

Use of a Borehole Color Video Camera to Identify Lithologies, Fractures, and Borehole Conditions in Bedrock Wells in the Mirror Lake Area, Grafton County, New Hampshire

By Carole D. Johnson¹

Abstract

A submersible color camera was used to describe bedrock lithologies and fractures in boreholes at the U.S. Geological Survey fractured-rock research site near Mirror Lake, Grafton County, New Hampshire. From June through August 1992, video surveys were completed in 29 bedrock wells that ranged in depth from 60 to 230 meters. Use of the submersible camera was prompted by a need to verify and provide additional descriptions of rock types identified in the wells. In two of the wells from which bedrock core was collected, video images together with drill cuttings were used to determine lithologies. These lithologies corresponded to lithologies determined directly from bedrock core samples collected from two wells. For wells from which core was not obtained, video images were used to improve the interpretations of the rock types that were based only on initial logs made at the time of drilling and later detailed examinations of drill cuttings. In addition, the images were used to inspect the conditions of the borehole walls for angularity, stability, or blockage.

INTRODUCTION

The Mirror Lake area is the site of a multidiscipline research effort to characterize fluid movement and chemical transport in fractured crystalline rock over a range of scales from meters to kilometers

(Shapiro and Hsieh, 1991). The bedrock domain in the Mirror Lake area is typical of New Hampshire and of most crystalline rock terranes associated with orogenic belts and, therefore, is structurally complex. The bedrock is predominantly sillimanite-grade pelitic schists and gneisses that have been intruded by anatectic granites, pegmatites, and basalts (Lyons and others, 1986). Fractures that have developed in response to tectonic stresses (Hardcastle, 1989) and sheeting fractures (Trainer and others, 1987) serve as conduits for fluid movement and chemical migration. The bedrock is overlain by 10 to 50 m of glacial deposits that cover approximately 97 percent of the bedrock surface. Therefore, the characterization of the rock types relies on subsurface exploratory drilling and other techniques. Twenty-nine bedrock wells, ranging in depth from 60 to 230 m, were drilled between 1979 and 1992 by use of the air percussion method. From June through August 1992, a color video camera was used to survey the wells and improve the interpretation of the subsurface. This paper describes the field procedure developed for identifying rock types, fractures and borehole conditions in the bedrock wells by use of a color video camera in the Mirror Lake area of New Hampshire.

DESCRIPTION OF EQUIPMENT

The equipment consists of a downhole camera and light source, an electrically powered winch, control unit, and video tape recorder (VTR) and monitor. The color video camera and light source are encased in a 9.2-cm-diameter housing, which is suspended from double steel-wrapped coaxial cable. On the land surface, a powered winch is used to raise and lower the camera in the borehole. A camera control unit encodes

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the depth of the camera; processes the analog image of the borehole; and provides downhole control of the light intensity, focus, and iris (or lens aperture), all of which enhance the video image. The processed image, including a superimposed digital depth readout, is sent to a VTR and a high-resolution monitor. This camera has two light attachments that allow for two different perspectives of the well: one looking down the well and the other looking at the side of the well. In order to view and adequately record the image, the VTR should have fast and slow forward and reverse speeds, freeze frame, four heads, and a real-time counter.

CAMERA-SURVEY TECHNIQUES

Two video surveys were completed in each of the 29 bedrock wells. For the first survey, the camera was set up to look down the borehole. From this perspective (fig. 1a), the borehole wall closest to the camera lens appears at the edge of the video image, and the bottom (the more distant views) of the well appears at the center. In the actual video image, however, the bottom of the well is blocked by the light attachment, which is supported by two rods. A planar feature (such as a fracture) that intersects the borehole at 90 degrees appears

as a circle, whereas a planar feature that intersects the borehole at less than 90 degrees appears as an ellipse. During the first survey, the occurrence of foliation, fractures, zones of borehole enlargement, and major changes in rock type and texture, were described. In addition, places to be closely viewed during the second survey were noted.

In the second survey, a light attachment that has a 360-degree rotational mirror tilted at 45 degrees to the camera lens to permit a side view of the borehole wall was used. A wide-angle lens directed downward toward the mirror allows a simultaneous view of the borehole wall adjacent to the mirror as well as a view down the well at the borehole below the mirror. The result is a composite image of the two views (fig. 1b). The mirror view appears at the center of the image. Surrounding the mirror view is the wide-angle view that looks beyond the edges of the mirror, and down the well, much like the perspective shown in figure 1a. This expanded view is useful when searching for individual fractures identified in the first survey or when tracing a fracture that is connected to or near other fractures. During the second survey, the rocks were viewed in greater detail than in the first survey, and more precise measurements of the locations and dips of major fractures were made.

BOREHOLE VIDEO IMAGES

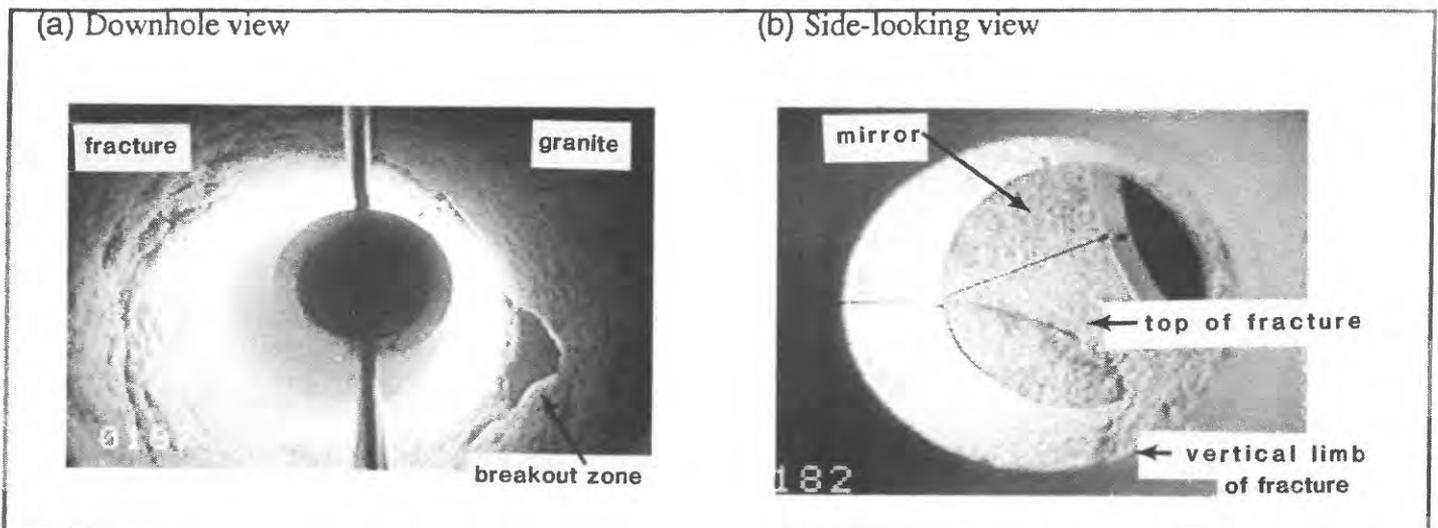


Figure 1. Example of borehole video images: (a) Downhole view of the well at a depth of 57 meters, showing a fracture in granite intersecting the well bore; (b) Side-looking mirror view superimposed on the downhole view at a depth of 55 meters.

IDENTIFICATION OF ROCK TYPES, FRACTURES, AND BOREHOLE CONDITIONS

Rock fragments and chips diverted up the hole by the force of the air and water from the drill rig were collected and described over 1.5-m-long intervals. Although mineralogy, texture, grain size, and color of the cuttings could be adequately described, identification of rock types was difficult. Rock chips measuring 1 to 2 mm in length are not always large enough to exhibit features of the source rock, such as foliation or banding. When rock chips from a short (1- to 1.5-m long) drilling interval include chips of granite and schist, it is impossible to determine from drill cuttings whether the well penetrated a schist xenolith in a granite, a granite dike in a schist host, or a contact between two rock types. Video surveys were completed in the 29 bedrock wells to positively identify the rock types. In two of the wells from which core was collected, lithologies compiled after examination of the drilling chips and borehole video surveys corresponded to the lithologies determined directly from 100 m of bedrock core. Thus, the video images provide a direct verification of fractures and the contacts between rock types. In addition, video images can be used to describe fracture zones that are missing or completely rubbed in the bedrock core. For wells from which core was not collected, video images were used to improve the interpretation of the rock types based only on drilling logs and drill cuttings. The video images were used to describe texture, grain-size, color, presence of fractures, foliation, folds, and faults, as well as the condition of the borehole. From the video images, the borehole wall could be identified as circular, extremely enlarged, or angular and jagged. The data from the video logs were used for assessing the stability and integrity of the borehole and for planning other tests, including the placement of packers for hydraulic or solute-transport tests.

ROCK TYPES

Four major rock types (schist, granite, pegmatite, and basalt) have been identified in the bedrock outcrops, drill cuttings and video images in the Mirror Lake area. Geologic names were not assigned to the rocks encountered in the boreholes, because of the localized nature of the sampling. However, in the following list, the schist and gneiss probably correspond to the metamorphic rocks of the Rangely Formation of

the Silurian age (Lyons and others, 1986). The granite is most likely anatectic, two-mica granite of the regional Concord Intrusive Suite of the Devonian age (Armstrong and Boudette, 1984; Lyons and others, 1986). These granites, derived from the melting of preexisting rocks, were injected into the overlying host rocks and commonly are found in sheetlike, tabular bodies. The basalt probably corresponds to the lamprophyric intrusions of Mid-Jurassic through Early Cretaceous age (McHone, 1984) and are found cross-cutting all other rock units.

Schists and gneisses.--Schists and gneisses are usually easy to identify by the foliated biotite, muscovite, and sillimanite. Some schist sections of the wells exhibit isoclinal folding, augens, banding, and (or) large felsic sections. Metasedimentary rocks typically are black, brown, green, yellow, or white. The coarse-grained biotites and muscovites reflect the light and appear bright and shiny, whereas fine-grained schists appear dark. In general, the schists and gneisses are much darker than the granites. The mirror attachment permitted a detailed view of some structural and stratigraphic features in the schists, such as the isoclinal fold in schistose bedding cored with a quartz layer, shown in figure 2.

BOREHOLE VIDEO IMAGE

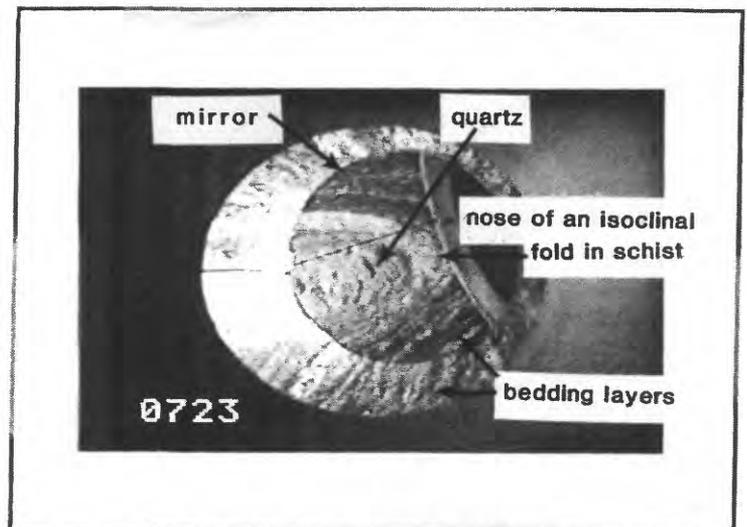


Figure 2. The nose of an isoclinal fold in schist seen using the side-looking mirror at a depth of 200 meters. Bedding layers can be traced around the nose of the fold and down the limbs of the fold.

Granite.--The granite is typically equigranular, medium-to-coarse grained, leucocratic, creamy white to gray with an occasional greenish tinge. Iron staining along fracture faces and within the rock matrix can be seen clearly in some of the video images. These rocks are usually medium grained and have a sugary texture. They occasionally exhibit weak foliation of biotites and muscovites, and sometimes contain strongly foliated biotite schlieren, which are oriented parallel to major structural features in the host rock (Armstrong and Boudette, 1984). These linear features are easily visible in the video image and can usually be differentiated from fractures. Local variations in granite composition, such as increased biotite or quartz content, appear as variations in shading along the borehole wall.

Pegmatites.--Pegmatites usually are the lightest and most reflective rocks in the boreholes. The contacts between the pegmatite and their host rocks were viewed with the mirror attachment. Some contacts were sharp and straight, whereas others were graded or wavy. Large individual crystals of muscovite, biotite, feldspar and quartz were observed and their lengths measured.

Basalt.--The darkest and least common rocks in the wells are the basalts. These rocks reflect little light because of their extremely fine-grained matrix and mafic-mineral content. However, felsic inclusions, including feldspar phenocrysts and cavity fillings, are highly reflective and discernible in the video image. Basalts crosscut both the granite and the schist, are present at a variety of depths and in a variety of widths, and range from subhorizontal to subvertical. Chill margins and vesicles were viewed with the mirror attachment.

FRACTURES

Fractures appeared in the video image as dark lines and were differentiated from other linear features by a change in relief or the continuity and smoothness of the wall. When the light source was below the fracture, the fracture was in shadow. In contrast, the borehole wall appeared smooth and continuous at other dark linear features, such as narrow basalt dikes and biotite schlieren. The borehole was significantly enlarged at some fractures. Other fractures had breakout zones only along part of the fracture, as shown in figure 1a.

During the first survey, fractures were described as being either single fractures or as fracture zones (multiple fractures that occur over a short distance). In addition, the intersection of the fracture along the entire borehole or only part of the borehole was noted. In the second survey, the fractures were further described as being horizontal, moderately dipping, or steeply dipping. Fracture apertures were only qualitatively described as being very tight, narrow, or wide, or a fracture zone with breakout. No attempt was made to measure the fracture width. Fractures were also described for the occurrence of mineralization or mineral coatings, including iron (with some migration into the rock matrix), grayish white clay, white calcite, and light white to brownish yellow quartz. Black manganese coatings were impossible to differentiate from dark minerals.

BOREHOLE CONDITIONS

In addition to providing rock type and fracture information, the video images were used to determine borehole conditions, including roughness and angularity of borehole walls, fractures with broken-out zones or borehole enlargement, alteration of the rock mass, scoring or rifling caused by drilling, blockage of the drill hole, and possible zones of falling rocks. The borehole shown in figure 3 is no longer circular,

BOREHOLE VIDEO IMAGE

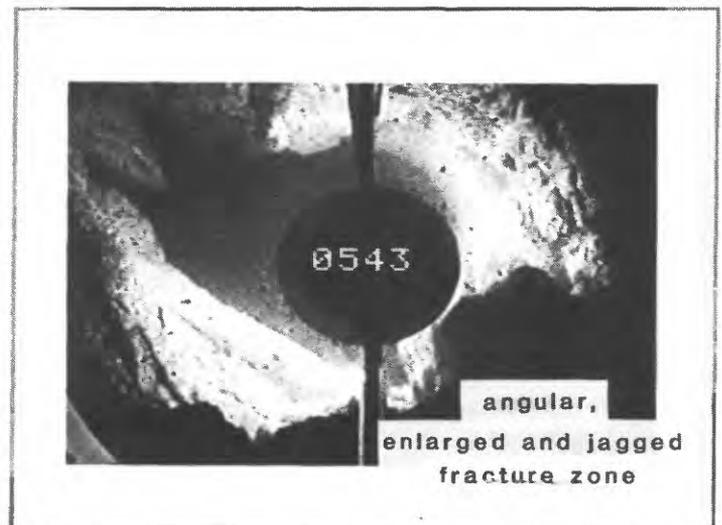


Figure 3. Downhole view of an enlarged and jagged breakout zone at a fracture zone at a depth of 165 meters, whereupon the well caved in.

but is now angular, jagged, and enlarged at this fracture zone. This well was originally drilled 30 m deeper than shown, but it caved in at this fracture zone. Enlarged and angular sections of the borehole that were identified in the video surveys were avoided when placing packers for hydraulic testing, tracer tests, and long-term water-level monitoring. Information on the condition of the borehole can be used to explain the results of other borehole tests.

SUMMARY AND CONCLUSIONS

Video cameras are effective tools for identifying rock types, fractures, foliation, folds and enlarged zones in the boreholes. Interpretations of rock types using video logs and drill cuttings agreed with interpretations of the core. In contrast, rock types could not always be determined from analysis of drill cuttings. The video images provided information about the distribution of rock types and the extent of the fractures that was not available from previously collected data, including data obtained by conventional drilling and borehole geophysical methods. Based on these merits, video cameras are a practical method for obtaining borehole data. The interpretation of the rock types from the video surveys will be used to calibrate borehole geophysical signals.

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Fracture Detection in Crystalline Rocks, Mirror Lake Area, Grafton County, New Hampshire

By F.P. Haeni¹, John W. Lane, Jr.¹, C.C. Barton², and David A. Lieblich¹

Abstract

Six surface-geophysical methods were used to detect saturated fractures in the upper 60 m (meters) of bedrock at the U.S. Geological Survey's fractured-rock research site in the Mirror Lake area, Grafton County, New Hampshire. Crystalline bedrock, consisting of foliated schists intruded by granite, pegmatite, and gabbro, underlies 3 to 10 m of glacial drift throughout the study area. Surface-geophysical methods included azimuthal seismic refraction, azimuthal Schlumberger direct-current- (DC) resistivity, square-array DC-resistivity, inductive-terrain conductivity, very-low-frequency (VLF) terrain resistivity, and ground-penetrating radar (GPR).

Azimuthal seismic-refraction and DC-resistivity methods measured directionally dependent physical properties of the crystalline rock at the Camp Osceola well field and in a ballfield 75 m southeast of Mirror Lake. The interpretation of the seismic-refraction P-wave data is that the primary fracture strike is 022.5° (degrees) with a secondary strike at 127° . The orientation of the anisotropy and probably the fractures, as determined from a quantitative interpretation of the original P-wave data, is 037° . The interpretation of the DC-resistivity data is that the primary fracture strike is 030° with a secondary strike at 150° . Inductive-terrain conductivity and VLF-terrain resistivity data show very small anomalies that have been interpreted as possible fractures or fracture zones having a strike of 045° . Processed

GPR data were used to determine the depth to bedrock and to locate numerous subhorizontal reflectors, which are interpreted to be fractures, fracture zones, and (or) foliation in the bedrock.

The strike interpreted from the surface-geophysical data correlates with the strike determined from bedrock outcrops, which are located 150 m from the Camp Osceola well field along Interstate 93. The outcrop data indicate a fracture-strike frequency maximum at 030° and a secondary maximum at 000° . Fracture dips range from 20° to 90° .

INTRODUCTION

The U.S. Geological Survey established a fractured-rock research site in the Mirror Lake area, Grafton County, New Hampshire (fig. 1) for the purpose of conducting multidisciplinary research on the flow of contaminants in fractured bedrock. As part of the study, surface-geophysical surveys to detect bedrock fractures and detailed mapping of bedrock outcrops have been conducted. This paper presents the results of surface-geophysical surveys and the mapping of fractures in bedrock outcrops in the Mirror Lake area.

Surface-geophysical methods have been used previously in a number of studies to detect saturated fractures in bedrock (Haeni and others, 1993; Lewis and Haeni, 1987). In most of these studies, a single geophysical method was used to define the predominant strike of steeply dipping fractures. The methods most commonly used were seismic refraction or direct-current- (DC) resistivity arrays rotated about a fixed centerpoint in order to measure azimuthal changes in the physical properties of the rock.

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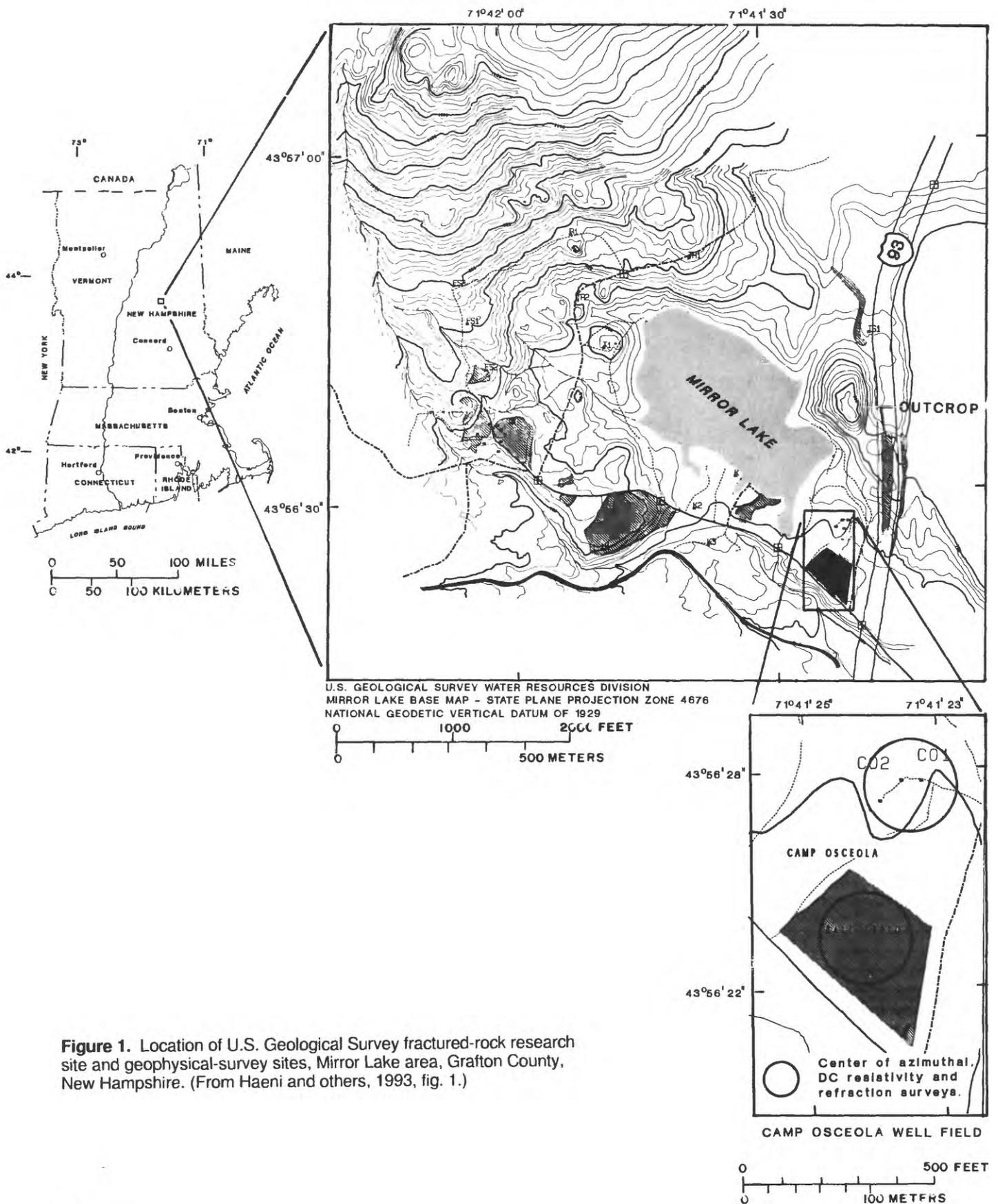


Figure 1. Location of U.S. Geological Survey fractured-rock research site and geophysical-survey sites, Mirror Lake area, Grafton County, New Hampshire. (From Haeni and others, 1993, fig. 1.)

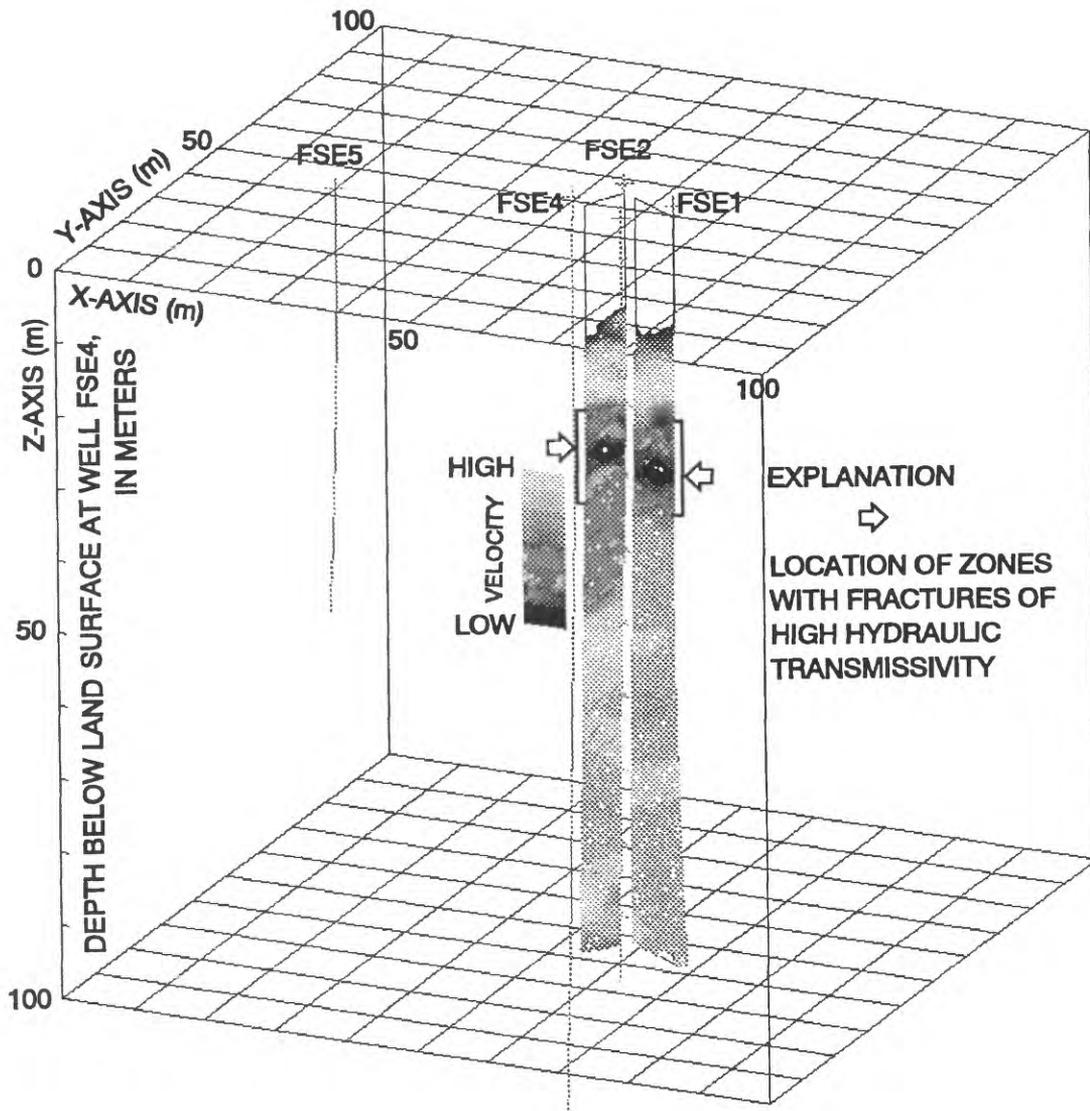


Figure 3. A pair of velocity tomograms in well pairs FSE1-FSE2 and FSE2-FSE4. The arrows indicate a zone that is known to have fractures with high hydraulic transmissivity. The large cube is 100 meters on a side and the grid is at 10 meter intervals. The gray scale goes from dark (low velocity) to light (high velocity).

has noted that large fracture apertures as measured with the acoustic televiewer do not always have high hydraulic transmissivity. Despite these complications, however, tomograms imaging rock electrical properties between wells at Mirror Lake do correlate with zones containing fractures of high hydraulic transmissivity.

Figure 3 shows a pair of velocity tomograms between well pairs FSE1-FSE2, and FSE2-FSE4 that

successfully image zones of fractures known to have high hydraulic transmissivity. These well pairs are at right angles to each other, so the view is into the tomograms as if looking into the pages of a half-opened book. The large cube is 100 m on a side, and the grid intervals are 10 m. The velocity gray-scale runs from dark (slow) to light (fast). The terms "slow" and "fast" are relative to the global average velocity in the tomogram. The actual values are not very important to the

EXPLANATION
 Possibly permeable ———
 Probably permeable ———
 Water Producing ———

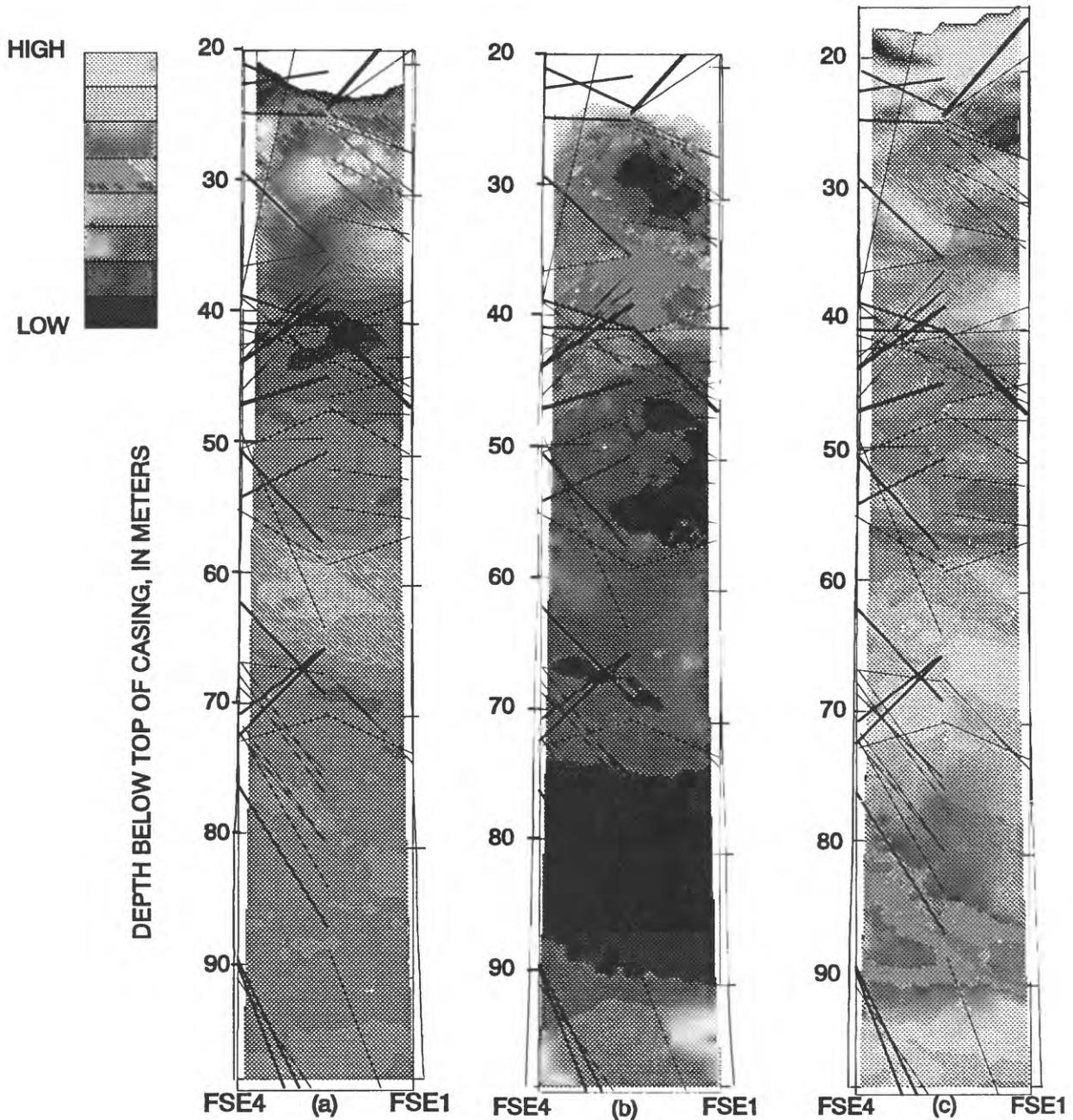


Figure 4. Three tomograms produced from the same data set between wells FSE4 (left) and FSE1 (right): (a) a velocity tomogram, (b) an attenuation tomogram, and (c) a dispersion tomogram. For this case it appears that (a) correlates best with the fractures that have high hydraulic transmissivity (marked with arrows). In each tomogram the gray scale is from dark (low) to light (high).

question of whether the tomograms visually image fracture zones. The arrows indicate the location of a zone that contains hydraulically permeable fractures (Paillet, 1991).

Figure 4 shows three tomograms produced from the same data set taken between wells FSE4 (left side of each panel) and FSE1 (right side). Figure 4a is a velocity tomogram formed from first arrival time picks, figure 4b is an attenuation tomogram formed from amplitude measurements, and figure 4c is a dispersion tomogram formed from pulse-width measurements. Superimposed on the tomograms are projections of fractures determined from acoustic televiewer logs of holes FSE4 and FSE1 (Paillet, 1991; Wright and others, 1996). The fractures seen in well FSE1 were projected in the plane defined by the FSE4-1 pair half way to well FSE4 and the fractures in well FSE4 were projected half way to well FSE1. The overlays are inexact because the tomograms include the effects of well deviation, and are therefore wider at the bottom than at the top, whereas the fracture projections neglect well deviation. Approximately 0.5 meter zones along each well have been excluded from each tomogram because calculated values immediately adjacent to the wells are not considered reliable. The gray scale runs from low to high in each tomogram. The actual calculated values for velocity, attenuation, or dispersion are not particularly important for the purpose of identifying visual correlations with fractures and thus have been omitted. According to Paillet, the projection angles are subject to errors of a few degrees, and it appears that relatively few fractures project very far in the FSE well field. Thus, the indicated projections are not definitive, but comparisons of projected fractures to the tomograms is of considerable interest. When well FSE4 is pumped and a flowmeter is used to find fractures that carry significant flow, it is determined that there are two fractures in well FSE1 and two in well FSE4 that have much higher hydraulic transmissivity than any other fractures. The projections of these fractures are denoted by the heaviest lines. The two fractures intersecting well FSE4 that have the highest transmissivity are in the 39 to 47-m deep zone. Of these, 80 percent of the water flows through the upper fracture. Consider the zone from 39 to 47 m deep in the tomograms. In this zone, the velocity tomogram (fig. 4a) seems to be responding to the presence of the fractures. Presumably there is more water in this zone than in adjacent zones. The attenuation tomogram (fig. 4b) shows an increase in attenuation in

this zone compared to the attenuation in the area below, but the local attenuation maximum is several meters above this zone. The dispersion tomogram has only subtle features in the region of the high-transmissivity fracture projections, but strong sharp features in other regions may correlate with other fractures.

