on the septum. The syringe was inserted into the septum. The valve on the radon assembly was closed further until the syringe could be filled with sample water with minimal effort. A minimum of 20 mL of sample water was used to rinse the syringe. Another 20 mL of water was collected. The syringe was withdrawn from the septum, held vertically, and 5 mL of sample water was forced out to

U.S. GEOLOGICAL SURVEY, WRD, GROUND-WATER QUALITY FIELD NOTES BQA-1 3/92 (3rd printing, 1st ed.)

Proj. Name, No. REDN NAWQA, 462712704 Date 9-7-95 Time 09:00

Loc. Well No. SF1S

Composite Samples? ☐ YES ☒ NO
If YES, indicate:
Dates
Times

Site I.D. 4 6 3 0 5 0 0 9 7 2 1 3 4 0 1

Sampled by M Menheer, P Larson, K Saylor

SMS Cntrl. No.

Record No. 99500342 Sample Purpose (71999) : 15.00

WELL DATA ☒ Well ☐ Open Hole ☐ Spring

Altitude, ft (72000) 995. Static water level, ft (72019) 14.62 * Casing vol. (gal.) 0.65

Depth top sample interval (72015) 9.3 Dia. inside (in.) 2.00 Purge vol. (gal.) 1.95

Depth bottom sample interval (72016) 18.70 Screened/ open interval Top : 9.30 Bottom : 18.70

Allowable draw-down (ft.) ____ * Casing Vol. (gal.) = 0.0408 X Dia. (in.)^2 X Height (ft) OR Cas. Vol. = H X F
Height = H = Well Depth - Static Water Level = ____ F = Casing volume factor

*** VOLUME FACTORS**

Dia. (in.)	Cas. Vol. Factor F
1.0	0.04
1.5	0.09
2.0	0.16
3.0	0.37
4.0	0.65
4.5	0.83
5.0	1.02
6.0	1.47
8.0	2.61
10.0	4.08
12.0	5.88
24.0	23.5
36.0	52.9

SAMPLING DATA

Location 135N53W16BBDBBA01 Date well last sampled 8-22-95

Minutes pumped before sampling (72004) 27 static water level when well last sampled 14.23

Sampler type (84164) 4046 Sampling condition (72006)

4010 = thief; 4020 = bailer; 4025 = double-valve bailer; 4100 = flowing well
PUMPS: 4030 = suction pump; 4040 = submersible; 4050 = squeeze; 4060 = gas recip.; 4070 = gas lift; 4080 = peristaltic; 4090 = jet; 8010.0 = other
0.10 = site was being pumped; 0.11 = site recently pumped
4. = flowing; 8. = pumping; 30. = seeping; 31. = nearby well pumping

Sampler ID REDN KECK #123

Sampler material : ☒ Stainless Steel ☐ Brass ☐ PVC ☐ Teflon ☐ Other Viton

Aquifer Name: 112 SNDL GW Color light brown Clarity cloudy

Sample extracted and processed under ☒ oxygenated ☐ nonoxygenated conditions

Sample contact with : ☒ atmosphere ☐ oxygen ☐ nitrogen ☐ other

Weather: Clear ☒ Partly Cloudy ☐ Cloudy Light Medium Heavy Snow Rain Calm ☒ Light Breeze ☐ Very Gusty Windy Very Cold ☒ Warm ☐ Hot Other

FIELD MEASUREMENTS

Q. Inst. (00059)	0.6	GPM	Eh (00090)	____ m volts
Temp. Water (00010)	9.3	°C	Alkalinity (39086)	484 mg/L
Temp. Air (00020)	8	°C	Bicarbonate (00453)	591 mg/L
pH (00400)	7.34	units	Carbonate (00452)	____ mg/L
Sp. Cond. (00095)	951	µS/cm 25°C	Hydroxide ( )	____ mg/L
Dis. Oxy. (00300)	0.5	mg/L	E. Coli (31633)	____ col./100 mL; Rmk ____
DO Sat. (00301)	____	%	FC (31625)	____ col./100 mL; Rmk ____
Bar. Press. (00025)	7.48	mm Hg	FS (31673)	____ col./100 mL; Rmk ____
			Other:	

Remarks WL = 16.72 - 2.10 = 14.62

pH meter B used for titration

SAMPLES COLLECTED

Nutrients ☒ TOC ☐
Major Ions ☒ DOC ☒
SOC ☐ Filt. ____ mL
BOD ☐ ____ ☐
COD ☐ ____ ☐

ORGANICS TR. ELEMENTS
Pesticide ☐ Unfiltered ☐
VOC ☐ Filtered ☐
BNA ☐ ____ ☐
Radiochemical ☐
Isotope ☒
Tritium ☒
☐

LABORATORY SCHEDULES
Lab Schedules Req. (or copy of lab request form attached ☐)

Lab Codes Add (A) Delete (D):

Checked by Date

Figure 5. Ground-water quality field notes form.

TEMPERATURE
Lab Thermometer ☐ Checked w/ASTM within ± 0.5 °C; Date _____
Down-Hole Sensor ☐ Describe

AMPULE LOT NUMBERS: nitric acid NA - 4364 -IGSI; mercuric chloride -; nitric acid/potassium dichromate -

pH A - 004027
Mtr W-no. B - 002688 METER Make/Model Orion / 250A

	electrode no.			electrode type		
	pH Buffer	pH Buffer Temp °C	Initial Reading	Adj. Reading	millivolts (redox meas)	Remarks
A	7.0	15.0	7.01	7.03		
A	10.0		10.11	10.11		Slope = 100.6
B	7.0	15.4	7.02	7.03		
B	4.0		3.97	4.00		Slope = 100.5

☒ unfiltered sample ☐ filtered sample

Temp correction factors for buffers applied? ☒ YES ☐ NO

stirrer used? ☐ YES ☒ NO
If yes, ☐ magnetic stirrer ☐ manually stirred

pH subsample from or pH measurement location : Churn | flow through chamber | single point at _____ depth | vertical avg of _____ points

Sample Temp = 9.3 °C

FIELD pH = 7.31 7.34 7.34 USE : 7.34

SPECIFIC CONDUCTANCE
Mtr W-no. 0905123 METER Make/Model Orion / 124

probe no.				
standard value	Temp Std °C	Initial Reading	Adj. Reading	Remarks
495	13.9	508		
744	13.8	764		
1000	14.0	1020		

correction factor applied? ☒ YES ☐ NO
☒ auto temp compensated meter
☐ manual temp compensated meter
corr. factor = _____

SC subsample from or SC measurement location : Churn | flow through chamber | single point at _____ depth | vertical avg of _____ points

FIELD CONDUCTANCE = 952 952 951 USE : 951

DISSOLVED OXYGEN W-no. 2295638 METER Make/Model Orion / 820

D.O. measurement location or D.O. subsample from : Churn | flow through chamber | single point at _____ depth | vertical avg of _____ points

Calibration : BOD bottle

☒ Air Calibration in Water ☐ Air Calibration Chamber in Air
D.O. Zero Check (using zero D.O. solution) ☐ YES ☒ NO
☐ Air-Saturation Deionized Water ☐ Calibration by Winkler Titration (attach Supplementary Winkler page)
Thermister Check ☐ YES ☒ NO

Slope = -1.06

BAR. PRESS _____ mm Hg; (mm = in. X 25.4)
Salinity Corr. Factor _____ H_2O Temp. _____ °C
Chart D.O. Sat. _____ mg/L
stirrer used? ☐ YES ☐ NO if yes, ☐ magnetic stirrer ☐ manually stirred
Meter D.O. Sat. _____ mg/L; Adjusted to _____ (if corr. factor applicable)

GROUND WATER D.O. = 0.5

QUALITY ASSURANCE SAMPLES
Were quality assurance samples collected?
☐ YES ☒ NO If YES indicate type(s) :

	Organic-free	DI	water from sampling site
Replicate	☐	☐	☐
Spike	☐	☐	☐
Field Blank	☐	☐	Supplementary page w/additional QA sample info attached ☐
Trip Blank	☐	☐	

Other ☐ Indicate Type(s) :

Calibration Notes and Remarks

Figure 5. Ground-water quality field notes form -- continued.

