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Chemical Analyses of Ground and Surface Water From Battle Brook Drainage Basin, Near Princeton, Minnesota

by

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Abstract

Research on the fate of agricultural chemicals in the Anoka Sand Plain in central Minnesota is being conducted by the U.S. Geological Survey and other federal and state agencies. Most of the research effort is focused on a 160-acre (6.5 x 10^5 square meters) Management Systems Evaluation Area (MSEA). It is hoped that the MSEA results will be applicable to all farms in the sand plain. To test this hypothesis, ground and surface water samples were collected in the entire Battle Brook drainage basin, which includes the test farm. A total of 27 ground-water samples and 29 surface-water samples were collected. This report presents the results of chemical analyses of the samples collected between June 24 and July 8, 1991. The chemical analyses include: field analyses of pH, dissolved oxygen, nitrate, nitrite, ammonia, sulfate, and carbonate; and laboratory analyses for a suite of major and trace cations and anions. On selected water samples and fertilizer samples, the isotopic composition of sulfur in sulfate and nitrogen in nitrate and ammonium were also determined.

Introduction

The Anoka sand plain in central Minnesota is heavily farmed. A major crop in this region is corn, which typically is given heavy applications of agricultural chemicals. These chemicals or their residues have been detected in shallow ground water and surface water. The primary goal of this project is to determine the fate of nitrogen- and sulfur-based fertilizers in the Battle Brook drainage basin and to investigate the geochemical processes influencing their transport or attenuation. Ground water, surface water, rain water, soil and plants were sampled in the Battle Brook basin, central Minnesota (fig. 1). The MSEA was more heavily sampled than surrounding areas within the basin. Water samples were analyzed in the field for pH; temperature; conductivity; three forms of nitrogen-- nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+); and sulfate (SO_4^{2-}). Samples were collected for later laboratory analysis for anions, cations, $\delta^{34}S$, and $\delta^{15}N$. Soil-, and plant-sample collection, analyses, and results will be presented elsewhere.

Battle Brook drains a low-relief, moderately wooded area of about 90 km^2. Maximum elevation is about 390 meters (m) above mean sea level; mean elevation of Elk Lake at the downstream end of the field area is 346 m. The boundaries of the Battle Brook drainage are defined by low-relief land-surface features, so the surface-water divide as shown in Figure 1 will not necessarily correspond to a ground-water divide. Land within the drainage area is heavily farmed. The dominant crop is corn, but wheat and soybeans are also grown. Although Battle

Brook flows through some fields, its course is generally through narrow wetlands. In the middle of our field area, the brook flows through a large wetland area, the Kunkel State Wildlife Management Area.

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Methods

Field Sampling and Analytical Methods

Most samples collected in this study were numbered according to the format, "91Mn-X," where 91Mn designates 1991 and Minnesota, and X is a sequential sample number: surface waters are numbered beginning with 1, ground waters begin with 101, and soil and plant samples begin with 201. Samples collected from multiport monitoring wells from the MSEA are numbered according to the format "Rn-X," where n is either 1 or 2 and represents the identification number of the multiport well and the value of X corresponds to the relative depth of the sampled port (sample depth increases with port number). Figure 2 shows a schematic diagram of a multiport monitoring well. The highest port (#1) was placed above the water table at the time of installation so that the uppermost water can be sampled if the water table rises.

Surface-water samples were collected from Battle Brook and adjacent wetlands, irrigation ditches, outlets of drain tiles (perforated drainage pipes beneath tilled fields), rain collectors, and three depths in Elk Lake (fig. 3). Ground-water samples were collected from existing domestic supply wells, the monitoring wells on the MSEA (fig. 4), and an auger hole in the Kunkel Wildlife Refuge. The southeastern half of the field area is covered by a layer of glacial outwash which forms a shallow aquifer characterized by high transmissivities (Lindholm, 1980). Many of the domestic wells draw water from this relatively shallow aquifer using sand points less than 10 m below the surface. The drilled wells are as deep as 90 m and produce water from a deeper aquifer. In the case of domestic wells, the existing pump was used to produce water, and a hose was connected to a spigot as close to the source as possible. If any treatment device (e.g. water softener) was installed that could not be bypassed, no sample was collected. Multiport wells and shallow auger holes were sampled with a peristaltic pump.

Three fertilizer samples (F designates fertilizer) were collected for sulfur and nitrogen isotope analyses, ammonium sulfate and sulfate-potassium-magnesium fertilizers from a local distributor (F21, F22) and a nitrogen-phosphorous-potassium fertilizer from a local farmer (F104).

Temperature was measured with a mercury-filled thermometer accurate to ±0.1°C. The temperature of each surface-water sample was measured as it was collected; care was taken to shade the thermometer. For the ground-water samples, temperature and conductivity were monitored as the well was pumped and samples were collected when these two parameters stabilized.

The pH of each sample was measured using an Orion model 407A [1] specific-ion meter with an Orion Ross combination pH electrode. Prior to each measurement, the meter/electrode assembly was calibrated to three pH standards at 25°C (pH 4.01, 6.86, and 9.18). The meter was first calibrated to the pH 6.86 standard and then various slope adjustments were made to calibrate the other two standards. Only minor adjustments were necessary (if any) at each sample site. The measurements are accurate to within ±0.05 pH.

Conductivity was measured using a Markson Model 10 conductivity meter. No conductivity standards were used in the field, so the conductivity values reported here are relative values and not absolute measurements of specific conductivity. TDS values were calculated from the analytical data as the sum of cations and anions for which analyses were performed.

Alkalinity was determined by titrating a known volume of sample with standardized sulfuric acid solutions (0.01686 *N* or 0.01620 *N*). Acid was added in small increments, usually less than 1 milliliter (ml), and the pH was recorded after each addition of acid. Titration curves were plotted to be sure that no significant non-carbonate alkalinity existed in the samples. In all samples, the only measurable inflections in the titration curves were attributable to carbonate species. Carbonate and bicarbonate concentrations were calculated from the titration results using equations given by Skougstad and others (1979). Analytical precision is within ±10%; detection limit is approximately 10 milligrams per liter (mg/L) in most cases. The field blank (91Mn-23) is reported as <1 mg/L because of the very small titrant volume required to overshoot the titration endpoint.

Nitrite was analyzed directly using the diazotization method in a kit available from Hach Company. This analytical procedure is sensitive only to nitrite. At least two nitrite standard additions were performed for samples that contained measurable nitrite. Standards used were prepared fresh every other day from pre-weighed sodium nitrite salt and deionized water. The nitrite standards were kept refrigerated when not in use. The detection limit is approximately 0.01 mg/L nitrite (as N).

Nitrate plus nitrite was determined in each sample using an analytical kit available from the Hach Company that quantitatively reduces nitrate to nitrite, followed by colorimetric determination of nitrite (Hach Company, 1989). Nitrate concentrations are the difference between the concentration measured by this method and the diazotization nitrite concentration. Each sample was analyzed initially with the high-range kit (0 - 30 mg/L N), followed by mid-range (0 - 4.5 mg/L N) or low-range (0 - 0.4 mg/L N) kits as needed. To increase the accuracy and precision of the analyses, at least two standard additions were performed for each sample in

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[1] Any use of trade, product, or firm names in this publication is for descriptive purposes only and does not imply endorsement by the U.S. Government.

which nitrate was detected. The final result was calculated from the results of the standard addition. The standard used for standard addition was prepared in the laboratory prior to leaving for the field area, and it was kept refrigerated for the duration of the field work. The detection limit is approximately 0.02 mg/L nitrate as N.

Ammonium was measured using the Nessler method available from Hach Company. Nessler reagent is added to a sample split and compared visually to an untreated split over which is superimposed a gradational color wheel. As for nitrite and nitrate, a minimum of two standard additions were performed for each sample in which ammonium was detected. The standards were prepared fresh in the field each week using preweighed ammonium chloride salt and deionized water. The ammonium standards were kept refrigerated when not in use. The ammonium concentration in a blank sample and the zero-concentration intercept of the standard additions was 0.4 mg/L. This value has been subtracted from all measured concentrations; corrected values are listed in the tables. The detection limit for this method is approximately 0.1 mg/L ammonium as N.

Concentrations of all nitrogen species are reported as parts per million as nitrogen (N). In the tables, the designations are N_x where x represents the individual species reported. For example, nitrate as N is designated N_{NO_3}.