CONCLUSIONS

Electromagnetic tomograms map changes in electrical properties. The presence of water-filled fractures will alter the local electrical properties, but so will lithologic differences. The tomograms presented here show correlation with some projected fractures but not others. In addition, the presence of water-filled fractures does not, in itself, produce high hydraulic transmissivity. Consequently, we believe that cross-borehole tomography will be a valuable tool for characterizing and mapping fractures, but must be used in conjunction with other geophysical measurements to achieve its full potential. We also conclude that more than one type of tomographic processing might be needed if we are to improve the ability to separate the effects of lithology from those caused by the presence of water-filled fractures.

ACKNOWLEDGMENT

We acknowledge F.L. Paillet for providing fracture projections from wells FSE1 and FSE4 and for providing digital data for fractures mapped with the acoustic televiewer in all of the FSE wells.

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Electromagnetic and Seismic Tomography Compared to Borehole Acoustic Televiwer and Flowmeter Logs for Subsurface Fracture Mapping at the Mirror Lake Site, New Hampshire

By David L. Wright¹, Gary R. Olhoeft¹, Paul A. Hsieh², Ernest L. Majer³, Frederick L. Paillet¹, and John W. Lane Jr.⁴

Abstract

Among the techniques used in research at the Mirror Lake site, Grafton County, New Hampshire, are electromagnetic (EM) and seismic tomography, borehole radar, borehole acoustic televiwer, and borehole flowmeter. Of these techniques, tomography and radar can probe several tens of meters between or around boreholes at that site with resolutions in the order of 1 meter, whereas televiwer data provides great detail at the borehole wall but little penetration. Flowmeter data, along with hydraulic tests and tracer tests provide information on hydraulic connectivity, but hydraulic paths between the wells can not be inferred from these data alone. We find from side-by-side comparison of electromagnetic and seismic tomograms of rock properties between wells FSE1 and FSE4 that both types of tomograms show the presence of fractures of high hydraulic transmissivity. We present velocity tomograms for two EM systems and one seismic system, attenuation tomograms for the two EM systems, and projections of fractures derived from acoustic televiwer logs. The pulsed transmitters used in the EM tomography at Mirror Lake produced wavelengths in the granite of about 2 m. The

seismic system produced wavelengths of about 1 m. Seismic and EM tomography can detect the presence of fractures whose aperture is much smaller than a wavelength but can not resolve fractures whose spacing is much less than the wavelength. Resolution—the ability to distinguish two nearby objects from one another—is determined by a number of factors, including spatial data density, but resolution usually can not be better than about half the wavelength used for probing regardless of whether the method is EM or seismic. It is possible to achieve some resolution improvement in low-attenuation environments, but a needed step to achieve maximum benefit from tomography is correlation of the tomograms with other hydrologic and geophysical information. Tomography is an art that is not fully mature but can be expected to improve in the future.

INTRODUCTION

Data have been recorded between 15 pairs of wells in the FSE field (fig. 1) with the radar/tomography borehole system developed by the U.S. Geological Survey (USGS) (Wright and others, this proceedings), and 18 pairs have been examined with a hole-to-hole seismic tomography system developed by Lawrence Berkeley National Laboratory. In addition, one pair of wells was studied tomographically using equipment leased from ABEM, a Swedish company. Because it was of some interest to compare results from three systems, all three were run

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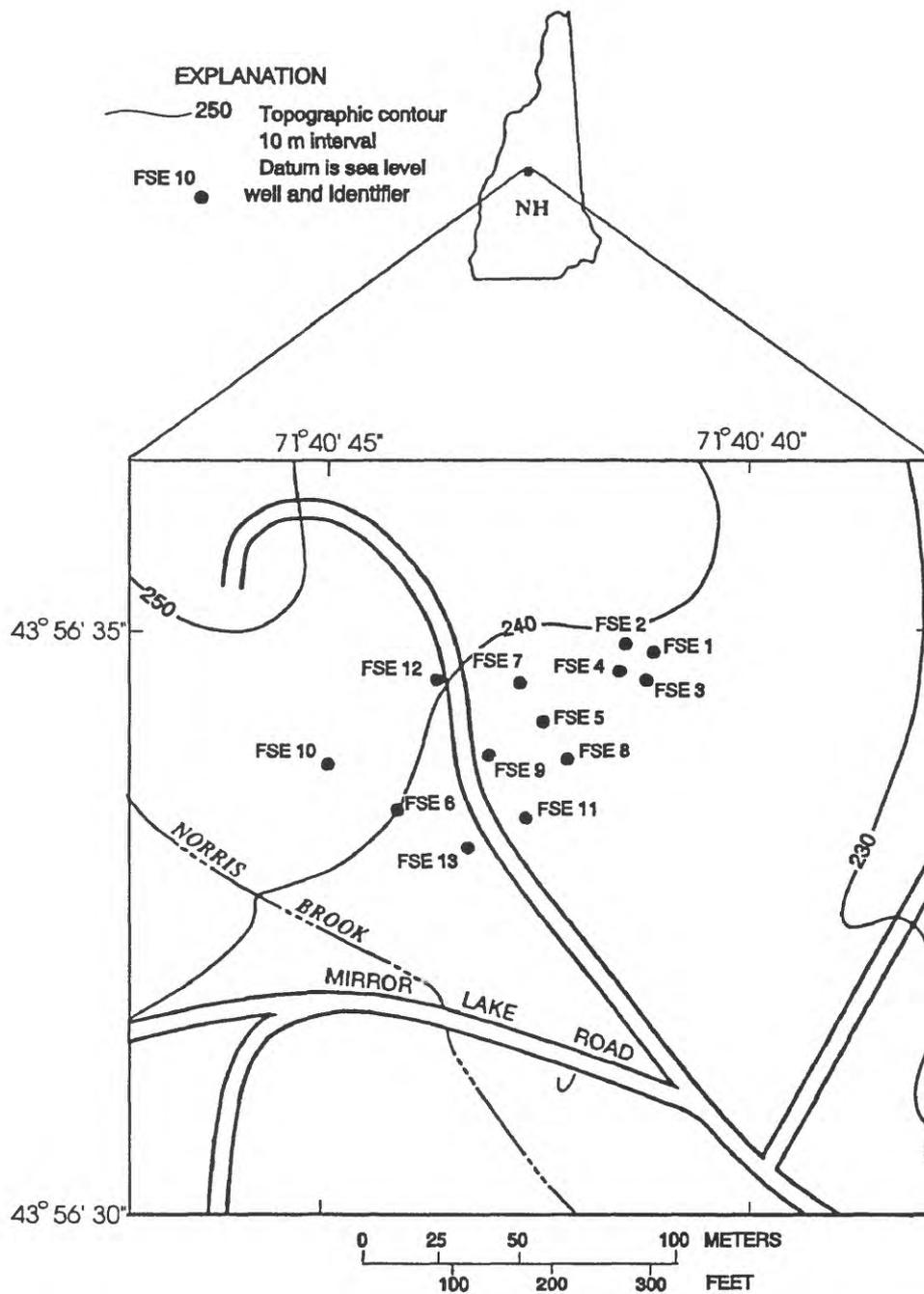


Figure 1. Location of the FSE well field at the Mirror Lake site in central New Hampshire. The geohydrologic setting of this area is given in Winter, 1984.

in the well pair FSE4-FSE1. This afforded a rare opportunity to see results in the same pair of wells that were obtained by different systems and processed by three independent groups by means of three different sets of software. Results of the borehole acoustic televiewer, flowmeter, and packer tests, which indicated the presence of the high-transmissivity fractures, were compared to the tomograms. The tomographic studies

at Mirror Lake are intended to aid hydrologists in the development of adequate 3-dimensional fracture-flow models, suggest other hydrologic applications of tomography, indicate limitations for applications of tomography in its present state in fractured crystalline rock, and identify directions in which the state-of-the-art could be enhanced for toxic-substances hydrologic studies.

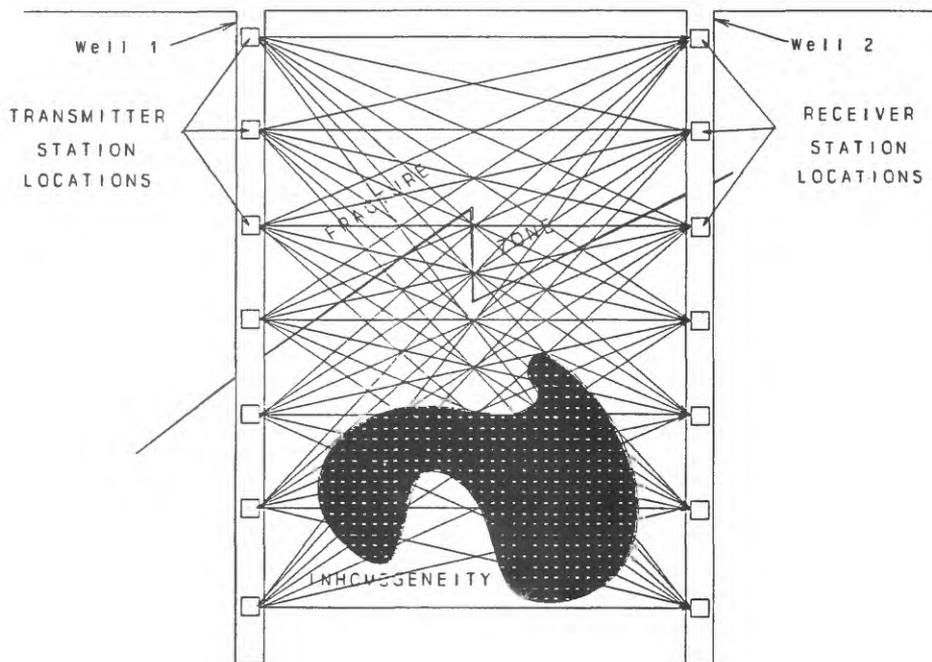


Figure 2. Generic tomography schematic for electromagnetic or seismic tomography. The number, spacing, and relative locations of the transmitter and receiver stations may vary.

BASICS OF TOMOGRAPHY

Tomography between boreholes is conceptually and mathematically similar to what is done when a medical computer-aided-tomography (CAT) scan is made, but the distances covered in borehole applications are much greater, the angular coverage is incomplete, and the resolution is much lower. The method of collecting data from boreholes is to record a number of measurements with a transmitter and receiver or string of receivers at various locations so that a number of raypaths pass through any particular volume of rock (fig. 2). For any given raypath, an average number for velocity, amplitude, or some other quantity is measured. If a water-filled fracture zone is present, it would be expected, for example, that the velocity would be lower for both electromagnetic (EM) and seismic waves than it would be in unfractured rock. Mathematical algorithms are applied to calculate an array of values for the mapped quantity at particular locations in the rock. The region between two boreholes is gridded, and calculated values are assigned to each area element, commonly referred to as a pixel. Frequently a smoothing algorithm is applied to visually enhance the display. The display

can be presented by using a color scale, a gray scale as in figures 3 and 4, contouring, or some combination of methods. Many algorithms are used for producing tomograms. Each has strengths and weaknesses. Much of the literature on tomography is dominated or motivated by medical applications (Herman, 1980). Applications of tomography to geophysics has grown rapidly, however, and there is now a substantial and growing literature applicable to geophysics (Dines and Lytle, 1979; Natterer, 1986; Kak and Slaney, 1988). There is still much art involved in producing tomograms. A "good" tomogram will be well constrained by the data from which it is derived and will visually reveal features of interest to the hydrologist, geologist, or geophysicist. Things that might be of great interest to the geologist, such as lithology, may be of less interest to the hydrologist who wants to know where the fractures are between wells and which fractures are hydraulically connected, and to quantify the hydraulic conductivity. A good tomogram from the hard-rock fracture-flow hydrologist's point of view will need to help answer those questions.

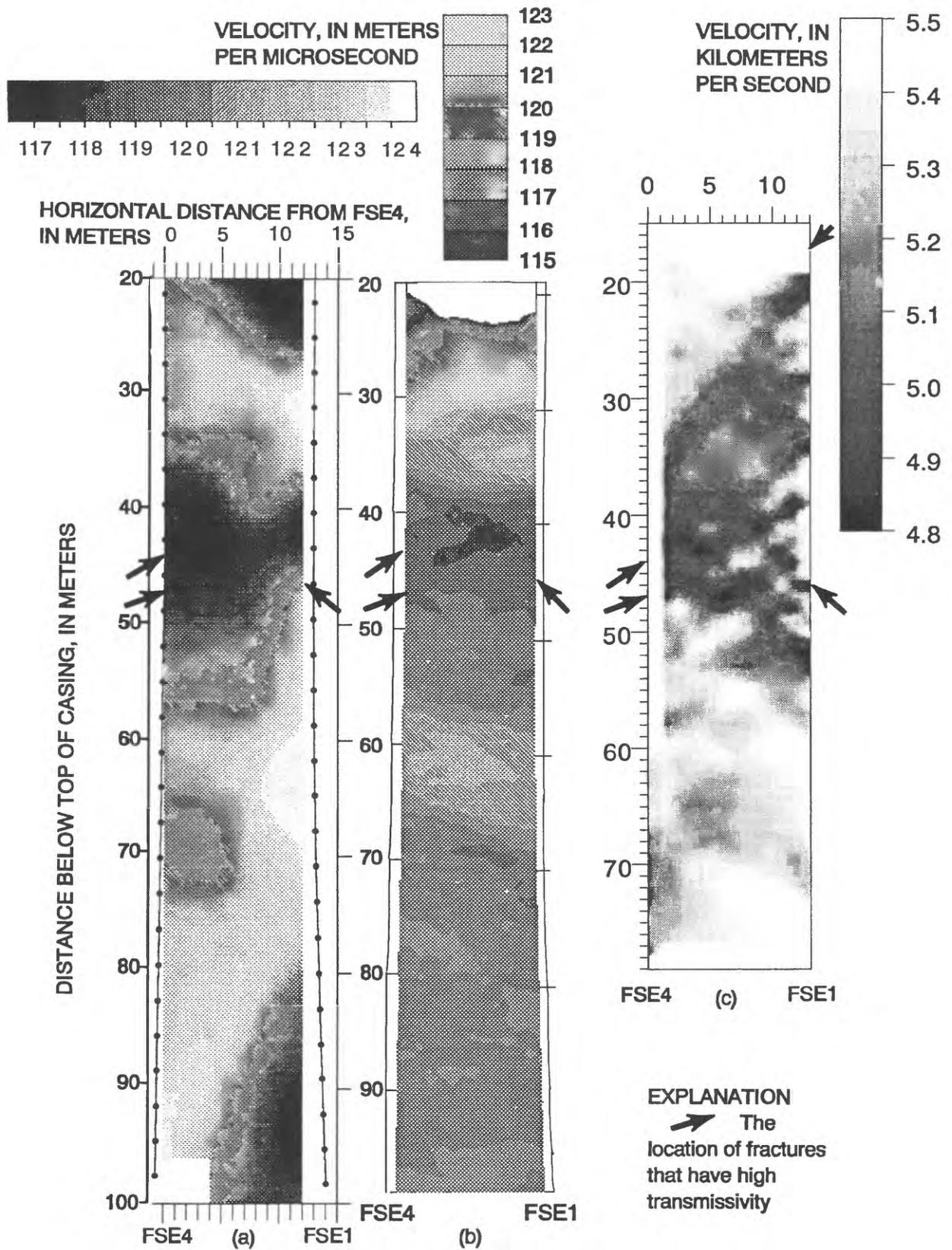


Figure 3. Electromagnetic velocity tomogram produced with the ABEM system (a), electromagnetic velocity tomogram produced with USGS system (b), seismic velocity tomogram produced with the Lawrence Berkeley National Laboratory system (c).

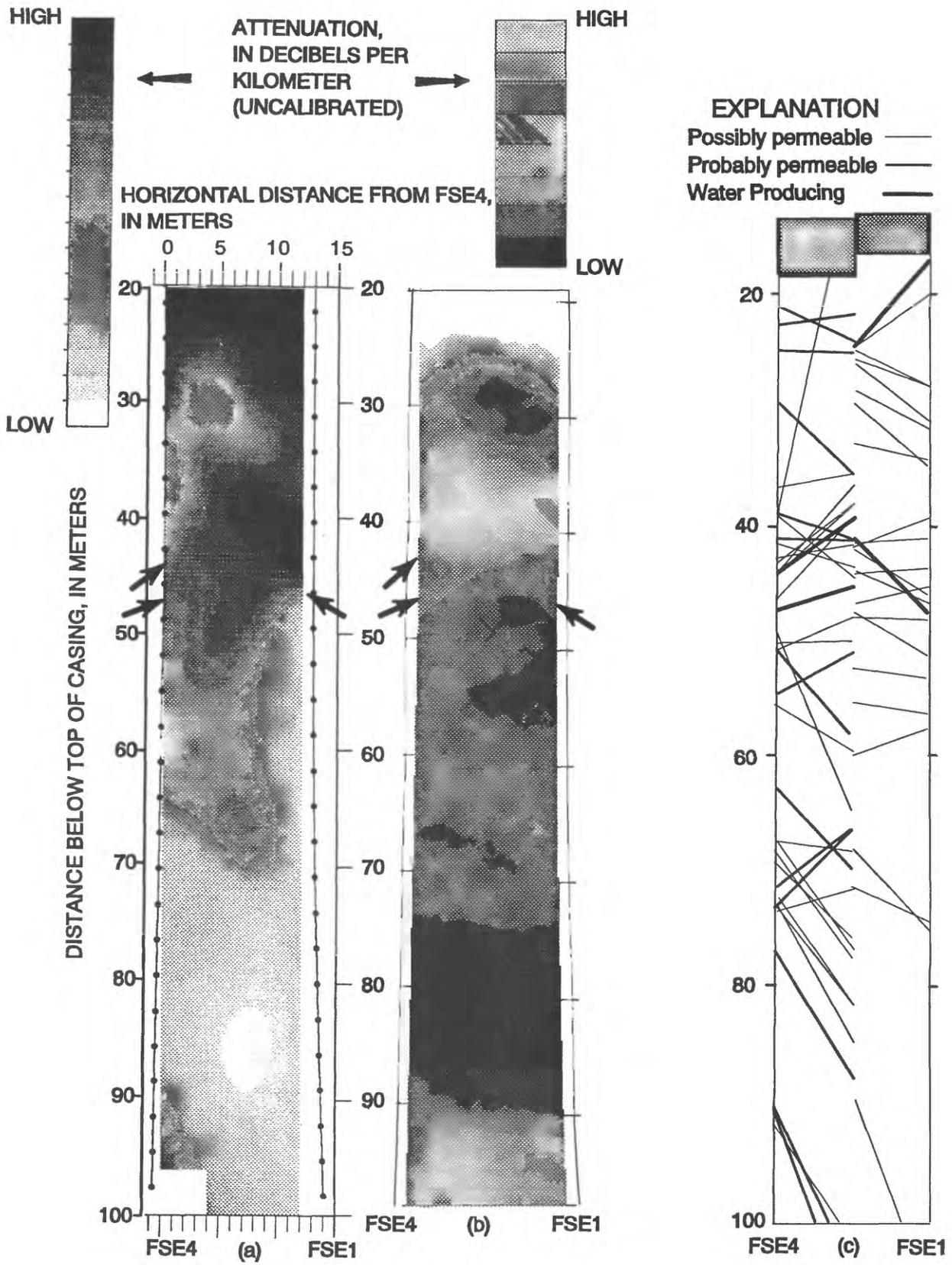


Figure 4. Electromagnetic attenuation tomogram produced with the ABEM system (a), electromagnetic attenuation tomogram produced with the U.S. Geological Survey system (b), fracture projections produced from the acoustic televiewer logs (c). The fractures with high hydraulic transmissivity are indicated with heavy lines.

EQUIPMENT AND MEASUREMENT METHODS

The ABEM radar system transmitter used in this study radiates a short pulse whose amplitude spectrum peaks at about 60 MHz. The transmitter was in well FSE1 and the receiver was in well FSE4. Data were recorded with the transmitter and receiver stationary at 3-m intervals.

In the case of the USGS radar, the 60-MHz transmitter (not identical to the ABEM transmitter) was in well FSE4 and the receiver was in well FSE1. Theoretically, the same system should produce identical tomograms, no matter which hole the transmitter was in, provided all other factors are equal. The method of data recording and processing did differ from those employed using the Swedish system, however. With the USGS system, the boreholes are logged with the probes moving at about 12 cm/s (25 ft/min) at constant depth offsets from one another. An exceptionally high-speed data acquisition system designed and built by the USGS (Wright and others, 1989) allowed averaging 512 waveforms for signal-to-noise improvement while recording the averaged data every 17 cm. Because half the data were used in producing the tomograms, the effective data interval was about 35 cm. Five different offsets were used. The maximum offset used was ± 10 m, so the steepest angle was about $\pm 38^\circ$.

The seismic equipment was developed and fabricated by scientists at the Lawrence Berkeley National Laboratory (LBL). The equipment consists of a seismic source, a receiver string, and a data-recording system. For the 1991 survey from which the displayed tomogram is derived, the seismic source consisted of a high-voltage, high-fidelity amplifier which delivers electrical pulses of 5 kV amplitude and 20 ms width through a coaxial cable to a downhole piezoelectric source. In this pulse mode, the generated seismic signal has a dominant frequency content in the 5 to 8 kHz range. For a seismic velocity of 5,000 m/s, the wavelength is approximately 1 m. Both the source and receiver stations were at 1-m intervals. The data-recording system consists of a computer with 16-bit analog-to-digital converter.

All three systems record the full waveform, so that any refinements in picking and processing could be applied to the original data in the future. All three systems also provide real-time computer-screen displays of the recorded waveforms so that the system operator can instantly detect gross system malfunction and have some assurance of the integrity of the recorded data without requiring playback or analysis.

One experimental factor should be mentioned that has been a problem for the radar systems, however. If the time base drifts, it will induce errors in the data. It is known that both the USGS and the ABEM systems sometimes have exhibited drift. For the 1992 field season, a new experimental procedure was used with the USGS system to allow detection, measurement, and correction for time-base drift, should it occur. The USGS data processing also includes a unique consistency test of the data quality (Olhoeft, 1988).

TOMOGRAMS AND FRACTURE PROJECTIONS AT THE FSE4-FSE1 WELL PAIR

Figure 3 is a side-by-side display of three velocity tomograms between well FSE4 (left side) and well FSE1 (right side). The gray scale renditions printed here are inferior in detail; color displays are commonly superior. Figure 3a shows a velocity tomogram produced from data acquired using the ABEM system. The tomogram was produced using proprietary ABEM software. The algorithm used by ABEM is of the conjugate gradient type. All of the possible raypaths were used in producing the ABEM tomogram. Because some of the rays that are produced by connecting every measurement station in well FSE4 to every station in well FSE1 are nearly vertical, the angular coverage is very good for this tomogram. Figure 3b shows a velocity tomogram produced from data recorded with the USGS system and processed with software written by the USGS (Olhoeft, 1988). The tomogram was produced using a variational filtered back-projection algorithm. Figure 3c was produced from data acquired with the LBL borehole seismic system. The manually picked first arrival time data were processed using an algebraic reconstruction technique (Peterson and others, 1985).

An attenuation tomogram produced with the ABEM system and software is shown in figure 4a. An attenuation tomogram produced with the USGS system and software is shown in figure 4b. The attenuation scales in figures 4a and 4b are not calibrated, but the relative values are sufficient for purposes of visual comparison. Figure 4c is produced by projecting fractures recorded with the acoustic televiewer from wells FSE4 and FSE1 (Paillet and others, 1987, Paillet and Kepucu, 1989, Paillet, 1991, Paillet, 1996). The fractures recorded in well FSE4 are projected in the plane of the wells from FSE4 half way to FSE1 and similarly for the fractures recorded in well FSE1. The projections are subject to errors of a few degrees, and the projections and other evidence

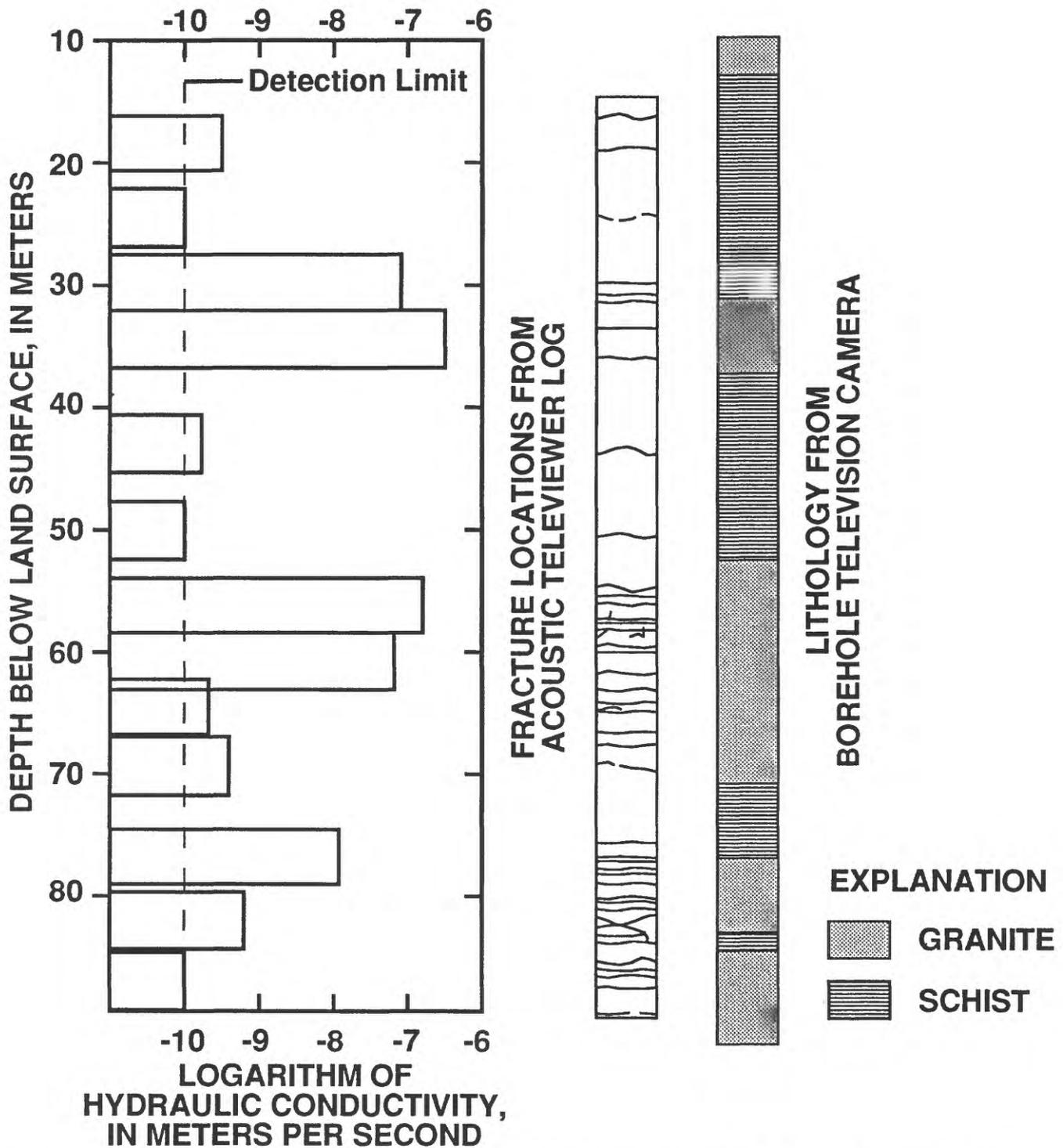


Figure 2. Hydraulic conductivity, acoustic televiewer and lithologic logs for borehole H-1 in the Mirror Lake watershed, Grafton County, New Hampshire.

borehole and then diffusing into the formation. Consequently, it is necessary to design a controlled environment for injecting traced fluid into bedrock formations for the purposes of conducting controlled-tracer tests.

A straddle-packer assembly is commonly used to isolate a permeable section of a bedrock well for hydraulic testing or the injection of traced fluids. A straddle-packer assembly consists of two packers, each with a flexible bladder that can be enlarged by

mechanical or pneumatic means to seal against the borehole wall. The interval between two packers is hydraulically isolated from the remainder of the borehole. A traced fluid can be injected into the straddled interval, and then the straddled interval can be flushed with tracer-free water. This procedure, however, does not guarantee that all of the traced fluid will be forced into the formation. Because of density differences between the ambient fluid and the traced fluid, or incomplete flushing in the straddled interval, some of the tracer can reside in the straddled section of the borehole and diffuse into the formation over time. This will affect the character of the temporal or spatial distribution of the tracer concentration in the formation and could result in erroneous interpretations of formation properties. Reducing the length of the straddled interval such that only the fracture is hydraulically isolated would eliminate this problem. However, it is difficult to reduce the distance between packers to less than 0.5 m, which could still cause problems in identifying the explicit temporal variation of the tracer concentration as it is introduced into the formation.

NEW TRACER INJECTION METHOD

To provide for the controlled injection of traced fluids into permeable sections of bedrock wells in crystalline rock, a new tracer injection system has been designed to seal off the permeable fractures intersecting the borehole between the straddle packers. The equipment is schematically depicted in Figure 3a. The equipment consists of 3 packers (labeled A, B, and C), and two valves controlling the "injection" and a "return" tubing.

The packers labeled A and C are inflated prior to the start of the hydraulic test to hydraulically isolate a section of the borehole where there is a permeable fracture (fig. 3b). Packer B is positioned so that it will block off the permeable fracture or fractures in the interval straddled by the top (A) and bottom (C) packers when it is inflated. Thus, relatively smooth borehole walls and only one or two closely spaced permeable fractures in the injection interval are required. These conditions are most likely to be encountered in crystalline rock.

Information on fracture location and hydraulic conductivity must be obtained prior to conducting the tracer test. For example, the location of fractures can be identified using a combination of borehole

geophysical logging tools such as the acoustic televiewer and caliper logs (Paillet, 1991) and a borehole television camera. The permeable sections of the borehole can be identified by using a flow meter while pumping water from the open borehole to identify locations where fluid enters the borehole from the formation (Hess, 1986). More exact measurements of hydraulic conductivity can be made using injection tests, similar to those described in the previous section (the results of which are shown in fig. 2).

Prior to starting the tracer test, the middle packer is inflated to block off the permeable fracture in the straddled interval (fig. 3c). A tracer solution is then prepared at land surface. The concentration of this tracer solution should be sufficient to achieve the desired injection concentration when it is mixed with the volume of tracer-free water residing between packers A and C. The injection and return valves are opened, and the tracer solution is then pumped through the "injection" tubing, and it is circulated between the packers. The mixed water returns to the surface through the "return" tubing and to the fluid reservoir containing the tracer solution (fig. 3d). With the middle packer inflated, none of the tracer is introduced into the formation. The tracer solution is circulated until it is well mixed in the reservoir at land surface and in the volume between packers A and B, and B and C. Once this is achieved, the injection and return valves are closed, and the volume and concentration of the water in the reservoir at land surface is measured.

The injection of the traced fluid is started by deflating the middle packer and opening the injection valve. The tracer is pumped down the injection tube and is forced into the formation (fig. 3e). The injection of traced fluid into the formation is terminated by inflating the middle packer to block the permeable fractures in the straddled interval (fig. 3f). The volume of water remaining in the fluid reservoir at land surface is then measured to determine the volume of the traced fluid injected into the formation.

The tracer solution between packer A and B, and B and C is then flushed with tracer-free water. This is done to ensure that the tracer is not introduced into the formation accidentally during the test or once the test is completed. The flushing of the tracer is conducted by opening the injection and return valves and using tracer-free water to flush the straddled interval through the "injection" tubing. The water exiting from the "return" tubing is monitored until the background concentration is achieved.