ALKALINITY

°C Temp	pH	△ pH	Vol acid DC or mL	△Vol acid DC or mL	△ pH / △ Vol acid
10.1	7.37	Initial			
	6.88	0.49	100	100	0.0049
	6.55	0.33	200	100	0.0033
	6.25	0.30	300	100	0.0003
	5.77	0.48	400	100	0.0048
	5.36	0.41	450	50	0.0082
	5.19	0.17	460	10	0.017
	5.16	0.03	462	2	0.015
	5.11	0.05	464	2	0.025
	5.08	0.03	466	2	0.015
	5.03	0.05	468	2	0.025
	4.97	0.06	470	2	0.03
	4.90	0.07	472	2	0.035
	4.82	0.08	474	2	0.04
	472	0.10	476	2	0.05
	4.61	0.11	4.78	2	0.055
	4.47	0.14	480	2	0.07
	4.31	0.16	482	2	0.08
→	4.14	0.17	484	2	0.085
	4.02	0.12	486	2	0.06
	3.90	0.12	488	2	0.06
11.9	3.80	0.10	490	2	0.05

Acid: [1.60 N] 0.1600 N 0.01639N OTHER _____

Acid Lot No. : 4126

Sample Volume : 100 mL

[X] Filtered [ ] Unfiltered

Sample stirred : [X] magnetically [ ] manually

pH: Start 7.37 End 3.80

DC (Digital Counts) or
Vol. titrated at End Point near pH 8.3 : -

Digital Counts or
Vol. titrated at End Point near pH 4.5 : 484

[X] Incremental Equivalence [ ] Fixed End Point [ ] Gran Titration

Date 9-7-95 Time 09:25

CALCULATIONS :

$$CO_3^{-2} = A \times \frac{F_1}{\text{mL sample}} \times CF \ *$$

$$HCO_3^{-1} = [B - 2(A)] \times \frac{F_2}{\text{mL sample}} \times CF; \ *$$

$$\text{ALKALINITY as } CaCO_3 = B \times \frac{F_3}{\text{mL sample}} \times CF \ *$$

FACTORS	DIGITAL COUNT TITRATION (DC) Using 0.1600 normal	Using 1.60 normal
F_1	12.0	120
F_2	12.2	122
F_3	10.0	100

A = DC or mLs acid from initial pH to endpoint near 8.3 = -

B = DC or mLs acid from initial pH to endpoint near 4.5 = 484

FACTORS	BURETTE * TITRATION (mL) Using ml of 0.01639 normal H_2SO_4
F_1	983.5
F_2	1000
F_3	820.2

* APPLY CORRECTION FACTOR (CF) IF ACID USED FOR BURETTE TITRATION HAS NONSTANDARD NORMALITY--
CF = corr. factor = H_2SO_4 normality/0.01639

(IMPORTANT : CF NOT APPLICABLE FOR THE DIGITAL TITRATION FACTORS SHOWN; use only with nonstandard normality BURETTE titration)

ALKALINITY (39086) 484 mg/L as $CaCO_3$

BICARBONATE (00453) 591 mg/L as HCO_3^{-1}

CARBONATE (00452) - mg/L as CO_3^{-2}

NOTE: ATTACH OUTPUT COPY IF ALKALINITY VALUES ARE CALCULATED USING A COMPUTER PROGRAM

OBSERVATIONS/CALCULATIONS :

Figure 5. Ground-water quality field notes form -- continued.

Miscellaneous Section (Notes/Calculations/Well Purge Log & Etc.)

WELL PURGE LOG

Time	Water Level blw MP LS	Draw Down feet 72040	Well Yield When Sampling gpm 00059	cfs	pH 00400	T °C 00010	SC 00095	DO 00300
08:51	Pump on						-water silty to sandy	
09:00	16.86	2.24	0.6				-flow turned to flow cell	
09:06	16.87	2.25	0.6		7.26	9.8	945	0.9
09:10	16.92	2.30	0.65		7.31	9.3	952	0.5
09:14	16.87	2.25	0.6		7.34	9.3	952	0.5
09:18	16.88	2.26	0.6		7.34	9.3	951	0.5
09:19	Sample began							
09:23	Sample end							
09.24	16.89	2.27			7.33	9.4	949	0.5
09:25	Pump off							
09:30	16.72	2.10						

E. COLI (31633)

Time collected : _____

Time in @ 35 °C : _____ Date : _____

Time in @ 44.5 °C : _____

Time out : Date :

Vol. (mL)	Count	Used in calculation?	Remarks *
Blank			
Blank			

* Remarks 1 = Less than 2 = Greater than 0 = Est. ct. K = non ideal ct.

Incub. Time 2 hrs @ 35 °C followed by :

filt. size _____ 20-24 hrs @ 44.5 °C

Ideal count 20-80 col.

E. COLI COUNT /100 mL_____; Rmk____

FECAL STREPTOCOCCI (31673)

Time collected : _____

Time in : _____ Date : _____

Time out : Date :

Vol. (mL)	Count	Used in calculation?	Remarks *
Blank			
Blank			

* Remarks 1 = Less than 2 = Greater than 0 = Est. ct. K = non ideal ct.

Incub. Time 46-50 hrs filt. size _____

Ideal count 20-100 col. Incub. Temp 35 °C

FS COUNT / 100 mL_____; Rmk_____

FECAL COLIFORM (31625)

Time collected : _____

Time In : _____ Date : _____

Time out : Date :

Vol. (mL)	Count	Used in calculation?	Remarks *
Blank			
Blank			

* Remarks 1 = Less than 2 = Greater than 0 = Est. ct. K = non ideal ct.

Incub. Time 22-26 hrs filt. size _____

Ideal count 20-60 col. Incub. Temp 44.5 °C

FC COUNT / 100 mL_____; Rmk_____

CALCULATIONS

Figure 5. Ground-water quality field notes form -- continued.

Table 1.—Ground-water-quality sample collection order and protocol

[mL, milliliter; C-18 SPE, carbon-18 solid phase extraction analytical method; µm, micrometer; PE, polyethylene bottle; HNO_3, nitric acid; N/A, not applicable; OWQ, Office of Water Quality; Tech. Memo., technical memorandum]

Schedule	Schedule name	Reference	Filter type	Bottle size/type	Fill method	Preservation	Holding time
2090	Volatile organic compounds	1	None	40 mL x 3/clear glass	No air space	Chill	14 days
2001	Pesticides (C-18 SPE)	2	Glass fiber (0.7 µm)	1 liter/amber glass	Leave air space	Chill	45 days
2050	Pesticides (activated carbon)	3	Glass fiber (0.7 µm)	1 liter/amber glass	Leave air space	Chill	45 days
2085	Dissolved organic carbon	4	Silver (0.45 µm)	250 mL/amber glass	Leave air space	Chill	42 days
2703	Trace elements	4, 5	Capsule (0.45 µm)	500 mL/acid-rinsed PE	Leave air space	1 mL HNO_3	42 days
2750	Major ions	5	Capsule (0.45 µm)	250 mL x 2/acid-rinsed PE	Leave air space	1 mL HNO_3	28 days
2752	Nutrients	5, 6	Capsule (0.45 µm)	125 mL/brown PE	Leave air space	Chill	8 days
1810	Radioactive elements	4, 7	Capsule (0.45 µm)	1 liter X 2/acid-rinsed PE	Leave air space	2 mL HNO_3	N/A
N/A	Field alkalinity	8	Capsule (0.45 µm)	250 mL/PE	No air space	Chill	1 day
2703	Trace elements	4, 5	None	250 mL/PE	Leave air space	None	42 days
2750	Major ions and silica	5	None	250 mL/PE	Leave air space	None	28 days
1369	Radon	4	None	10 mL x 2/clear glass	Leave air space	Mineral oil	3.8 days (half-life)
1565	Tritium	7	None	1 liter/PE	No air space	None	12.3 years (half-life)
1142	Stable isotopes	7	None	60 mL/clear glass	No air space	None	N/A

[1] Rose and Schroeder, 1995.
[2] Zaugg and others, 1995.
[3] Werner and others, 1996.
[4] Selected constituents(s) listed in Timme, 1995, method not yet published.
[5] Fishman and Friedman, 1989, U.S. Geological Survey OWQ Tech. Memo. 94.09.
[6] Patton and Truitt, 1992, U.S. Geological Survey OWQ Tech. Memo. 94.16.
[7] Thatcher and others, 1977.
[8] Koterba and others, 1995.