Sulfate (SO_4^{2-}) was determined in the field using a Hach DR-100 colorimeter and the barium chloride-turbidimetric method. In this analysis, sulfate is precipitated as barium sulfate. The turbidity of the solution depends on the amount of barium sulfate formed and is read directly as sulfate concentration. Two standard additions were performed for each sample containing detectable sulfate. Standards were prepared in the laboratory and kept refrigerated in the field. Minimum detectable concentration is approximately 5 ppm sulfate.

Laboratory Analytical Methods

Water samples were collected in the field and preserved for later laboratory analysis of anions, cations, nitrogen isotopes, and sulfur isotopes. The preservation technique depended on the intended analysis for each sample. All samples were filtered through 0.45 µm silver-metal membrane filters. The silver filters kill bacteria that may otherwise exist in the sample. If bacterial activity is not halted in the sample, spurious anion and isotope analyses may result. Samples used for anion analyses were filtered only and received no other treatment. Samples for cation analyses were acidified to pH <2 with concentrated hydrochloric acid (HCl) to prevent precipitation of hydrous iron oxides or other metals.

Anions other than dissolved inorganic carbon were determined in the laboratory by ion chromatography. Samples were compared to calibration curves derived from four standards and a blank. The detection limits for each constituent are: F^-, 0.1 mg/L; Cl^-, 0.2 mg/L; N_{NO_2}, 0.03 mg/L; N_{NO_3}, 0.02 mg/L; PO_4^{3-}, 0.1 mg/L; and SO_4^{2-}, 0.2 mg/L. The precision of the ion chromatography analyses is within ±10%, and were almost always within 10% of the field measurements of detectable nitrate, nitrite, and sulfate. The concentrations of sulfate in Battle Brook samples measured by the ion chromatograph was not detectable in field analyses. These samples are brownish yellow in color due to dissolved organic compounds that may interfere with the field turbidimetric technique.

Cation samples were analyzed by inductively coupled argon plasma atomic emission spectroscopy (ICP). Internal laboratory quality control was maintained by running standards as unknowns, by running duplicate samples, and in some cases by running multiple dilutions of individual samples. Detection limits vary from one element to another, and are represented by the qualified (<) values in Tables 5, 6, and 7. The precision of the ICP method is within ±10%.

Nitrogen isotope analyses were performed on N_2 gas produced and purified by a sealed-tube combustion method (Kendall and Grim, 1990). Solid fertilizer samples were ground, homogenized, and loaded into 9 mm Vycor glass tubes with 3 g granular Cu, 0.2g CaO powder, and 2 g CuO wire. The Vycor tubes were evacuated, sealed with a torch, and placed in a muffle furnace programmed to hold at 850°C for 2 h, then cooled at 40°C/h to room temperature. Water samples containing more than about 1 mg/L N as nitrate or ammonium were concentrated by freeze-drying in flasks, re-dissolved in 1-2 ml deionized water, then freeze-dried again in 9mm Vycor glass tubes. Ammonium-rich samples were adjusted to pH 3 with H_2SO_4 before freeze-drying. Freeze-dried salts were sealed in the glass tubes with Cu, CaO, and CuO and combusted, as were the fertilizers. All sample sizes were adjusted to yield aliquots of approximately 10 μmoles of N_2 gas, which were expanded into a Finnigan MAT 251 isotope ratio mass spectrometer. All samples were prepared and analyzed at least twice. The N isotope measurements were calibrated by analyzing identical preparations of standard nitrate and ammonium salts and solutions and are reported as mean $\delta^{15}N$ values[2] relative to atmospheric N_2 (0.0 ‰). The overall uncertainties of the mean $\delta^{15}N$ values are estimated to be about ±0.3 ‰ or better.

Sulfur isotope analyses were performed on SO_2 gas produced and purified by a quartz reduction process. Solid fertilizer samples were ground, homogenized, and dissolved in hot 6*N* HCl. The solution was filtered and the solid residue discarded. Bromine-saturated distilled water was added to the filtrate and boiled until the bromine was expelled. $BaSO_4$ was precipitated by adding 10 wt. % $BaCl_2$ solution to the filtrate, boiling the solution for 15 minutes, and allowing it to digest overnight on low heat. The $BaSO_4$ precipitate was filtered, washed with deionized H_2O, and dried. The dried precipitate was loaded into a boat, covered with quartz sand (buffer for the oxygen isotopic composition of the SO_2). The boat was then loaded into a reaction tube, evacuated on a combustion-vacuum line, and heated until the $BaSO_4$ decomposed to SO_2. The SO_2 gas was expanded into a Nuclide isotope ratio mass spectrometer. Twenty percent of the samples were prepared and analyzed twice. The S isotope measurements were calibrated by analyzing standard sulfur salts, and are reported as $\delta^{34}S$ values[2] relative to Cañon Diablo Troilite S (0.0 ‰). The overall uncertainties of the $\delta^{34}S$ values are estimated to be about ±0.2 ‰.

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[2] δX (‰) = $[(R_{sample} - R_{standard})/R_{standard}] \times 1000$, where R is the isotopic ratio in the sample or standard ($^{15}N/^{14}N$ for X = ^{15}N and $^{34}S/^{32}S$ for X = ^{34}S).

Results

Sample descriptions and field results for the analyses described above are presented in Table 1 for surface-water samples and Table 2 for ground-water samples. The last column in Table 2, labeled "Fe," is the response of the homeowner to our question of whether they experienced a problem with iron contamination in their water. Such contamination would be noted by iron staining of plumbing fixtures or laundry. Only positive responses are recorded in the table. Field results of samples from the multiport monitoring wells are in Table 3. All of the multiport samples have high concentrations of nitrate; five of the six samples exceed the drinking-water standard of 10 mg/L nitrate as N. The multiports also exhibit dramatic changes in concentration of some constituents over small depth intervals.

Laboratory results of anion analyses are presented in Table 4. Cation analyses are presented in Table 5 for surface-water samples, in Table 6 for ground-water samples, and in Table 7 for samples from the multiport samplers at the MSEA site. Silver concentrations shown in the tables are an artifact of the field preservation technique wherein the samples were filtered through silver-metal membrane filters. The fact that the silver concentrations are an artifact is supported by the observation that samples 91Mn-20, 91Mn-21, 91Mn-22, and 91Mn-23 (three rain-water samples and a field blank, respectively) all contain low or below detection concentrations of nearly every dissolved constituent except silver. There is no evidence to suggest contamination of any other element by the silver filters. Isotope results are in Table 8.

Many of the surface-water samples have rather high concentrations of dissolved iron. The processes responsible for such high iron concentrations are currently being investigated. In some of these samples rapid oxidation of dissolved iron and subsequent precipitation of ferric oxyhydroxides hindered sample filtration. Therefore, the actual dissolved iron concentrations may be higher than those listed in Tables 5, 6 or 7.

The chemistry of the waters can be depicted graphically on a Piper diagram, as shown in Figure 5. To construct this figure, equivalents per liter of cations or anions are normalized to 100% of their total. Sodium and potassium are added together, as are chloride and nitrate. Cations are plotted on the triangular field in the lower left portion of the diagram, anions to the lower right. Details on how to construct and interpret Piper diagrams are given in numerous textbooks, for instance Davis and DeWiest (1966). The figure shows that the cation compositions of the multiport samples are nearly the same as those of the surface-water samples; the ground-water cation compositions are somewhat more variable. For most samples, calcium is the predominant cation, although several of the ground-water samples plot within the central field of no cation predominance. Carbonate is the dominant anion in most of the samples, although 5 of 6 multiport samples and the two drain tile samples show a predominance of Cl + NO_3 in approximately equal concentrations. Close inspection of the anion composition of the ground-water samples reveals two clusters of samples: one with extreme predominance by dissolved carbonate; the other with somewhat lower carbonate concentrations. In general, the former represents deeper (drilled) wells while the latter cluster is mostly shallower ground water (sand-point wells). These two groups of samples most likely are drawn from different aquifers.

Nitrate and sulfate concentrations in surface-water samples are much lower than those in the ground-water samples and the multiport samples (figs. 5 and 6). Only shallow ground-water samples (<8 m) had nitrate concentrations exceeding 1 mg/L N_{NO_3}; deeper ground waters had uniformly low nitrate concentrations. The highest nitrate concentrations were recorded in the multiport samples and from the two drain-tile outlets. In contrast to those of nitrate, sulfate concentrations in ground water are independent of well depth.