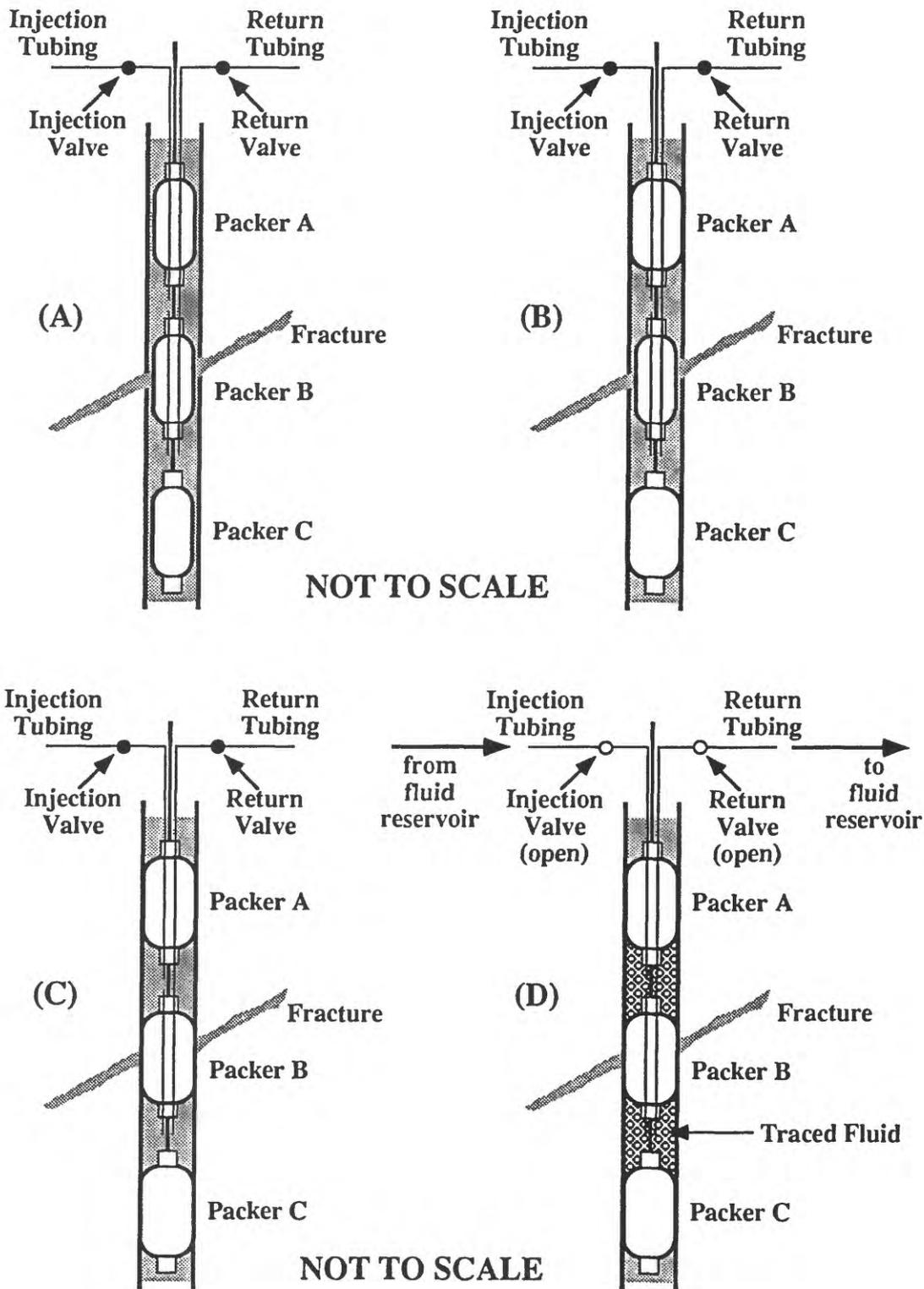


Figure 3. (a) New straddle packer assembly used for the controlled injection of traced fluids. (b) Packers A and C inflated to isolate injection interval in bedrock well. (c) Packer B inflated to seal permeable fracture in the injection interval. (d) Injection and return valves opened and traced fluid is circulated to mix in volume between packers A and B, and B and C. (e) Packer B deflated and injection valve opened to inject traced fluid into permeable fracture. (f) Packer B inflated to terminate injection; injection and return valves opened and tracer-free water circulated to flush traced fluid between packers A and B, and B and C.

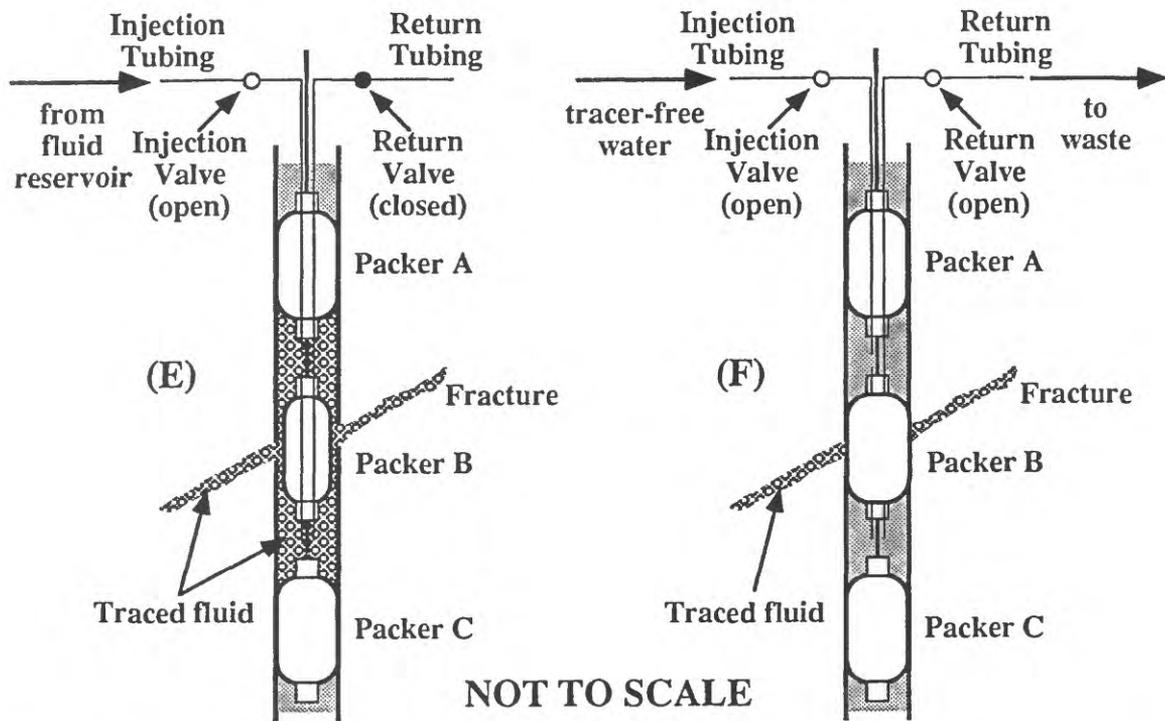


Figure 3. (a) New straddle packer assembly used for the controlled injection of traced fluids. (b) Packers A and C inflated to isolate injection interval in bedrock well. (c) Packer B inflated to seal permeable fracture in the injection interval. (d) Injection and return valves opened and traced fluid is circulated to mix in volume between packers A and B, and B and C. (e) Packer B deflated and injection valve opened to inject traced fluid into permeable fracture. (f) Packer B inflated to terminate injection; injection and return valves opened and tracer-free water circulated to flush traced fluid between packers A and B, and B and C—Continued.

SUMMARY

The interpretation of controlled tracer experiments in subsurface terranes requires a knowledge of the temporal variation in the concentration of the traced fluid as it is injected into the formation. Because of abrupt spatial changes in hydraulic properties in fractured rock, it is difficult to perform the controlled injection of traced fluid in open sections of bedrock wells. Density differences between the ambient fluid and the traced fluid, and the lack of adequate circulation of the traced fluid in the borehole usually results in a residual concentration in the borehole that diffuses into the formation.

A new method for the injection of traced fluid into permeable intervals in bedrock wells uses a string of three inflatable packers. This newly designed injection apparatus permits the controlled injection of traced fluids into fractures within a hydraulically isolated section of a borehole. Prior to the tracer injection, the middle packer is used to seal off the fractures in the injection interval, allowing downhole mixing of the tracer with borehole fluid. After a uniform mixture is achieved, the middle packer is deflated to allow injection of the traced fluid into the formation. The equipment requires smooth borehole

walls and no more than a few closely spaced permeable fractures.

In this paper, operation of the new injection apparatus is presented for the instantaneous injection of a known volume of traced fluid into the formation. The equipment can also accommodate other injection procedures, such as the continuous injection of traced fluids into the formation.

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Field Instrumentation for Multilevel Monitoring of Hydraulic Head in Fractured Bedrock at the Mirror Lake Site, Grafton County, New Hampshire

By Paul A. Hsieh¹, Richard L. Perkins², and Donald O. Rosenberry³

Abstract

An adjustable and removable instrument, consisting of commercially available components, was developed for monitoring hydraulic heads at several depth intervals in bedrock wells. The intervals are isolated from each other by packers. Each interval is connected to an open pipe, so that the water level in the pipe equals the hydraulic head in the interval. The water levels are monitored by a potentiometer-float system and automatically recorded by a datalogger. The water levels are also measured manually by a water-level probe to check periodically the automatic measurements. The hydraulic-head monitoring instrument can be removed from the well to accommodate activities such as geophysical logging, water sample collection, or hydraulic testing. This instrumentation has been installed at 12 bedrock wells at the Mirror Lake site.

INTRODUCTION

Accurate measurement of hydraulic head is essential for monitoring fluid flow in the subsurface. In particular, a measurement of the vertical distribution of hydraulic head is needed to determine the vertical component of fluid flow. In shallow alluvial material, the vertical distribution of hydraulic head can be measured by installing a cluster of piezometers screened at different depths. In most bedrock environments, the cost of drilling and casing multiple

wells to different depths is prohibitively high, so that the hydraulic heads at different depths must be measured in a single well. However, an open well can perturb the natural flow field by connecting highly permeable fracture zones that are unconnected in the absence of the well. Therefore, packers are generally needed to divide the well into separate intervals and to isolate the highly permeable fracture zones from one another. To complicate matters, the well could be needed for other purposes, such as collecting water samples, geophysical logging, and testing new instruments. Accordingly, any instrument installed in the well must be removable. This paper describes a removable instrument developed for multilevel monitoring of hydraulic heads in bedrock wells at the U. S. Geological Survey Toxic Substances Hydrology research site in the Mirror Lake area, Grafton County, New Hampshire.

DESIGN CRITERIA

To accommodate the many uses of a bedrock well, the hydraulic-head monitoring instrument is designed according to the following criteria: (1) The instrument had to divide the well into several intervals so that the hydraulic head in each interval could be measured separately. (2) Each interval had to be connected to an open pipe, so that the hydraulic head could be measured either manually with a water-level probe, or automatically with a potentiometer-float device or an electronic pressure transducer. The manual measurements would provide checks on the automatic measurements. (3) The instrument had to be removable so that the well can be used for purposes such as geophysical logging, water quality sampling, or hydraulic testing. Upon completion of work, the instrument would be reinstalled in the well. (4) The

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instrument had to be adjustable so that the monitored interval could be modified should the need arise. (5) The instrument had to be made of components that are commercially available to minimize the need for specialized fabrication.

DESCRIPTION OF INSTRUMENT

Figure 1 is a schematic diagram showing the instrument set up for multilevel monitoring of hydraulic head in a bedrock well. The well is cased through the overburden and is left as an open hole below the casing. Two packers are suspended on 3-cm-inside-diameter (i.d.) steel pipes. When inflated with air, the rubber bladder of the packer swells and presses against the borehole wall, creating a pressure-tight seal. The two packers separate the well into three intervals: A, B, and C. The hydraulic head in each interval is a composite of the hydraulic heads in the transmissive fractures that intersect the interval. In many cases, the interval contains a single, highly transmissive fracture or fracture zone that dominates the hydraulic head in the interval.

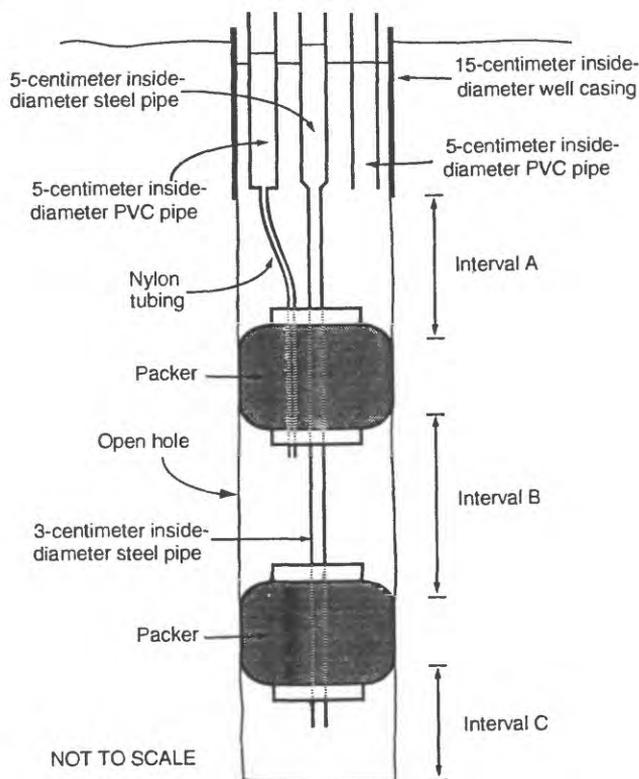


Figure 1. Instrument for multilevel monitoring of hydraulic head in a bedrock well.

Each interval is connected to a 5-cm i.d. pipe so that the water level in the pipe equals the hydraulic head in the interval. The 5-cm i.d. is needed to accommodate a potentiometer-float system for automatic water-level measurement. Hydraulic head in the bottom (C) interval is measured in the 5-cm i.d. steel pipe that is connected to the 3-cm i.d. steel pipe on which the packers are suspended. The hydraulic head in the middle (B) interval is measured in a 5-cm i.d. polyvinyl-chloride (PVC) pipe that is connected to the interval by means of a nylon tubing. The hydraulic head in the upper (A) interval is the water level in the well casing. This water level is also measured through a 5-cm i.d. PVC pipe to avoid tangling the float with tubing in the well. Not shown in figure 1 are the nylon tubing used to inflate the packers.

A potentiometer-float system (Rosenberry, 1990a) is used to measure water levels in the 5-cm i.d. pipes (fig. 2). The wire on which the float and counterweight are suspended is wrapped around the wheel of a potentiometer. As the water level changes, the float moves, turning the wheel and changing the electrical resistance of the potentiometer. This change in resistance is converted back to water level and recorded by a datalogger. Under controlled laboratory

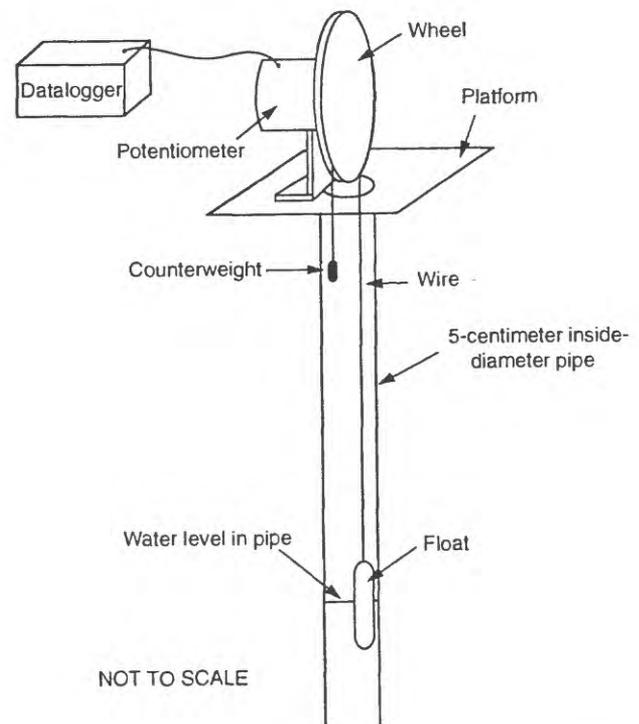


Figure 2. Potentiometer-float method for measuring water level in the 5-centimeter-inside-diameter pipe.

conditions, this potentiometer-float system can detect a water level change of 0.1 cm. However, during long-term operation in the field, the wire may gradually slip against the potentiometer wheel, causing a larger error. A study by Rosenberry (1990b) shows that, during long-term operation, water levels are measured by a potentiometer-float system with an accuracy of ± 1 cm.

In principle, the well can be divided into more than three intervals by installing more than two packers. In practice, the number of intervals is limited by the number of pipes that can fit inside the well casing. Because a minimum inside diameter of 5 cm is needed to accommodate the float, only three pipes can fit inside a 15-cm i.d. well casing. Reducing the pipe diameter allows additional intervals to be monitored, but requires the use of a smaller float, which lessens the sensitivity of the recorder to water-level changes. Accurate measurement of water-level change in a smaller diameter pipe may require the use of alternative water-level sensors such as electronic pressure transducers.

INSTALLATION OF INSTRUMENT

Before installing the hydraulic-head monitoring instrument, some preliminary information is needed to select appropriate locations for packer placement. In general, packers are placed between the highly transmissive fractures to isolate them from each other. These highly transmissive fractures can be identified by hydraulic testing with straddle packers, or by measurement of flow in borehole during pumping (Paillet and others, 1987). A packer should be placed where the borehole wall is smooth and unfractured to achieve a pressure-tight seal. A caliper log is extremely helpful for identifying locations where the borehole wall is rough or broken; such sections in the borehole should be avoided. Borehole-image logs, such as those made by borehole viewers and video cameras, provide detailed information on fracture locations.

Once the packer placements are selected, the instrument can be installed in the well. In general, a well-servicing vehicle (work-over rig) or a tripod-winch assembly is needed to lower the packers and pipes into the well. The depth range of each interval can be easily adjusted by cutting the 3-cm i.d. steel pipes to the desired length. Installing the three 5-cm-diameter i.d. pipes requires special care, because all three pipes are lowered simultaneously into the well.

The PVC pipes are affixed to the steel pipe by steel bands.

After the packers are lowered into position and are inflated, a platform is attached to the well head. The potentiometers are then mounted on the platform. The well-head installation, including the datalogger, is covered by an aluminum box, which provides shelter from rain and snow.

MONITORING HYDRAULIC HEADS IN THE MIRROR LAKE AREA

Monitoring hydraulic heads in fractured bedrock is part of an interdisciplinary study on fluid flow and chemical transport in fractured rocks at the U. S. Geological Survey Toxic Substances Hydrology research site in the Mirror Lake area in central New Hampshire (fig. 3). As discussed by Shapiro and Hsieh (1991), the objectives of this study are to develop monitoring and testing methods for characterizing ground-water flow and solute transport in bedrock, and to establish a site for long-term study. Although the Mirror Lake area is not contaminated, the techniques and understanding developed in this study are directly transferable to other fractured rock sites where ground water has been contaminated with chemical wastes.

As of early 1993, multilevel hydraulic-head monitoring instruments have been installed in 12 bedrock wells. Hydraulic heads are recorded automatically once every hours. Each well is inspected once a week to check that the instrument is working properly. Several packers tend to leak air and must be repressurized from time to time. During each visit, water levels are measured manually for comparison with the automatic measurements. As more experience is gained from this operation, the frequency of visit will decrease to approximately one visit per month.

Figure 4 illustrates the hydraulic heads recorded at well site FS3 during 1991. During this period, hydraulic heads were manually measured once a week. Interval A in the bedrock well extends from the bottom of casing (depth of 11.6 m) to a depth of 25.5 m below land surface. Interval B extends from a depth of 26.2 m to 59.2 m. Interval C extends from a depth of 59.9 m to the bottom of the well (depth of 196.6 m). In addition to the heads in the bedrock well, figure 4 also shows the heads in three nearby piezometers installed at depths of 4.3 m, 6.7 m, and 8.8 m in the glacial drift overlying the bedrock. The decrease of hydraulic head with depth suggests a downward component of flow from the glacial drift into the bedrock at this well site.

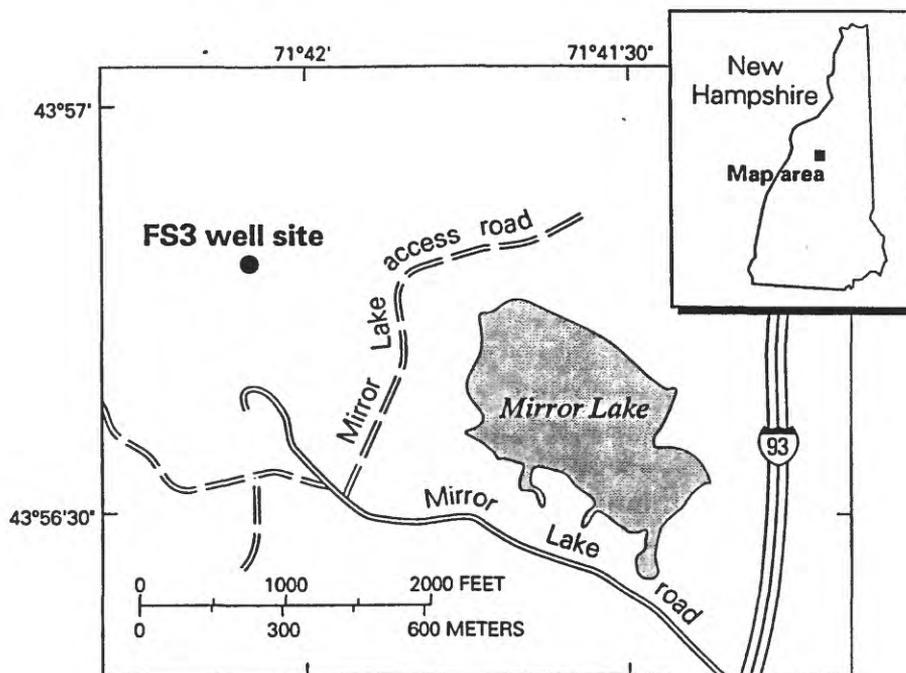


Figure 3. Location of the FS3 well site in the Mirror Lake area in New Hampshire.

SUMMARY

An adjustable and removable instrument has been developed to monitor the hydraulic heads in packer-isolated intervals in a bedrock well. The hydraulic head in each interval can be monitored by measuring the water level in an open pipe connected to the interval. Because the pipes are open, automatic water-level measurements can be made using a potentiometer-float system. Periodic manual measurements using a water-level probe provide a check of the automatic measurements. The instrument

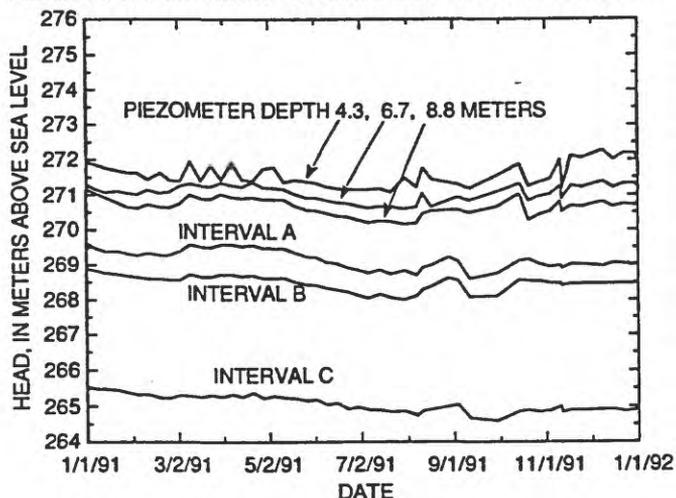


Figure 4. Hydraulic heads in intervals A, B, and C in bedrock well FS3 and in three nearby piezometers installed in glacial drift at depths of 4.3, 6.7, and 8.8 meters below land surface.

can be removed from the well to accommodate activities such as geophysical logging, water-sample collection, and hydraulic testing. This instrumentation has been installed at 12 bedrock wells at the Mirror Lake site.

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Factors Affecting Recharge to Crystalline Rock in the Mirror Lake Area, Grafton County, New Hampshire

By Philip T. Harte¹ and Thomas C. Winter²

Abstract

The effects of local and regional-flow processes on recharge to crystalline rock are investigated by use of numerical, cross-sectional models of ground-water flow, comparison of vertical-head gradients between lower piezometers in drift and upper bedrock wells, and chemical mass-balance models of net differences in water chemistry. This paper describes factors that control recharge to crystalline rock in the Mirror Lake area. Four principal factors that affect bedrock-recharge patterns are (1) relief of land and bedrock surface above ground-water discharge areas, (2) lateral trends in bulk-rock horizontal hydraulic conductivity, (3) local topographic features, and (4) drift stratigraphy. Factors 1 and 2 control the regional distribution of bedrock recharge, whereas the local distribution of bedrock recharge is controlled by factors 3 and 4.

INTRODUCTION

The spatial distribution of bedrock recharge from overlying unconsolidated deposits is an important factor in delineating areas susceptible to the advective transport of contaminants. Crystalline-rock aquifers in many areas of the country that have been glaciated have few surface exposures. The low hydraulic conductivity of these aquifers can cause the water table to be shallow and to be present primarily in

the overlying unconsolidated drift in humid environments. Few studies have evaluated the distribution of bedrock recharge from overlying drift, although Keeler and others (1988) have indicated that unconsolidated deposits can control rates of bedrock recharge.

This paper describes factors that affect bedrock recharge from overlying glacial drift. Two numerical, steady-state cross-sectional models of ground-water flow are used to evaluate recharge processes: (1) A model of a generalized hillside-valley system representative of New England and (2) A model of the Mirror Lake area. Results of the modeling experiments are compared to the distribution of vertical head between glacial drift and bedrock at 14 locations, and to the vertical distribution of ground-water chemistry at 2 locations (FS3 and FS1) in the Mirror Lake area (fig. 1).

FACTORS AFFECTING BEDROCK RECHARGE FOR HYPOTHETICAL SYSTEMS

The model of the hypothetical setting is patterned after the generalized characteristics of the physiography and hydrogeology encountered in the Mirror Lake area and elsewhere in the glaciated northeast United States (fig. 2). The geologic setting consists of fractured crystalline rock overlain by a largely continuous mantle of glacial till, which in turn is overlain in places by stratified drift. A detailed discussion of the setting, finite-difference model (McDonald and Harbaugh, 1988), model assumptions and boundaries, and sensitivity tests is given in Harte (1992). The bulk hydraulic properties of the fractured crystalline rock are viewed as an equivalent porous medium over the dimensions of the investigation.

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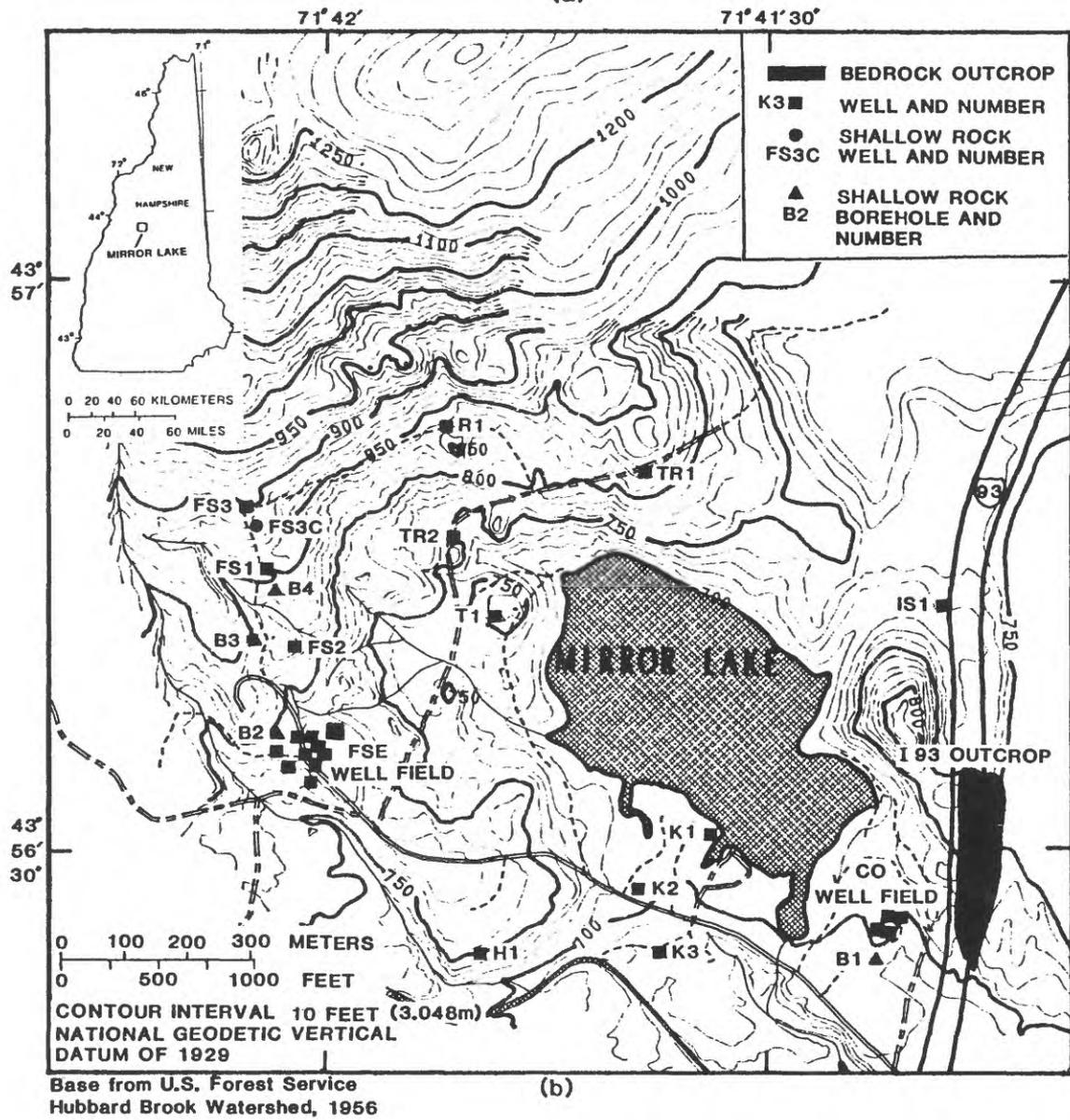
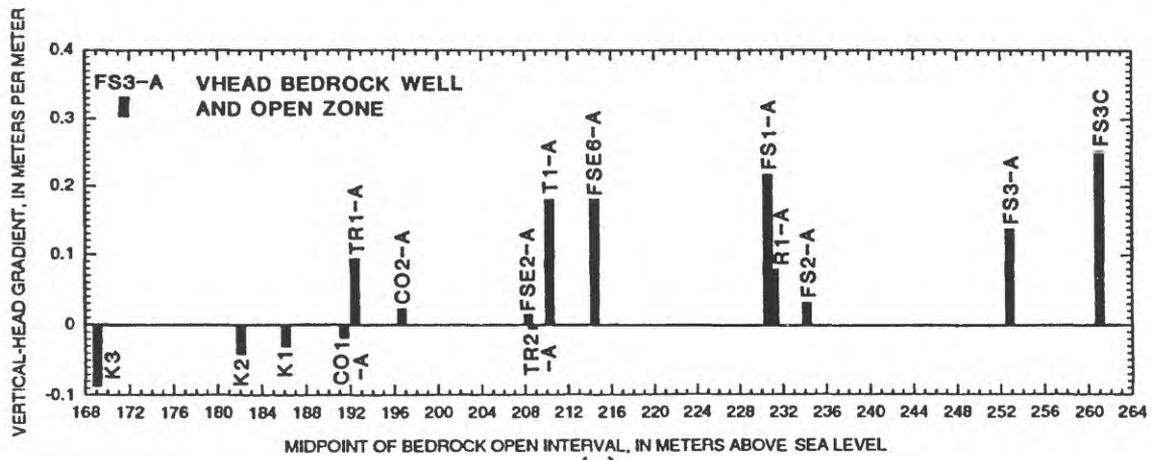


Figure 1. Vertical-head gradients between lower drift and upper bedrock from bedrock well nests (a), and location of well nests and shallow rock boreholes in the Mirror Lake area, Grafton County, New Hampshire (b) (modified from U.S. Forest Service, written commun., 1956).

The Transport of Inorganic Contaminants in a Sewage Plume in the Cape Cod Aquifer, Massachusetts

By Brigid A. Rea¹, Douglas B. Kent², Linda C. D. Anderson², James A. Davis²,
and Denis R. LeBlanc³

Abstract

The active and abandoned sewage-disposal beds at the Massachusetts Military Reservation sewage-treatment plant are a major source of inorganic contaminants, such as zinc, copper, and phosphate, in the Cape Cod aquifer, Massachusetts. The distribution and mobilities of these chemical constituents around the sewage-treatment plant are strongly affected by geochemical processes; extensive adsorption results in confinement of the most intensive concentrations to the near-source region, including currently used and abandoned disposal facilities. Beyond the disposal facilities, zinc and copper movement continues to be controlled by sorption processes. Zinc and copper contamination was present at the same depths, although copper concentrations were much lower than those of zinc. Phosphate concentrations were high in the suboxic zone near the source and are controlled by adsorption to sediments. Phosphate concentrations in the anoxic zone were much lower and likely are controlled by ferrous phosphate solubility.

INTRODUCTION

Inorganic contaminants in the subsurface travel at widely variable rates. The mobility of contaminants is strongly dependent on their speciation, aquifer pH, redox reactions, and mineral composition of the aquifer

material (Davis and Kent, 1990; Sposito, 1984). In this paper, we report on the processes that affect the distribution of sewage-derived phosphate, zinc (Zn) and copper (Cu) in the ground water near the sewage-effluent disposal beds (also termed "sand beds") at the U.S. Geological Survey Cape Cod Toxic Substance Hydrology Research site (fig. 1). A contrast in relative rates of transport is made between the two cations (Zn and Cu) and phosphate (an oxyanion) on the basis of expected ion-adsorption phenomena. Cation adsorption generally increases with an increase in pH, whereas anion adsorption decreases with an increase in pH.

In a previous paper (Rea and others, 1991), we described a small plume of dissolved Zn in a transition zone between pristine recharge water (infiltrated precipitation) and suboxic sewage-contaminated water; the 2-m-thick plume extended approximately 350 m downgradient from the sewage disposal beds (fig. 1). We postulated that the mobility of Zn was controlled by sorption reactions, which are affected by pH and Zn concentration. Concentrations of dissolved Zn in equilibrium with sorbed Zn on the aquifer solids decrease with increasing pH; above pH 6.0, Zn concentrations in equilibrium with sorbed Zn are often below detection (Rea and others, 1991). At constant pH, the amount of Zn sorbed increases with increasing Zn concentration until the maximum sorptive capacity is achieved (Davis and Kent, 1990; Sposito, 1984). In the sewage-contaminated zone, Zn can move only after the available sorption sites are saturated with sorbed Zn and other metals that compete for sorption sites. In the transition region, decreased pH, resulting from the mixing with pristine ground water, enhances Zn mobility enough to cause the observed Zn plume (Rea and others, 1991).