Table 2.—Quality-control blank-sample collection order and protocol

[mL, milliliter; C-18 SPE, carbon-18 solid phase extraction analytical method; µm, micrometer; PE, polyethylene bottle; HNO_3, nitric acid]

Schedule	Schedule name	Filter type	Bottle size/type	Fill method	Preservation	Blank water
2090	Volatile organic compounds	None	40mL x 3/clear glass	No air space	Chill	Organic blank
2001	Pesticides (C-18 SPE)	Glass fiber (0.7 µm)	1 liter/amber glass	Leave air space	Chill	Organic blank
2050	Pesticides (Activated carbon)	Glass fiber (0.7 µm)	1 liter/amber glass	Leave air space	Chill	Organic blank
2085	Dissolved organic carbon	Silver (0.45 µm)	125 mL/amber glass	Leave air space	Chill	Organic blank
2750	Major ions	Capsule (0.45 µm)	250 mL/amber glass	Leave air space	1 mL HNO_3	Inorganic blank
2752	Nutrients	Capsule (0.45 µm)	125 mL/brown PE	Leave air space	Chill	Inorganic blank
1810	Radioactive elements	Capsule (0.45 µm)	1 liter x 2/acid-rinsed PE	Leave air space	2 mL HNO_3	Inorganic blank
2750	Major ions	Capsule (0.45 µm)	500 mL/PE	Leave air space	Chill	Inorganic blank
2750	Major ions	None	250 mL/PE	Leave air space	None	Inorganic blank

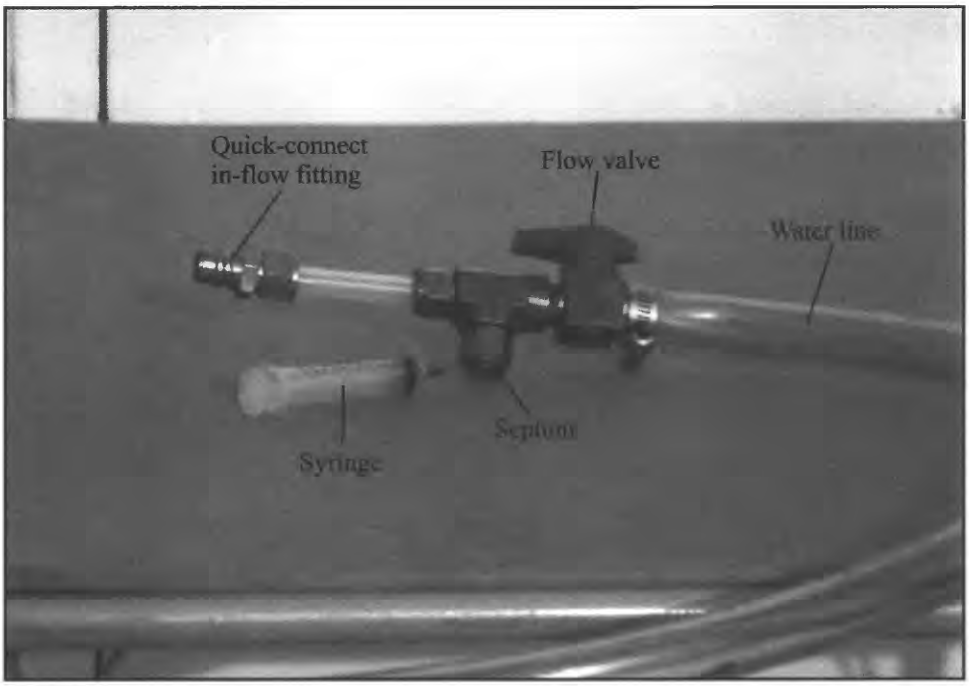

Figure 6. Photograph of radon-sampling assembly.

remove any air that may have been collected in the syringe. Two vials half filled with mineral oil were used to collect the sample. With the tip of the syringe in the mineral oil, near the bottom of the sample vial, 10 mL of water was slowly dispensed. Five mL of water was left in the syringe to assure the accuracy of the volume dispensed. The entire procedure was repeated with a second vial. The two vials were shaken for 30 seconds and shipped the same day to the laboratory.

The tritium and stable isotope samples were both collected without rinsing the bottles. Also, both of the bottles were filled to overflowing and conical caps were used to avoid air bubbles in the sample.

All samples requiring chemical preservation were treated shortly after they were collected. Gloves were changed before beginning to use each type of preservative, and a separate preservation chamber was used for each type of preservative. All sample bottles were opened in the preservation chamber, treated, and immediately recapped. The samples that needed to be chilled were immediately placed in coolers filled with ice.

When the last sample had been collected, the flow of water was diverted to the flow-through cell. A final set of field parameters were recorded. The pump and the sampling equipment were cleaned using the field decontamination protocols, as described later in this report, and the alkalinity samples were titrated as described by Koterba and others (1995, p. 62).

Alkalinity was determined on site by incremental equivalence titration, within several hours after the sample was collected. A Hach digital titrator, 1.6 normality (sulfuric acid titrant), 100 mL of sample water, an Orion 250A pH meter, a Teflon-coated magnetic spinbar, and a battery-powered magnetic stirrer were used (Koterba and others, 1995, p. 62-70).

During 1994, two alkalinity samples were titrated at each site; a filtered (0.45 micrometer filter) and an unfiltered sample. Alkalinity values for 123 pairs of titrations were determined, representing a wide range (45-742 mg/L as calcium carbonate). The data from these two methods were very similar, with no detectable method bias. The lack of bias was confirmed statistically by a paired t-test. Differences in alkalinity between paired samples appeared to be within the precision of the method. The relative percent difference (100 x [unfiltered alkalinity - filtered alkalinity] / [unfiltered alkalinity + filtered alkalinity]) between unfiltered and filtered alkalinity ranged from -4.64 to 4.23 percent, with a mean of -0.047 percent. The number of filtered and unfiltered alkalinity data sets with a relative percent difference (absolute value) of less

than 1.99 was 110. Therefore, beginning in November 1994, only filtered samples were titrated for alkalinity.

The samples were sent to the NWQL for analysis. The chilled samples were shipped in a cooler, with ice, daily from the field by a next-day delivery service. Samples with longer holding times were shipped at the end of the week (U.S. Geological Survey, Technical Memorandum 92.06, 1992). The tritium sample, stable isotope sample, and a duplicate major ions sample were archived in the Mounds View, Minnesota office of the USGS for possible analysis at a later date. A list of the supplies used to ship samples is listed in the Supplemental Information section at the end of this report.

Sample Filters and Bottles

Several types of filters were used to process groundwater samples. DOC samples were collected using an Osmonics, Inc., 0.45 µm pore size, 47 mm diameter, silver filter held in a Gelman Sciences pressure barrel filtration unit.

A stainless steel filter unit was used to collect all of the filtered samples, except DOC, during the 1993 field season. A 0.7 µm pore size, 142 mm diameter, prebaked, glass-fiber filter held on a stainless steel filtration unit was used to filter the pesticide samples. A 0.45 µm, 142 mm diameter cellulose nitrate filter was used on the same filtration unit to collect the rest of the filtered samples.

The stainless steel filter unit was used only for pesticide sampling following the 1993 field season. The reasons for this were:

(1) The physical size of the stainless steel filter unit was large, making it difficult to use in the sample collection chamber.

(2) The filter unit had several parts with grooves and threads, which made it difficult to clean thoroughly.

(3) The filter unit was made of stainless steel, which became worn with continued use and cleaning. This made sealing the filter to avoid leaks increasingly difficult and could possibly allow unfiltered water to be collected along with the sample. Also, these worn areas were places contaminants could accumulate.

(4) This type of filter was prone to clogging (loading) due to sediment in the water, which led to a time-consuming process of changing the filter.

(5) The filter could not be used to filter trace-element samples because of possible contamination from the metal filter unit.

These problems were eliminated by the use of capsule filters (Horowitz and others, 1994). Disposable 0.45 µm Gelman capsule filters were used during the 1994 and 1995 field seasons.

Capsule filters and sample bottles were rinsed with DI water prior to sampling trips. The procedure for this rinsing, or pre-conditioning, is as follows:

(1) gloves were worn during the pre-conditioning;

(2) the capsule filters were rinsed with 1 liter of DI water;

(3) the filter was held so that the rinse water entered the filter at the bottom and flowed out at the top to ensure that the whole capsule filter was filled and rinsed;

(4) following this rinse, excess DI water was removed by shaking the filter;

(5) the filter was double bagged with plastic bags and chilled on ice or in a refrigerator until use; and

(6) pre-conditioned filters were used within 5 to 8 days.

Sample bottles were rinsed three times with DI water, filled half full with DI water, and recapped. The DI water was poured out in the sample-collection chamber just prior to the field rinse with sample water and the collection of the sample.

Field Trip Preparation

The following checklist outlines the preparation done before leaving for a field trip. Several of the items were done only when required, not before every field trip.

(1) Perform routine maintenance on the meters.

(2) Charge or replace batteries.

(3) Clean the sampling equipment.

(4) Collect QC blank samples.

(5) Fill water containers.

(6) Pre-condition filters and bottles.

(7) Fill coolers with ice.

(8) Assemble well data, maps, and field plans for field trip.

(9) Contact well owners.

(10) Restock vehicle with equipment and supplies.

Sampling Equipment Decontamination

Sampling equipment was cleaned weekly in the Mounds View, Minnesota office of the USGS before each sampling trip and between each sampling site in the field, to minimize the possibility of sample contamination by the equipment. QC samples were collected routinely to assess potential contamination by equipment or sampling procedures. A complete list of supplies used in the decontamination process is listed in the Supplemental Information section at the end of this report.

Office decontamination of sampling equipment (tubing, flow-manifold, pesticide filter, DOC filter, sample chambers, graduated cylinders, and beakers) included the following steps:

(1) Clean washbasins with a Liquinox-tap water solution, then rinse with tap water.

(2) Disassemble and soak equipment in a 2 percent Liquinox-tap water solution for 30 minutes.