The $\delta^{15}N$ values in oxygen-rich waters from the MSEA multiports R1 and R2 are less than or equal to zero, and decrease slightly with depth. The low average values are consistent with fertilizer sources (e.g., Sample F21) for most of the nitrate. Sample R2-6 has an anomalously high $\delta^{15}N$ value and relatively low nitrate and dissolved oxygen concentrations, all of which could be qualitatively consistent with the presence of some partially denitrified water or with changes in the amounts and types of fertilizers used in the past. The highest $\delta^{15}N$ value (+11.2) is for nitrate in Well 103 and may indicate either animal waste input or partial denitrification. Other nitrate-rich waters have intermediate $\delta^{15}N$ values that could indicate mixed nitrogen sources (fertilizers, manure, and/or plant degradation products) or partial reactions.

Although the data are sparse, there is a systematic trend of increasing $\delta^{34}S$ values in ground water with depth. Sulfate in surface water is enriched in ^{34}S relative to that in shallow ground water by as much as 8‰. The ^{34}S-depletion in the shallow ground water probably reflects biological cycling of the sulfur instead of contamination by fertilizer sulfur because the fertilizer sulfur is ^{34}S-enriched relative to the sulfate in the shallow ground water.

Summary

Several generalizations can be made from the data:

- High nitrate concentrations were observed only in effluents from the drain tiles, shallow ground-water wells, and in the multiport wells. Deeper ground water (>8 m) and surface water contained little or no nitrate.
- Sulfate concentrations generally are higher in ground water than surface water, and unrelated to well depth.
- Nitrite was observed in only a few samples, and then only in very low concentrations.
- Ammonium was detected in nearly every surface-water sample. The surface waters also had generally low dissolved oxygen concentrations.
- Anaerobic conditions in Battle Brook are consistent with fairly high iron concentrations (up to 5.7 ppm) and low sulfate concentrations.
- Nitrogen isotope data indicate a variety of potential sources for nitrate in the ground and surface water. Values of $\delta^{15}N$ in the shallow MSEA multiport samples are closest to fertilizer values.

- Sulfur isotopes in ground water from deep wells are different from those in ground water from shallow wells. The difference may be due to sampling distinct waters from different aquifers or bacterial-mediated reactions in shallow ground water.
- From other work being done at the MSEA site, it is inferred that discharge of shallow ground water is an important source of water for Battle Brook. This hypothesis is supported by the relative similarity of cation compositions of the shallow ground waters with those of the surface waters (fig. 5). Anion compositions differ somewhat, possibly because nitrate and/or sulfate are reduced as ground water discharges through wetlands.

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Table 1- Results of field analyses of surface-water samples (n.d. means not detected, n.a. means not analyzed). Abbreviations are as follows: T°C, temperature in Celsius; Cond, conductivity; DO, dissolved oxygen. Sources are as follows: BB, samples from Battle Brook; ID, samples from irrigation ditches; blank, distilled water from laboratory; DT, samples from drain-tile outlets; EL, samples from Elk Lake (depth of sample in parentheses). Conductivity values are for relative reference only and were not calibrated to standards.

Sample Number	Source	T °C	Cond µmho/cm	pH	DO ppm	HCO_3 mg/L	SO_4 mg/L	N_{NO_3} mg/L	N_{NO_2} mg/L	N_{NH_4} mg/L
91Mn-1	BB	24.1	100	6.7	8	42	n.d.	1	<.01	0.7
91Mn-2	BB	20.2	280	7	0	98	n.d.	<.02	<.01	1.0
91Mn-3	BB	21	240	6.89	0	86	n.d.	<.02	<.01	1.0
91Mn-4	BB	21.1	280	6.85	0	98	n.d.	<.02	<.01	0.8
91Mn-5	BB	22.5	425	7.71	5.8	123	n.d.	0.10	<.01	0.8
91Mn-6	BB	22.3	420	7.69	5.1	118	n.d.	0.10	0.03	0.6
91Mn-7	BB	23.1	420	7.5	0.7	121	n.d.	0.06	<.01	0.6
91Mn-8	BB	22.7	380	7.2	0	83	n.d.	<.02	<.01	0.3
91Mn-9	BB	21.9	410	7.29	0	123	n.d.	<.02	<.01	1.5
91Mn-10	BB	22	415	7.61	2	121	n.d.	<.02	<.01	1.1
91Mn-11	BB	22.3	460	7.6	0	129	n.d.	0.13	0.03	1.5
91Mn-12	ID	23.9	300	7.42	0	93	n.d.	<.02	<.01	0.9
91Mn-13	BB	31	195	7.28	1	66	n.d.	<.02	<.01	0.4
91Mn-14	BB	28.3	230	7.37	6.1	65	n.d.	0.20	0.02	0.4
91Mn-15	BB	24.25	160	9.18	9.1	67	n.d.	<.02	<.01	<0.1
91Mn-16	BB	22.7	200	7.1	0	76	n.d.	<.02	<.01	1.0
91Mn-17	ID	14.7	290	7.51	5.2	64	n.d.	1	0.03	0.3
91Mn-18	BB	24	240	7.31	0	77	n.d.	<.02	<.01	0.6
91Mn-19	BB	22.1	265	7.4	0.6	85	n.d.	0.14	<.01	0.4
91Mn-20	rain	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a..	n.a.	n.a.
91Mn-21	rain	n.a.	n.a.	n.a.	n.a.	n.a.	1	0.07	0.02	0.8
91Mn-22	rain	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.	n.a.	n.a.	0.7
91Mn-23	blank	n.a.	n.a.	5.67	n.a.	<1	<5	<.02	<.01	<0.1
91Mn-24	DT	15.3	425	6.41	3.4	56	23	13	0.10	0.4
91Mn-25	DT	14.9	460	5.91	5.7	<10	12	28	0.06	<0.1
91Mn-26	BB	21.5	260	7.04	1.5	91	n.d.	<.02	<.01	0.8
91Mn-27	EL (0m)	25.7	150	9.4	9.8	64	8	0.06	<.01	<0.1
91Mn-28	EL (2m)	23.9	195	9.1	7.4	62	7	0.02	<.01	0.2
91Mn-29	EL (3m)	23.4	200	9.02	7.1	63	8	<.02	<.01	<0.1

Table 2- Results of field analyses of ground-water samples. Depths are given in meters below land surface. Abbreviations are defined in the caption for Table 1. The last column in Table 2, labeled "Fe," is the response of the homeowner to our question of whether they experienced a problem with iron contamination in their water.

Sample Number	depth meters	T °C	Cond µmho/cm	pH	DO ppm	HCO_3 mg/L	SO_4 mg/L	N_{NO_3} mg/L	N_{NO_2} mg/L	N_{NH_4} mg/L	Fe
91Mn-101	59	9.9	560	7.51	0	118	38	<.02	<.01	0.5	yes
91Mn-102	27	9.2	470	7.7	0	160	<5	<.02	<.01	0.6	
91Mn-103	7	10.4	215	6.62	0	46	25	5	0.12	0.2	
91Mn-104	19	14.8	300	8.02	0	84	25	0.24	<.01	<0.1	
91Mn-105	8	10.3	170	8.43	0	38	34	<.02	<.01	0.1	
91Mn-106	17	11.8	535	8.27	0	119	65	<.02	<.01	0.3	
91Mn-107	17	11.2	415	7.82	0	95	36	0.30	0.10	0.1	
91Mn-108	5	10.9	840	7.29	5.1	139	59	11	<.01	0.1	
91Mn-109	?	9.8	370	7.35	0	115	17	0.80	<.01	<0.1	
91Mn-110	?	10.9	320	5.97	2.3	64	12	7	<.01	<0.1	
91Mn-111	22	9.5	400	7.8	0	103	18	0.60	0.04	0.1	
91Mn-112	91	9.7	465	7.71	0	139	20	0.02	<.01	<0.1	
91Mn-113	17	11.5	380	7.82	0	79	36	<.02	<.01	<0.1	
91Mn-114	32	9.8	340	7.6	0	113	<5	<.02	<.01	15	yes
91Mn-115	?	9.7	180	8.6	0	76	3	<.02	<.01	0.6	
91Mn-116	26	9.5	255	8.2	0	86	8	<.02	<.01	0.3	yes
91Mn-117	8	10.7	300	7.61	0	72	31	<.02	<.01	0.4	yes
91Mn-118	8	9.4	220	8.1	0	53	18	6	0.20	<0.1	yes
91Mn-119	8	8.5	485	7.5	0	159	8	0.66	0.03	<0.1	
91Mn-120	8	10.3	240	7.2	3.3	21	8	16	0.80	<0.1	
91Mn-121	0.3	19.5	740	6.83	0	167	nd	<.02	<.01	7.0	yes

Table 3- Results of field analyses of samples collected from multiport samplers R1 and R2 at the MSEA site. Abbreviations are defined in the caption for Table 1.