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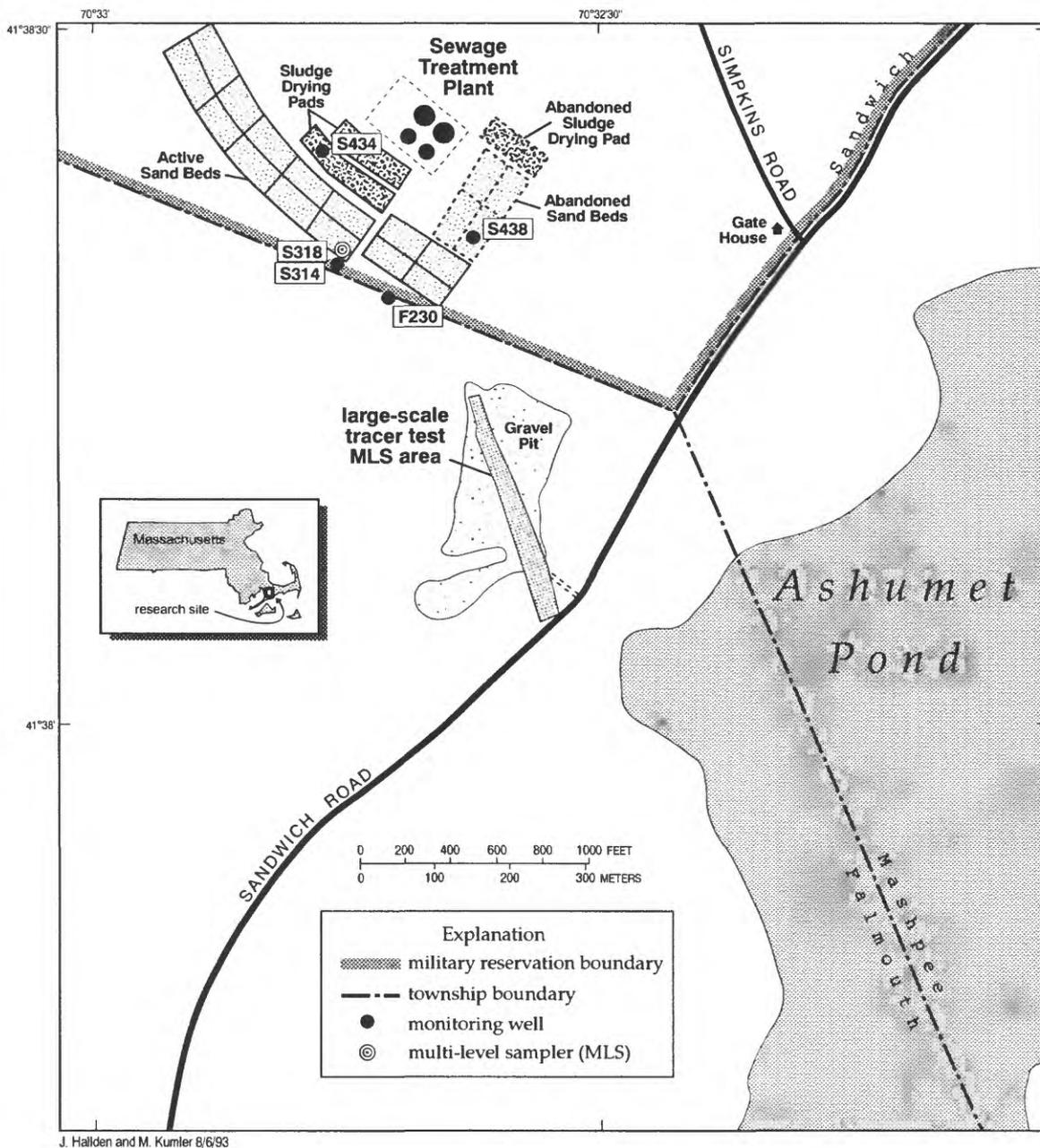


Figure 1. Location map showing the Massachusetts Military Reservation Sewage Treatment Facility, and well sites.

Zn in the sewage effluent is likely derived from pipe corrosion (Foerstner and Van Lierde, 1983). This led us to look for elevated concentrations of other metal ions, in particular Cu and lead (Pb). Both Cu and Pb adsorb to minerals more strongly than does Zn (Sposito, 1984; Dzomback and Morel, 1990). Consequently, contamination of the aquifer by these metals is expected to be limited to an area near the source;

however, mobilization of these metals could occur in response to changes in the ground-water chemistry.

Phosphate contamination has been reported previously in the Cape Cod aquifer (LeBlanc, 1984; Gschwend and Reynolds, 1987). Recently, local communities have become concerned that the contribution of phosphate from the Massachusetts Military Reservation (MMR) sewage-treatment plant may be

and the subsequent flux of water and CO₂ through the unsaturated zone to the water table.

Significant vertical variations of chemical constituents can indicate one or more components of inhomogeneity of the chemical system. This inhomogeneity complicates development of a single quantitative mass-transfer model. The simulation process is further complicated by the difficult task of collecting chemical data along true flow paths in a water-table aquifer for comparison with results of geochemical mass-transfer models.

CO₂ IN THE UNSATURATED ZONE

In order to improve the understanding of CO₂ variability in recharge water in the project area, it was necessary to analyze for CO₂ concentrations in the unsaturated zone for the different land uses. Because much of the production of CO₂ occurs in the root zone of the soil and subsoil, the CO₂ concentration can vary significantly from season to season and with depth within the unsaturated zone (Reardon and others, 1979; Wood and Petraitis, 1984).

Land Use

Although the project area contains parks, residential areas, golf courses, a wildlife sanctuary, Otis Air Base, and other land uses, four principal types of land cover affect CO₂ production in the unsaturated zone. These are: areas where vegetative cover is sparse to absent, such as gravel pits and utility right-of-ways; mixed hardwood and conifer woodlands; grassy areas of parks, and much of Otis Air Base; and landscaped residences, and golf courses (fig 2).

Methods

Twenty sites in the project area were selected to sample and analyze soil gases (fig 2). Four were selected to show typical analytical results (fig. 3a-3d). Gas samples were withdrawn through a 1/2-inch-diameter hollow probe driven to a specified depth. Concentration profiles of CO₂ in unsaturated zone gas were obtained at each site to depths of up to 12 ft. Samples were collected over five consecutive seasons represented by the months of November 1991, February 1992, May 1992, July 1992, and November 1992. Samples were collected by first withdrawing the

unsaturated-zone gases at a rate of 1 L/min with a peristaltic pump through intake slots near the base of the probe set to the specified depth. A constant value could usually be obtained by pumping for about 1 minute per ft of probe. Samples were withdrawn through the silicon tubing attached to the probe using a 50-mL plastic syringe with needle. The sample was immediately injected into a field gas chromatograph, which was equipped with a thermal conductivity detector. Peak separation of the CO₂ component of the gas was achieved using a micro-column packed with the HayesSep A and following the conditions of temperature and flow rate recommended in the user's manual for the equipment. The chromatograph contains an internal reservoir that accurately subsamples and passes the gas through the analytical column. Analytical precision was ± 1 percent and accuracy was ± 2 percent. Concentration of CO₂ was measured in parts per million, volume/volume. Calibration of the instrument was achieved using commercial standard gases.

Results of Gas Sample Analyses

Selected sites representative of results of the sampling for four significant land uses (Site a, grassy field; Site K, gravel pit; Site O, woodland; Site Q, golf course) are shown in figures 3a-d. Ranges of CO₂ concentrations given below represent approximate ranges of values in the subsurface from the actual data at each site. The smallest concentrations of CO₂ were in the gravel-pit areas where CO₂ ranged from about 500 to 2,000 ppm. Much of the vegetation had been removed at these locations, and the generation of CO₂ at the root zone was probably limited. The woodland areas contained the next smallest concentrations of CO₂--about 2,000 to 8,000 ppm. Woodlands were characterized by a moderate density of hardwood-conifer mix of trees, and low density ground cover with some decaying vegetation and mulch. CO₂ data from the woodlands overlapped CO₂ data for uncultivated grassy areas--about 6,000 to 8,000 ppm. Uncultivated grassy areas were covered with slow-growing grasses that were maintained by occasional mowing but were not watered or fertilized. The largest concentrations of CO₂ were found in the cultivated grassy areas on the golf courses--10,000 to 50,000 ppm. Hybrid grasses, high growth density, intense watering, and fertilization are conducive to elevated production of CO₂ in the root zone.

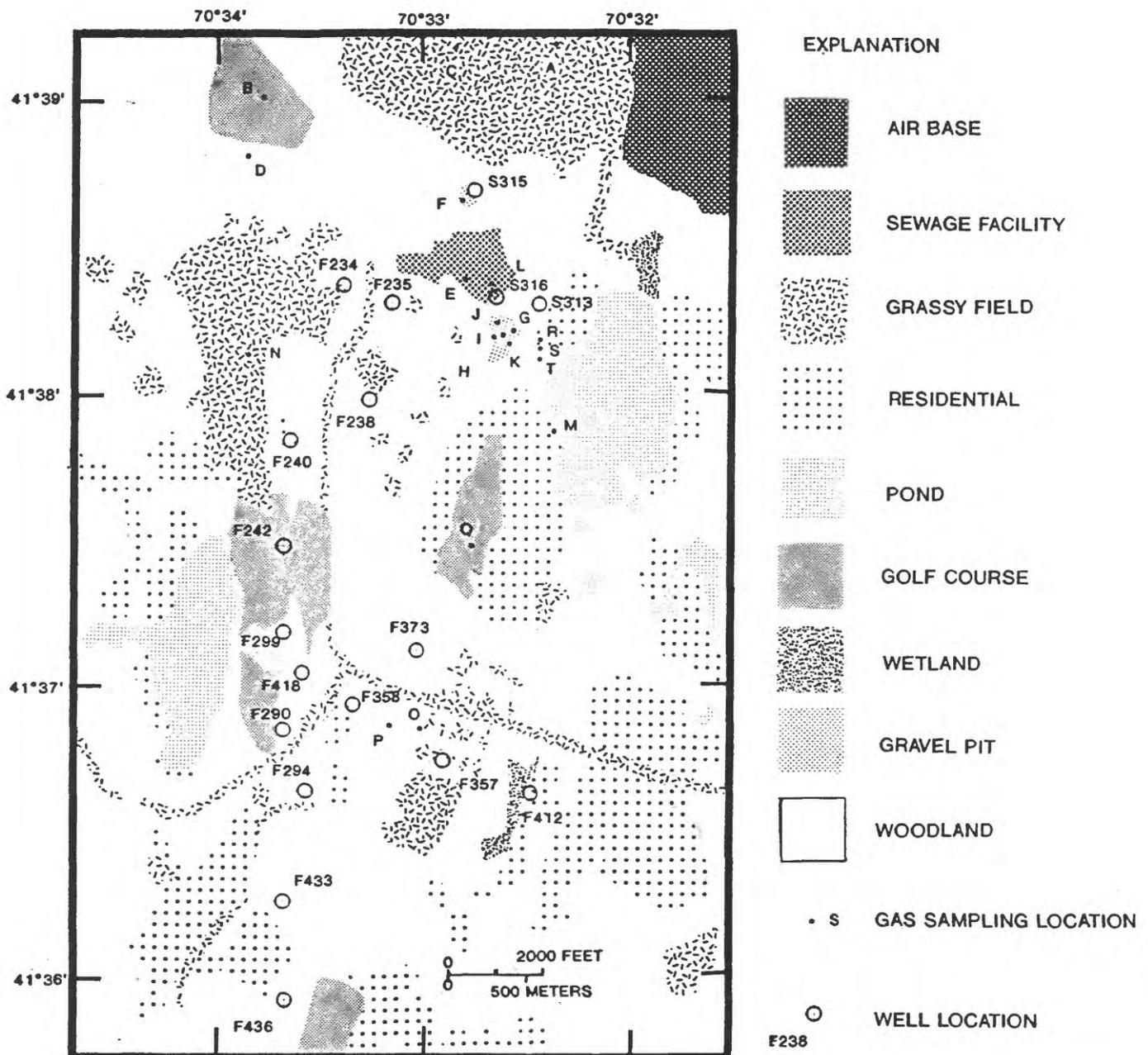


Figure 2. Land-use map in the vicinity of Otis Air Base, Cape Cod, Massachusetts, showing well cluster locations and unsaturated-zone-gas sampling locations.

Sampling Borehole Flow to Quantify Aquifer Cross-Contamination by Volatile Organic Compounds

By Ronald A. Sloto¹

Abstract

A combination of borehole geophysical methods, measurements of vertical borehole flow, and analyses of borehole-fluid samples were used to assess the extent of aquifer cross-contamination in the Stockton Formation in Hatboro, Pennsylvania. The Stockton consists of interbedded nonmarine sandstone and siltstone-mudstone. Most industrial, public-supply, and monitoring wells drilled into the Stockton Formation are constructed as open holes with short casings and are open to multiple water-bearing zones. Caliper, fluid-resistivity, fluid-temperature, natural-gamma, and single-point-resistance logs were run in 19 boreholes 149 to 656 feet deep to locate water-bearing fractures and determine zones of vertical borehole-fluid movement. The direction and rate of vertical borehole-fluid movement was measured by injecting a slug of high-conductance fluid at a specific depth in the borehole and monitoring the movement of the slug with the fluid-resistivity tool. After intervals of borehole flow were determined, samples of moving fluid were extracted from nine boreholes at a rate less than that of the measured borehole flow and analyzed for volatile organic compounds. An estimated 80.9 kilograms per year of volatile organic compounds were moving downward through the sampled boreholes from the contaminated, upper part of the aquifer to the lower part, which is tapped by public-supply wells. Trichloroethylene accounts for 94 percent and 1,1,1-trichloroethane accounts for 3 percent of the compounds.

INTRODUCTION

Many public supply, industrial, and monitoring wells in the United States are completed as open holes that obtain water from several formations or from several water-bearing zones in a single formation. The advantage to this construction practice is that a much greater yield can be obtained than if a well is open to a single formation or water-bearing zone. The disadvantage is that these boreholes, which connect several aquifers or water-bearing zones, commonly short circuit the ground-water-flow system and act as conduits for the transport of contaminants. The existence and magnitude of this problem is largely undetermined.

This paper presents some of the results of a study done by the U.S. Geological Survey (USGS) in cooperation with the U.S. Environmental Protection Agency (USEPA) to identify and assess cross-contamination by abandoned multiaquifer boreholes. A combination of borehole geophysical methods, measurements of vertical borehole flow, and analyses of borehole-fluid samples were used to assess the extent of aquifer cross-contamination in the Stockton Formation in Hatboro, Pa. The purpose of this paper is to show how those techniques were used to identify and determine the magnitude of cross-contamination.

Location and Description of Study Area

The study area is part of Hatboro Borough in Montgomery County, Pa. (fig. 1). It is centered around an older industrial area typical of many other communities in southeastern Pennsylvania. Much of the industry dates back to or prior to the World War II era. Industrial and public-supply wells drilled into the Stockton Formation were constructed as open holes with short casings and are open to multiple water-bearing zones. Downward fluid movement in

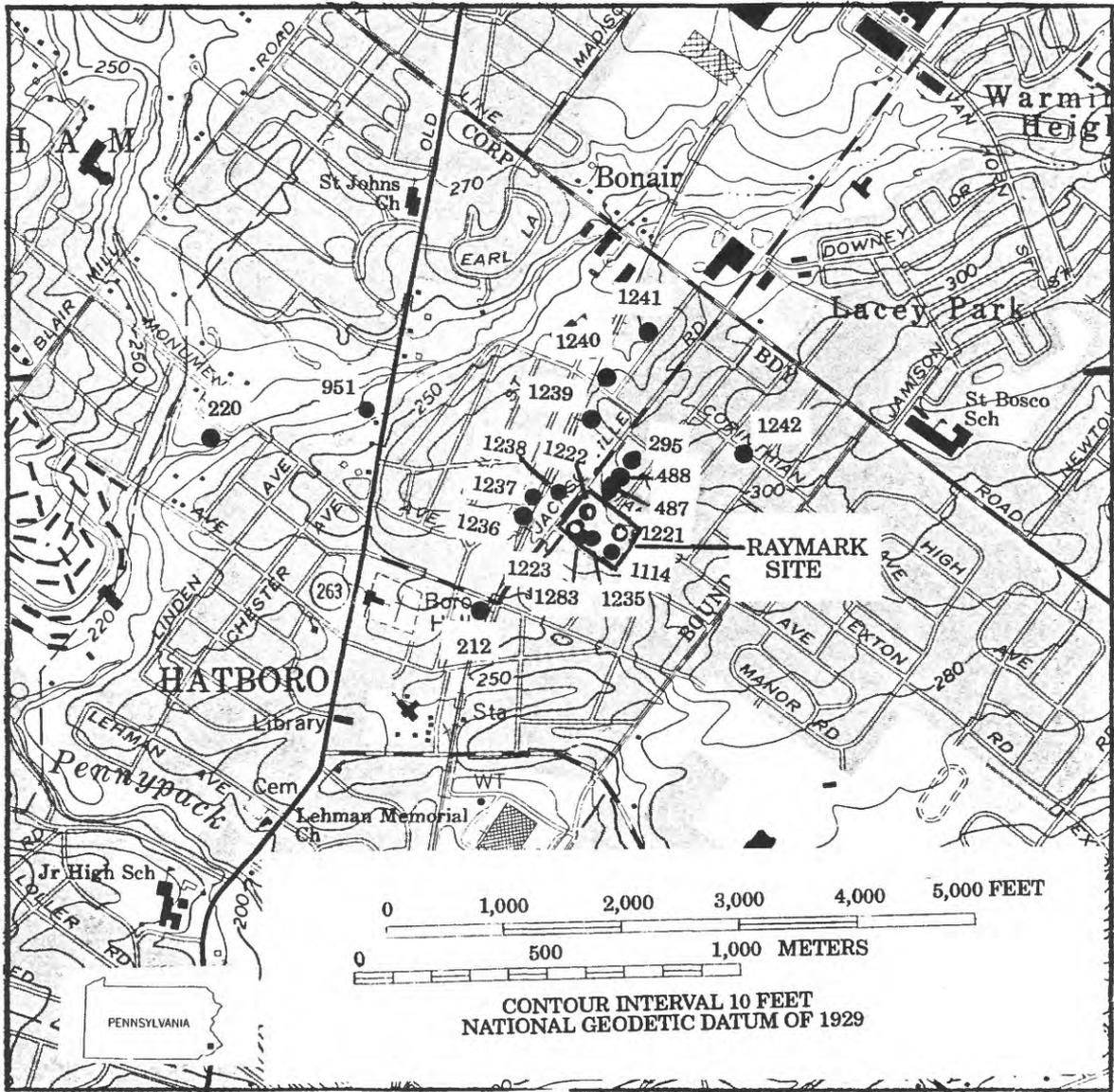
¹U.S. Geological Survey, Malvern, Pa.

75°07'

75°05'

40°11'

40°10'

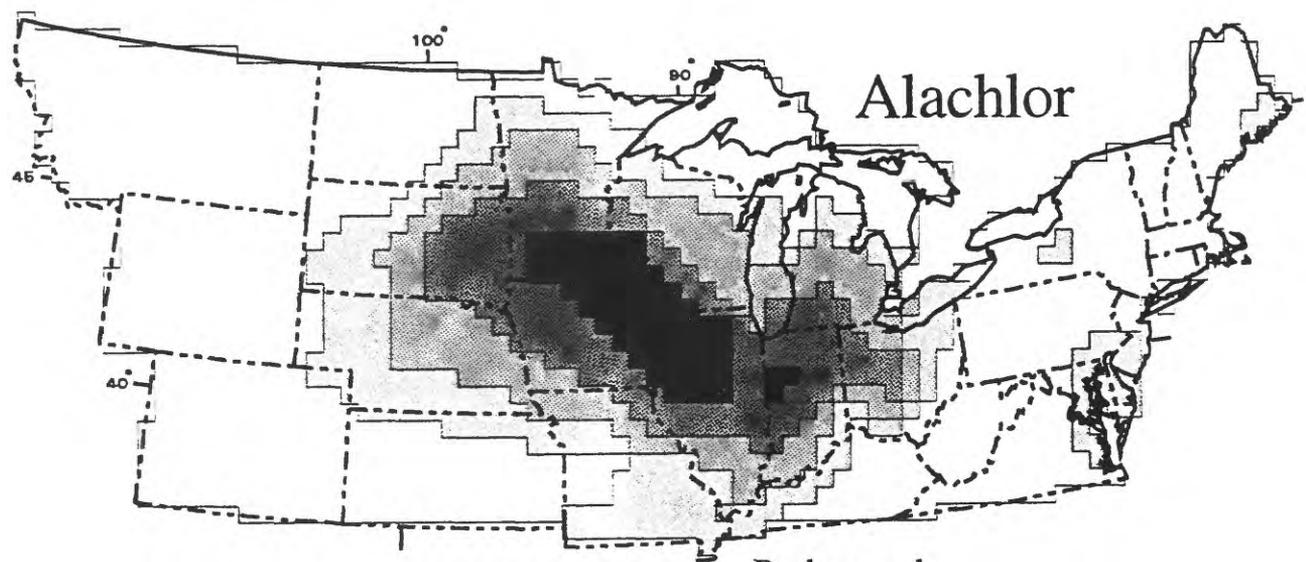
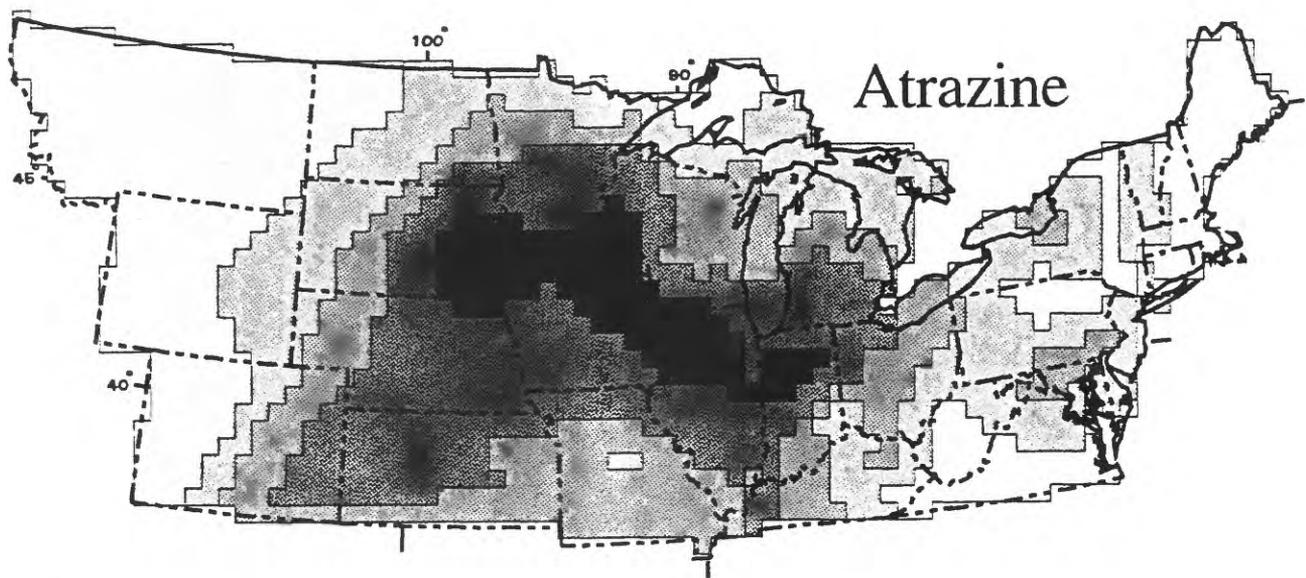


Base from U.S. Geological Survey Hatboro 1:24,000, 1983

EXPLANATION

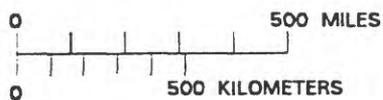
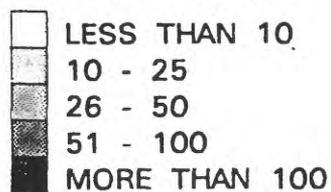
- 1236 BOREHOLE AND IDENTIFICATION NUMBER (Prefix MG omitted from number)
- 1221 MONITORING WELL CLUSTER AND IDENTIFICATION NUMBER (Prefix MG omitted from number)

Figure 1. Location of boreholes and monitoring-well clusters.



EXPLANATION

DEPOSITION, IN
MICROGRAMS PER SQUARE
METER PER YEAR



Background
Area

Study Area

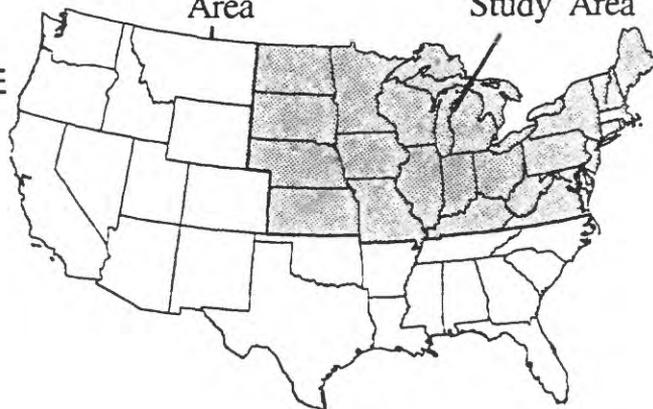


Figure 5. Estimated deposition of atrazine and alachlor in precipitation throughout the midwestern and northeastern United States, January through September 1991.

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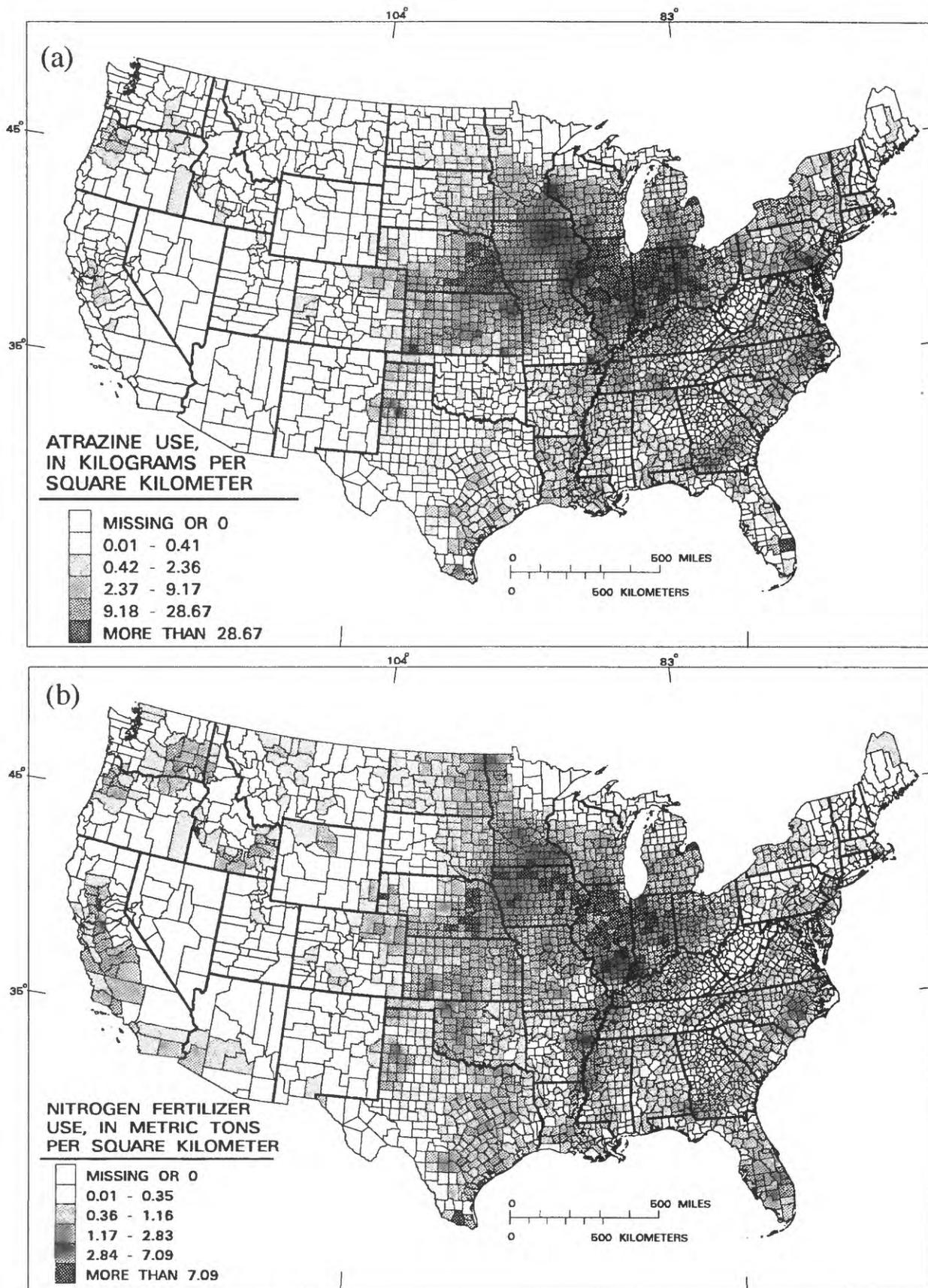


Figure 3. Estimated county-level: (a) atrazine use; (b) nitrogen fertilizer use, July 1, 1990, to June 30, 1991.

Table 2.--Estimated annual application of atrazine, alachlor, cyanazine, metolachlor, and nitrogen as commercial fertilizer in metric tons, in the Mississippi and several tributary basins

Sampling station name	Upstream drainage area in square kilometers	Estimated application, in metric tons				
		Atrazine	Alachlor	Cyanazine	Metolachlor	Nitrogen
Mississippi at Baton Rouge, La.	2,914,000	20,600	18,500	8,170	15,800	6,263,000
Mississippi at Thebes, Ill.	1,847,000	13,400	12,200	6,210	11,000	4,055,000
Missouri River at Hermann, Mo.	1,357,000	6,280	4,660	1,970	3,490	1,930,000
Ohio River at Grand Chain, Ill.	526,000	5,060	4,900	1,440	3,440	1,133,000
Mississippi River at Clinton, Iowa	222,000	1,440	2,040	1,590	1,630	607,000
Platte River at Louisville, Nebr.	222,000	1,600	1,030	464	444	425,000
Illinois River at Valley City, Ill.	69,000	1,960	1,880	715	1,760	450,000
White River at Hazelton, In.	29,000	711	851	214	424	143,000

Table 3.-- Goodness of fit statistics for regression relations of agricultural chemical transport, April 1991 through March 1992, with annual use

	Atrazine	Alachlor	Cyanazine	Metolachlor	Nitrate
Pearson product-moment correlation coefficient	0.994	0.889	0.983	0.997	0.968
Multiple R-square	0.989	0.790	0.967	0.994	0.936
P(F)-value	0.0000	0.0032	0.0000	0.0000	0.0001
Slope of regression line	1.56	0.22	1.68	0.79	15.47

from this study can be compared with results from these other studies. Hall and others (1972) estimated atrazine transport in runoff water was 2 percent of the amount applied at the recommended rate. Squillace and Thurman (1992) estimated that 1.5 to 5 percent of the atrazine applied was transported from the Cedar River basin in 1984. Wauchope (1978) estimated that 2 to 5 percent of herbicides applied as wettable

powders (includes atrazine and cyanazine) and 1 percent of other herbicides (including alachlor), were lost in runoff. The results of the present study indicate slightly smaller loss of herbicides than estimated by Wauchope (1978) and Hall and others (1972). The difference could be the result of basin-to-basin variability, climatic conditions particular to the year of study, or changing agricultural management systems

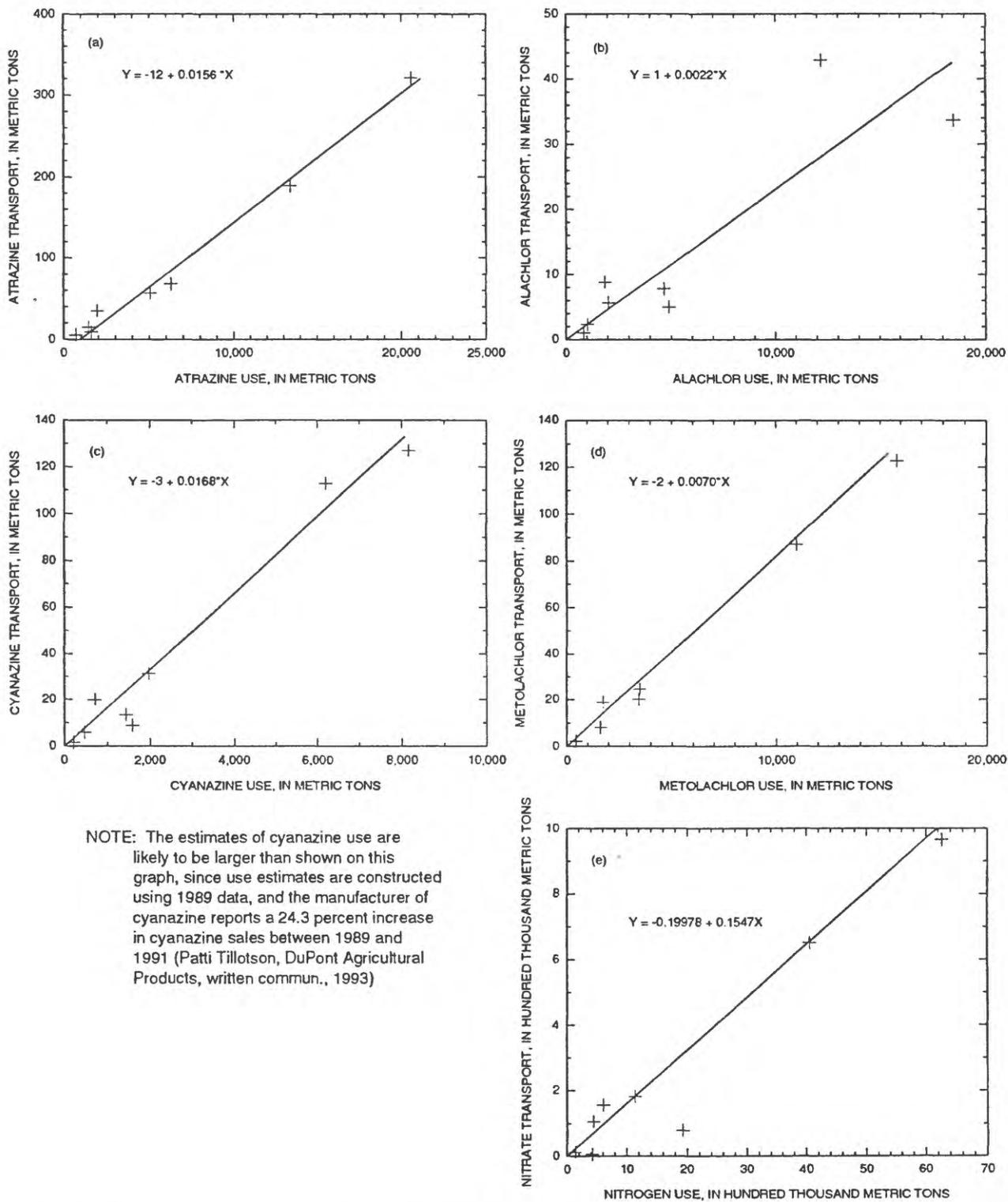


Figure 4. Graphs showing agricultural chemical transport as a function of use in the Mississippi River and several tributaries for: (a) atrazine, (b) alachlor, (c) cyanazine, (d) metolachlor and (e) nitrate.