(3) Put on powderless latex gloves.

(4) Wash all of the equipment with sponges and non-metallic brushes.

(5) Change gloves.

(6) Rinse all of the equipment with tap water.

(7) If sampling for trace elements, rinse all non-metallic equipment with 5 percent HCl.

(8) Change gloves.

(9) Rinse all of the equipment with DI water.

(10) If sampling for pesticides, rinse the pesticide plate filter unit and forceps with methanol, let air dry, reassemble plate filter and wrap in aluminum foil.

(11) Wrap clean equipment with aluminum foil or plastic, if sampling for trace elements.

Cleaning the pump and pump tubing involved two people using a "clean hands", "dirty hands" method. One person wore gloves, handled the pump and the tubing, and was considered the "clean hands" person. This person avoided touching anything except the pump or the tubing. The "dirty hands" person assisted by turning the pump on or off, and refilling the standpipe with water as necessary (Horowitz and others, 1994, p. 8-9).

Office decontamination of the sampling pump included the following steps:

(1) Place the pump in the standpipe and coil pump tubing into a clean washbasin.

(2) Fill the standpipe and washbasin with a 2 percent Liquinox tap-water solution.

(3) Soak pump and tubing for 30 minutes.

(4) Put on gloves.

(5) Wash the external surface of the pump tubing with a sponge or a non-metallic brush.

(6) Pump Liquinox tap-water solution through the pump tubing at least 5 times. This water may be recirculated after some water has been pumped completely through the line.

(7) When an adequate volume of water has been pumped (5 to 7 gallons), let the pump run until the water has been removed from the pump tubing.

(8) Change gloves.

(9) Lift the pump out of the standpipe and the tubing out of the washbasin.

(10) Rinse the exterior of the pump and pump tubing with tap water. Place the tubing in a clean rinsed basin.

(11) Pour out the water remaining in the standpipe and rinse it with tap water.

(12) Place the pump back in the standpipe and fill it with tap water.

(13) Pump tap water through the tubing until the Liquinox tap-water solution is removed. Do not recirculate the tap water.

(14) Repeat steps 8 through 13 using DI water instead of tap water

(15) If sampling for organics, repeat steps 8 through 13 using methanol (the methanol may be recirculated). Then repeat steps 8 through 13 again using DI water instead of methanol.

(16) Recoil the pump tubing on its reel.

(17) Wrap the pump in aluminum foil or plastic, if sampling for trace elements, and cover the pump tubing reel with a plastic bag.

The Gelman barrel DOC filtration unit was initially cleaned in a Liquinox tap-water solution followed by a tap and DI water rinse. QC blank samples collected following this cleaning showed problems with contamination. The barrel filter was then cleaned by rinsing it with DI water and wiping it dry with powderless tissue paper. The Liquinox detergent was determined to be the cause of the contamination. The DOC QC blank values are discussed at greater length in the Quality Control section of this report.

The equipment was also cleaned in the field between sampling sites. The procedures were the same as the office cleaning with the following exceptions:

(1) The exterior of the tubing on the flow-manifold was not washed.

(2) The equipment, pump, and tubing were not soaked.

(3) The Liquinox tap-water solution was reduced to 0.1 percent Liquinox.

(4) The acid, methanol, and second DI rinse were not done.

After the 1993 field season the sample-collection chambers were cleaned by rinsing with DI water and replacing the chamber bag. The sample-preservation chambers were cleaned and their chamber bags were replaced at the end of each week, not between each site.

Field decontamination of sampling equipment included the following steps:

(1) Place the sampling equipment in a clean washbasin.

(2) Fill the washbasin with a 0.1-0.5 percent Liquinox tap-water solution.

(3) Put on gloves.

(4) Wash all of the equipment with sponges and non-metallic brushes.

(5) Change gloves.

(6) Rinse all of the equipment with tap water.

(7) Rinse all of the equipment with DI water.

(8) If sampling for pesticides rinse the pesticide plate filter unit and forceps with methanol, let air dry, reassemble plate filter and wrap in aluminum foil.

(9) If sampling for trace elements, place clean equipment in plastic bags.

(10) Place a clean bag on the sample collection chamber between each site.

Field decontamination of the sampling pump included the following steps:

(1) Place the pump in the standpipe and coil the pump tubing into a clean washbasin.

(2) Fill the standpipe and washbasin with a 0.1-0.5 percent Liquinox tap-water solution.

(3) Put on gloves.

(4) Wash the external surface of the pump tubing with a sponge or a non-metallic brush.

(5) Pump Liquinox-tap water solution through the pump tubing at least 5 times; this water may be recirculated after some water has been pumped completely through the line.

(6) When an adequate volume of water has been pumped (5-7 gallons), let the pump run until the water has been removed from the pump tubing.

(7) Change gloves.

(8) Lift the pump out of the standpipe and the tubing out of the washbasin.

(9) Rinse the pump and pump tubing with tap water, place the tubing in a clean rinsed basin.

(10) Pour out the water remaining in the standpipe and rinse it with tap water.

(11) Place the pump back in the standpipe and fill it with tap water.

(12) Pump tap water through the tubing until the Liquinox tap-water solution is removed. Do not recirculate the tap water.

(13) Repeat steps 8 through 13 using DI water instead of tap water. The DI water may be recirculated after some water has been pumped completely through the line.

(14) Recoil the pump tubing on its reel.

(15) Wrap the pump in aluminum foil or plastic, if sampling for trace elements, and cover pump tubing reel with a plastic bag.

Quality Control

To assess the quality of analytical data from this study, QC samples were routinely collected and analyzed. These samples collected were in addition to

laboratory QC samples, which were routinely analyzed to calibrate analytical instruments, validate analytical data, and compare analyses with other laboratories (described, in part, by Friedman and Erdmann, 1982). Field QC samples from this study were used to assess the entire process of collecting, handling, shipping, preserving, and analyzing of samples; and the reporting of analytical results. Uncertainty and bias introduced in each of these steps provides information about the overall uncertainty and bias of reported data. This section defines the main types of QC samples used, and the following section summarizes QC data for the analytical schedules used in this study.

Replicates

Samples were (usually 2, or, less often, 3) collected sequentially so they would be expected to be nearly identical in composition. Data from the analysis of the replicate samples were used to assess variability of the overall sampling and analytical process.

The procedure for collecting a replicate sample was to fill a second (duplicate) and in some case a third (triplicate) bottle with sample water. Replicate sample(s) were collected immediately following the regular sample in the same sample collection order (table 1). The filter was changed before the collection of duplicate and again before collection of triplicate samples.

Data from replicate-sample analyses were reviewed by calculating a CV for each analyte, for each set of replicates. For each group of replicate samples, the CV was plotted against the mean. These plots were used to assess how CV's varied as a function of concentration.

For many analytes, CV's showed no relation to concentration. For these analytes, a single, pooled CV was calculated for summarizing data variability.

For some analytes the CV's of a replicate set were large and (or) highly variable at low concentrations, but relatively low and constant at higher concentrations. For these analytes, the replicate data were split into low-concentration (mean was less than 5 or 10 times the MDL) and high-concentration (mean was greater than or equal to 5 or 10 times the MDL) groups. Separate pooled CV's were calculated for each group. Analytical data commonly are more variable, on a relative basis, at low concentrations (relative to the MDL).

A problem in summarizing variability of data from this study is that low-concentration data often were reported to only one significant figure. This causes highly variable CV's. For example, values of 0.14 and 0.16 would be rounded to 0.1 and 0.2, respectively, producing large relative differences (as indicated by a large CV), although the absolute difference in concentrations is fairly small. Conversely, concentrations rounded to the same value (such as 0.16 and 0.24, both rounded to 0.2) yield an artificially low CV of zero.

Pooled CV's were calculated to summarize the variability of each analyte. CV's were squared for pooling, and a weighted mean (weighted to degrees of freedom of each set of replicates) was calculated, as recommended by Anderson (1987, p. 44-45). The pooled CV is the square root of the weighted mean of the squared CV's. Concentrations reported as less than the MDL were not included in this analysis. Cases in which one replicate group had an unusually high CV, at concentrations greater than 10 times the MDL, were treated as outliers and were omitted from the pooled CV calculation.

Blanks

Blank samples were collected using water that had undetectable concentrations of the analytes of interest. The blank water was processed through all sampling equipment, collected, and sent to the NWQL for analysis to determine if any step of the sample collection or analysis process contaminated the samples.

Two types of blank samples were collected. Office equipment blanks were collected in the USGS laboratory in Mounds View, Minnesota to check the sampling equipment for contamination under controlled, indoor conditions. Equipment blanks also were collected in the field, under ambient conditions that could include dust, aerial pesticide spraying, or other potential sources of sample contamination. Distilled "blank" water obtained from the QWSU in Ocala, Florida was used for blank samples for inorganic analyses. HPLC reagent-grade water (Baker Analyzed, J.T. Baker Co.) was used for blank samples for organic chemical analyses. Each lot of blank water used for this study was analyzed by the NWQL. An equipment blank was processed in the USGS laboratory in Mounds View, Minnesota, prior to each field season, so that the results could be reviewed prior to sampling each year. The sample collection order and the type of blank water used for this sampling is listed in table 2.