Sampler R1

Sample Number	T °C	Cond µmho/cm	pH	DO ppm	HCO_3 mg/L	SO_4 mg/L	N_{NO_3} mg/L	N_{NO_2} mg/L	N_{NH_4} mg/L
R1-2	16.6	265	7.38	2.3	45	1	17	0.03	0.1
R1-4	13.3	360	6.83	3.7	29	1	20	0.35	0.4
R1-6	12.3	570	7.79	8.1	87	0	14	0.22	<0.1

Sampler R2

Sample Number	T °C	Cond µmho/cm	pH	DO ppm	HCO_3 mg/L	SO_4 mg/L	N_{NO_3} mg/L	N_{NO_2} mg/L	N_{NH_4} mg/L
R2-2	15.5	260	8.01	8	31	1	14	0.03	<0.1
R2-4	16.5	440	7.48	4.7	43	0.5	22	0.04	0.1
R2-6	12.8	295	8.18	1.8	67	12	8	0.03	0.1

Table 4- Laboratory analytical results for anions. Samples were analyzed by ion chromatography. All values are given as mg/L. Nitrite and nitrate are reported as N.

Surface-water samples:

Sample No.	F^-	Cl^-	NNO_2	NNO_3	PO4^{3-}	SO4^{2-}
91Mn-1	0.6	2.6	<0.03	0.16	<0.1	1.5
91Mn-2	0.4	4.4	<0.03	0.16	<0.1	0.7
91Mn-3	0.5	1.3	<0.03	<0.02	<0.1	0.7
91Mn-4	0.4	2.2	<0.03	<0.02	<0.1	0.7
91Mn-5	0.7	11	<0.03	0.45	<0.1	3.8
91Mn-6	0.2	9.5	<0.03	0.36	<0.1	21
91Mn-7	0.8	11	<0.03	0..22	<0.1	1.8
91Mn-8	0.2	16	<0.03	<0.1	<0.1	11
91Mn-9	0.5	7.1	<0.03	<0.1	<0.1	1
91Mn-10	0.5	6.1	<0.03	<0.1	<0.1	1.2
91Mn-11	0.4	11	<0.03	1.3	<0.1	2.9
91Mn-12	0.9	3.2	<0.03	<0.1	<0.1	0.7
91Mn-13	0.4	5.1	<0.03	0.16	<0.1	1.1
91Mn-14	0.4	7.9	<0.03	0.38	<0.1	11
91Mn-15	1.1	5.2	<0.03	<0.02	<0.1	8.1
91Mn-16	0.2	4.4	<0.03	0.16	<0.1	1.9
91Mn-17	0.2	13	<0.03	1.2	0.2	30
91Mn-18	0.2	6.9	<0.03	0.16	<0.1	4.9
91Mn-19	0.1	5.1	<0.03	0.29	<0.1	7.2
91Mn-20	0.4	0.8	<0.03	0.59	<0.1	1.4
91Mn-21	0.2	0.5	0.03	0.18	0.4	0.8
91Mn-22	0.2	0.4	0.06	0.12	0.5	0.6
91Mn-23	0.1	<0.2	<0.03	<0.02	<0.1	0.6
91Mn-24	0.1	45	<0.03	6.5	<0.1	19
91Mn-25	<0.1	47	<0.03	28	<0.1	13
91Mn-26	0.1	1.5	<0.03	<0.02	<0.1	0.8
91Mn-27	<0.1	4.5	<0.03	0.11	0.1	7.7
91Mn-29	0.3	4.2	<0.03	<0.02	0.2	7.4

Table 4- (continued)

Ground-water samples:

Sample No.	F^-	Cl^-	N_{NO_2}	N_{NO_3}	PO_4^{3-}	SO_4^{2-}
91Mn-101	0.3	21	<0.03	<0.02	<0.1	38
91Mn-102	0.1	0.5	0.21	<0.02	0.2	1.7
91Mn-103	0.1	10	<0.03	3.4	<0.1	26
91Mn-104	0.2	11	<0.03	0.47	<0.1	25
91Mn-105	<0.1	13	<0.03	<0.02	<0.1	31
91Mn-106	0.1	29	<0.03	<0.02	<0.1	57
91Mn-107	0.2	18	<0.03	0.63	<0.1	33
91Mn-108	0.1	17	<0.1	72	<0.1	50
91Mn-109	<0.1	1.3	<0.03	1.1	<0.1	17
91Mn-110	<0.1	9.8	<0.03	4.5	<0.1	11
91Mn-111	<0.1	1.1	0.18	.43	<0.1	18
91Mn-112	0.2	9.9	<0.03	0.16	<0.1	17
91Mn-113	<0.1	25	<0.03	<0.02	<0.1	34
91Mn-114	<0.1	1.1	0.21	<0.02	<0.1	0.7
91Mn-115	0.1	0.7	0.15	<0.02	<0.1	1.4
91Mn-116	0.1	1.9	0.37	<0.02	0.2	6.7
91Mn-117	0.1	9.4	<0.03	<0.02	<0.1	33
91Mn-118	0.1	4.4	0.24	3.8	<0.1	18
91Mn-119	<0.1	2	0.52	1.2	<0.1	9.7
91Mn-120	<0.1	8.5	<0.03	18	<0.1	9.4
91Mn-121	0.8	12	<0.03	<0.02	<0.1	96

Multiport samples:

Sample No.	F^-	Cl^-	N_{NO_2}	N_{NO_3}	PO_4^{3-}	SO_4^{2-}
R1-2	0.1	12	<0.03	14	<0.1	1.8
R1-4	<0.1	19	<0.03	19	<0.1	1.2
R1-6	<0.1	17	<0.03	16	<0.1	1.5
R2-2	<0.1	13	<0.03	16	<0.1	1.6
R2-4	<0.1	21	<0.03	22	<0.1	1.5
R2-6	<0.1	8.8	1.0	2.5	<0.1	8.8

Table 5- Samples of surface water from Battle Brook drainage. All samples were below detection in: Be (<1 ppb); Bi (<10 ppb); Co (<3 ppb); Ga (<5 ppb); Mo (<10 ppb); Pb (<10 ppb); Sn (<6 ppb); V (<6 ppb); and Zr (<1 ppb). Total dissolved solids (TDS) was calculated as the sum of all cations and anions.

Sample Number	Ag ppb	Al ppm	B ppb	Ba ppb	Ca ppm	Cd ppb	Cr ppb	Cu ppb	Fe ppm	K ppm
91Mn-1	140	0.1	13	37	21	5	<1	<10	1.3	0.9
91Mn-2	140	0.2	9	64	44	3	2	21	2.3	0.4
91Mn-3	350	0.3	10	53	39	4	7	<10	4.3	0.6
91Mn-4	210	0.3	<5	62	43	6	2	11	5.7	0.5
91Mn-5	27	0.1	14	59	56	1	2	<10	0.60	1.5
91Mn-6	27	0.1	13	62	57	<1	6	<10	0.80	1.1
91Mn-7	41	0.1	14	63	55	1	6	<10	0.90	1.2
91Mn-8	20	<.1	12	50	45	<1	8	<10	0.40	0.8
91Mn-9	140	0.2	9	77	55	3	5	<10	2.0	0.4
91Mn-10	130	0.2	12	77	55	2	4	<10	1.3	0.4
91Mn-11	80	0.1	14	73	60	1	7	<10	0.8	1.5
91Mn-12	200	0.1	8	53	43	1	5	<10	3.0	0.5
91Mn-13	210	0.2	6	46	33	4	14	<10	2.9	1.2
91Mn-14	120	0.1	10	33	38	3	5	<10	0.8	1.0
91Mn-15	97	0.5	13	36	30	5	10	<10	0.1	1.3
91Mn-16	150	0.1	7	38	37	4	14	<10	1.9	1.2
91Mn-17	88	<.1	10	40	45	2	5	<10	0.2	1.1
91Mn-18	64	<.1	8	37	42	<1	3	<10	0.7	0.9
91Mn-19	73	<.1	10	44	45	<1	1	<10	0.6	0.5
91Mn-20	160	<.1	6	4	2.3	<1	<1	<10	<.05	0.3
91Mn-21	160	<.1	<5	7	1.5	1	4	<10	0.06	0.4
91Mn-22	170	<.1	<5	5	0.7	<1	2	<10	<.05	0.2
91Mn-23	26	<.1	<5	<2	0.2	<1	<1	<10	<.05	0.0
91Mn-24	28	<.1	15	79	50	2	<1	<10	0.06	3.7
91Mn-25	26	<.1	27	100	45	2	<1	<10	0.06	1.4
91Mn-26	190	<.1	10	110	41	<1	1	<10	3.6	0.5
91Mn-27	39	<.1	13	33	27	2	10	<10	0.3	1.1
91Mn-29	76	0.1	13	36	27	2	55	10	0.4	1.2

Table 5- continued.