Table 4.--Estimated transport, April 1991 through March 1992, as a percentage of use for atrazine, alachlor, cyanazine, metolachlor, and nitrate, in the Mississippi River and several tributaries

Sampling station name	Estimated transport as a percentage of use				
	Atrazine	Alachlor	Cyanazine	Metolachlor	Nitrate
Mississippi at Baton Rouge, La.	1.56	0.18	1.55	0.78	15.44
Mississippi at Thebes, Ill.	1.41	0.35	1.82	0.79	16.05
Missouri River at Hermann, Mo.	1.09	0.17	1.59	0.71	4.14
Ohio River at Grand Chain, Ill.	1.13	0.10	0.93	0.59	16.06
Mississippi River at Clinton, Iowa	1.05	0.28	0.56	0.50	25.86
Platte River at Louisville, Nebr.	0.58	0.23	1.27	0.57	1.33
Illinois River at Valley City, Ill.	1.83	0.47	2.77	1.07	23.78
White River at Hazelton, In.	0.80	0.12	0.80	0.50	8.04
Value from regression of transport with use, all basins	1.56	0.22	1.68	0.79	15.47

(including changes in application method and rate); However, the difference is likely to be a function of the area studied and the design of the experiments. The experiments summarized by Wauchope (1978) were mostly field-scale studies with study plots less than 2 ha, not basin-scale studies as used in the present study. In the study by Hall and others (1972), field runoff was maximized by experimental design and plot construction.

Estimates of nitrogen transport as a percentage of nitrogen use calculated for this study (table 4) are well within the range of values (1.5 to 64 percent) observed during 1979-90, but are somewhat lower than the reported long-term average (24.7 percent) in a small basin in Iowa (Lucey and Goolsby, 1993). In their review of nitrate contamination in the United States, Spalding and Exner (1991) indicated that nitrate in surface water is more of a problem in the Northeast, where runoff is high, and in the Midwest, where tile drainage contributes to surface-water flow, and less of a problem in the High Plains States. Results from this study also indicate that annual nitrogen transport, as a percentage of nitrogen use, is greater in

the Ohio and Illinois river basins than for the Platte and Missouri river basins (table 4).

Possible causes of variations in nitrate transport from east to west include differences in agricultural practices, population density, climatic conditions, and surficial materials. These possible causes need to be tested in future studies. The strength of the relations between agricultural chemical use and agricultural chemical transport (table 3) indicates that rates of chemical use could be as important in determining regional vulnerability to surface-water contamination as other hydrogeological factors, such as aquifer type, soil type, and agricultural management systems.

SUMMARY

Estimates of agricultural chemical use compiled using a GIS and estimates of agricultural chemical transport calculated from periodic water-quality sampling and daily mean stream flow data were compared using linear regression models for the Mississippi River and several of its tributaries in the midwestern United States. Results indicated that, during April

1991 through March 1992, estimated masses equivalent to about 15 percent of the commercial fertilizer, 1.6 percent of the atrazine and cyanazine, 0.8 percent of metolachlor, and 0.2 of the alachlor used in the basins were transported in the dissolved phase out of the basins by rivers.

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Relation of Nitrate Concentrations in Surface Water to Land Use in the Upper-Midwestern United States, 1989-90

By David K. Mueller¹, Barbara C. Ruddy¹, and William A. Battaglin¹

Abstract

As part of a study on contamination from agricultural chemicals, nitrate data were collected during several synoptic surveys at a large number of surface-water sites in 10 midwestern states during 1989-90. These data were analyzed using logistic regression to relate discrete categories of nitrate concentrations to land use in the drainage basins upstream from the sampling sites. The nitrate data were divided into three categories representing background concentrations, elevated concentrations, and concentrations that exceeded the U.S. Environmental Protection Agency maximum contaminant level for drinking water. Land-use data were derived from spatial-digital data available from several sources in national data bases. The explanatory variables selected for the best-fit model were percentile of streamflow at the time of sampling, acreage of the basin in corn, acreage in soybeans, density of cattle, and population density. All these variables have qualitative relations to nitrate sources, mobilization, or transport. Classification of nitrate categories from this model was 80 percent accurate in comparison to observed categories. The accuracy of the model was better for classification into categories that represented lower concentrations; however, incorrect classifications were not biased either high or low. Results from this study indicate that land-use data can be useful in analyses of water-quality conditions in large regions and that logistic regression is a valuable technique for use in such analyses.

INTRODUCTION

Large quantities of agricultural chemicals, including herbicides and nitrogen fertilizers are applied each year to farmland in the upper-midwestern United States. These applications, in conjunction with the moderately large solubility and mobility of some herbicides and nitrate, create the possibility for substantial contamination of surface and ground water. In 1989, the U.S. Geological Survey (USGS) began a regional study of herbicides and nitrate in surface waters of a 10-State area (fig. 1). Synoptic sampling surveys were conducted in the spring and summer of 1989 and 1990 and in the fall of 1989. Analysis of regional synoptic data is an important aspect of several programs within the USGS, including the National Water Quality Assessment Program (NAWQA) and the Toxic Substances Hydrology Program. The results of herbicide analyses from these samples have been presented previously (Goolsby and others, 1991, Thurman and others, 1991).

This paper presents results of the nitrate-data analysis -- specifically, the concept that nitrate concentrations in the synoptic samples are related to land-use data derived from large-scale geographic data bases. Also, statistical models that can be used to estimate nitrate concentrations from land-use data are evaluated.

SOURCE OF DATA

Surface-water samples were collected at 141 sites in Illinois, Indiana, Iowa, Kansas, Minnesota, Missouri, Ohio, Nebraska, South Dakota, and Wisconsin (fig. 1). Sampling sites were selected to be proportional to corn production in each State (D.A. Goolsby, U.S. Geological Survey, written commun., 1989, 1990). Within States, site selection was based

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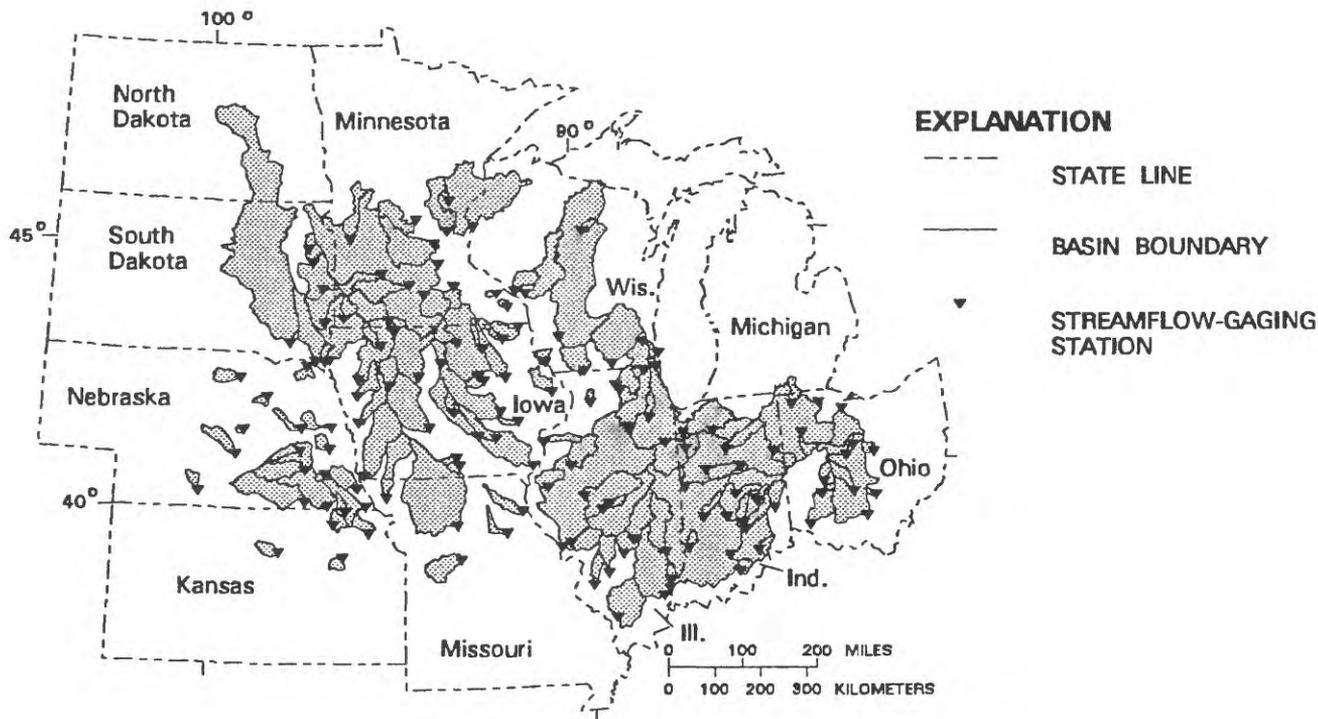


Figure 1. Location of selected stream-sampling sites and upstream drainage basins in the upper midwestern United States.

on geographic distribution and drainage-basin area. Most sites were located at existing USGS streamflow-gaging stations.

Samples were collected three times in 1989: (1) spring (March-May), before the application of herbicides, but not necessarily prior to application of nitrogen fertilizers; (2) summer (May-July), during the first major runoff event after application of herbicides; and (3) fall (October-November), after the first killing frost. Samples were analyzed for selected herbicides and for dissolved nitrite plus nitrate (hereinafter referred to as nitrate). Field measurements of temperature, pH, and specific conductance were made and streamflow was either measured or derived from a rating curve.

Fifty sites were resampled during the spring and summer of 1990. Selection of these sites was based on ranking the samples collected during the summer of 1989 according to the total herbicide concentration. The sampling sites were divided into three equal groups. Twenty-five sampling sites were randomly selected from the group that contained the highest concentrations; 13 sampling sites were randomly selected from the middle group; and 12 sampling sites were

randomly selected from the group that contained the lowest concentrations. Two additional sampling sites were selected in northeast Iowa from basins that were not sampled in the summer of 1989 because of drought.

Geographic data for the study area were obtained from several sources. Agricultural data, including land use, crop types, and livestock, were collected for the 1987 Census of Agriculture (U.S. Bureau of Census, 1989). Data on nitrogen fertilizer sales during 1989 and 1990 were obtained from the U.S. Environmental Protection Agency (USEPA) (1990). Although these data are for sales, they were considered to represent fertilizer application as well. Population data were collected for the 1990 Census of Population and Housing (U.S. Bureau of Census, 1990). All data were retrieved from Geographic Information System (GIS) data bases, stored as 1:2,000,000-scale digital maps of the coterminous United States. The agricultural and fertilizer data were stored by county. The population data were stored by census geographic units (block groups).

Digital data extracted from these sources were used to compute values for the drainage basin

upstream from each surface-water sampling site. A computerized GIS procedure was used to areally weight the extracted data and sum it by basin. When basins were nested (a large basin can contain several smaller basins), the data for the smaller basins were summed to derive the information for the large basin.

The final step in development of the data was to convert the basin data to units that were independent of basin size. For the geographic data, this conversion was done by dividing the data values by basin area. Streamflow at the time of sampling was converted to a percentile value on the basis of the flow-duration relation for daily streamflow at the site. Percentile of flow has been shown to be preferable to actual streamflow in making comparisons among basins of different sizes and, consequently, different flow regimes (D.R. Helsel, U.S. Geological Survey, written commun., 1993). Daily streamflow records were not available for five sampling sites; therefore, flow percentiles could not be computed and those basins were omitted from subsequent analyses. Also, one basin was

omitted because no samples were collected during the spring or summer sampling periods in either 1989 or 1990. The resultant data set contained values for 135 basins, having drainage areas that ranged from 89 to about 19,000 mi² (square miles). The variables in this data set are listed in table 1.

STATISTICAL METHODS

The initial attempt to relate nitrate concentrations at each site to land use in the upstream drainage basin was made by using multiple linear regression (MLR). However, no satisfactory MLR models were identified. Logistic regression was selected as an alternative method.

Logistic regression commonly is used when the response variable is discrete or categorical, rather than continuous (Helsel and Hirsch, 1992, p. 393). The logistic regression model is similar to the MLR model in that a set of explanatory variable is used to estimate the value of a response variable. The response variable

Table 1. Variables (attributes) included in the final data set

[mg/L, milligrams per liter; acre/mi², acres per square mile; number/mi², number per square mile; ton N/mi², tons nitrogen per square mile]

Variable (attribute)	Units	Minimum	Median	Maximum
Dissolved nitrite plus nitrate, as nitrogen	mg/L	< 0.1	2.5	19
Percentile of flow	none	.5	67.5	99.5
Total harvested cropland	acre/mi ²	57.1	345	480
Acreage in corn, including silage	acre/mi ²	3.06	149	267
Acreage in soybeans	acre/mi ²	.51	126	239
Acreage in grain (wheat, oats, and rye)	acre/mi ²	1.69	15.9	192
Acreage in hay	acre/mi ²	4.25	25.4	158
Pastureland, including pastured woodland	acre/mi ²	6.04	49.4	397
Woodland, not pastured	acre/mi ²	1.09	11.3	75.5
Cattle	number/mi ²	5.09	55.3	176
Hogs	number/mi ²	.99	98.3	448
Poultry (chickens and turkeys)	number/mi ²	.05	32.3	6,280
Fertilizer application	ton N/mi ²	1.38	14.3	27.2
Population density	number/mi ²	1.58	32.8	1,960

in logistic regression is the log of the odds ratio, $p/(1-p)$, where p is the probability of a data value being in one of the possible categories (Helsel and Hirsch, 1992, p. 395-396). The logistic regression equation is

$$\log\left(\frac{p}{1-p}\right) = b_0 + bX,$$

where, b_0 = the intercept, X = the vector of k explanatory variables, and b = the vector of slope coefficients for each explanatory variable, so that $bX = b_1X_1 + b_2X_2 + b_kX_k$.

The slope coefficients are fit to the categorical data by the method of maximum likelihood (Helsel and Hirsch, 1992, p. 397). This method optimizes the likelihood that the observed data will be estimated from a given set of slope coefficients.

To create a discrete variable, observed concentrations of nitrate (as nitrogen) in each sample were divided into three categories: less than 3 mg/L, 3 to 10 mg/L, and greater than 10 mg/L. A total of 359 samples from the 135 sites during four synoptic sampling periods (spring and summer, 1989 and 1990) were included in this data set. More than one-half of the observations (192) were in the first category, which was considered to include background concentrations of nitrate in the study area. Observations in the second category (138) were considered elevated but were less than the USEPA maximum contaminant level (MCL) of 10 mg/L for drinking water (U.S. Environmental Protection Agency, 1986). Observations in the third category (29) exceeded the MCL. The categorized nitrate data for samples collected during the spring and summer of 1989 are shown in figure 2.

Best-fit logistic regression models were selected to estimate nitrate concentrations from land-use data by using a stepwise procedure. Explanatory variables were added to the model in order of significance, if the significance level (p -value) of the slope coefficient was less than or equal to 0.15. As variables were added, previously entered variables could be removed if their p -values increased to greater than 0.20

To decrease the possibility of collinearity (cross correlation among the independent variables), the list of explanatory variables used in model fitting was restricted. Fertilizer application and total cropland were strongly correlated with corn and soybean acreage; therefore, fitting procedures were applied to two sets of explanatory variable: one set included fertilizer and total cropland data, and the other included corn and soybean acreage data. All the other explanatory

variables listed in table 1 were included in both sets. Slope coefficients were determined separately for spring and summer data. Separate coefficients also were determined for classification between the low (concentrations less than 3 mg/L) and medium (3 to 10 mg/L) nitrate categories and between the medium and high (greater than 10 mg/L) categories. Overall, four sets of coefficients were determined using the same selected group of explanatory variables. A model consisted of the selected variables and the four sets of coefficients.

Models were compared on the basis of their capability to classify nitrate concentrations correctly. First, the model was used to estimate the probabilities of nitrate concentrations being in a particular category for each sample. Estimated probabilities were computed for the same data set used to fit the model. The classified category was selected to be the one with the maximum probability. The accuracy of the model was determined by comparing the classified category to the observed category.

RESULTS AND DISCUSSION

Two best-fit models were selected—one from each set of explanatory variables. For the variable set that included fertilizer and total-cropland data but no data on individual crop types, the selected explanatory variables were percentile of flow, fertilizer application, and population density. The logistic regression fit to these explanatory variables is referred to as model 1 in this paper. Comparisons of nitrate categories estimated by model 1 to observed nitrate concentrations are listed in table 2. The overall accuracy of the model is determined by the total percentage of correct classifications. For model 1, 73 percent of the classifications were correct. However, only 34 percent of the observations greater than 10 mg/L were correctly classified. Also, model 1 might be biased because most of the incorrect classifications were low.

Model 2 was fitted by use of the set of explanatory variables that included crop types, but not fertilizer application or total cropland. The selected explanatory variables from this set were percentile of flow, acreage in corn, acreage in soybeans, cattle, and population density. Accuracy results for model 2 also are listed in table 2. The overall accuracy of correct classifications was 80 percent, which is a slight improvement over that of model 1. Most of this improvement was attributed to better accuracy in

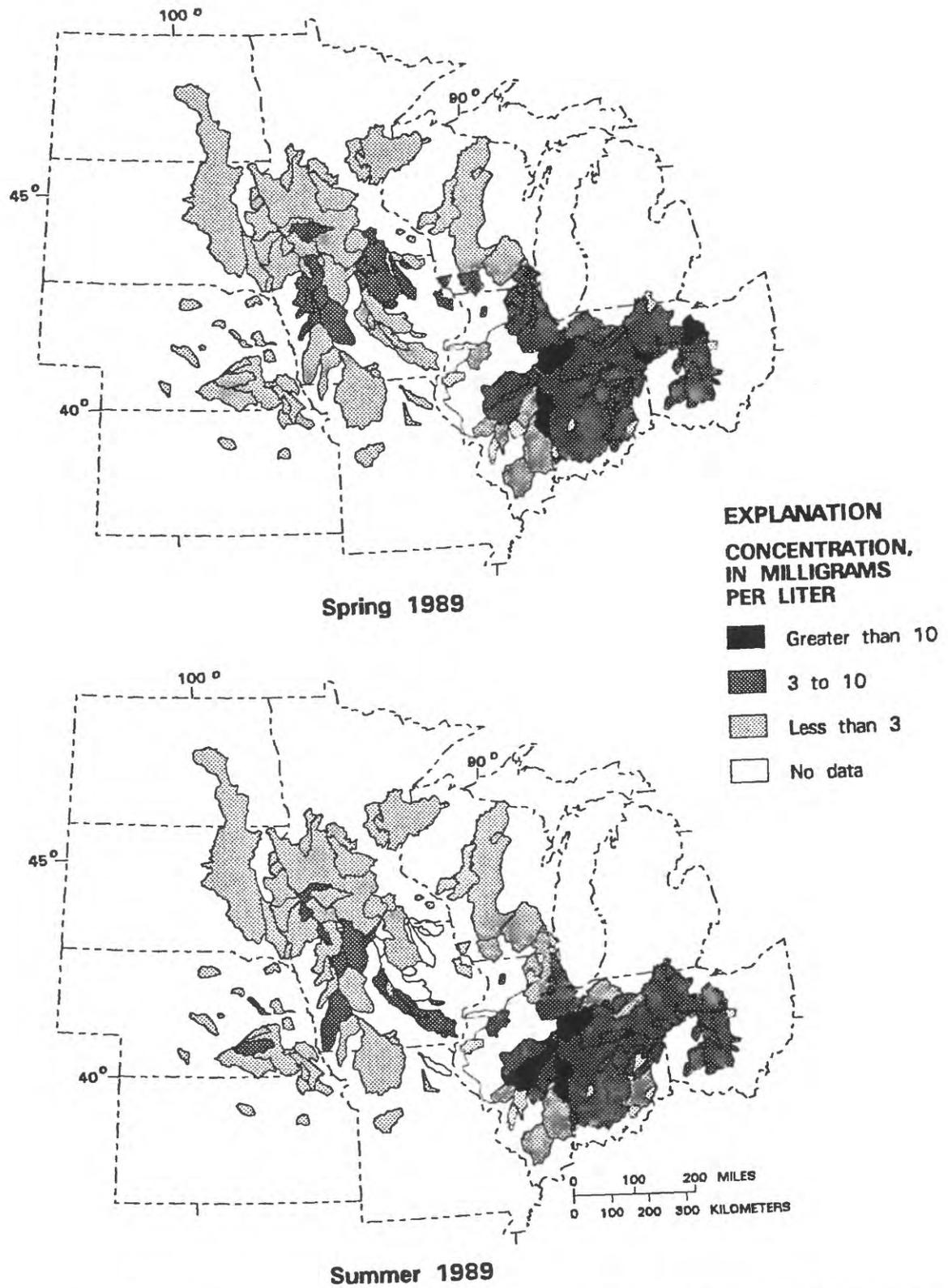


Figure 2. Geographic distribution of concentrations of dissolved nitrite plus nitrate as nitrogen, in selected streams in the upper-midwestern United States, displayed by drainage basin, for samples collected during the spring and summer 1989.

Table 2. Observed nitrate categories and category classifications from the logistic regression models

[mg/L, milligrams per liter; --, not applicable]

Category (mg/L)	Observed	Classified correct		Classified low		Classified high	
		Number	Percent	Number	Percent	Number	Percent
Model 1 (percentile of flow, fertilizer application, and population density)							
< 3	192	164	85	--	--	28	15
3 - 10	138	87	63	42	30	9	7
> 10	29	10	34	19	66	--	--
Total	359	261	73	61	17	37	10
Model 2 (percentile of flow, acreage in corn, acreage in soybeans, cattle, and population density)							
< 3	192	166	86	--	--	26	14
3 - 10	138	104	75	27	20	7	5
> 10	29	16	55	13	45	--	--
Total	359	286	80	40	11	33	9

classifying the higher concentrations. Classifications from model 2 were correct for 75 percent of the observed nitrate concentrations in the medium (3 to 10 mg/L) category and for 55 percent of the observed nitrate concentrations in the high (greater than 10 mg/L) category. This accuracy is a substantial improvement over model 1. Also, the incorrect classifications were about evenly distributed between high and low values, so model 2 does not seem to be biased.

The spatial distribution of the classification accuracy using model 2 for data from the spring and summer of 1989 is shown in figure 3. Incorrect classifications, both low and high, are distributed in a relatively uniform pattern throughout the study area. This result indicates that the model classifications are not geographically biased. Therefore, the accuracy of the model does not seem to depend on correlation of the explanatory variables with regional geography.

Generally, model 2, which is based on crop-type data, is superior to model 1, which is based on fertilizer data. Model 2 also is reasonably accurate in categorizing nitrate concentrations in the outflow from a variety of basins on a regional and seasonal scale. Model classifications do not seem to be biased in either magnitude or geographic distribution. These

results lead to two primary conclusions. First, the level of nitrate contamination in midwestern streams is most strongly related to streamflow and to several characteristics of the upstream basin, including the areal extent of corn and soybean production, the density of cattle, and the population density. This list seems logical because each variable has a qualitative relation to nitrate. Streamflow results from basin runoff, which provides the mechanism for mobilization and transport of nitrate. In the model, as the percentile of flow increases, the probability increases that nitrate concentration will be in a higher category. Corn and soybeans are the major crops in the region, and their extent in the basin logically should be related to the use of all fertilizers, including commercial fertilizers and manure. Cattle also could be related to fertilizer use because they are a primary source of manure. Perhaps if data were available on actual fertilizer application, rather than only on fertilizer sales, a better model based on fertilizer instead of crop-type and livestock data could be developed. Population density is related to outflow from sewage-treatment plants, which generally are point sources of nitrate or of ammonia (a nitrogen species that can readily oxidize to nitrate). Even

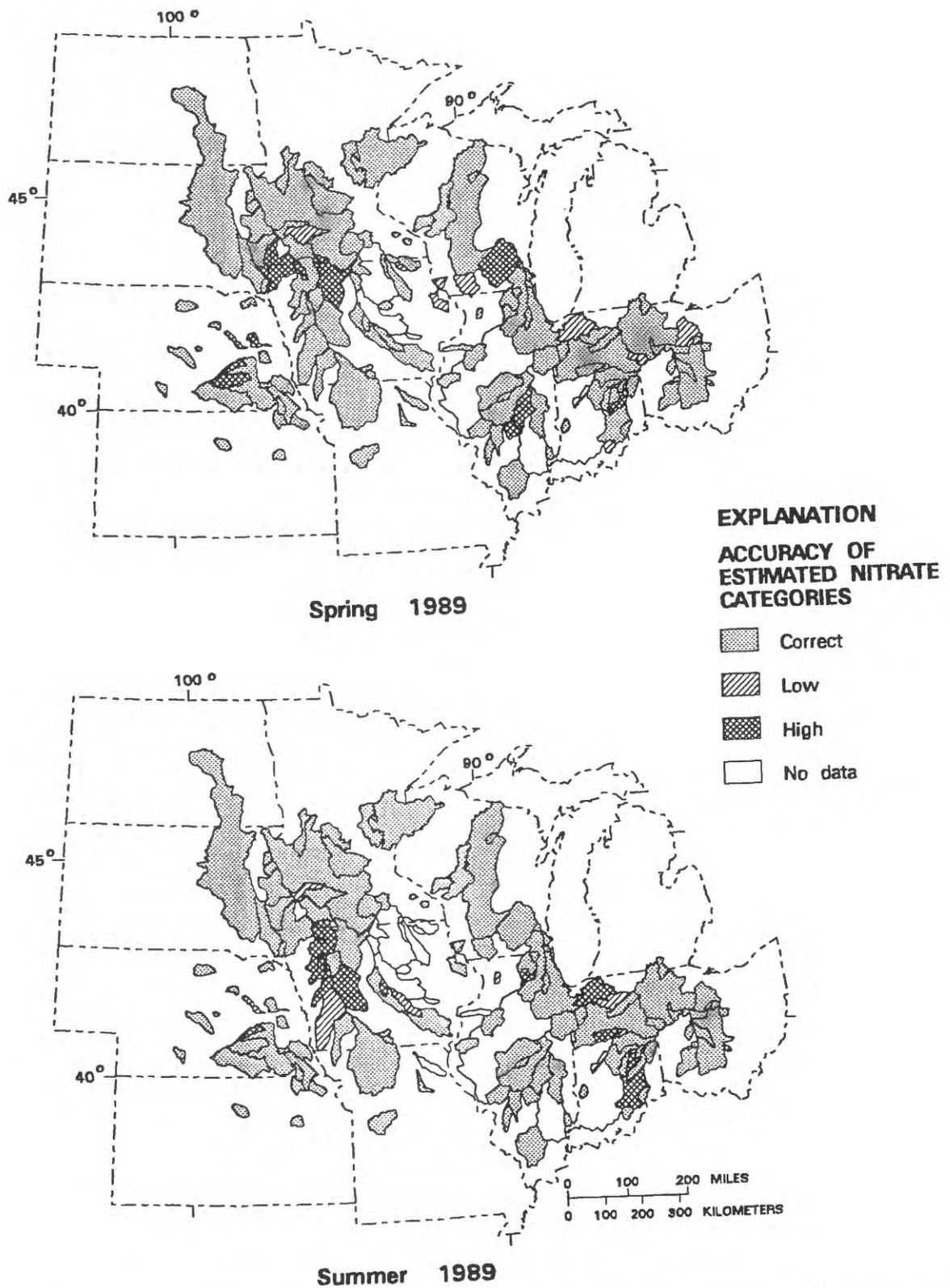


Figure 3. Accuracy of nitrate-concentration categories estimated from logistic model 2 based on comparison to concentrations in samples collected during the spring and summer of 1989.

in rural areas, population density likely is related to nitrate contamination from septic system leachate.

A second conclusion is that an adequate model can be developed by relating synoptic water-quality data to regionally derived geographic data. All the explanatory variables in the model were retrieved from large GIS data bases that had, at best, a county-scale resolution. Yet these data were adequate to classify 80 percent of the observed nitrate concentrations correctly in outflow from a variety of basins.

The implication of these conclusions is that land-use data can be used to analyze water-quality conditions within large regions. Reasonable models can be developed for relating water quality to land use. These models can be adequate, even if the land-use data are extracted from large-scale data bases. Refinement of the models might be possible by collecting more precise land-use data in the basins upstream from sampling sites. More precise explanatory data could improve the accuracy of model classifications. The models could be used to identify other basins in the region where surface-water contamination might be a problem. Models from different regions could be compared to identify similarities and differences in the land-use factors that affect water quality in the regions. Logistic regression is a valuable technique for the development of these models.

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Reconnaissance Data for Selected Herbicides and Two Atrazine Metabolites in Surface Water of the Midwestern United States: Chemical Analysis by Immunoassay and Gas Chromatography/Mass Spectrometry

By Elisabeth A. Scribner¹, E. Michael Thurman¹, and Donald A. Goolsby²

Abstract

Water-quality data were collected from 147 rivers and streams during 1989-90 for an assessment of selected preemergent herbicides and two atrazine metabolites in 10 Midwestern States. All water samples were collected by depth-integrating techniques at three to five locations across each stream. Sites were sampled three times in 1989: before application of herbicides, during the first major runoff after application of herbicides, and in the fall during a low-flow period when most of the streamflow was derived from ground water. About 50 sites were selected by a stratified random procedure and resampled for both pre- and post-application herbicide concentrations in 1990 to verify the 1989 analytical results. Laboratory analyses consisted of enzyme-linked immunosorbent assay (ELISA) with confirmation by gas chromatography/mass spectrometry (GC/MS). The data have been useful in (1) studying herbicide transport, (2) comparing the spatial distribution of the post-application concentrations of 11 herbicides and 2 atrazine metabolites (deethylatrazine and deisopropylatrazine) in streams and rivers at a regional scale, (3) examining the annual persistence of herbicides and their metabolites in surface water, and (4) assessing whether the two atrazine metabolites can be used as indicators of surface- and ground-water interaction.

INTRODUCTION

During 1987-89, about 136 million pounds per year of four major herbicides were applied in a 10-State region (table 1). The herbicides alachlor, atrazine, cyanazine, and metolachlor accounted for about 73 percent of the herbicides applied (Gianessi and Puffer, 1990). The intense use of these herbicides with their partial water solubility and mobility cause them to leach into ground water, to run off in surface water, as well as to be transported aerially and to occur in precipitation (Goolsby and others, 1990). Runoff from fields immediately after herbicide application substantially increases herbicide concentrations in streams and rivers as reflected by increased concentrations of these herbicides in the Mississippi River (Goolsby and others, 1991a). Potentially serious problems concerning nonpoint-source contamination of surface- and ground-water supplies are associated with this agricultural chemical use. Drinking-water quality also is affected because conventional water-treatment practices do not remove these herbicides because they are soluble (Goolsby and others, 1990).

This paper presents the water-quality data collected during the reconnaissance study of surface water in the midwestern United States. This paper (1) describes the occurrence, distribution, and concentrations of nitrite plus nitrate and selected preemergent herbicides and two metabolites, (2) describes the geographic and seasonal distribution of nitrite plus nitrate and commonly used herbicides in streams of different size throughout the 10-State area, and (3) examines the usefulness of a low-cost immunoassay analysis for determining herbicide concentrations in a regional-scale reconnaissance study (Goolsby and others, 1990). The study area includes the following states: Illinois, Indiana, Iowa, Kansas, Minnesota, Missouri, Nebraska, Ohio, South Dakota, and Wisconsin (fig. 1).

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Table 1. Quantities of four major herbicides applied in 10 agricultural Midwestern States, 1987-89

[From Gianessi and Puffer, 1990; values shown are in millions of pounds of active ingredient per year]

State	Alachlor	Atrazine	Cyanazine	Metolachlor
Illinois	8.0	8.5	3.1	8.1
Indiana	6.9	5.7	1.7	3.5
Iowa	6.4	5.6	3.7	8.5
Kansas	1.9	4.7	0.2	2.2
Minnesota	4.0	1.5	2.8	2.4
Missouri	1.8	3.1	1.2	1.6
Nebraska	3.8	7.1	1.8	1.9
Ohio	3.7	3.8	1.6	4.0
South Dakota	1.9	0.5	0.3	1.0
Wisconsin	1.3	2.7	1.7	1.4
Total	39.7	43.2	18.1	34.6
Total of four major herbicides: 135.6				

METHODS

Sampling Design

The 147 sampling sites were selected at U.S. Geological Survey (USGS) streamflow-gaging

stations by a stratified random-sampling procedure designed to ensure geographic distribution and regional-scale interpretation of the data. The number of sites per State was proportional to the amount of corn and soybean production in each state, and sites were chosen randomly by county. The drainage area of the hydrologic units in which streams were sampled ranged from 66 to more than 700,000 mi², with a median drainage area of 770 mi². Most of the streams were sampled three times in 1989: before application of herbicides (March or April); after application and during the first major runoff (May or June); and in the fall during a low-flow period (October or November) when most of the streamflow was derived from ground water.

One-third of the streams sampled in 1989 were resampled during 1990 before herbicide application (March or April) and after herbicide application (May or June). The streams sampled in 1989 were ranked from largest to smallest total herbicide concentrations; 50 percent of the streams sampled in 1990 were randomly selected from the upper one-third, 25 percent from the middle one-third, and 25 percent from the lower one-third of the streams according to the ranked concentration.