The following evaluations were made for each analyte in the blank samples:

(1) If an analyte was not detected or was always less than the concentrations in ground-water-quality

samples, contamination was presumed to be insignificant; and,

(2) If analyte concentrations in QC blank samples exceeded concentrations in any of the ground-water-quality samples, this was considered an indication of a potential contamination problem. Further examination was made to determine the extent of sample contamination. Occasional, low-level blank-sample contamination may be unavoidable for some constituents, and does not preclude usefulness of ground-water-quality data for those constituents. Frequent, high-concentration contamination (concentrations comparable to or greater than those in ground-water-quality samples) indicates a problem in the sample collection and analysis procedures, which may preclude usefulness of data for quantitative purposes.

Ground-Water Matrix Spikes

Ground-water matrix spikes are ground-water QC samples to which known amounts of target analytes have been added. Spiked samples were used to assess bias and precision of pesticide analyses (Schedules 2001 and 2050). Low recoveries of spiked analytes could indicate degradation of analytes, analytical interference from the sample matrix, and (or) poor analytical recovery. The NWQL assesses the last of these separately with laboratory-control spike samples (Zaugg and others, 1995).

Replicate, field-collected pesticide samples were spiked with 100 microliters (µL) of spike solution following collection. The NWQL verified analyte concentrations in spike solutions, which were about 1 nanogram per µL (ng/µL) for schedule 2001 and 10 ng/µL for schedule 2050. The solution was added to the samples using a micropipet fitted with a single-use, disposable, glass capillary tip. Field spike samples, field spike replicates, and lab spike samples were collected, although the last two were not collected with every spike sample. The lab spike was a sample bottle, containing HPLC-grade water, which was taken into the field, opened and spiked, then shipped back to the lab.

Spike-recovery data for each pesticide were analyzed in several steps. First, if the pesticide was detected in a paired ground-water sample, the ground-water concentration was subtracted from the spiked-sample concentration. If QC replicate samples were collected, the mean concentration was used. Next, the concentration was converted to mass of recovered pesticide, divided by mass of added pesticide, and multiplied by 100. Spike-recovery calculations are more accurate if the analyte is at low concentration (or less than MDL) in the ambient ground-water-quality sample. If the amount of analyte in the ambient ground-water-quality sample approaches or exceeds the amount added to QC spiked samples, the spike recovery tends to be masked by uncertainty (imprecision) in the data.

Surrogates

Surrogates are added to samples, in a known amount, to provide a means of assessing analytical recovery for each analysis. Surrogates are chemicals that should have similar properties to the analytes of interest. They should not interfere (or co-elute, as in chromatography) with quantitation of the analytes of interest. In this study, surrogates were used only for the pesticide analytical schedules. The surrogates are added to samples immediately prior to extraction, and in this study, all extractions of ground-water-quality and QC samples were performed at the NWQL.

Surrogate data are reported as percent recovery of added surrogate. Some researchers use surrogate-recovery data to adjust measured pesticide concentrations to account for low and(or) variable recovery of analytes (measured concentrations are divided by percent surrogate recovery). To assess the usefulness of surrogate data for correcting pesticide concentrations from this study, linear regressions of spike-recovery versus surrogate-recovery data for the matrix-spike samples were examined. The results, not presented in detail herein, showed that surrogate recoveries could be used to adjust measured concentrations of some pesticides.

Summary of Quality-Control Data

This section summarizes ground-water QC data collected by the Red River Basin study unit in 1993-95 by laboratory schedule. Timme (1995) documents constituents by schedule number, and gives information about sample bottles used, also see table 1 and table 2. Where available, references to analytical methods are given herein. The references for each of the methods are summarized in table 1. Pritt and Raese (1992) document quality-assurance/quality-control procedures.

Schedule 1369—Radon

Three sets of duplicate samples were collected. The pooled CV for these sample sets is 20 percent. No other QC sampling was done for radon.

Schedule 1810—Radium-226 and Uranium

Three sets of duplicates for radium and five sets for uranium had values greater than their respective MDL's. For radium, two sets of replicates were near the MDL; thus, the pooled CV of 17 percent is influenced by data from low-concentration analyses where data are rounded to one significant figure. Uranium results were reproducible, with a pooled CV of 2.1 percent. These constituents were not detected in blank samples, indicating there was no sample contamination.

Schedule 1043/2703—Trace Elements

Table 3 summarizes QC data for trace elements. Blank samples for trace elements are only summarized herein if the source of blank water was the QWSU in Ocala, Florida.

Replicate QC data are limited for trace elements. Most of the data was reported below MDL's. Several trace elements were infrequently detected in ground water therefore only one to four sets of duplicate measurements for each analyte was reported above the MDL. Arsenic, barium, cobalt, molybdenum, nickel, and aluminum occurred in reproducible quantities. Chromium, copper, and zinc had pooled CV's from 0-19 percent at concentrations greater than five times the MDL, at lower concentrations the pooled CV's were substantially greater.

Trace elements in ground-water-quality samples had concentrations reported as less than the MDL. Therefore the presence of trace elements greater than the MDL in blank samples suggests a potential for contamination in low concentration trace element ground-water-quality samples. Several trace elements were not detected in any blank samples. Barium, chromium, and copper were occasionally detected. Zinc and aluminum occurred frequently in blank samples. In some samples, trace element concentrations in QC blank samples exceeded those in many ground-water-quality samples. Maximum aluminum and copper concentrations in QC blank samples exceeded those in ground-water-quality samples thereby precluding quantitative use of data for these elements. A possible source of contamination may be the metallic components of the sampling pumps which contain copper, zinc, chromium, and aluminum. Fine particles derived from aquifer sediments could become entrained in sampling equipment, and cause metal contamination, although the cleaning procedures have attempted to minimize this possibility.

Schedule 2750—Major Ions and Silica

QC data for major ions and silica are summarized in table 4. Manganese was determined by both the trace element and major ion schedules. If both major ions and trace elements were analyzed in a given sample, the manganese value from the trace element analysis was used.

Analyses of most major ions were quite reproducible, with pooled CV's of less than 5 percent. Pooled CV's for potassium, silica, and iron (greater than 10 times the MDL) were less than 10 percent. Fluoride, bromide, and low-level iron measurements were more variable.

Potassium and bromide were not detected in any blank samples. Sodium and chloride were infrequently detected, and always at concentrations lower than the minimum concentration detected in ground-water-quality samples. Fluoride was detected in only 2 of 31 blank samples, each time at the MDL of 0.1 mg/L. Sulfate was infrequently detected in blank samples, at concentrations of 0.1 (the MDL) to 0.3 mg/L. Two ground-water-quality samples had similarly low sulfate concentrations (<0.1 mg/L); therefore the potential for sulfate contamination in the ground-water-quality samples was considered quite low. Silica was frequently detected in blank samples, but always at concentrations lower than in ground-water-quality samples.

Manganese was a low-level contaminant in 13 of 34 blank samples, with a maximum concentration of 4.0 µg/L. Sixty-eight of 323 ground-water-quality samples had manganese concentrations less or equal to the highest blank sample concentration.

Iron contaminated three-fourths of the blank samples, with a maximum concentration of 27 µg/L. Seventy-three ground-water-quality samples had iron concentrations less than the MDL of 3.0 µg/L; 134 had concentrations less than or equal to the highest blank sample iron concentration. Thus, iron contamination likely interferes with low-level iron determinations in ground-water-quality samples. A source of iron contamination may be steel components of the submersible sampling pump.

The blank-sample data indicate that the analytical methods are sufficient for higher levels of manganese and iron, and for distinguishing between high- and low-concentrations. Contamination appears to be insignificant above about 5 µg/L for manganese, and about 30 µg/L for iron.

Table 3.—Summary of quality-control data for trace elements

[MDL, maximum detection limit; N, number of samples; µg/L, micrograms per liter; <, less than; --, not detected; CV, coefficient of variation; Replicate data are summarized only where concentrations exceed the MDL. For chromium, copper, and zinc, replicate sets were divided into high concentration (greater than times the MDL) and low concentration groups.]