Sample Number	Li ppb	Mg ppm	Mn ppb	Na ppm	Ni ppb	Si ppm	Sr ppb	Ti ppb	Zn ppb	TDS ppm
91Mn-1	<2	4.9	230	2.9	8	5.4	45	<1	41	85
91Mn-2	<2	15	660	3.9	38	11	94	2	32	180
91Mn-3	<2	12	980	2.6	10	11	85	2	10	160
91Mn-4	<2	14	1000	2.8	13	12	98	<1	15	180
91Mn-5	2	18	750	6.0	17	9.0	110	<1	5	230
91Mn-6	2	19	890	5.8	9	9.1	110	<1	5	250
91Mn-7	2	19	830	5.9	9	9.6	120	<1	8	230
91Mn-8	3	16	200	7.2	11	8.2	97	<1	3	190
91Mn-9	3	19	1500	5.1	12	9.4	110	<1	6	220
91Mn-10	2	19	1500	5.0	10	9.3	120	2	3	220
91Mn-11	3	19	1800	5.9	9	9.7	120	<1	<2	240
91Mn-12	<2	13	570	3.3	8	11	87	<1	<2	170
91Mn-13	<2	7.5	610	3.8	14	10	65	<1	10	130
91Mn-14	<2	8.0	200	4.0	8	7.1	67	<1	8	150
91Mn-15	<2	9.4	23	3.9	13	3.7	59	2	10	130
91Mn-16	<2	8.4	2200	3.6	15	9.9	72	2	14	150
91Mn-17	<2	8.9	490	4.6	7	8.8	72	<1	4	180
91Mn-18	<2	8.8	270	3.7	14	8.0	77	<1	3	160
91Mn-19	<2	11	140	3.5	5	8.5	76	<1	2	170
91Mn-20	<2	0.4	9	0.5	<5	0.3	4.0	<1	7	9
91Mn-21	<2	0.3	12	<.2	<5	0.2	3.4	<1	14	6
91Mn-22	<2	0.1	12	<.2	<5	0.1	1.7	2	9	3
91Mn-23	<2	0.0	1	<.2	<5	0.1	0.3	<1	2	1
91Mn-24	3	20	40	8.5	<5	11	160	<1	15	280
91Mn-25	<2	15	20	7.0	7	11	260	<1	14	260
91Mn-26	<2	13	1000	2.7	<5	12	93	<1	24	170
91Mn-27	<2	9.5	23	3.7	11	6.1	58	<1	3	130
91Mn-29	<2	9.4	24	3.7	39	5.9	59	2	4	120

Table 6- Samples of ground water from Battle Brook drainage. All samples were below detection in: Be (<1 ppb); Bi (<10 ppb); Co (<3 ppb), except 91Mn-121 (6 ppb); Cu (<10 ppb), except 91Mn-108 (17 ppb); Ga (<5 ppb); Mo (<10 ppb); Pb (<10 ppb); Sn (<6 ppb); Ti (<1 ppb), except 91Mn-118 (2 ppb); V (<6 ppb), except 91Mn-113 (11 ppb); and Zr (<1 ppb). Total dissolved solids (TDS) was calculated as the sum of all cations and anions.

Sample Number	Ag ppb	Al ppm	B ppb	Ba ppb	Ca ppm	Cd ppb	Cr ppb	Fe ppm	K ppm
91Mn-101	8	0.1	<5	89	62	1	<1	3.3	1.8
91Mn-102	48	0.1	20	76	63	<1	1	0.06	1.6
91Mn-103	20	<.1	19	24	29	<1	<1	0.06	1.2
91Mn-104	19	0.1	15	33	39	<1	<1	<.05	1.5
91Mn-105	8	<.1	7	54	30	<1	<1	0.06	0.7
91Mn-106	13	0.2	18	62	52	<1	<1	0.06	2.0
91Mn-107	9	0.1	29	33	35	<1	2	0.06	2.0
91Mn-108	14	<.1	277	61	76	<1	1	<.05	2.1
91Mn-109	57	<.1	11	41	60	<1	<1	<.05	0.8
91Mn-110	26	<.1	12	22	38	<1	5	0.06	0.7
91Mn-111	78	<.1	15	74	52	<1	1	0.06	1.2
91Mn-112	15	<.1	343	22	40	<1	<1	<.05	2.2
91Mn-113	13	<.1	15	42	47	<1	<1	<.05	1.3
91Mn-114	22	<.1	34	150	37	<1	4	2.2	2.2
91Mn-115	51	<.1	39	21	23	<1	<1	0.06	1.1
91Mn-116	49	<.1	13	15	41	10	2	0.06	0.9
91Mn-117	12	<.1	<5	110	50	<1	2	3.0	0.9
91Mn-118	24	<.1	30	19	35	<1	<1	<.05	0.7
91Mn-119	20	<.1	27	81	81	<1	<1	<.05	4.9
91Mn-120	23	<.1	18	17	28	1	<1	<.05	0.9
91Mn-121	87	<.1	<5	190	67	2	<1	64.	0.7

Table 6- continued.

Sample Number	Li ppb	Mg ppm	Mn ppb	Na ppm	Ni ppb	Si ppm	Sr ppb	Zn ppb	TDS ppm
91Mn-101	8	21	330	6.9	7	17	86	79	290
91Mn-102	4	25	370	6.8	<5	14	130	18	270
91Mn-103	3	11	190	5.1	5	11	69	10	160
91Mn-104	3	16	22	7.9	<5	8.0	120	2	200
91Mn-105	<2	7.5	100	2.9	<5	9.3	47	3	130
91Mn-106	<2	37	60	9.0	<5	7.3	210	<2	310
91Mn-107	4	26	46	15	<5	7.6	210	4	230
91Mn-108	<2	18	11	52	<5	11	320	30	440
91Mn-109	2	16	5	2.3	<5	12	69	24	230
91Mn-110	<2	11	2	3.4	<5	9.9	68	17	170
91Mn-111	2	14	120	2.8	<5	11	110	11	210
91Mn-112	5	19	23	40	<5	9.9	470	78	280
91Mn-113	3	17	50	5.8	<5	8.8	99	53	220
91Mn-114	3	13	130	10	6	17	92	16	210
91Mn-115	<2	8.1	17	16	<5	5.2	140	10	130
91Mn-116	<2	10	72	3.9	<5	11	77	5	160
91Mn-117	<2	5.8	430	3.5	<5	12	64	9	190
91Mn-118	<2	7.7	200	2.9	<5	8.6	62	5	150
91Mn-119	2	16	910	4.7	<5	11	190	16	290
91Mn-120	<2	9.4	16	5.0	<5	11	83	13	170
91Mn-121	2	19	2800	4.8	<5	15	150	48	450

Table 7- Multi-port samples on MSEA site. All samples were below detection in: Al (<0.1 ppm); Be (<1 ppb); Bi (<10 ppb); Cd (<1 ppb); Co (<3 ppb); Cu (<10 ppb); Ga (<5 ppb); Fe (<0.05 ppm); Li (<2 ppb), except R1-4 (3 ppb); Mo (<10 ppb); Ni (<5 ppb); Pb (<10 ppb); Sn (<6 ppb); V (<6 ppb); and Zr (<1 ppb). Total dissolved solids (TDS) was calculated as the sum of all cations and anions.