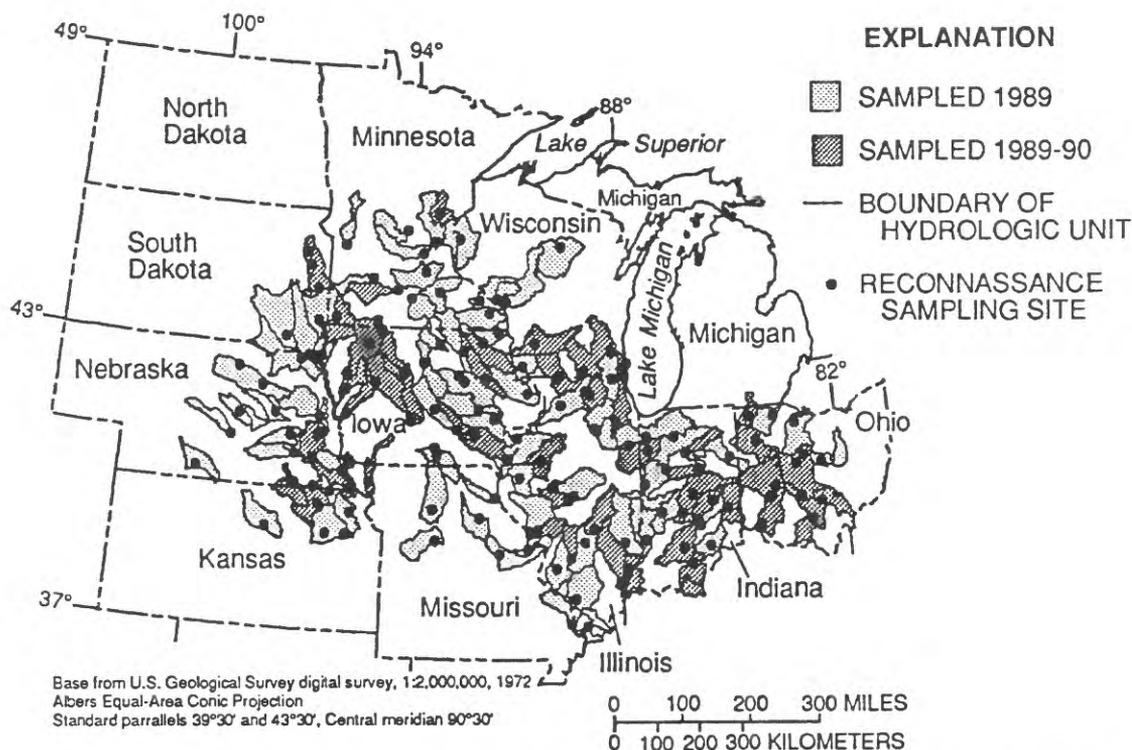


Figure 1. Location of study area, hydrologic units, and sites sampled in 1989 and 1990, in the midwestern United States. (From Thurman and others, 1992, fig. 1A.)

Predicting Nitrate-Nitrogen and Atrazine Contamination in the High Plains Aquifer in Nebraska

By A.D. Druliner¹ and T.S. McGrath¹

Abstract

Three statistical models, developed through the Toxic-Waste--Ground-Water Contamination Program of the U.S. Geological Survey, were used to predict the concentrations of nitrate-nitrogen and atrazine and the probability of atrazine detections in ground water in Buffalo and Hall Counties, south-central Nebraska. The models use a combination of hydrochemical, hydrologic, soils, and land-use explanatory variables, and ARC/INFO techniques to generate maps showing predicted concentrations of the selected contaminants. Confirmational testing of the models and comparison of maps of predicted concentrations to maps of observed concentrations showed that the statistical models were reasonable predictors of nitrate-nitrogen and atrazine concentrations in ground water of the High Plains aquifer in south-central Nebraska.

INTRODUCTION

Today, farmers in Nebraska, like farmers throughout most agricultural States across the Nation, rely on fertilizers and pesticides to maximize crop yields and to sustain productivity. Mineral fertilizers, such as nitrogen, and broadleaf herbicides, such as atrazine, have been applied annually over large areas of Nebraska for more than 30 years. In 1989, Nebraska farmers applied an estimated 662,000 tons of nitrogen (as N) fertilizers--an amount slightly less than amounts applied earlier in the decade (Nebraska Department of Agriculture, 1980; 1990). In 1987, an estimated 28.6 million pounds of herbicide was applied in Nebraska (Baker, and others, 1990)--an 18 percent increase over

1982 estimates even though planted acreages actually declined by about 13 percent during the 6-year period. As a result of the intensive use of agricultural chemicals (Gormly and Spalding, 1979), ground water in many areas of the State is contaminated with nitrate-nitrogen concentrations in excess of the U.S. Environmental Protection Agency's (1991) maximum contamination level of 10 mg/L for drinking water and contains trace concentrations of atrazine (Exner and Spalding, 1990). However, not all ground water in areas of Nebraska where these chemicals are regularly used is contaminated to the same extent (Chen and Druliner, 1987), suggesting that one or more combinations of physical factors are affecting the transport of these contaminants to the ground water.

The U.S. Geological Survey conducted a nonpoint-source ground-water contamination study in Nebraska to investigate the relations among concentrations of nitrate-nitrogen and atrazine in ground water and quantifiable physical factors. During the first phase of the study, Chen and Druliner (1987) investigated the presence of selected agricultural chemicals in ground water in parts of the High Plains aquifer and performed a preliminary investigation of the effects of selected physical factors on ground-water contamination by nitrate-nitrogen and atrazine. One of the specific objectives of the second phase of the study was to develop techniques that could be used to recognize or predict areas of potential ground-water contamination by selected agricultural chemicals.

This paper describes three statistical models developed as part of the second phase of the study that relate nitrate-nitrogen and atrazine concentrations in ground water to hydrologic, land-use, and soils variables in Nebraska. The models are used to predict nitrate-nitrogen and atrazine concentrations and atrazine detections in ground water in Buffalo and Hall Counties, south-central Nebraska (area 1, fig. 1), and the predictions are compared to observed concentrations of nitrate-nitrogen and atrazine in ground water in the same area.

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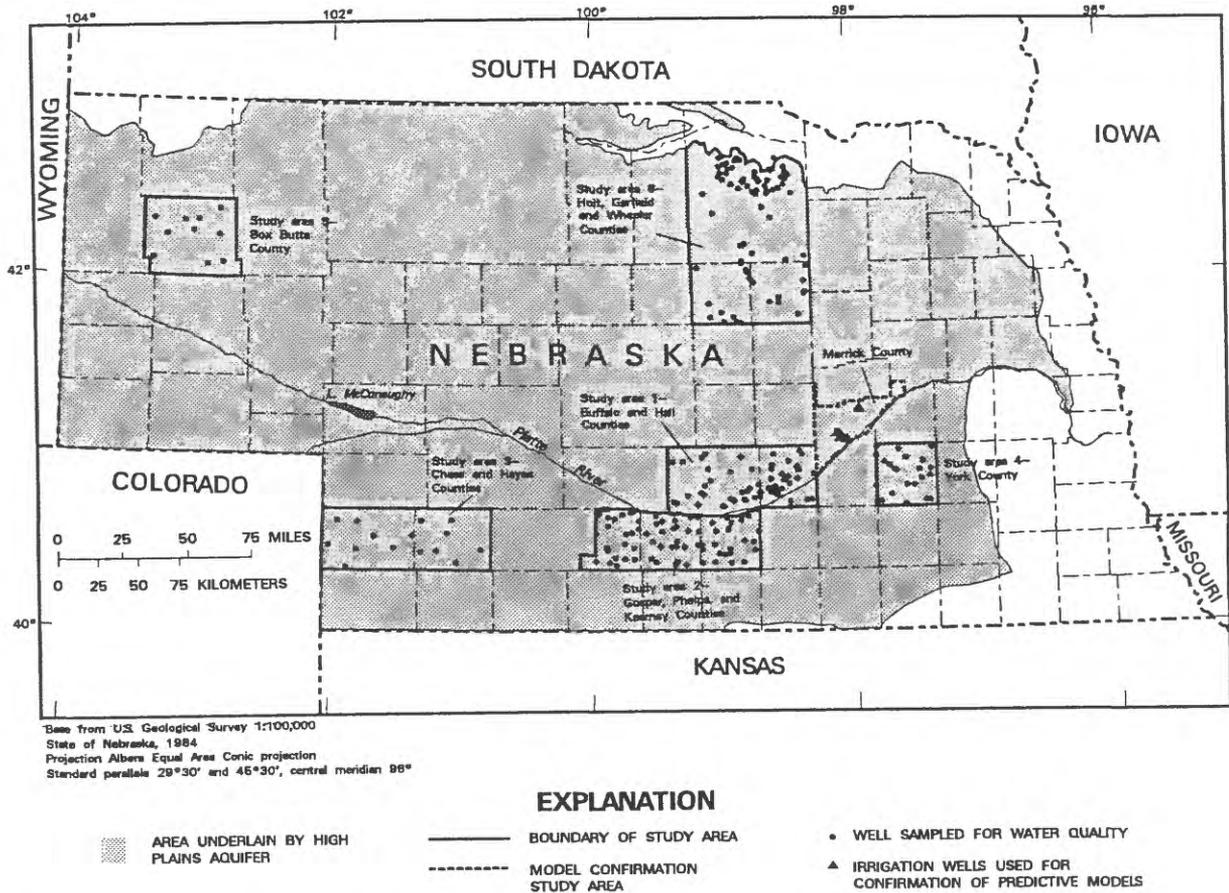


Figure 1. Extent of the High Plains aquifer in Nebraska, the location of ground-water sampling sites in the six study areas, and the location of Merrick County.

APPROACH

Six study areas encompassing 12 counties of Nebraska were selected in an effort to investigate a variety of hydrologic, land-use, and soils factors that could affect ground-water contamination by agricultural chemicals (fig. 1). More than 70 explanatory variables were tentatively identified as possibly affecting ground-water contamination. Some examples of these variables are depth to water, average hydraulic conductivity, fertilizer application amounts, tillage type, soil slope, and soil permeability. Water-quality samples were collected from 268 irrigation, domestic, public, and stock wells in the six study areas during a 4-year period (1984-87). Data quantifying the explanatory

variables were compiled for each of the 268 well sites and compared to nitrate-nitrogen concentrations in the ground water at each site. Similarly, data describing explanatory variables for 210 of the well sites were compared with atrazine concentrations in the ground water. Data for all six areas, as well as for single areas, were used to construct a variety of statistical models that could be used to predict areas of present or potential ground-water contamination.

DESCRIPTION OF STUDY AREAS

The six study areas contain from one to three counties each, and all are underlain by the High Plains aquifer (fig. 1). A variety of locations was selected to

provide a wide range of hydrochemical, hydrologic, soils, and land-use conditions in addition to targeting some areas of existing and potential ground-water contamination by agricultural chemicals. A brief description of the hydrology, land-use, and soils variables follows.

The High Plains aquifer is generally unconfined and consists of silt, sand, and sandstone of Tertiary Age with some calcareous cement and local zones of coarse sand and gravel and (or) overlying clay, silt, and sand of Quaternary age. In the six study areas, the High Plains aquifer is from 100 to 400 ft thick and is underlain by relatively impermeable clay of Cretaceous age. Recharge, chiefly from precipitation, occurs throughout most of the High Plains aquifer in the study areas. Additional recharge is provided by seasonal irrigation return flows, losing reaches of streams and rivers, and leakage from canals. Discharge from the aquifer in all areas occurs primarily through irrigation-well pumpage; secondary losses occur from evapotranspiration and ground-water discharge to streams, lakes, and canals.

The soils overlying the High Plains aquifer vary with the local topography and underlying geology. Soils in the study areas range from loamy, sandy soils in the Platte River Valley (areas 1 and 2) and adjacent to the Sand Hills (area 6) to clayey and silty soils in area 4 (Kuzila and others, 1990).

Irrigated corn is the dominant crop in five of the six areas and typically receives larger application amounts of nitrogen fertilizer and pesticides than other crops grown in Nebraska. Nitrogen most commonly is applied as anhydrous ammonia, which is usually injected into the ground prior to planting time. During the 1980's, nitrogen sales in the six study areas fluctuated from 100,000 to 150,000 tons/yr (Nebraska Department of Agriculture, 1980; 1990). The most commonly used pesticide on row crops in Nebraska is atrazine, a pre-emergent herbicide used to control broadleaf weeds in corn and sorghum. An estimated 13.4 million pounds of atrazine was applied in Nebraska in 1988 (Baker and others, 1990).

METHODS

Multiple linear-regression techniques as described by Minitab (1989) and SAS (1990) were used to generate statistical models with nitrate-nitrogen and atrazine concentrations as the dependent variables. Stepwise, stepwise forward, stepwise backwards, best-regres-

sion, maximum R, R-squared, and logistic regression methods were used. In the Minitab stepwise-regression efforts, a minimum F-statistic of 1.8 was used to determine which explanatory variables would remain in the models even though all models containing explanatory variables with F-statistics less than 4 (and with T-ratio less than 2) were later rejected. The maximum R and R-squared techniques in SAS were designed to maximize the R-square values (percentage of explained variation) for each model by stepwise selection of explanatory variables, or by considering all combinations of explanatory variables, respectively. The Lillifores test (Iman and Conover, 1983) was used to ensure that the residuals for each of the representative models were normally distributed at the 95-percent confidence level. Plots of the residuals as a function of the predicted values were examined for each model to reveal trends that might indicate the presence of untested variables.

Logistic regression methods were used to develop models predicting the probability of atrazine detections in ground water with atrazine data that were converted to detect or nondetect values. Through a maximum-likelihood methodology, this technique produced multiple-regression models that predicted the probability of the presence or absence of the dependent variable at the specified threshold value. The goodness-of-fit for the logistic models was determined by comparing the percentages of correct and incorrect predictions rather than through coefficients of determination. Models were considered acceptable if they represented logically plausible relations with the explanatory variables and if the probability of exceeding the Chi-square statistic was less than 0.05 for each explanatory variable included in the model.

RESULTS

A number of multiple linear-regression models were produced with nitrate-nitrogen and atrazine concentrations as the dependent variables. Models were generated using data for all of the sampled areas, and other models used subsets of the data based on individual study areas. The best of these models explained from 50 to 68 percent of the variation (coefficient of determination) observed in the dependent variables. Logistic models using just atrazine concentrations as the dependent variables yielded predicted accuracies up to 81 percent when compared to the input data. Examples of these models are presented in table 1.

Table 1. Regression models used to predict concentrations of nitrate-nitrogen and atrazine and the probability of atrazine detections in ground water

Explanatory variables	Regression coefficients	T-ratio	P-value
Model A: Nitrate-nitrogen concentration (multiple-linear regression)			
Intercept	21.890	2.00	0.047
Specific conductance	.014902	6.01	0
Average hydraulic conductivity of the unsaturated zone	.080430	4.72	0
Median well-completion date in 1-mile radius	-.43650	1.96	.050
Coefficient of determination = 0.68			
Model B: Atrazine concentration (multiple-linear regression)			
Intercept	-1.46360	-6.40	0
Nitrate-nitrogen concentration	.0035944	6.05	0
Depth to water	-.006926	2.52	.015
Number irrigated acres in 1.7-mile radius	.0007743	2.02	.048
Coefficient of determination = 0.61			
Model C: Probability of atrazine detection (logistic regression)			
Explanatory variables	Regression coefficients	Chi-square	P-value
Intercept	-5.6503	6.6052	0.010
Nitrate-nitrogen concentration	.1822	14.3439	0
Water-table gradient	-959.1	11.0128	.001
Percentage of clay in soil	-.0559	4.8374	.028
Logarithm of well depth	-2.0797	4.8282	.028
Percentage total correct identifications: 81			

Model A was formulated using only data from area 1. The model predicted nitrate-nitrogen concentrations using specific conductance, the average hydraulic conductivity of the unsaturated zone, and the median completion date of irrigation wells within a 1-mi radius of the sampled well. Specific conductance is believed to be an indirect measure of nitrate-nitrogen concentration, as nitrate-nitrogen was one of the principal anions in many of the collected water samples. The average vertical hydraulic conductivity of the unsaturated zone demonstrated that increased perme-

ability of the sediments enhanced the likelihood of ground-water contamination by nitrate-nitrogen. The median completion date of irrigation wells within a 1-mi radius showed that sites that had been under irrigation the longest had an increased probability of ground-water contamination by nitrate-nitrogen.

Model B was formulated using only data from area 1. The model predicted atrazine concentrations using nitrate-nitrogen concentration, depth to water, and the number of irrigated acres in a 1.7-mi radius of the sampled well and explained about 61 percent

Table 2. Results of comparisons of observed nitrate-nitrogen and atrazine concentrations from sites in Merrick County with predicted concentrations and probabilities of detection from selected models
[mg/L, milligrams per liter; µg/L, micrograms per liter]

	Model A:		Model B:	Model C:
Observed nitrate-nitrogen concentration (mg/L)	Predicted nitrate-nitrogen concentration (mg/L)	Observed atrazine concentration (µg/L)	Predicted atrazine concentration (µg/L)	Probability of atrazine detection greater than 0.05 µg/L
28	4.1	.60	.26	1.0
21	4.4	.30	.16	.95
16	18	Not analyzed	Not determined	Not determined
8.8	15	.50	.06	.84
18	15	.60	.13	.97
16	6.8	.60	.12	.90
21	12	1.4	.16	.97
4.3	7.2	.30	.04	.71
P-values from Wilcoxon rank sign test	0.16 ¹		0.02	

¹ P-values greater than 0.05 are not significantly different at the 95-percent confidence level.

of the variation observed in atrazine concentrations. The presence of nitrate-nitrogen as an explanatory variable was not surprising given the overall correlation coefficient of 70 percent between nitrate-nitrogen and atrazine concentrations analyzed for this study. This supports the assumption that many of the factors affecting the transport of nitrate-nitrogen into the ground water also possibly affect the transport of atrazine. The depth-to-water variable demonstrates the greater likelihood of contamination with atrazine in areas with shallow water tables. The number of irrigated acres in a 1.7 mi radius of the sampled well is a measure of the intensity of irrigated agriculture and represents the effects of adjacent land use on water quality and the significance of lateral ground-water flow paths.

Model C was a logistic model using data from all study areas. The model predicted the probability of atrazine detections at or larger than the 0.01 µg/L detection limit using nitrate-nitrogen concentration, gradient of the potentiometric surface, percentage of clay in the soil, and the logarithm of well depth as

explanatory variables. The presence of the potentiometric gradient in the model logically maintains that areas with flat gradients and relatively slow rates of ground-water flow may tend to accumulate atrazine at the water table faster than areas with relatively steep gradients. The percentage of clay represents the importance of soil permeability, and the log of well depth again demonstrates that deeper water supplies are not as easily contaminated by agricultural chemicals as shallow water supplies.

The overall effectiveness of the models was tested in two ways. First, water from eight irrigation wells in Merrick County (fig. 1), which is adjacent to area 1, was collected and analyzed for nitrate-nitrogen and atrazine concentrations independently of the data used to produce the models. Data quantifying the explanatory variables for each of the models were collected for each ground-water sampling site and predicted concentrations, or probabilities of detection, were compared to observed concentrations (table 2). The Wilcoxon rank sum test (Minitab, 1989), which compares population medians, showed

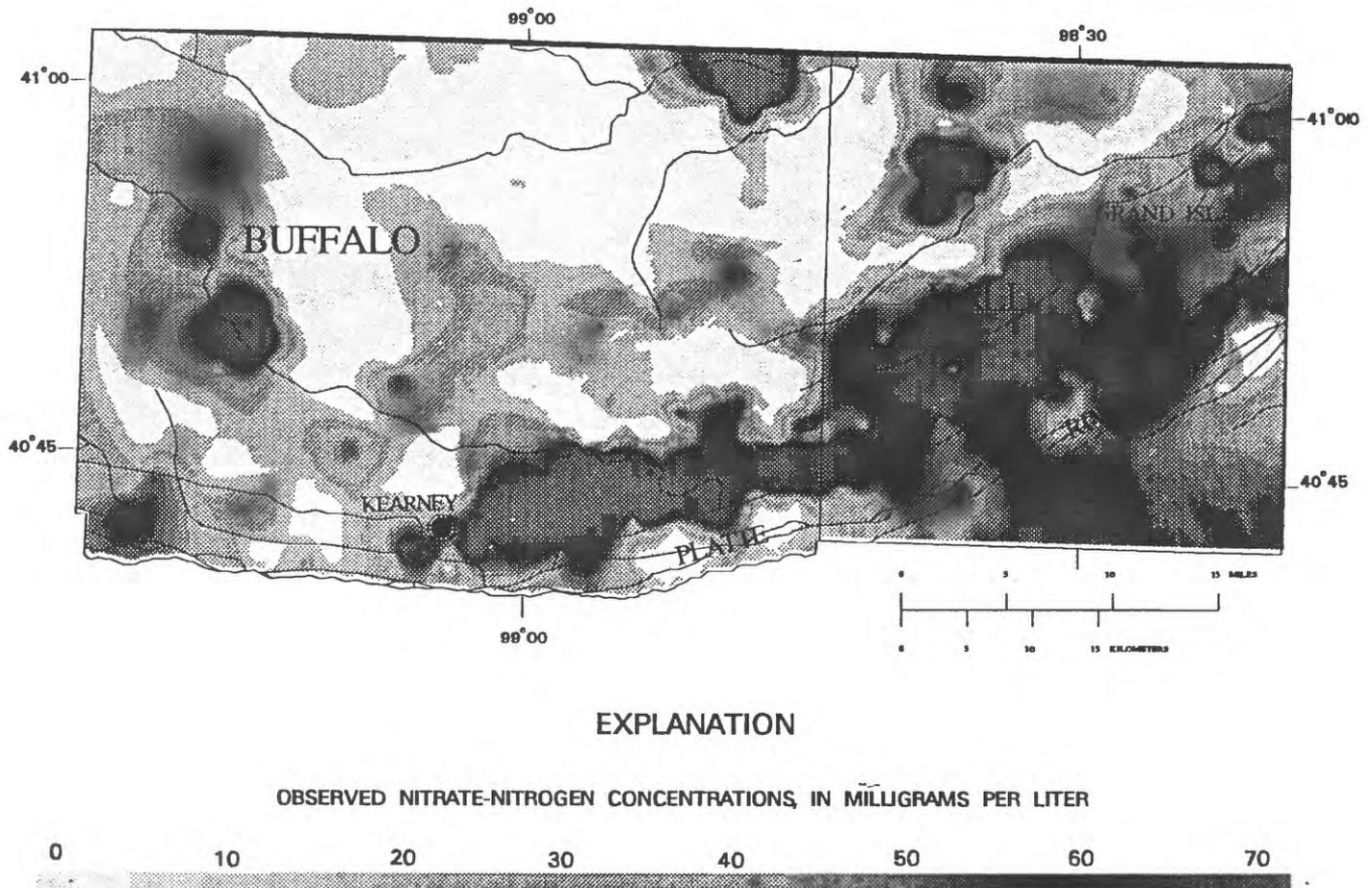


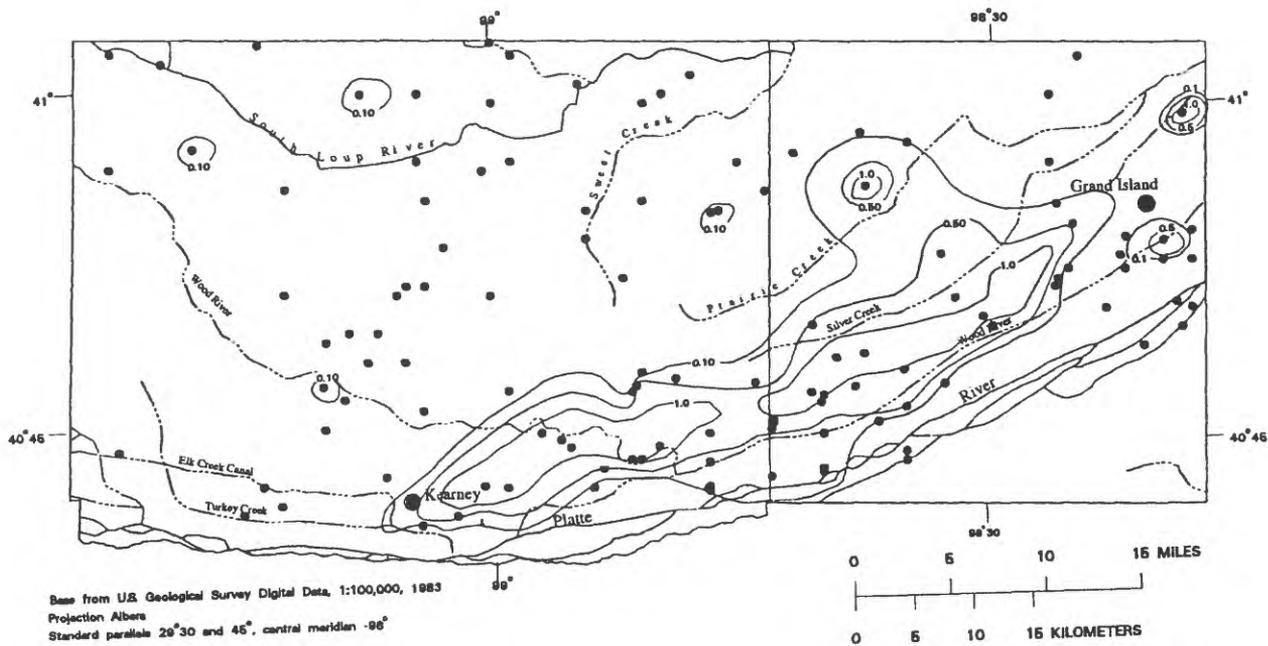
Figure 2. Distribution of observed nitrate-nitrogen concentrations in Buffalo and Hall Counties, south-central Nebraska.

that the predicted nitrate-nitrogen concentrations were statistically similar to the observed concentrations at the 95-percent confidence level and that the atrazine concentrations predicted by model B were statistically smaller than observed atrazine concentrations. Model C predicted probabilities of atrazine detection of 0.71 to 1.0 for the seven irrigation wells for which atrazine data are available.

The second means of testing the models was through comparison of maps of observed and predicted ground-water concentrations of nitrate-nitrogen and atrazine (figs. 2-6). The predictive maps of nitrate-nitrogen and atrazine concentrations and probability of atrazine detection (figs 4-6) were

selected to represent each of the explanatory variables in the models. The surfaces for each model were overlaid, and the predictive equations were solved using the explanatory variable values for each cell. The maps predicting nitrate-nitrogen and atrazine concentrations and probabilities of atrazine detection were compared to maps showing observed nitrate-nitrogen and atrazine concentrations generated from data sources other than those used to produce these models (Exner and Spalding, 1990).

In comparing the maps of observed and predicted concentrations, note that both the predicted nitrate-nitrogen and atrazine concentrations and the probability of atrazine detections look quite similar to the maps



EXPLANATION

- LINE OF EQUAL OBSERVED ATRAZINE CONCENTRATION IN GROUND WATER
 —Interval in Micrograms per liter, is variable
- ◆ LOCATION OF WELL FROM WHICH WATER WAS COLLECTED FOR ATRAZINE

Figure 3. Distribution of observed atrazine concentrations through 1989 in Buffalo and Hall Counties, south-central Nebraska.

of observed concentrations. Both maps of observed and predicted contamination show a generalized belt of ground-water contamination in the lowlands adjacent to the Platte River with some areas of larger concentrations superimposed on it. The upland areas north of the Platte River, where the depth to water is greater and where row-crop agriculture is less intense, show much smaller observed and predicted concentrations of nitrate-nitrogen and atrazine. Even in the upland areas, subtle effects, such as small stream drainages, are revealed by the predictive maps as being slightly more susceptible to ground-water contamination by agricultural chemicals than other upland areas. The fine detail shown on the predictive maps is the result of much

larger data sets describing the explanatory variables (usually an order of magnitude larger) than the observed nitrate-nitrogen and atrazine data sets.

CONCLUSIONS

Multiple-regression and logistic regression techniques appear to be well suited for the generation of predictive ground-water-quality models. Although the models explained only 50 to 68 percent of the variation in nitrate-nitrogen and atrazine concentrations in ground water, the predicted concentrations and probabilities of detection generally agreed with observed contaminant concentrations from the eight wells in

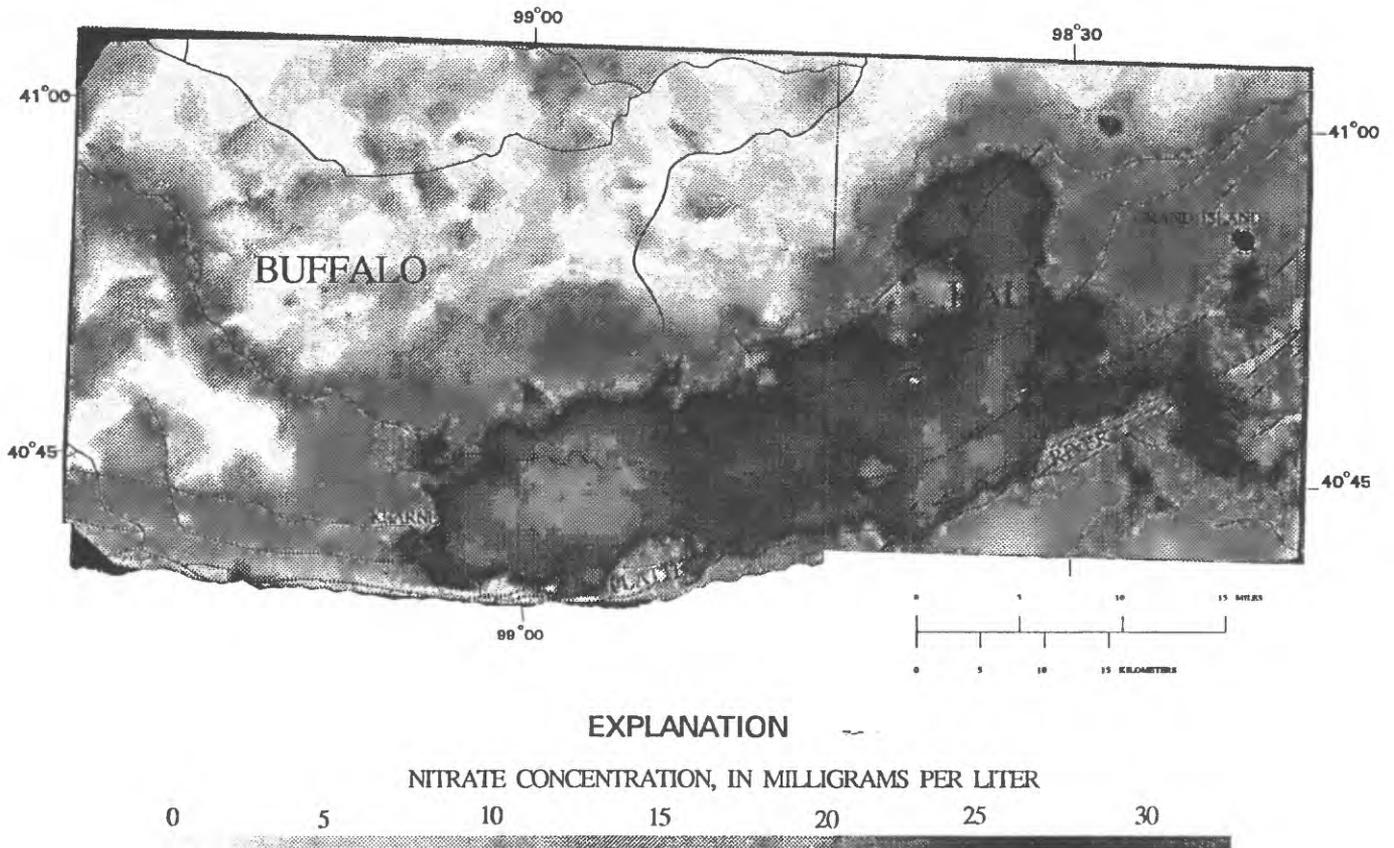


Figure 4. Distribution of predicted nitrate-nitrogen concentrations in ground-water in Buffalo and Hall Counties, south-central Nebraska.

Merrick County, and maps of predicted concentrations and probabilities of detection closely agreed with maps of observed concentrations of nitrate-nitrogen and atrazine in ground water in area 1.

The coupling of regression and logistic models that predict ground-water quality with a geographic information system, such as ARC/INFO, can be a powerful tool for evaluating models as they are generated and for utilizing the models after they have been completed. The modeling and graphic representation permits the

user to define basic relations between selected ground-water contaminants and physical factors that may be affecting those concentrations and to use the relations to better define areas of potential ground-water contamination beyond the immediate areas of observed water-quality data sites. In fact, the explanatory variable data sets are commonly orders of magnitude larger than the dependent variables and can yield much larger coverages with finer detail than is possible with most contaminant data bases.