		Ambient ground water				Blanks				Replicates			
			Concentration					Concentration					
Analyte	MDL	N	Minimum (µg/L)	10th percentile	Maximum (µg/L)	N	N>MDL	Minimum (µg/L)	Maximum (µg/L)	N	Number of groups	Concentration range	Average CV
Aluminum	1.0	29	<1.0	<1.0	11	5	5	4.0	14	6	3	all	0.0
Antimony	1.0	29	<1.0	<1.0	<7.0	5	--	<1.0	--	--	--		--
Arsenic	1.0	55	<1.0	<1.0	49	7	--	<1.0	--	6	3	all	0
Barium	1.0	41	6.0	10	520	6	2	<1.0	19	8	4	all	12.3
Beryllium	1.0	41	<.5	<.5	<7	6	--	<.5	--	--	--		--
Cadmium	1.0	41	<1.0	<1.0	1	6	--	<1.0	--	--	--		--
Chromium	1.0	41	<1.0	<3.0	22	6	3	<1.0	9.0	8	4	all	23.5
Cobalt	1.0	41	<1.0	<1.0	8.0	6	--	<1.0	--	2	1	all	0
Copper	1.0	41	<1.0	<1.0	62	6	3	<1.0	101	6	3	all	39.9
Lead	1.0	41	<1.0	<1.0	10	6	--	<1.0	--	--	--		--
Molybdenum	1.0	41	<1.0	<2.0	27	6	--	<1.0	--	4	2	all	11.2
Nickel	1.0	41	<1.0	<1.0	23	6	--	<1.0	--	2	1	all	0
Selenium	1.0	39	<1.0	<1.0	1.0	6	--	<1.0	--	--	--		--
Silver	1.0	39	<1.0	<1.0	1.0	6	--	<1.0	--	--	--		--
Zinc	1.0	41	<2.0	3.0	1,000	6	5	<3.0	20	8	4	all	34.3
										6	3	high	18.7
										2	1	low	60.6

Table 4.—Summary of quality-control data for major ions and silica

[Concentrations in milligrams per liter, except iron, which is in micrograms per liter. MDL, method detection limit in milligrams per liter, except for iron and manganese, which are in micrograms per liter; N, number of samples; <, less than; --, not detected; CV, coefficient of variation. Replicate data are summarized only where concentrations exceed the MDL. Chloride, bromide, and manganese each had one set of replicates with atypically bad reproducibility; these were treated as outliers and deleted from the summary. For iron, replicate sets were divided into high (greater than 5 times the MDL) and low concentration ranges.]

		Ambient ground water				Blanks					Replicates			
			Concentration					Concentration						
Analyte	MDL	N	Minimum	10th percentile	Maximum	N	N>MDL	Minimum	90th percentile	Maximum	N	Number of groups	Concentration range	Average CV
In milligrams per liter:														
Calcium	0.02	323	1.8	61	510	32	31	<0.02	1.2	3.5	61	28	all	2.2
Magnesium	.01	323	.57	14	500	32	29	<.01	.29	1.2	61	28	all	2.8
Potassium	.1	323	<.1	.6	83	32	0	<.1	--	--	61	28	all	6.4
Sodium	.2	323	1.0	1.9	3,400	32	6	<.1	.40	.9	61	28	all	2.2
Bromide	1.0	322	<.01	.01	8.4	31	--	<.01	--	--	59	27	all	19
Chloride	.1	329	.4	1.4	4,800	32	7	<.1	.20	.3	58	27	all	3.7
Sulfate	.1	322	<.1	4.0	2,700	32	7	<.1	.20	.3	61	28	all	2.3
Floride	.1	322	<.1	<.1	3.1	31	2	<.1	--	.1	50	23	all	11
Silica	.01	323	8.8	20	52	32	29	<.01	.98	4.5	61	28	all	5.3
In micrograms per liter:														
Iron	3.0	323	<3.0	<3.0	9,700	32	24	<3.0	12	27	51	23	all	12
	40	18	high	7.5										
	11	5	low	21										
Manganese	1.0	323	<1.0	<1.0	1,500	34	13	<1.0	--	4.0	--	--	--	--

Schedule 2752—Nutrients

QC data for nutrient analyses are summarized in table 5. Replicate nutrient analyses exhibited large ranges in CV's at low (near MDL) concentrations. These large ranges in CV's are partially a result of rounding to one significant figure at low concentrations, as discussed earlier. Absolute differences in concentrations were generally small. Nutrient analyses were more reproducible, as indicated by CV's, at concentrations greater than or equal to 10 times the MDL. Nitrite plus nitrate, and nitrite, which was infrequently detected, had pooled CV's of less than 10 percent. The other nutrients were split into low- and high-concentration groups (less than 10 times the MDL, and greater than or equal to 10 times the MDL, respectively) for summary. Analyses of high-concentration samples were the most reproducible. Low-concentration replicates showed fairly large CV's, although absolute differences in concentration were fairly small.

In general, QC blank samples for nutrients had little or no detectable contamination. Ammonia plus organic nitrogen was not detected in any blank samples. Nitrite and orthophosphate were infrequently detected at the MDL. Nitrite plus nitrate and dissolved phosphorus were detected infrequently, and at concentrations near the MDL. Ammonia was detected frequently at levels ranging from 0.01 mg/L (the MDL) to 0.04 mg/L. This low level of contamination was observed by the NWQL in routine ammonia analyses. Therefore, low-level (less than about 0.05 mg/L) measurements of ammonia are subject to contamination.

Schedule 2001—Pesticides

Schedule 2001 pesticides, determined by the method of Zaugg and others (1995), were infrequently detected in ground water in this study. Replicate QC data are insufficient to characterize variability in these data; see the section on Ground-Water Matrix Spikes. Sixteen QC blank samples were collected. Atrazine was the only pesticide detected (in a single sample at a concentration of 0.012 µg/L). The ground-water-quality sample collected directly prior to the collection of this blank sample had no detectable atrazine; therefore, it is unlikely that the contamination of this blank was due to cross-contamination from sampling equipment.

QC spike data, summarized in table 6, were used to assess recovery of pesticides added to ground-water-quality samples. Most pesticides had mean recoveries between 75 and 110 percent. Exceptions are desethylatrazine, benfluralin, *p,p'*-DDE, malathion, methyl parathion, metribuzin, pendimethalin, *cis*-permethrin, phorate, terbacil, and trifluralin.

The variability of pesticide data, indicated by the standard deviation and CV of spike-recovery data, varies among compounds. For many compounds, variability is relatively low (CV less than 20 percent). Highly variable recoveries (CV greater than 40 percent) were observed for terbacil, disulfoton, carbaryl, propargite, azinphos-methyl, and *cis*-permethrin. One spiked sample was omitted from the calculation of atrazine recovery because the paired ground-water-quality sample had a high atrazine concentration relative to the amount added to the spiked sample. Acetochlor was not analyzed during the early part of this study, and was spiked in only two samples.

In describing this method, Zaugg and others (1995) reported highly variable recoveries for carbofuran, carbaryl, terbacil, and azinphos-methyl. When detected, concentrations of these compounds are now reported as "estimated". Two of the compounds we found to have poor performance from the Red River Basin spike recovery data (propargite, high variability; and *cis*-permethrin, low recovery and high variability), but were not noted as problematic by Zaugg and others (1995).

Three surrogates were added to every pesticide schedule 2001 sample as a means of assessing method performance for every analysis. Recovery statistics for these compounds, for 182 regular and replicate ground-water samples, are presented in table 7. Surrogate recoveries were typically good (close to 100 percent). Concentrations of pesticides in ground water were not corrected for surrogate recovery.

Schedule 2050—Pesticides

Schedule 2050 pesticides determined by the method of Werner and others (1996) were infrequently detected in ground water in this study. Reproducibility is assessed with spiked samples, discussed below. None of the analytes were detected in any of the 17 QC blank samples collected for this schedule.

Not all schedule 2050 pesticides were in each spike solution used during this study. Thus, spike data (summarized in table 8) are limited, especially for some analytes. Of the 31 compounds that were spiked in at least five samples, 17 had mean spike recoveries between 60 and 105 percent. Recoveries of schedule 2050 pesticides tended to be more variable than for schedule 2001 analytes, and were occasionally very low including a few recoveries of zero percent. Of the 31 compounds considered, CV's ranged from 18 to 164 percent. CV's were less than 30 percent for only 9 of the 31 compounds. CV's exceeded 50 percent for 10 of the 31 compounds, indicating highly variable recoveries.

Table 5.—Summary of quality-control data for nutrients

[Concentrations in milligrams per liter. MDL, method detection limit; mg/L, milligrams per liter; N, number of samples; <, less than; --, not detected; CV, coefficient of variation.