Sample Number	Ag ppb	B ppb	Ba ppb	Ca ppm	Cr ppb	K ppm	Mg ppm
R1-2	33	22	29	40	2	1.8	8.8
R1-4	20	26	45	40	1	2.4	7.5
R1-6	31	13	26	63	2	0.9	17
R2-2	18	12	16	32	<1	0.7	8.7
R2-4	20	11	33	47	<1	1.1	14
R2-6	24	9	20	41	<1	0.5	10

Sample Number	Mn ppb	Na ppm	Si ppm	Sr ppb	Ti ppb	Zn ppb	TDS ppm
R1-2	64	2.5	8.6	150	2	150	190
R1-4	21	2.6	8.8	210	5	69	190
R1-6	8	2.9	9.9	96	<1	30	270
R2-2	21	2.4	9.5	68	<1	23	170
R2-4	42	2.6	6.8	180	<1	59	240
R2-6	8.8	2.6	10.	53	<1	23	160

Table 8- Results of S and N isotope analyses of samples of fertilizer (F), ground water, surface water, and multiports. The $\delta^{15}N$ values are relative to atmospheric nitrogen and $\delta^{34}S$ values to Cañon Diablo Troilite standard.

Sample no.	Notes	$\delta^{15}N_{NO_3}$ ‰	$\delta^{15}N_{NH_4}$ ‰	$\delta^{34}S_{SO_4}$ ‰
91Mn-24	drain tile	+7.8		+2.3
91Mn-25	drain tile	+6.4		+3.9
91Mn-26	Battle Brook			+3.2
91Mn-27	Elk Lake (0m)			+1.7
91Mn-28	Elk Lake (2m)			+3.7
91Mn-101	well (59m)			+2.7
91Mn-103	well (7m)	+11.2		
91Mn-105	well (8m)			-4.5
91Mn-106	well (17m)			+0.9
91Mn-107	well (17m)			-1.3
91Mn-109	well (?m)			+2.7
91Mn-110	well (?m)			+2.2
91Mn-111	well (22m)			-4.5
91Mn-112	well (91m)			+5.8
91Mn-113	well (17m)			-0.2
91Mn-114	well (32m)		+3.0	
91Mn-117	well (8m)			-2.6
91Mn-118	well (8m)	+6.6		-4.8
91Mn-120	well (8m)	+3.7		
91Mn-121	auger hole (0.3m)		+1.6	
R1-2	multiport	0.0		
R1-4	multiport	-0.7		
R1-6	multiport	-1.5		
R2-2	multiport	-0.4		
R2-4	multiport	-1.2		
R2-6	multiport	+2.8		+1.5
F21	N21-P0-K0-S24*	-0.3		+9.6
F22	N0-P0-K22-S11			+9.3
F104	N27-P14-K14 + urea	+1.5		-0.6

*Element followed by its percentage by weight in the fertilizer

Figure Captions

Figure 1. Map of the Battle Brook drainage area in central Minnesota. A large wetland area is shown in the center of the drainage area, although extensive wetlands are developed throughout the area adjacent to the main channel of Battle Brook. Within the wetland area, the Kunkel State Wildlife Management Area is shown by the dot-dash line.

Figure 2. Schematic diagram of a multiport monitoring well.

Figure 3. Location of surface-water sample sites including drain tiles.

Figure 4. Location of ground-water samples including multiport monitoring wells.

Figure 5. Piper diagram showing chemical composition of surface- and ground-water samples.

Figure 6. Histogram showing frequency of sulfate and nitrate concentrations in surface waters, ground water from domestic and monitoring wells, and effluent from drain tiles.

Figure 1

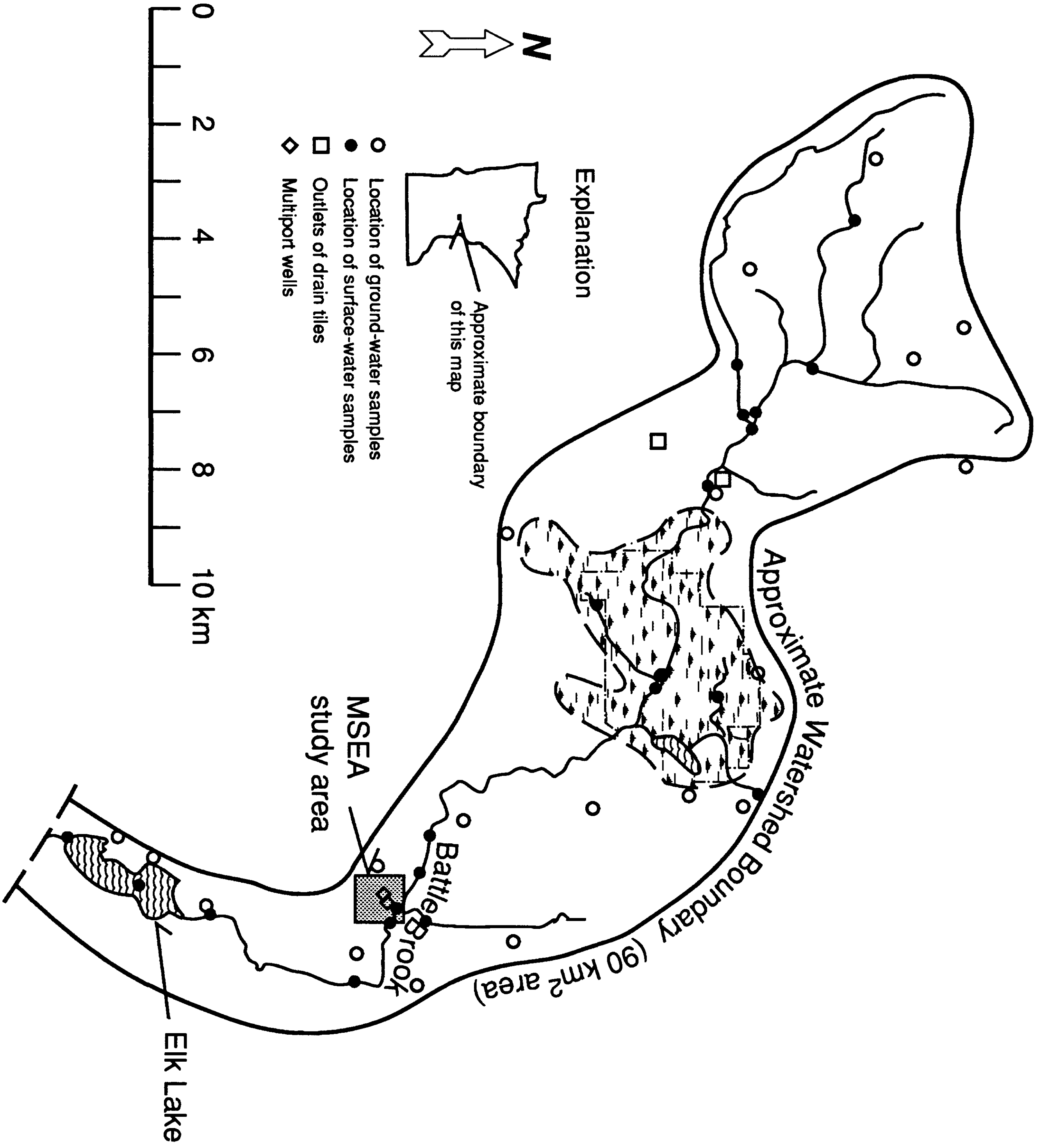

Approximate Watershed Boundary (90 km² area)
MSEA study area
Battle Brook
Elk Lake
N
Explanation
Approximate boundary of this map
○ Location of ground-water samples
● Location of surface-water samples
□ Outlets of drain tiles
◇ Multiport wells
0
2
4
6
8
10 km