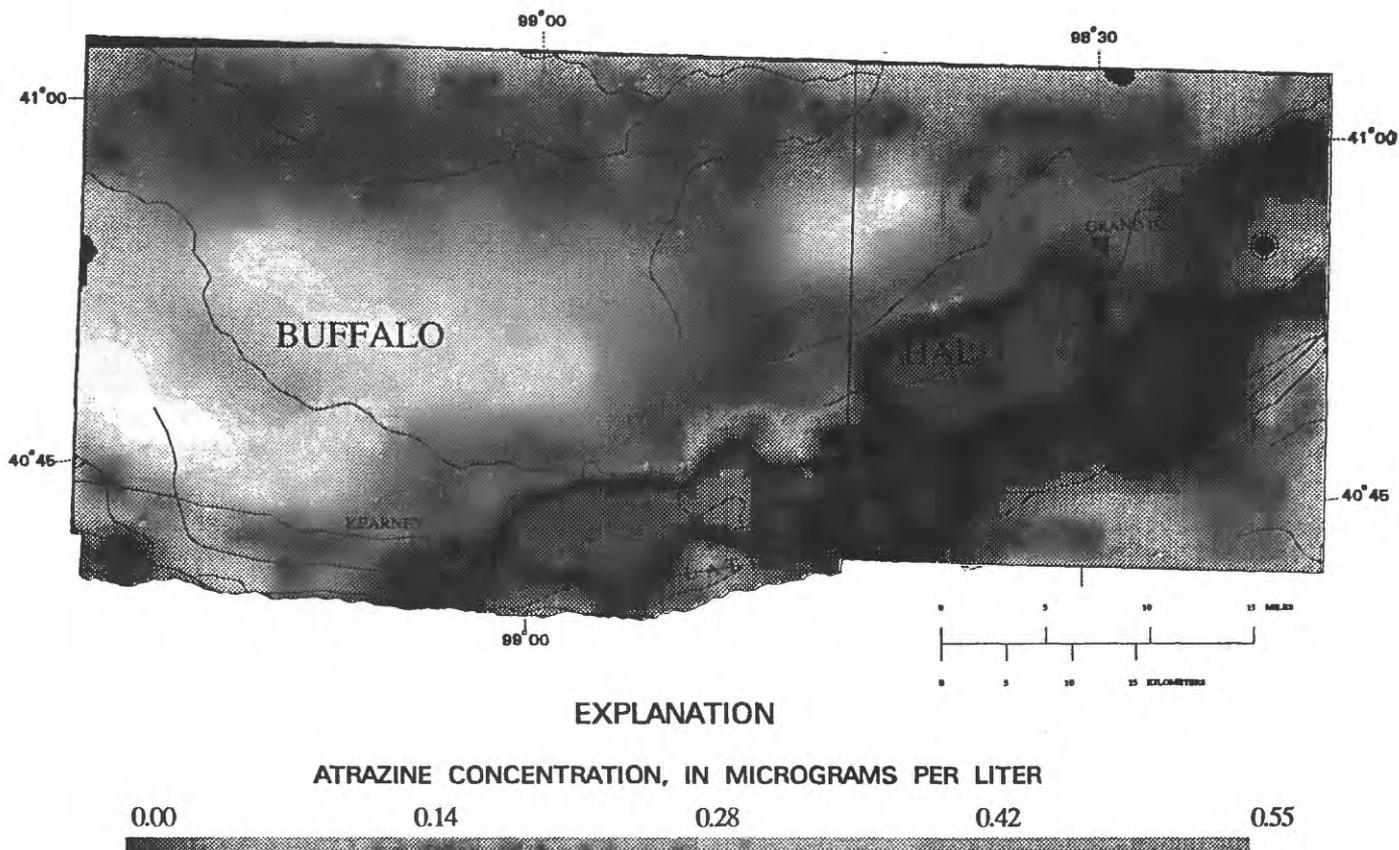


Figure 5. Distribution of predicted atrazine concentrations in ground-water in Buffalo and Hall Counties, south-central Nebraska.

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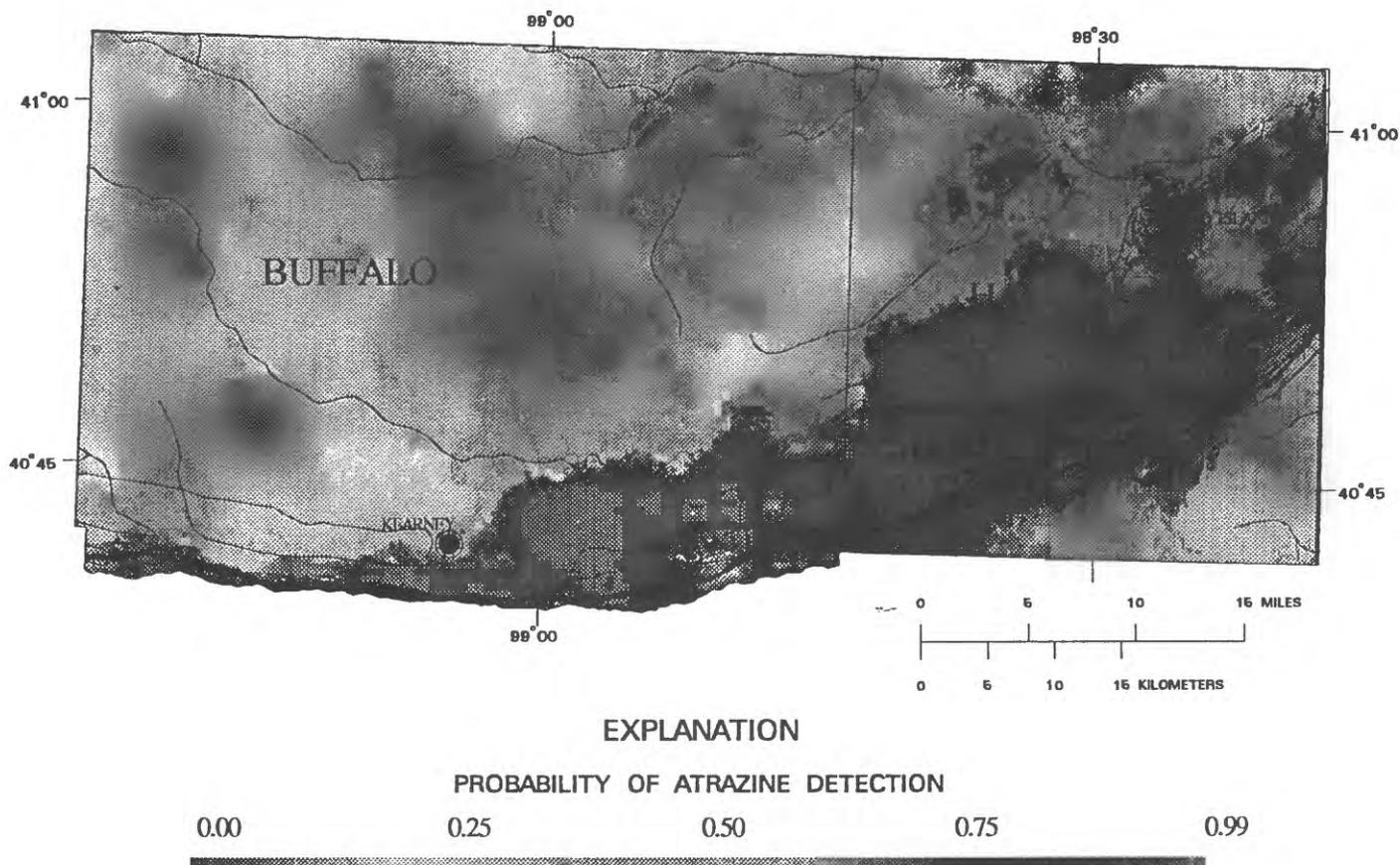


Figure 6. Distribution of probability of atrazine detection greater than or equal to 0.01 micrograms per liter in ground water in Buffalo and Hall Counties, south-central Nebraska.

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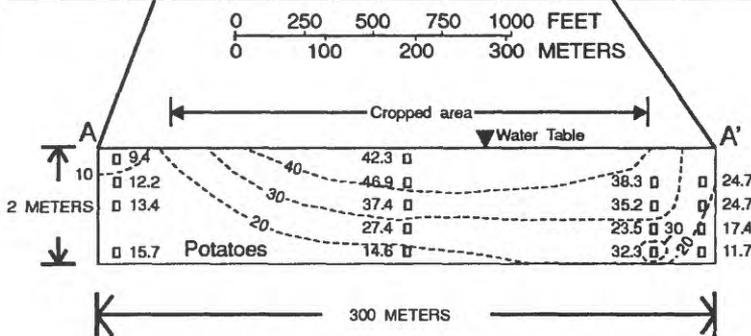
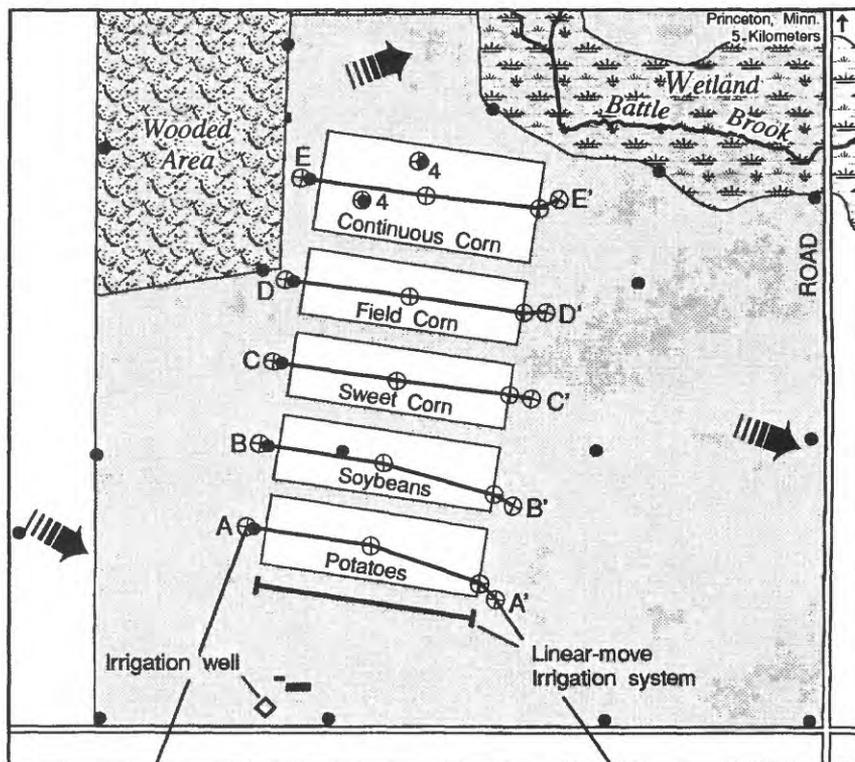
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The research area is located in the northeast quarter of section 18, township T35N, range R26W.

EXPLANATION

- | | | | |
|----------|---|--|--|
| | Cropped area and 1991 crop type | | Data point, number indicates chloride concentration, in milligrams per liter |
| | Research area, including cropped areas | | Observation well, number indicates number of wells at site |
| | Direction of ground-water flow, January, 1991 | | Multiport well |
| A—A' | Line of section | | Building |
| ---20--- | Approximate line of equal chloride concentration, interval in 10 milligrams per liter | | |

Figure 1. Layout of the Princeton, Minnesota, Management Systems Evaluation Area and example illustrating contouring of chloride concentrations along a cross section beneath the potato-cropped area, April 1992.

Table 1. Application rates of agricultural chemicals on crops at the Princeton, Minnesota, Management Systems Evaluation area, 1991

[All application rates are broadcast rates; band, application of herbicide only over row, amount is one-third of the total amount per hectare for broadcast application. kg/ha, kilograms per hectare; --, not applied]

Agricultural chemical	Potatoes		Soybeans		Sweet corn		Field corn		Continuous corn	
	Total rate kg/ha	Month(s) applied								
Fertilizer										
Potash (potassium chloride)	504	April	112	April	112	April	112	April	112	April
Nitrogen	224	April and June	--	--	157	April and June	157	April and June	157	April and June
Herbicide										
Atrazine	--	--	--	--	1.70 band	May	1.70 band	May	1.70	May
Alachlor	--	--	2.25 band	May	2.25 band	May	2.25 band	May	2.25	May
Metribuzin	0.56	May	0.56 band	May	--	--	--	--	--	--
Metolachlor	1.12	May	--	--	--	--	--	--	--	--

A buffer area around and between the cropped areas (fig. 1) was planted with a mixture of timothy and smooth brome grass. Agricultural chemicals were not applied in this buffer area. The entire 65-ha field was planted in alfalfa during 1981-89 and in corn during 1990, prior to the implementation of the MSEA farming systems in spring 1991. Detailed records of farming practices and chemical applications during this period were not available.

The ground-water-quality sampling network at the Princeton MSEA consists of 29 observation wells and 22 multiport wells (fig. 1). In addition, 14 observation wells are located off the 65-ha field (not shown in fig. 1). Observation wells were used to measure water levels monthly and to determine background concentrations of agricultural chemicals. These wells are constructed of 5.1-cm inside-diameter (i.d.) galvanized-steel or polyvinyl chloride (PVC) casing with 0.6-m-long screens located at the water table or 0.15-m-long screens installed deeper in the aquifer. The multiport wells are located 21 m upgradient, in the middle, at the downgradient edge, and 25 m downgradient (slightly

less than the distance ground water travels in 1 year) of each cropped area (fig. 1). Each multiport well consists of six, 0.6-cm i.d. stainless-steel tubes housed in a 5.1-cm i.d. PVC casing; each tube has a 3-cm-long screened interval (port) which is external to the PVC casing. The sampling ports were installed at 0.5-m intervals with the uppermost port 0.5 m above the water table to allow sample collection if the water table rose.

Water samples were collected during 1991 at four different times from all multiport wells, selected onsite observation wells, and Battle Brook (fig. 1). These samples were collected before the application of agricultural chemicals (April), twice during the growing season (June and August), and in the late fall after crops were harvested (December). Sample-collection and laboratory-analysis quality-assurance/quality-control protocols were followed (MSEA Steering Committee, written commun., 1991). Specific conductance, pH, temperature, dissolved oxygen concentration, and oxidation-reduction potential of ground water were measured during pumping at each sampling site.

Water samples were collected once these properties stabilized. Alkalinity titrations were performed the same day in the field. Water samples were collected and analyzed for dissolved major cations and anions, nutrients, and selected herbicides and herbicide metabolites (atrazine, de-ethylatrazine (DEA), de-isopropylatrazine (DIA), alachlor, chloroalachlor, 2,6-diethylalanine, metolachlor, and metribuzin). Gas chromatography/mass spectrometry was used to determine herbicide concentrations (P.D. Capel, U.S. Geological Survey, written commun., 1991).

GROUND-WATER QUALITY, 1991

Concentrations of selected water-quality constituents in the upper 2 m of the saturated zone were contoured along a cross section extending beneath each MSEA cropped area (figs. 1-4). The contouring is somewhat speculative because of the wide horizontal spacing of the data points. Contour intervals were selected that best emphasized contrasts in constituent concentrations along each cross section.

Because potash (potassium chloride) fertilizer was applied only to the cropped areas (fig. 1 and table 1) and because chloride moves conservatively with ground water, chloride was used as a tracer of water recharged through the cropped areas. Where concentrations of chloride and nitrate nitrogen (nitrate-N) were clearly greater beneath a cropped area than upgradient, contours were drawn to reflect the interpretation that the source of the higher concentrations was recharge of chemicals from the overlying cropped area. For example, beneath the potato cropped area during April 1992 (fig. 1), the 20-mg/L chloride contour was extended to the upgradient (west) end of this area because the source of the higher chloride concentrations was considered to be downward movement of chloride to ground water from the cropped area.

Most of the closed contours in figures 1-4 are artifacts of the contour intervals selected. The closed contour around the 32.3-mg/L chloride concentration in figure 1, for example, likely represents a volume of water that was recharged through the overlying potato-cropped area. This volume of water could have become isolated within water that had lower chloride concentrations because of temporal variations in fluxes of water and chemicals to the saturated zone. Other closed contours in figures 1-4, particularly for the herbicides, likely represent mixing of waters in the aquifer and are not related to the MSEA farming systems. For atrazine

and DEA, the contour intervals chosen were the reporting and detection limits for each compound. Because there is uncertainty associated with the reproducibility of these herbicide analyses near their detection limits, there is also uncertainty associated with the locations of the herbicide-concentration contour lines (figs. 2, 3, and 4).

Chloride.—Chloride concentrations (23-26 mg/L) greater than background (2-19 mg/L) were first detected in the upper 1 m of the saturated zone beneath the field corn-cropped area (fig. 2) during the June 1991 sampling period, about 1.5 months after application. Chloride concentrations (33-37 mg/L) greater than background were first detected in the upper 1 m of the saturated zone beneath the potato- (fig. 3) and soybean-cropped areas during the August 1991 sampling period, about 4 months after application. Chloride concentrations (21-31 mg/L) greater than background were first detected in the upper 1 m of the saturated zone beneath the sweet corn and continuous corn during the December 1991 sampling period, about 7.5 months after application. On the basis of these times of first detection of elevated chloride concentrations, the estimated time of travel of water and chloride moving through the unsaturated zone was 1 to 7.5 months. These travel times are maximum values because the sampling periods were not frequent enough to identify first arrival of the chloride tracer. In addition, relatively high background concentrations (2-19 mg/L) of chloride partially conceal increases in chloride concentrations that could have resulted from recharge through the MSEA cropped areas. These travel times are comparable with a travel time of 75 days determined in a dye-tracing study done during 1991 (Delin and others, 1992b).

The April 1992 data reflect the affects of agricultural practices in 1991 and earlier on ground-water quality because agricultural chemicals had not yet been applied for the 1992 growing season. Additional inputs of chloride and continued spread of chloride through the aquifer occurred during spring 1992 (figs. 2-4) when approximately 6.4 cm of recharge occurred. Chloride concentrations were greatest beneath the potato-cropped area (fig. 4), reflecting that the chloride (potash fertilizer) application on the potato-cropped area was 4.5 times greater than that used with any other crop (table 1). Chloride concentrations in April 1992 in the upper 1 m of the saturated zone beneath the cropped areas ranged from 20 to 50 mg/L compared with concentrations of 2 to 19 mg/L away from the cropped

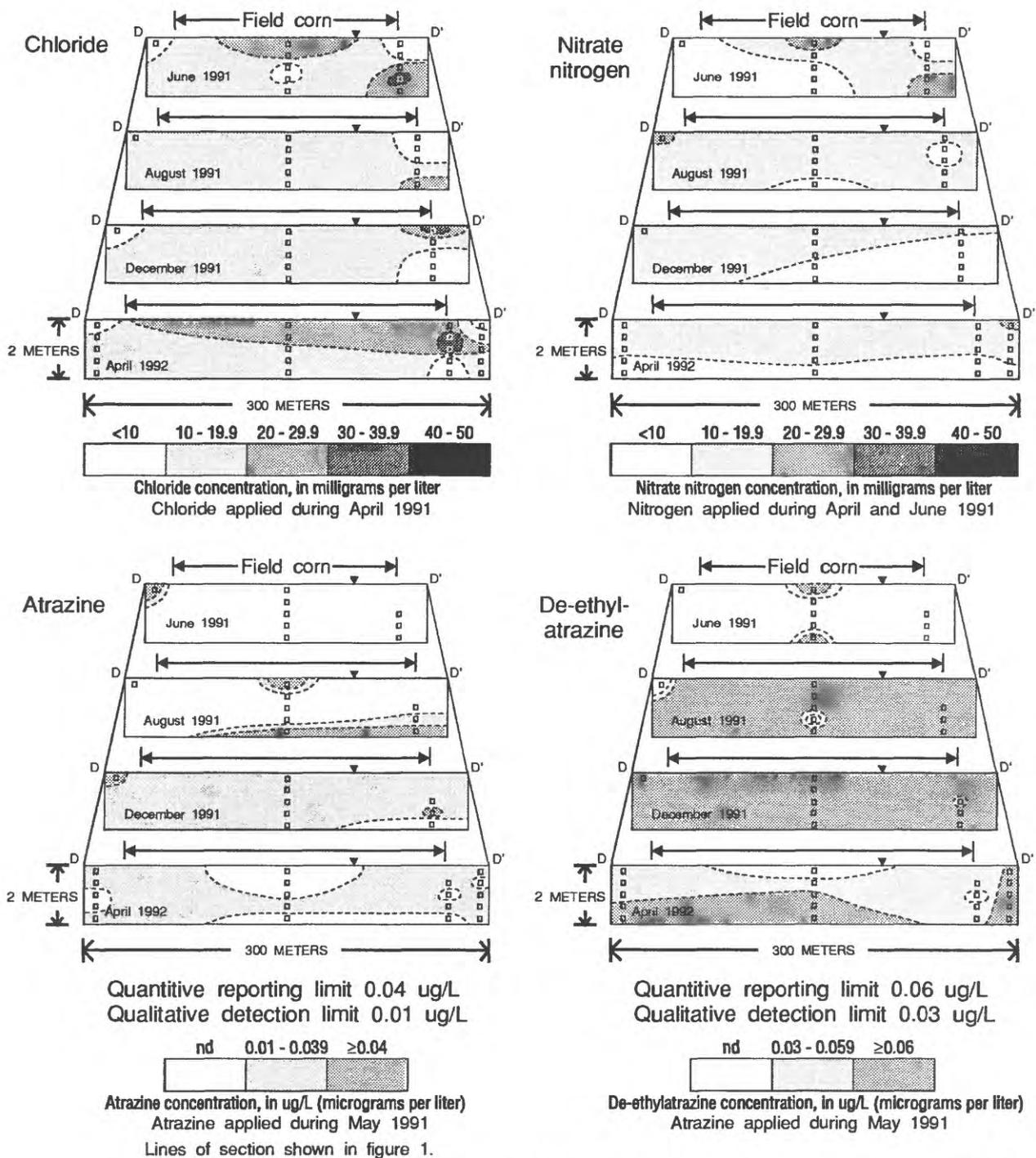
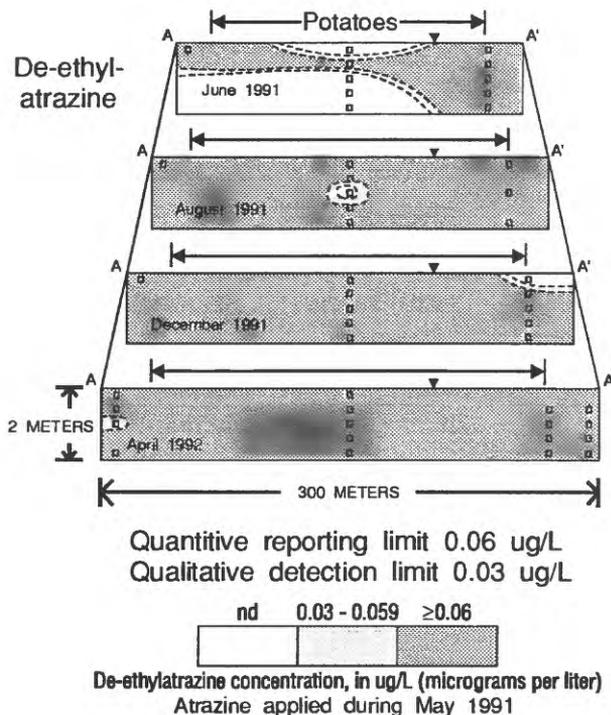
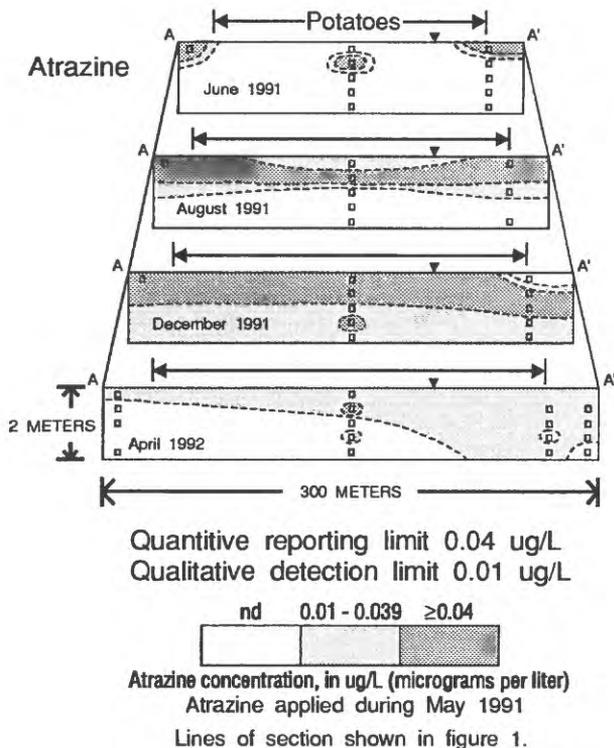
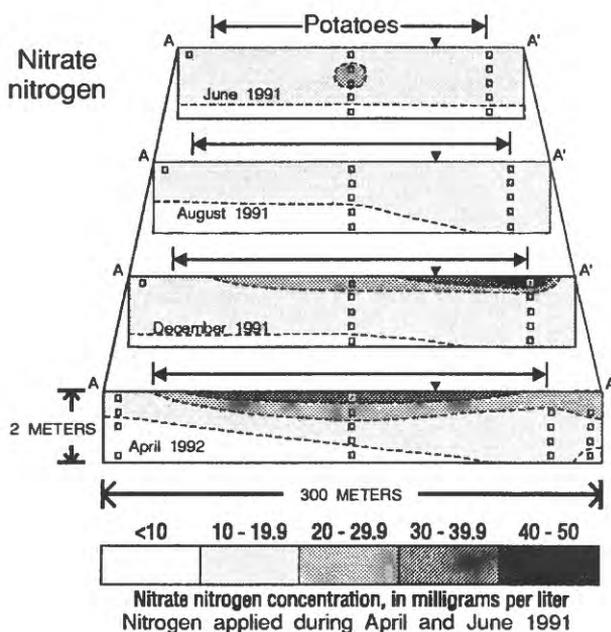
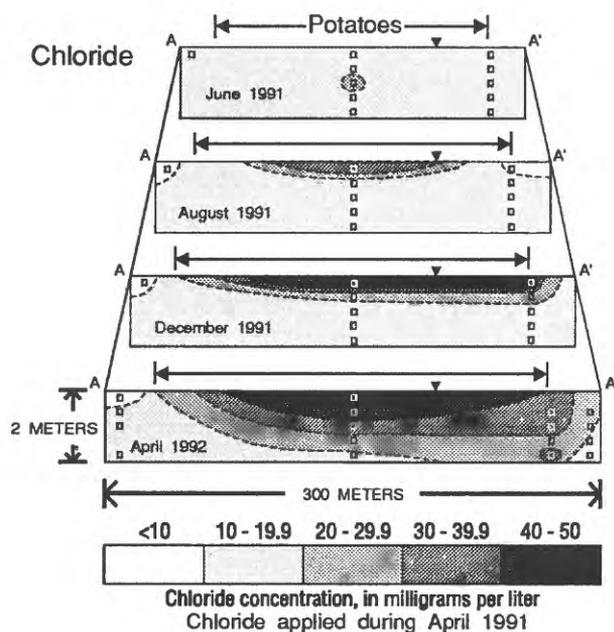


Figure 2. Chloride, nitrate nitrogen, atrazine, and de-ethylatrazine concentrations along a cross section beneath the field-corn cropped area during the June 1991 through April 1992 sampling periods at the Princeton, Minnesota, Management Systems Evaluation Area.



EXPLANATION

- ▽— Water-table
- - - - - Approximate line of equal chemical concentration
- ◄————► Cropped area
- August 1991 Sampling period date
- nd Below the detection limit
- Data point

Figure 3. Chloride, nitrate nitrogen, atrazine, and de-ethylatrazine concentrations along a cross section beneath the potato-cropped area during the June 1991 through April 1992 sampling periods at the Princeton, Minnesota, Management Systems Evaluation Area.

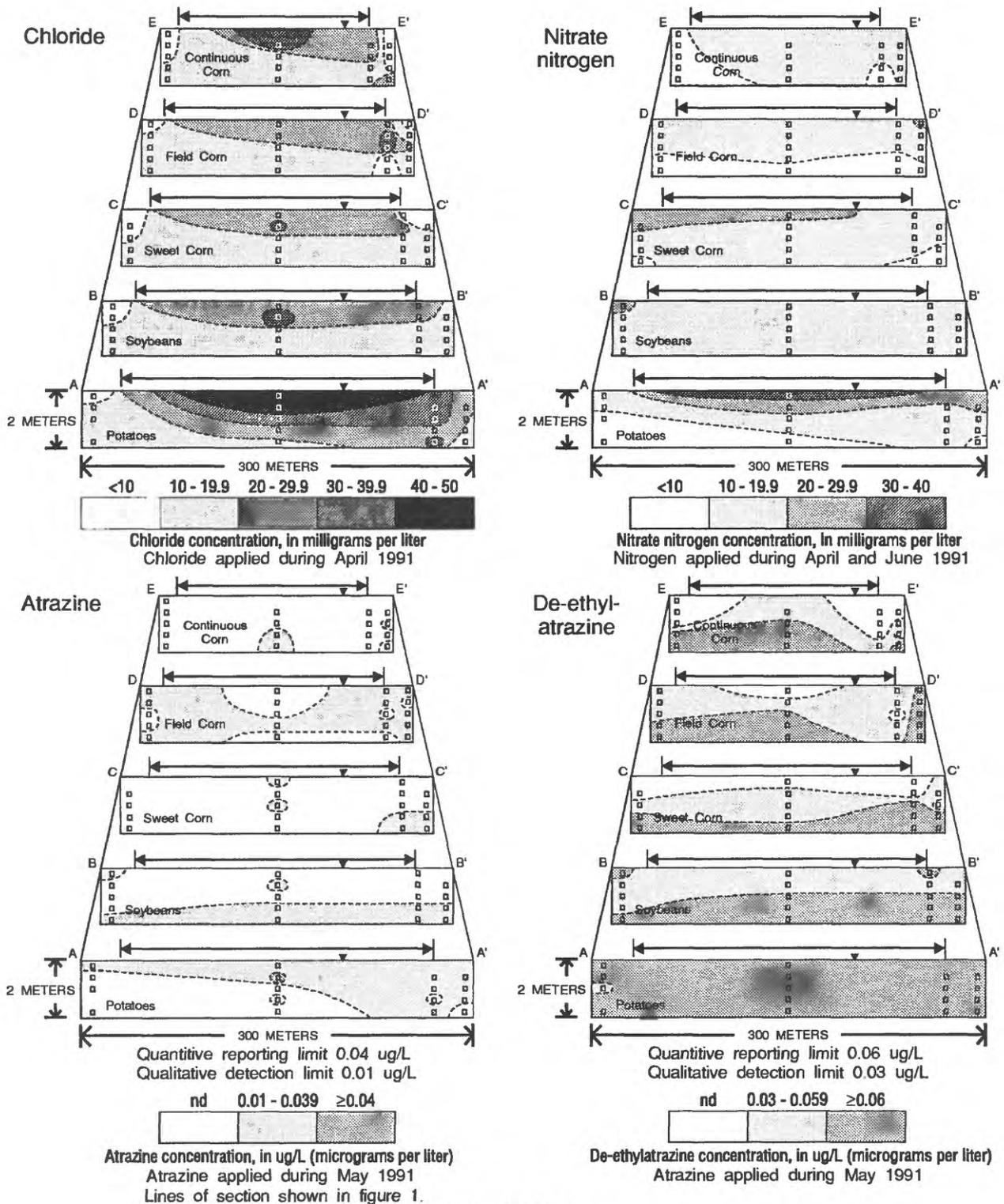


Figure 4. Chloride, nitrate nitrogen, atrazine, and de-ethylatrazine concentrations along a cross section beneath cropped areas at the Princeton, Minnesota, Management Systems Evaluation Area, during the April 1992 sampling period.

Spatial Variability of Unsaturated-Zone Properties in Relation to Topography in a Sand-Plain Setting near Princeton, Minnesota

By G.N. Delin¹, M.K. Landon¹, R.W. Healy², and H.W. Olsen³

Abstract

The spatial distribution of preferential flow paths and unsaturated-zone properties in two topographic settings were determined from a dye-tracing and trenching study done at the Management Systems Evaluation Area (MSEA) near Princeton, Minnesota. The topographic settings are upland and lowland sites about 78 m (meters) apart that differ in elevation by 1.4 m. A 3 percent solution of rhodamine-WT dye was applied uniformly as a tracer to a 3.5- by 6-m area at both sites at 10-day intervals from July 5 through September 13, 1991. After application of the dye, a 3- by 2-m trench was dug to a depth of 2 m in the middle of each dye-application area to locate the dye and to collect soil samples.

Water samples were collected periodically from a multiport well, located 2.5 m horizontally downgradient of each dye-application area, to estimate the time-of-travel of recharge water through the unsaturated zone. The dye was first detected in ground water about 100 days after application. On the basis of average ground-water velocity at the Princeton MSEA of 10 cm/d (centimeters per day), the transport velocity of dye through the unsaturated zone was calculated to be 3.7 cm/d at the lowland site and 5.3 cm/d at the upland site. The dye moved 2 m vertically through the saturated zone over a horizontal distance of about 9 m, whereas a steady-state ground-water-flow model predicted less than 0.2 m of vertical movement.

A total of about 450 soil samples were collected from the sides and bottom of the trenches

for analyses of bulk density, dye fluorescence, grain-size distribution, hydraulic conductivity, moisture-retention characteristics, organic-carbon content, and volumetric moisture content. The distribution of dye through the unsaturated zone was highly variable at the upland and lowland sites. Dye movement was greatest beneath the furrows and least beneath the corn rows. Preliminary results indicate the dye moved preferentially in response to tillage patterns (corn rows and furrows), microtopography, presence of plant roots, differences in total organic carbon, and coarser-grained heterogeneities in the unsaturated zone. Visible dye distribution did not correlate strongly with bulk density, saturated hydraulic conductivity, moisture-retention characteristics, and volumetric moisture content.

INTRODUCTION

Two factors that affect water movement through the unsaturated zone are spatial variability of soil properties (Delhomme, 1979; Sharma and others, 1980; and Russo and Bresler, 1981) and topography (Meyboom, 1966). Spatial variability of soil properties affects the pathways and rates of water movement. Among the important soil properties that can affect water movement are bulk density, grain-size distribution, hydraulic conductivity, moisture-retention characteristics, organic-carbon content, and volumetric moisture content. This study was designed to evaluate the effects of spatial variability of these soil properties on the distribution of preferential flow paths in upland and lowland areas in sandy soils.

This paper describes preliminary results of ongoing studies by the U.S. Geological Survey of unsaturated-zone properties at the Management Systems Evaluation Area (MSEA) near Princeton, Minn. (fig. 1).