		Ambient ground water				Blanks					Replicates			
			Concentration (mg/L)				Concentration (mg/L)							
Analyte	MDL (mg/L)	N	Minimum	10th Percentile	Maximum	N	N>MDL	Minimum	90th percentile	Maximum	N	Number of groups	Concentration range	Average CV
Ammonia, as nitrogen	0.01	323	<0.01	<0.015	4.5	29	18	<0.01	0.03	0.04	43	19	all	13
											22	9	high	3.1
											21	10	low	19
Nitrite, as nitrogen	.01	323	<.010	<.010	1.1	29	1	<.01	--	.01	4	2	all	6.6
Ammonia plus organic nitrogen	.2	312	<.200	<.200	4.7	29	--	<.2	--	--	30	13	all	12
											2	1	high	3.0
											28	12	low	12
Nitrite plus nitrate,	.05	323	<.05	<.05	76	29	5	<.05	.13	.30	21	10	all	3.0
Dissolved phosphorus	.01	312	<.01	<.01	.84	29	8	<.01	.01	.03	29	14	all	28
											9	4	high	7.3
											20	10	low	34
Orthophosphate, as phosphorus	.01	323	<.01	<.010	.84	29	3	<.01	.01	.01	31	14	all	38
											6	3	high	14
											25	11	low	41

Table 6.—Summary of spike-recovery data for schedule 2001 pesticides

[MDL, method detection limit; µg/L, micrograms per liter; N, number of samples; CV, coefficient of variation, or standard deviation expressed as a percentage of the mean; mean and standard deviation are in units of percent recovery.]

Analyte	MDL (µg/L)	Spike recovery			
		N	Mean (percent)	Standard deviation (percent)	CV (percent)
Acetochlor	0.009	2	87	1.1	1.3
Alachlor	.009	18	95	15	16
Atrazine	.001	17	89	13	15
Desethylatrazine	.002	17	34	9.2	27
Azinphos-methyl	.001	18	82	72	88
Benfluralin	.002	18	59	15	25
Butylate	.002	18	90	5.4	6.0
Carbaryl	.003	18	85	41	48
Carbofuran	.003	18	101	37	37
Chlorpyrifos	.004	18	81	15	19
Cyanazine	.004	18	89	23	26
DCPA (dacthal)	.002	18	104	18	17
p,p'-DDE	.006	18	63	7.8	12
Diazinon	.002	18	85	16	19
Dieldrin	.001	18	92	14	15
Diethylanaline	.003	18	90	8.3	9.2
Disulfoton	.017	18	81	52	64
EPTC (eptam)	.002	18	86	11	13
Ethalfluralin	.004	18	71	21	30
Ethoprop	.003	18	86	15	17
Ethyl parathion	.004	18	75	14	19
Fonofos	.003	18	80	10	13
α-HCH	.002	18	85	14	17
γ-HCH (lindane)	.004	18	92	15	16
Linuron	.002	18	105	37	35
Malathion	.005	18	74	25	34
Methyl parathion	.006	18	68	16	24
Metolachlor	.002	18	100	19	19
Metribuzin	.004	18	61	14	23
Molinate	.004	18	87	12	14
Napropamide	.003	18	96	16	17
Pebulate	.006	18	91	15	16
Pendimethalin	.004	18	56	17	30
cis-permethrin	.005	18	27	17	63
Phorate	.002	18	66	20	30
Prometon	.018	18	84	15	18
Pronamide	.003	18	77	15	19
Propachlor	.007	18	89	10	11
Propanil	.004	18	83	18	22

Table 6.—Summary of spike-recovery data for schedule 2001 pesticides—continued

Analyte	MDL (µg/L)	Spike recovery N	Mean (percent)	Standard deviation (percent)	CV (percent)
Propargite	0.013	18	110	97	88
Simazine	.005	18	79	15	19
Tebuthiuron	.010	18	86	21	24
Terbacil	.007	18	68	29	43
Terbufos	.013	18	83	23	27
Thiobencarb	.002	18	98	18	18
Triallate	.001	18	86	13	15
Trifluralin	.002	18	60	15	25

Table 7.—Summary of surrogate-recovery data for schedule 2001 pesticides in water

[*d*10, decadeuterated compound; *d*6, hexadeuterated compound]

Chemical name	Mean percent recovery	Standard deviation (percent)	Minimum (percent)	Maximum (percent)
Diazinon, *d*10	92.0	20.4	38.8	149
Terbuthylazine	96.8	13.0	60.3	136
Hexachlorocyclohexane, *d*6	92.0	18.2	55.0	170

Dicamba had good recoveries in 5 of 8 spiked samples (mean=82 percent), but low recoveries in 3 of 8 spiked samples (mean=10 percent). Oxamyl had consistent recoveries in 5 of 7 spiked samples (mean=21 percent), but very low recoveries in 2 of 7 spiked samples (mean=2.9 percent). Picloram had good recoveries in 3 of 5 spiked samples (mean=69 percent), but recoveries of zero and 31 percent in the other 2 spiked samples. Bromoxynil, methomyl, and DNOC recoveries were good in 6 of 7 samples (mean=84, 64, and 67 percent, respectively); these compounds were not recovered in one spiked sample. Mean recovery of aldicarb in 6 of 9 spiked samples was 54 percent, and was 15 percent in 3 of 9 spiked samples. Mean recoveries of 2,4-DB in 7 of 9 spiked samples was 52 percent, but in 2 of 9 spiked samples was 20 percent.

Analyzing a larger data set of laboratory-control spiked samples and field-submitted spiked samples, the NWQL found that recoveries usually were fairly good, but substantially more variable than for the schedule 2001 method (Werner and others, 1996; U.S. Geological Survey, internal memorandum, NAWQA/NWQL Quality Assurance Committee for Schedule 2050/2051 Pesticide Method, Dec. 1, 1995). Method performance varied by analyte, and by time period for each analyte. During some time periods, recoveries of certain analytes were highly variable, including recoveries of zero percent for a small percentage of spiked samples. The NWQL considers analytical data for compounds that had low and(or) highly variable recoveries to be appropriate only for qualitative purposes. These compounds include 1-naphthol, chlorthalonil, dichlobenil, DNOC, and esfenvalerate. In addition, aldicarb sulfone, aldicarb sulfoxide, carbaryl, MCPB, methiocarb, and oxamyl had low and(or) highly variable recoveries in QC spiked samples from this study.

The main concern over low recoveries is that of low-biased data, including false negatives (compounds that are in a sample at concentrations greater than the detection limit, but which fail to be detected because of analytical problems). Concentration ranges and frequencies of detection are potentially low-biased for such compounds, although the extent to which this is a

Table 8--Summary of spike-recovery data for schedule 2050 pesticides

[MDL, method detection limit; µg/L, micrograms per liter; N, number of samples, CV, coefficient of variation, or standard deviation expressed as a percentage of the mean; --, not determined]

Analyte	MDL (µg/L)	Spike recovery			
		N	Mean (percent)	Standard deviation (percent)	CV (percent)
Acifluorfen	0.035	2	77	4.5	5.8
Aldicarb	.016	9	42	23	55
Aldicarb sulfone	.016	7	25	30	120
Aldicarb sulfoxide	.021	7	71	39	55
Bentazon	.014	9	71	28	39
Bromacil	.035	7	90	20	22
Bromoxynil	.035	7	72	34	47
Carbaryl	.008	9	42	31	74
Carbofuran	.028	9	68	23	34
3-hydroxycarbofuran	.014	2	76	28	37
Chloramben	.011	2	68	8.7	13
Chlorothalonil	.035	9	20	30	150
Clopyralid	.050	2	0	0	--
2,4-D	.035	9	65	17	26
2,4-DB	.035	9	44	21	48
Dacthl, mono-acid (DCPA)	.017	1	77	--	--
Dicamba	.035	8	54	41	76
Dichlobenil	.020	2	60	8.6	14
Dichlorprop	.032	9	78	21	27
Dinoseb	.035	9	80	25	31
Diuron	.020	9	50	21	42
DNOC	.035	7	58	29	50
Esfenvalerate	.019	2	48	5.7	12
Fenuron	.013	9	91	34	37
Fluometuron	.035	9	69	14	20
Linuron	.018	8	68	18	26
MCPA	.050	9	61	11	18
MCPB	.035	2	70	7.7	11
Methiocarb	.026	8	53	37	70
Methomyl	.017	7	55	26	47
1-naphthol	.007	9	4.7	6.9	146
Neburon	.015	9	67	20	30
Norflurazon	.024	2	91	9.3	10
Oryzalin	.019	2	104	9.3	8.9
Oxamyl	.018	7	16	11	69
Picloram	.050	5	48	32	67
Propham	.035	8	103	28	27

Table 8--Summary of spike-recovery data for schedule 2050 pesticides—continued

Analyte	MDL (µg/L)	Spike recovery N	Spike recovery Mean (percent)	Spike recovery Standard deviation (percent)	Spike recovery CV (percent)
Propoxur	0.035	7	62	21	34
Silvex	.021	9	70	16	23
2,4,5-T	.035	9	73	26	36
Triclopyr	.050	2	39	4.0	10

problem cannot be determined because "true" concentrations are unknown.

The problem of false negatives is likely to be more widespread than the opposite situation of false positives (where a detection is reported when the "true" concentration is less than the MDL). The NWQL is highly confident that when a compound is detected at concentrations greater than the detection limit, the compound has been properly identified and quantified.

Two surrogates were initially used for this method. Toluic acid was removed from the method because of poor recovery. The remaining surrogate, BDMC, had a mean recovery of 54 percent (range: 0-138 percent; standard deviation: 30 percent) in 170 samples from this study.