Figure 2

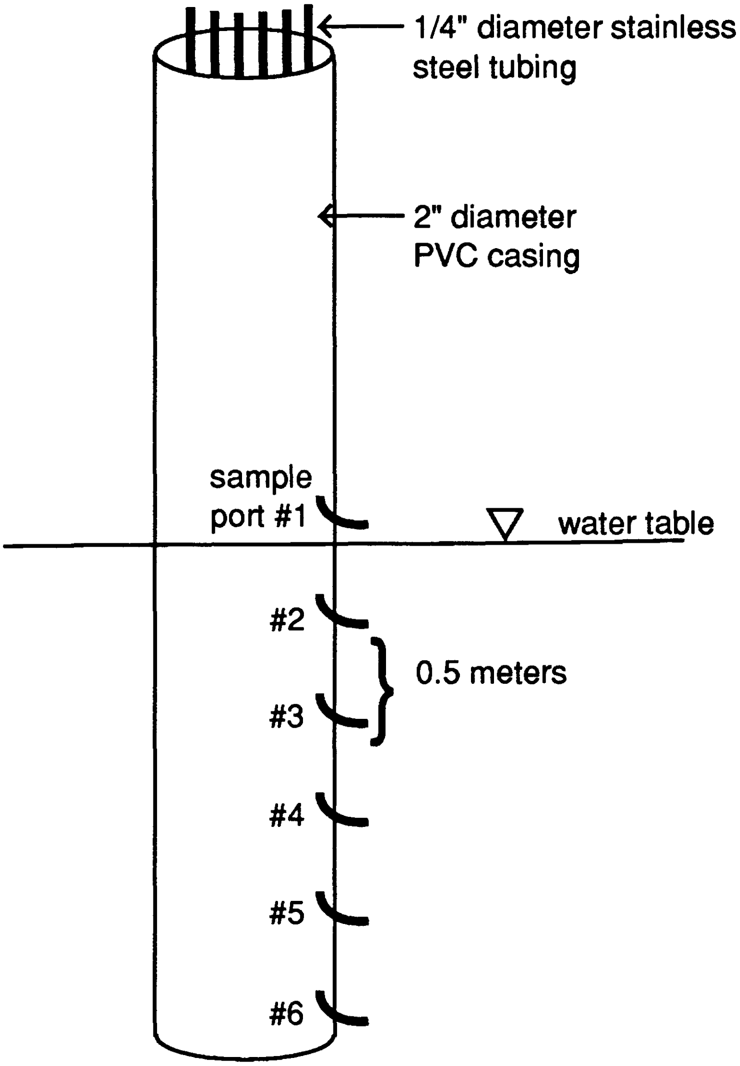
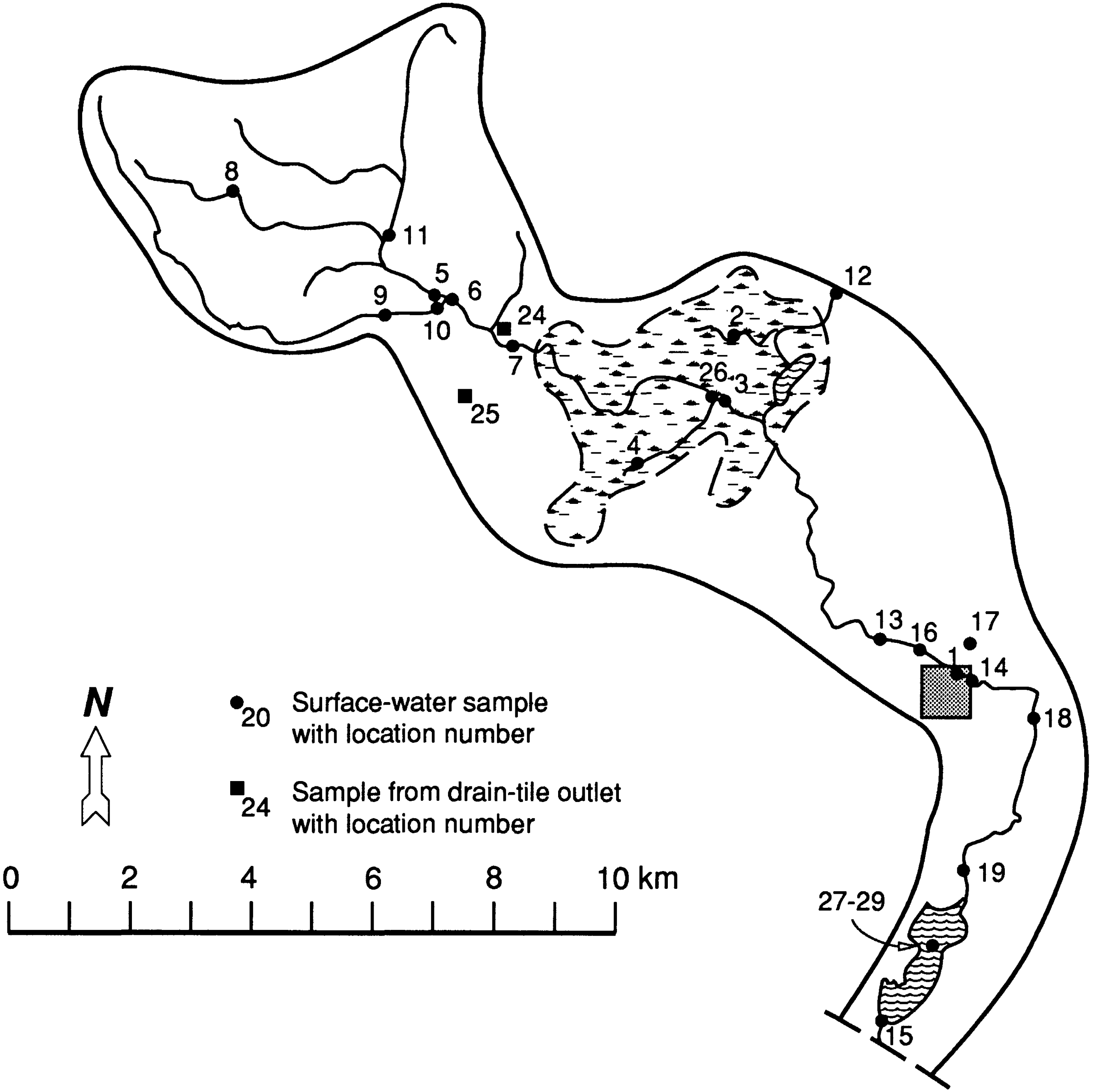

1/4" diameter stainless steel tubing
2" diameter PVC casing
sample port #1
water table
#2
0.5 meters
#3
#4
#5
#6

Figure 3



8
11
5
6
9
10
24
7
25
12
2
26
3
4
13
16
17
1
14
18
19
27-29
15
N
●20 Surface-water sample with location number
■24 Sample from drain-tile outlet with location number
0
2
4
6
8
10 km

Figure 4

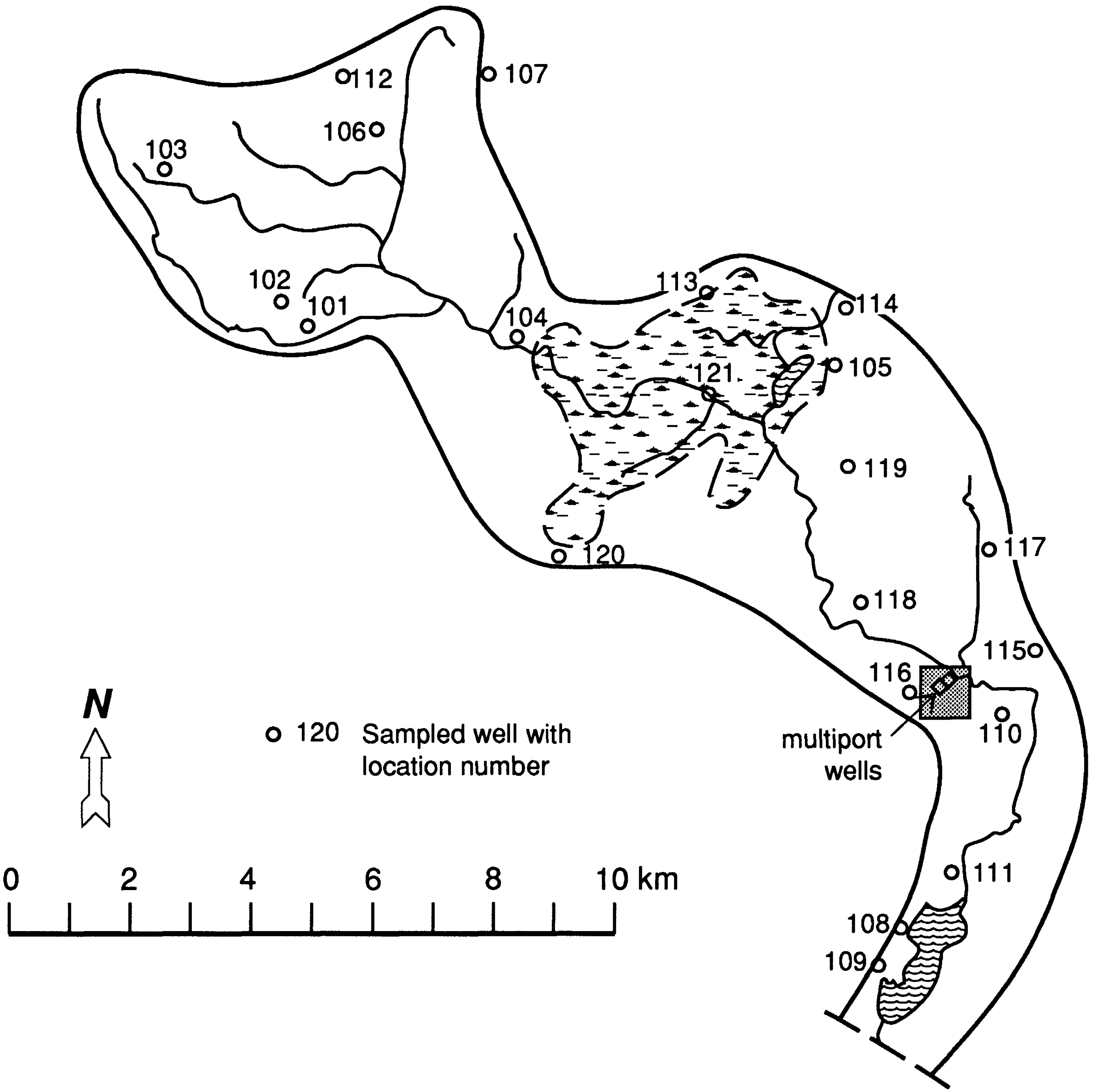

112
107
103
106
102
101
104
113
114
121
105
119
120
117
118
115
116
multiport wells
110
111
108
109
N
120 Sampled well with location number
0
2
4
6
8
10 km

Figure 5

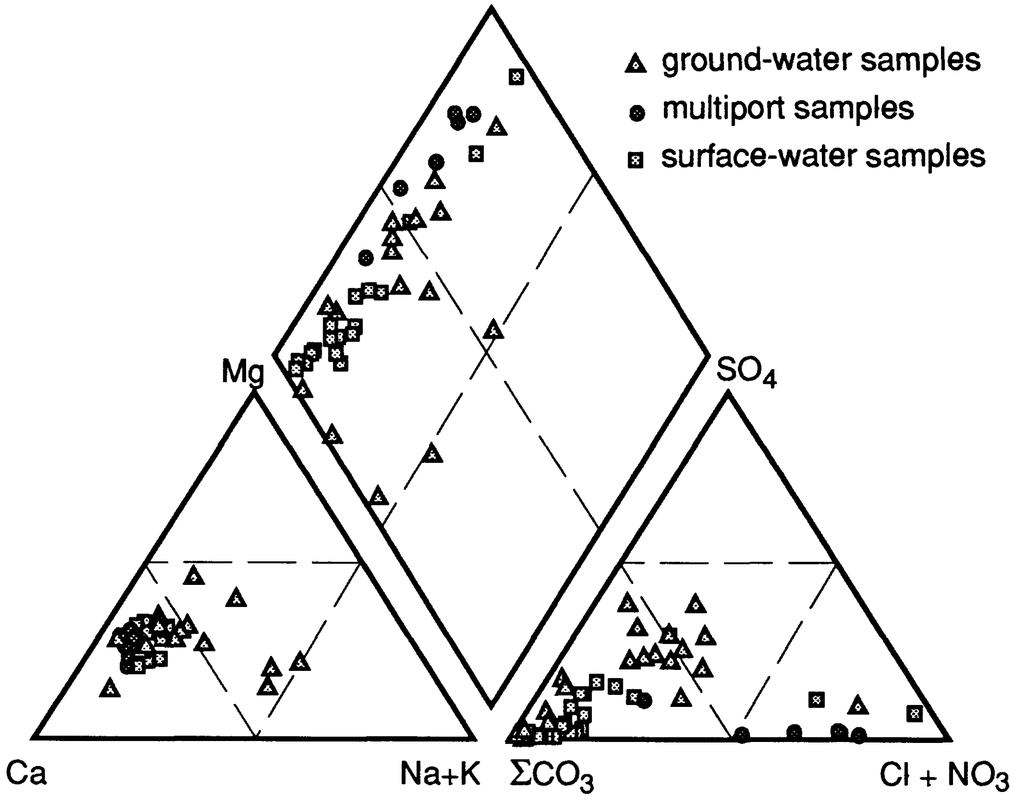
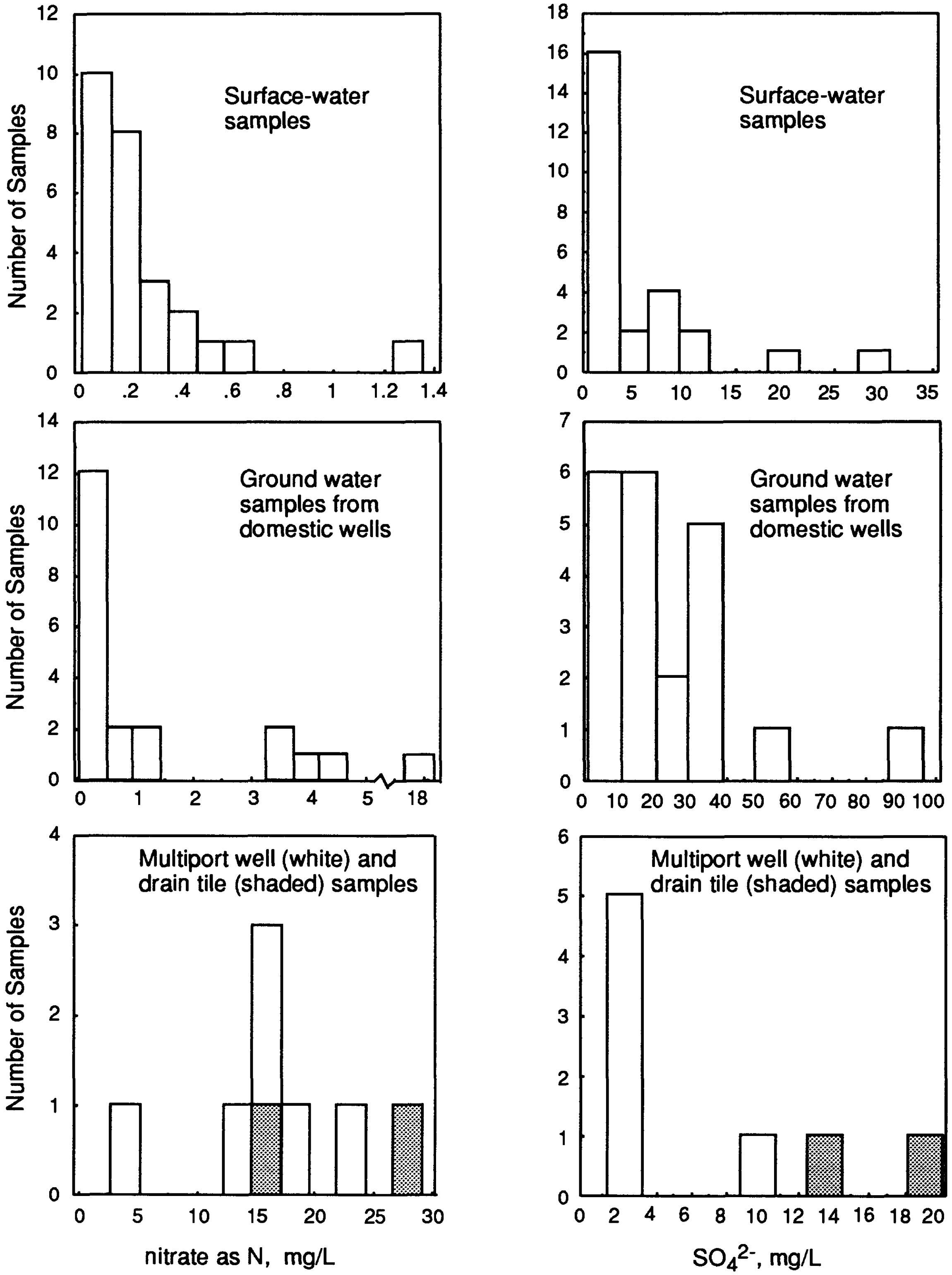

▲ ground-water samples
● multiport samples
▣ surface-water samples
Mg
SO4
Ca
Na+K
ΣCO3
Cl + NO3

Figure 6


Surface-water samples
Ground water samples from domestic wells
Multiport well (white) and drain tile (shaded) samples
Number of Samples
0
2
4
6
8
10
12
14
0
.2
.4
.6
.8
1
1.2
1.4
0
1
2
3
4
5
18
0
5
10
15
20
25
30
nitrate as N, mg/L
0
2
4
6
8
10
12
14
16
18
0
1
2
3
4
5
6
7
0
5
10
15
20
25
30
35
0
10
20
30
40
50
60
70
80
90
100
0
2
4
6
8
10
12
14
16
18
20
SO4 2-, mg/L