Schedule 2085—Dissolved Organic Carbon

DOC analyses were usually highly reproducible (pooled CV=5.5 percent). One set of replicates was omitted from the calculation because it was an outlier (variability in that set was much greater than the remaining sets of replicates).

All QC blank samples were contaminated with DOC. Although the range of DOC concentration in blank samples (0.1-63 mg/L) was similar to that of ground-water-quality samples (0.3-70 mg/L). Seventy-five percent of the DOC concentrations in blank samples were less than or equal to 0.8 mg/L; in contrast, 90 percent of the ground-water-quality samples exceeded 0.9 mg/L. Blank samples tended to have lower DOC concentrations. Thus, DOC sample contamination, presumably from sampling equipment, potentially interferes with its accurate determination at low levels in ground water (less than about 1 mg/L). While effective at minimizing cross contamination for many constituents (for example, pesticides and nutrients), the cleaning procedures, which use liquid detergent, may have contaminated the sampling equipment with DOC. Sampling equipment was initially cleaned daily in the field with liquid detergent. All equipment was rinsed with DI water after cleaning. When contamination was discovered, the DOC barrel filter was no longer washed with detergent. It was rinsed with DI water and wiped dry with powder-less laboratory tissues. This change in procedure did not yield noticeably lower DOC concentrations in blank samples. The contamination could have been coming from any of the sampling equipment, the pump, the manifold, or the tubing.

It is likely that DOC contamination from detergent is much greater in QC blank samples than in ground-water-quality samples. QC blank samples are collected immediately after cleaning the equipment, with only a small quantity of water being "wasted" prior to sample collection. In contrast, the large volume of ground water pumped through the sampling pump, tubing, and equipment while purging the well and monitoring field parameters before collecting the ground-water-quality DOC sample, provides a more effective rinse.

Schedule 2090—Volatile Organic Compounds

VOC samples (ground-water-quality and QC) were infrequently collected in this study. One QC blank sample was collected using organic-free blank water. Chloroform was the only analyte detected; its concentration was 0.4 µg/L, which is twice the MDL.

One QC sample of DI water, from the USGS laboratory in Mounds View, Minnesota, was analyzed to determine possible VOC contaminants. This sample contained the following VOC's (concentrations in µg/L): dichlorobromomethane (1.0), chlorodibromomethane (0.7), chloroform (1.5), 1,2-dichloropropane (0.3), and toluene (0.3). The first three chemicals are trihalomethanes, or THM's, and are frequent contaminants in chlorinated municipal water supplies. 1,2-dichloropropane and toluene are common industrial solvents. Based on this sample, minimal or no contamination of sampling equipment from DI water is expected for most analytes. All of the compounds

detected were less than 10 times the MDL of 0.2 µg/L. Because the sampling equipment is thoroughly purged when sampling wells, such low-level contamination of DI water would probably not impart detectable quantities of VOC's to ground-water-quality samples.

To summarize, data from quality-control samples collected throughout this study show that for most constituents, the sampling and analytical procedures yield reproducible data. Bias from sample contamination is minimal or nonexistent for most constituents. Some constituents were detected in QC blank samples at low levels, comparable to low-concentration ground-water-quality samples.

QC blank-sample data indicate problems for some constituents. Aluminum, copper, and DOC concentrations in QC blank samples overlapped with those in ambient samples. True concentrations of these constituents in ground water may be less (perhaps substantially less) than reported concentrations. The greater volume of water flowing through the sampling equipment likely minimizes DOC contamination in ground-water-quality samples compared to QC blank samples, which are collected directly after cleaning.

Systematic bias from poor analytical recovery is minimal for most pesticides. Schedule 2001 tends to be accurate and reproducible for most compounds; exceptions are carbofuran, carbaryl, terbacil, and azinphos-methyl (Zaugg and others, 1995). Variable propargite recoveries, and low, variable cis-permethrin recoveries in spiked samples from this study were observed.

Schedule 2050 typically yields lower, more variable analytical recoveries than schedule 2001. Occasionally and sporadically, very low (including zero percent) recoveries were observed in schedule 2050 analyses. Schedule 2050 data for pesticides in ground water are therefore possibly low-biased, and may include false negatives. The following pesticides were poorly quantified by schedule 2050, and are only appropriately analyzed for qualitative purposes: 1-naphthol, chlorthalonil, dichlobenil, DNOC, and esfenvalerate (Werner and others, 1996). In addition, aldicarb sulfone, aldicarb sulfoxide, carbaryl, MCPB, methiocarb, and oxamyl occasionally had low and(or) highly variable recoveries in spiked samples from this study.

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Supplemental Information

The following is a complete list of the equipment used for ground-water sampling by the Red River of the North Basin NAWQA study unit.

Sample Collection Equipment

1. Well development equipment:
   - 1.7 in. hand pump (Brainard-Kilman)
   - Centrifugal pump
   - Inertial pump
   - Stop watch
   - Calibrated bucket
   - Well development log book
   - Orion conductivity meter
   - Conductivity standards
2. Sampling pump equipment:
   - Submersible pump (Keck, Grundfos)
   - Teflon tubing discharge line (3/8 in. ID), with Swagelock stainless steel quick-connections
   - Deep cycle marine battery
   - Battery charger
   - Jumper cables
   - Anti-back siphoning device
   - Generator (if required for submersible pump)
   - Threaded connections and tubing for domestic well taps
3. Field parameter measurement equipment:
   - Hydrolab Scout II
   - Flow-through chamber (Geotech)
   - Dissolved-oxygen meter (Orion model 820)
   - Dissolved-oxygen calibration chart
   - Barometer
   - Air thermometer
   - Conductivity meter (Orion model 124) and conductance standards
   - pH meter (Orion model 250A) and standardizing buffers
   - Manuals for meters
   - Extra storage solutions
4. Pesticide sample filtration unit:
   - Stainless-steel filter unit
   - Glass-fiber baked filter (0.7 µm, 142 mm diameter)
   - Teflon tubing fittings
   - Pesticide spike kit
5. Dissolved organic carbon sample filtration unit:
   - Silver filters (0.45 µm, 47 mm diameter) (Osmotics, Inc.)
   - Stainless-steel Gelman barrel filter unit
   - Deionized water
   - Organic blank water
   - Graduated cylinder, glass, 100 mL
   - Nitrogen gas tank
   - Nitrogen gas desiccant assembly
   - Nitrogen gas tank quick-connect assembly
   - Stainless steel forceps
6. Inorganic sample filtration unit:
   - Filters (0.45 µm, capsule or cellulose nitrate filter papers)
7. Sample collection equipment:
   - Flow manifold
   - Sample-collection chamber
   - Clear 50 in. by 50 in., plastic bags for sample-collection chambers
   - Trays to hold sampling equipment and sample bottles
   - Teflon connector tubing with quick connects
   - Rigid polycarbonate bell and corrugated Teflon tubing
   - Radon sample-collection assembly
   - Radon syringe and needles for radon assembly
   - Squeeze bottles for methanol and organic blank water
8. Alkalinity titration equipment:
   - Digital titrator (Hach)
   - Acid cartridges for digital titrator, 0.16 and 1.6 normality H_2SO_4 (sulfuric acid)
   - Delivery tubes for acid cartridges
   - Beaker, glass, 250 mL
   - Graduated cylinder, glass, 100 mL

Battery powered magnetic stirrer

Teflon-coated magnetic stir bars

pH meter (Orion 250A) and standardizing buffers

9. Sample Preservation Supplies and Apparatus:

$HgCl_2$ (mercury chloride) ampoules

HNO_3 (nitric acid) ampoules, 1 mL

HNO_3 ampoules, 2 mL

Sample-preservation chamber

Clear 50 in. by 50 in. plastic bags for sample-preservation chambers

Coolers with ice

Decontamination Supplies

1. Decontamination Supplies:

Disposable single-use latex gloves (powderless)

Washbasins for cleaning

Teflon pump standpipe

Detergent (Liquinox)

Sponges

Brushes for cleaning

Squeeze bottles

Tap water

Deionized water

Methanol, HPLC grade

Methanol waste bottle

Powderless laboratory tissues (Kimwipes)

Paper towels

Cloth towels

Aluminum foil

Garbage bags

Sample Shipping and Other Supplies

1. Sample shipping supplies:

Coolers

Strapping tape

Overnight shipping forms

Analytical service request forms

Return address labels

Cardboard boxes

Plastic garbage bags (large and small)

Sealable plastic bags

2. Other supplies:

Inorganic blank water

Organic blank water

Sample bottles

Bottle labels

Indelible markers

E-line, for measuring water levels

Steel tape, for measuring water levels

Field notebook

Field note forms

Well information

Sampling protocols

Calculator

Camera

Film

Maps

Safety goggles

Knife

Batteries (D cell, 9V, AA)

Garden hose