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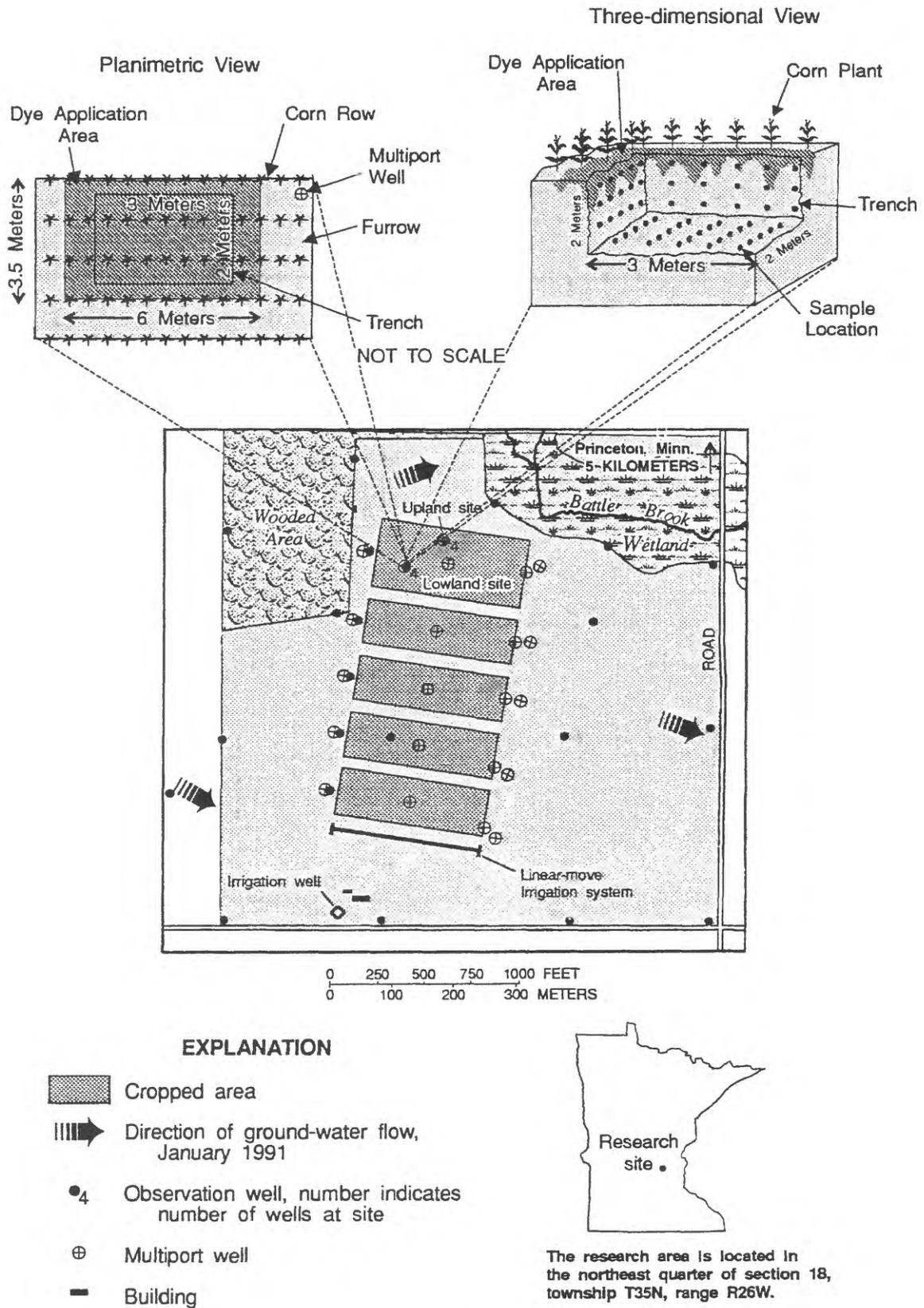


Figure 1. Layout of the Princeton, Minnesota, Management Systems Evaluation Area.

Nitrogen Uptake and Soil Water Variability Across a Sand Plain Landscape

By J.A. Lamb¹, M.D. Tomer², J.L. Anderson³, and R.H. Dowdy⁴

Abstract

Research at the Northern Cornbelt Sand Plains Management Systems Evaluation Area at Princeton, Minnesota, was conducted to characterize the variability of whole-plant nitrogen uptake and soil-water content under a continuous corn-cropping system. The soil was a Zimmerman fine sand (mixed, frigid, Alfic Udipsamment). Nitrogen fertilizer was applied uniformly in 1991 and 1992. In 1991 and 1992, corn whole-plant samples were collected in 15-meter intervals along a 244-meter-long transect to determine nitrogen uptake. In 1992, plastic neutron-moisture-meter access tubes were placed to a depth of 2 meters every 20 meters along the same transect. Nitrogen uptake ranged from 115 to 157 kilograms nitrogen per hectare in 1991 and 92 to 132 kilograms nitrogen per hectare in 1992. Mean uptake of nitrogen was 24 kilograms per hectare greater in 1991 than it was in 1992. Soil-water content ranged from 10 to 15 centimeters for the upper 1.7-meter depth interval on July 23, 1992. The area where nitrogen uptake in 1992 was least is a sideslope area where the surface soil was driest. Leaching may have occurred during recharge events during the growing season at this and positions in the terrain.

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INTRODUCTION

The Northern Cornbelt Sand Plains Management Systems Evaluation Area (MSEA) program is a multi-agency, multistate initiative to evaluate the effects of present and modifications to present agricultural management systems on water quality in a sand plain areas in Minnesota, North Dakota, South Dakota, and Wisconsin. The Northern Cornbelt Sand Plains MSEA program is a cooperative study primarily between the U.S. Department of Agriculture-Agricultural Research Service, the University of Minnesota Soil Science Department, and the U.S. Geological Survey.

Ground water contamination from agricultural management systems is caused by numerous complex processes. An objective of the MSEA project is to evaluate agricultural systems with the goal of minimizing adverse effects of agricultural management practices on ground water. Nitrogen (N) fertilizer is necessary for profitable corn production; however, N fertilizers combined with N mineralized from soil organic matter can be major sources of ground-water contamination. N fertilizer traditionally has been uniformly applied on production fields. The Northern Cornbelt Sand Plains MSEA has been investigating the effect of landscape variability on N uptake by crops and on soil-water content. N in soils and fertilizer can be removed by processes such as plant uptake and removal, leaching of nitrate-N through the soil, erosion of soil, and denitrification by bacteria. Because of typically high infiltration rates for the sandy soils at the Northern Cornbelt Sand Plains MSEA, offsite losses of N resulting from erosion are negligible. The purpose of this paper is to examine the relation of N uptake by corn to soil-water content across a typical sand-plain terrain.

MATERIALS AND METHODS

The Northern Cornbelt Sand Plains MSEA, Princeton, Minn., site (45°31'34"N. and 93°37'8"W.) was established in 1991 on the Anoka Sand Plain

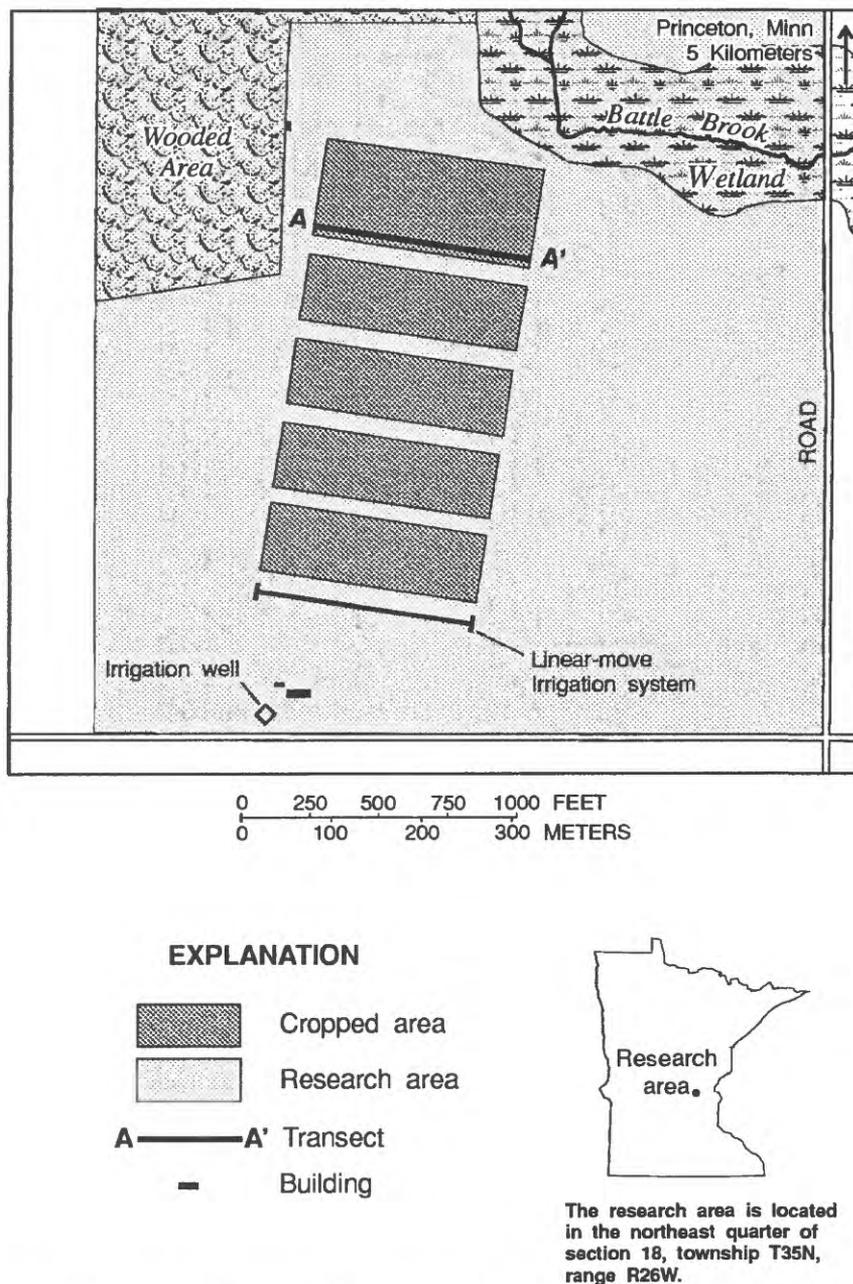


Figure 1. Princeton, Minnesota, Management Systems Evaluation Area and transect used for nitrogen-uptake and soil-water-content measurements.

located 90 kilometer (km) northwest of Minneapolis, Minn. The predominant soil is a Zimmerman fine sand (mixed, frigid, Alfic, Udipsamment). Topographic relief at the 64 hectare (ha) Princeton MSEA is less than 3 meters (m). Generally, the unsaturated zone consists of fine- to medium-grained sand, and the saturated zone consists of medium- to coarse-grained sand. Discontinuous layers of silt and very fine-grained sand as thick as 20 centimeters (cm) are present in the unsaturated and saturated zones. A predominantly clayey till underlies the surficial aquifer. During 1991, the average depth to the water table was about 3.7 m below land

surface, and the saturated thickness ranged from 4 to 16 m. The direction of ground water flow generally is from west to east at about 8 centimeters per day (cm d^{-1}). Ground-water recharge rates generally range from 10 to 20 centimeters per year (cm yr^{-1}).

Five 1.8- to 2.7-ha cropped areas are aligned with the predominant direction of ground-water flow at the Princeton MSEA (fig. 1) where three agricultural management systems are being evaluated: (1) Corn-soybean crops are rotated under ridge (conservation) tillage, split N application, N application adjusted for N mineralized from previous legume crop (soybean), and

banding of herbicides (application of herbicide directly over the plant row. Application area is a third of area covered by a broadcast application, the area where herbicide is applied receives it at the same rate) in cropped areas A and C. (2) Sweet corn and potato crops are rotated with conventional full-width (disk or chisel) tillage and a similar "banded" application of herbicides for sweet corn and conventional full-width tillage and broadcast application of herbicides for potatoes in cropped areas B and D. (3) Corn is grown in consecutive years (continuous corn) under conventional full-width tillage and broadcast application of herbicides in cropped area E. The buffer around the cropped areas (fig. 1) was planted with a mixture of timothy and smooth brome grass to which agricultural chemicals were not applied. Before the implementation of the MSEA agricultural management systems in spring 1991, the entire 67 ha field was planted in alfalfa during 1981-89 and in corn during 1990. Additional details are in Landon and others (1993) and Anderson and others (1991).

The continuous corn system was used for this study. N fertilizer, irrigation water, and pesticides were uniformly applied in the 2.7-ha crop area. The corn was fertilized with a total of 156 kilograms of nitrogen per hectare (kg N ha^{-1}) in 1991 and 168 kg N ha^{-1} in 1992. An adapted corn hybrid was planted during the first week of May in 1991 and 1992. A transect was established 9 m (10 crop rows) north of the southern boundary of the continuous corn-crop area (fig. 1). The 244-m-long transect was chosen to represent a variety of terrains. Plastic access tubes were installed to a depth of 2 m along the transect with 20-m spacing in 1992.

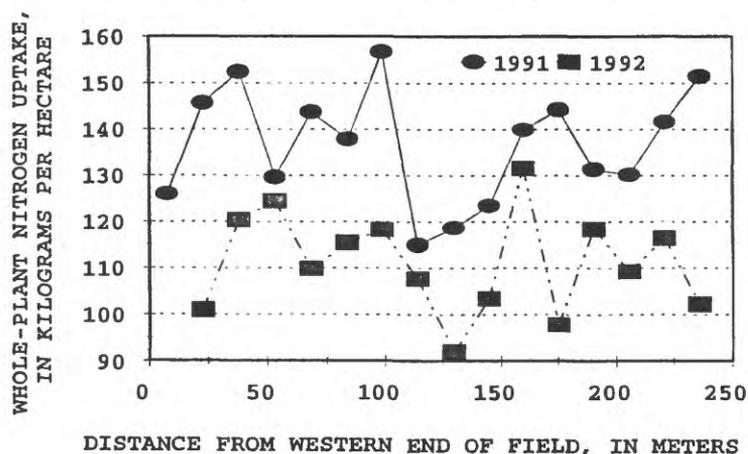


Figure 2. Corn whole-plant nitrogen uptake in kilograms per hectare for continuous corn in 1991 and 1992 at the Princeton, Minnesota Management Systems Evaluation Area along transect A-A' (transect shown in fig. 1).

These access tubes were used to measure soil-water concentration on a volumetric basis with a neutron moisture meter in multiple-day sequences that began after previous significant rainfall or irrigation. The soil-water content for a specific soil layer was determined by multiplying the soil water concentration by the thickness of the soil layer from which the data were derived.

Samples of above-ground corn-plant biomass (grain plus stover) were collected at physiological maturity from 2-m by 1-m areas located every 15 m along the transect. N concentration was measured by means of Kjeldahl digestion techniques. Whole-plant N uptake was then calculated by multiplying the biomass times N concentration.

RESULTS AND DISCUSSION

Whole-plant N uptake along the transect at physiological maturity for 1991 and 1992 is illustrated in figure 2. N uptake ranged from 115 to 157 kg N ha^{-1} in 1991 and 92 to 132 kg N ha^{-1} in 1992. Mean N uptake was 24 kg N ha^{-1} greater in 1991 than it was in 1992 (table 1). This difference in N uptake was caused by the reduced N concentration in 1992 as a result of cooler growing conditions compared to those in 1991. Whole-plant biomass for both years was similar (table 2). The coefficient of variation for N uptake in 1992 (9.7 percent) was slightly greater than that in 1991 (9.1 percent). N uptake was not the same along the transect in each year although there were some similarities. Greater N uptake occurred in areas 35 to 40 m, 90 to 100 m, and

Table 1. Descriptive statistics for corn whole-plant nitrogen uptake in 1991 and 1992 at the Northern Cornbelt Sand Plains Management Systems Evaluation Area near Princeton, Minnesota

Year	Nitrogen uptake (kilograms per hectare)		Coefficient of variation (percent)
	Mean	Range	
1991	136	115 - 157	9.1
1992	112	92 - 132	9.7

Table 2. Descriptive statistics for corn whole-plant biomass in 1991 and 1992 at the Northern Cornbelt Sand Plains Management Systems Evaluation Area near Princeton, Minnesota

Year	Plant biomass (megagrams per hectare)		Coefficient of variation (percent)
	Mean	Range	
1991	14.3	11.6 - 18.1	12.1
1992	14.5	10.7 - 18.2	13.6

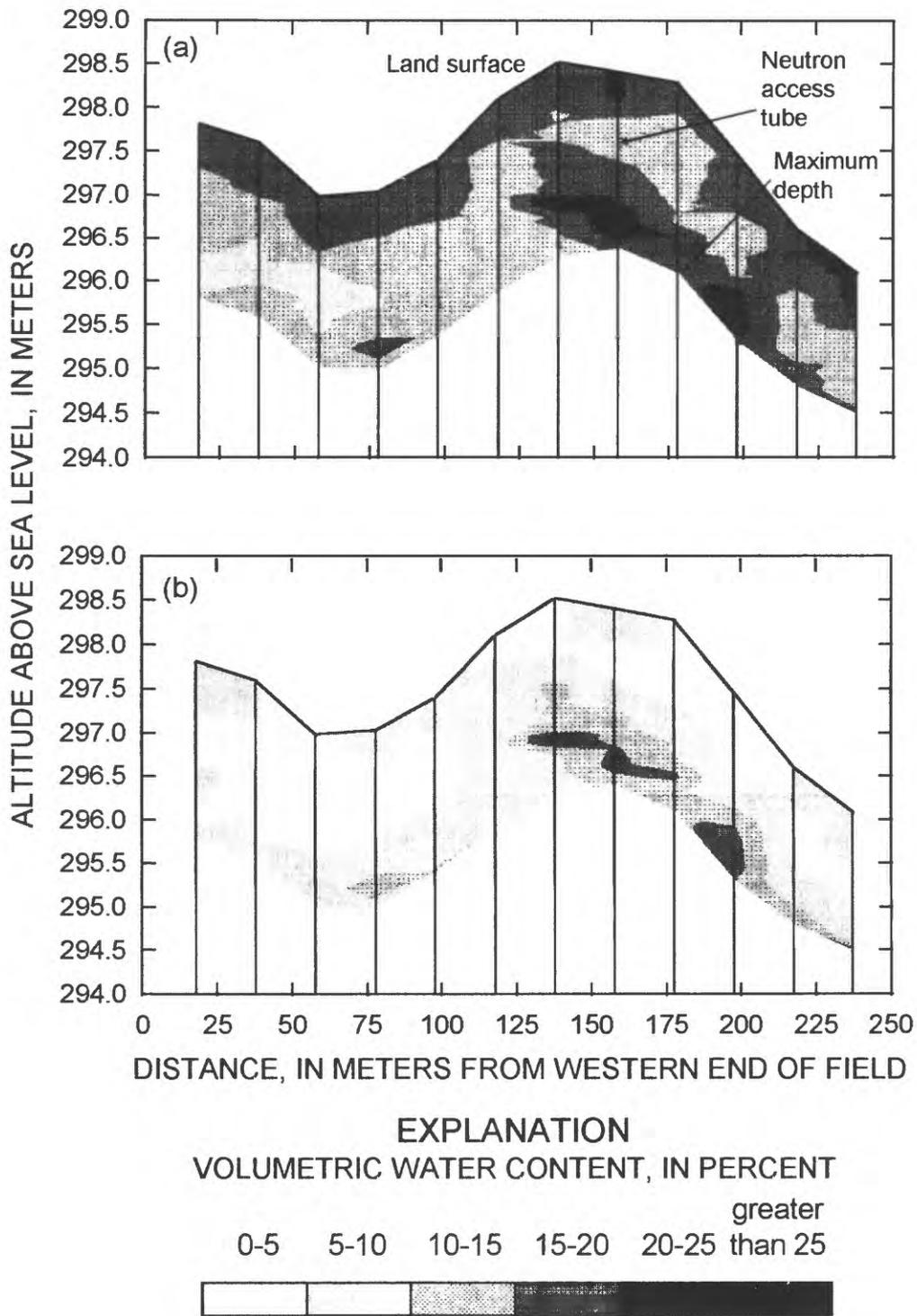


Figure 3. Cross section of the (a) wettest and (b) driest soil-water conditions measured during the 1992 growing season along transect A-A' (transect shown in fig. 1).

160 to 165 m from the western end of the field in both years, whereas less than average N uptakes occurred in the area 110 to 150 m along the transect (fig. 2). The N uptakes are local maximums in 1991 and local minimums in 1992 at three locations along the transect (23, 69, and 177 m). The N uptakes are local maximums in 1992, local minimums in 1991 at two locations along the transect (54 and 192 m). These results suggest that the large differences in N uptake occur in similar places each year. There is not a strong correlation between years and location for N uptake ($r = 0.24$).

Soil in the vadose zone is not homogeneous. Thin illuvial horizons (lamellae) are present in the 1- to 1.7-m-depth interval throughout the Princeton, Minn.. MSEA, usually in topographically high terrain. These layers may retard or divert soil-water movement, thereby affecting potential loss of N by leaching and plant N uptake. The spatial variability of soil-water content illustrated in figure 3 is caused by the perching of soil water above the lamellae. The greatest perching of soil water occurred at the hilltop position in the area 125 and 175 m along the transect (fig. 3). Rates of water loss caused by crop use or drainage after rainfall or irrigation were slower where the degree of perching was greatest. During dry periods in the growing season, soil-water content in the upper 1-m depth interval was least along sideslope positions, which coincide with areas of least N uptake, particularly the west-facing slope in the area 110 to 140 m along the transect. N uptake by plants may have been limited by poor surface- and subsurface-water retention relative to that at other locations, resulting in reduced crop growth and an increased potential for leaching of N.

After irrigation on July 23, 1992, soil-water content in the 1.7-m depth interval ranged from 10 to 15 cm. Soil-water content was least at the western end of the transect, where subsoils are coarse and lamellae are absent, and greatest in upland positions where soil-water perching occurs. Soil-water content also was small on sideslope positions where the surface soil horizon is thinner than it is along the rest of the transect. Water loss from crop use and drainage during July 23 -August 3, 1992, ranged from 3.5 to 5.5 cm. If the differences in soil-water content and soil water losses from crop use and drainage were considered, there is a potential for variations in the amount of N that could be transported vertically to ground water,

even over a relatively short horizontal distance of the transect (244 m).

Considering soil-water content and N uptake, the area where plant uptake of N was least was also the area where the potential for leaching of N was greatest (sideslopes). The variability in plant N uptake and soil-water content indicate that the processes involved in the removal of N from the soil and the transport of N to the ground water are complex. Accordingly, monitoring the effects of an agricultural-management practice on ground-water quality and in identifying the predominant process affecting the movement of N to the ground water will be difficult. These results strongly suggest that knowledge of the location of a particular site with a managed area is important in interpreting effects of agricultural-management systems.

SUMMARY

Variability in corn N uptake and soil-water content was very complex along a 244-m-long transect at the Northern Cornbelt Sand Plains MSEA near Princeton, Minn. N uptake by corn had ranged from 115 to 157 kg ha⁻¹ in 1991, and 92 to 132 kg ha⁻¹ in 1992. The mean N uptake was 24 kg ha⁻¹ greater in 1991 than it was in 1992, indicating that annual fluctuations in N uptake occur and were similar in 1991 and 1992 as measured by range in uptake and coefficient of variation. The correlation of N uptake and location along the transect during 1991 and 1992 was not good ($r = 0.24$). Soil-water content in the upper 1.7 m depth interval along the transect varied from 10 to 15 cm on July 23, 1992. The least N uptake occurred in 1991 and 1992 in a sideslope area where surface soils were dry because of a lack of subsurface lamella to slow vertical water movement. Therefore, the loss of N by leaching may be increased in sideslope areas.

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Geophysical Investigations of Heterogeneity and Scale at the Princeton, Minnesota, Management Systems Evaluation Area

By Jeffrey E. Lucius¹ and Gary R. Olhoeft¹

Abstract

The U.S. Geological Survey collected more than 1 gigabyte of ground penetrating radar (GPR) data in 1991 at the Princeton, Minnesota, Management Systems Evaluation Area (MSEA) to generate detailed images of the subsurface and to determine the three-dimensional spatial variability of hydrogeologic properties. The Princeton MSEA is located on the Anoka glacial outwash sand plain northwest of Minneapolis-St. Paul. The GPR system transmitted electromagnetic pulses that propagated through the ground. The pulses were partially reflected back to the GPR antennas when they encountered changes in electrical properties (which are controlled by water content, bulk density, lithology, and porosity). The GPR data were computer processed to produce geometrically correct images of the subsurface. Reflector continuity, amplitude, configuration, and spatial frequency were analyzed in the GPR images to determine lithologic structure, depositional processes, moisture content, stratification patterns, and grain-size distributions. Changes in water-table capillary fringe thickness, areas of possible focused recharge, areas consisting of eolian or other fine-grained deposition, and undulations of the till surface were identified. The GPR images were also correlated with lithology logs from sampling wells. For agricultural sites with very little or no clay near the surface, ground penetrating radar offers a fast, cost-effective, high-resolution method for extending information acquired at

INTRODUCTION

Agricultural pesticides, herbicides, and fertilizers are intended for the plant and root zone of the shallow subsurface. Sometimes, however, these chemicals migrate downward into the water-saturated zone and affect ground-water quality. The MSEA program is part of a multiscale, interagency project to evaluate the effects of agricultural practices on ground-water quality. An objective of the MSEA program is to improve our understanding of the processes and factors affecting the transport and fate of agricultural chemicals in a particular hydrologic system. The U.S. Geological Survey (USGS) has been conducting investigations to determine the three-dimensional spatial variability of hydrogeologic properties by use of GPR. The overall objective was to determine the usefulness of geophysical methods to hydrologic investigations in an agricultural setting. The specific objectives were to (1) generate high-resolution images of the subsurface geology and (2) characterize the hydrogeologic heterogeneity in terms of length-scales and statistical distributions—important factors in understanding three-dimensional patterns of ground-water flow.

The investigations were conducted at the MSEA (fig. 1) located on the Anoka Sand Plain near Princeton, Minnesota (approximately 100 kilometers (km) northwest of Minneapolis and St. Paul) during January, April, and October of 1991. The near-surface material at the site is glacial outwash that consists of mixtures of fine-to-medium and medium-to-coarse sand and gravel with discontinuous, thin silty layers (Delin and others, 1992). A loamy sand soil is present at the surface. The outwash is underlain by glacial till below the water table. Topography at the site is relatively flat; relief is about three meters (fig. 1). Average annual precipitation is about 76 centimeters (cm).

The GPR system used in this study was a Subsurface Interface Radar (SIRTM) System-7 manufactured by Geophysical Survey Systems, Inc. The system

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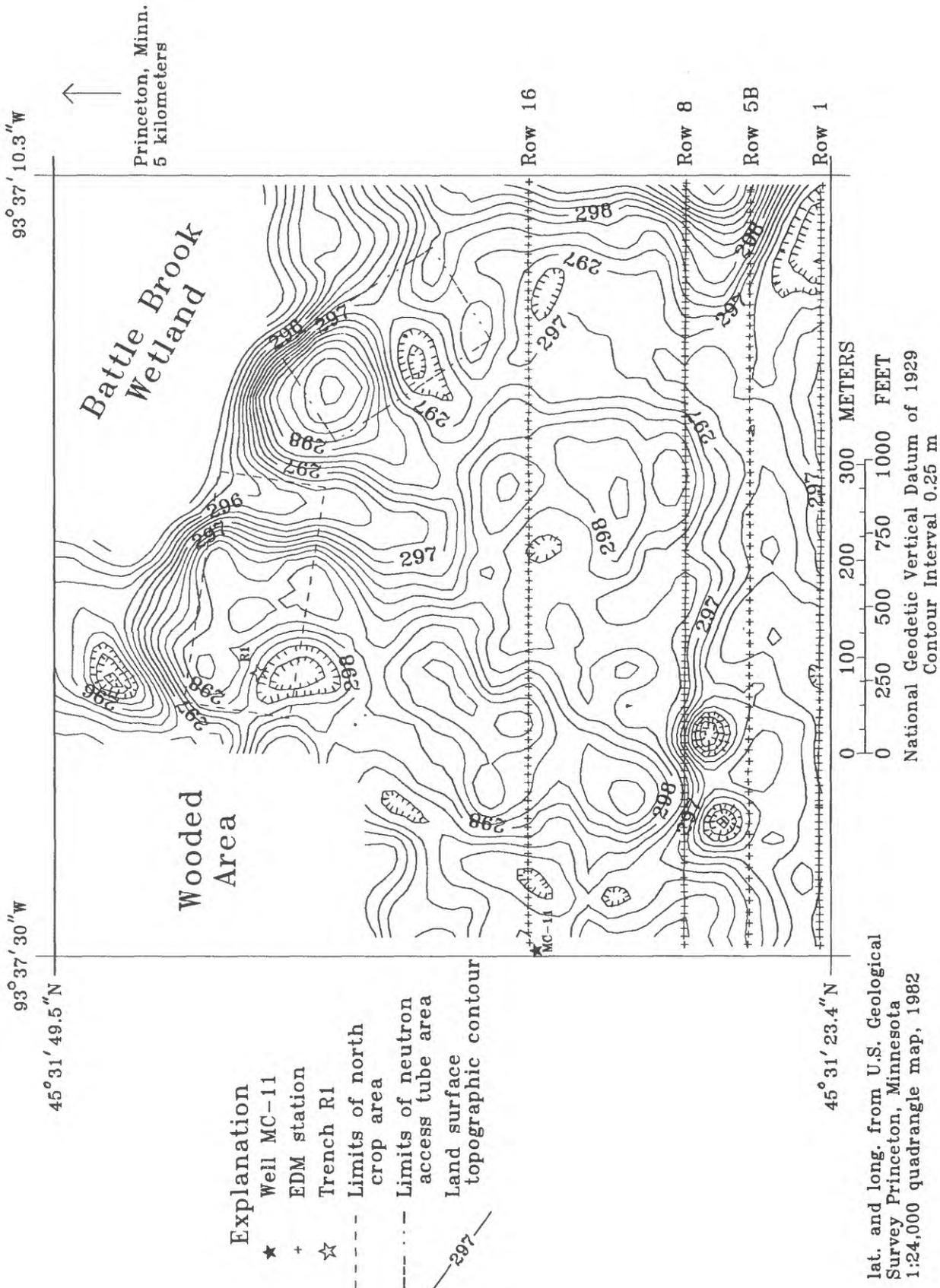


Figure 1. Land-surface topography at the Princeton, Minnesota, Management Systems Evaluation Area.

periodically transmits radio-frequency electromagnetic pulses into the ground. The pulses propagate through the earth and are partially reflected back to the GPR antennas when they encounter changes in relative dielectric permittivity and conductivity. These changes are dominantly controlled by water content, bulk density, lithology, and porosity which are in turn affected by sedimentological processes and hydrological conditions. Radar antennas having center-frequencies of 80, 300, and 500 megahertz (MHz) were used. Depth of penetration of the electromagnetic pulses into the earth is approximately inversely proportional to antenna frequency. However, resolution of subsurface features approximately proportional to antenna frequency. Surveys were performed by slowly pulling the antennas in a pickup truck across the ground surface. The reflected signals were recorded on digital magnetic tape. A continuous recording acquired on a straight heading is called a traverse.

In January 1991, GPR data were collected on 40 west-to-east traverses spaced 20 m apart across the truck-accessible parts of the MSEA using 300-MHz antennas to obtain a comprehensive view of the site subsurface. In April 1991, traverses using the 80-MHz antennas were conducted on selected areas of the site and on adjacent roads to partly determine the variability of the underlying till. A detailed survey of the northernmost crop area (fig. 1) was also performed using the 300-MHz antennas. In October 1991, data from 300-MHz and 500-MHz antennas were collected over one of the areas to be trenched (trench R1, fig. 1). Data also were collected near the neutron-probe access tubes in the spatial variability plot (fig. 1) to compare GPR data to the moisture variations measured by neutron probes. In all, more than a gigabyte of GPR data was collected. More than 3,500 stations were topographically surveyed to record the locations of the traverses.

The purpose of this paper is to (1) present a sample of the subsurface images generated from GPR data that show local variations in hydrogeology, (2) compare GPR data to lithology logs of wells at the site, and (3) discuss the utility of GPR for agricultural-site characterization. Chi-square tests were performed on GPR reflector-length histograms of adjacent 20-m-long sections along selected traverses to quantify the heterogeneity of the subsurface and to identify sections of a traverse that are statistically similar. Those results were presented in Lucius and Olhoeft (1993) and are not discussed in detail here.

GROUND PENETRATING RADAR-GENERATED CROSS-SECTIONS

The GPR horizontal-sampling interval along the traverses was about 2 to 3 cm; this interval varied slightly according to antenna towing speed. The vertical sampling interval depends on how the GPR system was adjusted; and ranged from about 2 to 4 cm. Vertical resolution is a function of antenna frequency, signal wavelength in the ground, data-collection rate, and speed of the radar-wave propagating in the ground. Although the GPR system can detect thin layers, those layers must be separated by about one wavelength or constructive and destructive interference of closely-spaced reflected waveforms will complicate interpretation. The estimated radar wavelengths in the ground (using a relative dielectric permittivity of 4 measured in dry sand at the site) were 1.8 meter (m) for the 80-MHz antennas, 0.5 m for the 300-MHz antennas, and 0.3 m for the 500-MHz antennas.

The GPR data were computer processed to correct for geometric distortions inherent in the data-collection process and to produce a more tractable data set for characterization of the subsurface or estimation of the hydraulic properties. A background trace (the average of all traces in a traverse) was subtracted from each raw trace to minimize system noise in the data. A running-average filter, approximately 0.5 m in length, was applied to the raw data to improve the signal-to-noise ratio. For display, data placement was horizontally corrected for variations in towing speed. Then a time-to-depth conversion was determined (based on bulk relative dielectric permittivity of 4 above the water table and 6.5 below the water table and above the till) and used to convert the recorded time sections into approximate depth sections; static corrections were applied to adjust for elevation changes. The result was (approximately) geometrically correct images of the subsurface.

Gray-scale images of processed 300-MHz data along two west-to-east traverses are shown in figure 2 (locations of the two traverses are shown in fig. 1). Elevations are approximate because the time-to-depth conversion (using a relative dielectric permittivity of 4 for the entire section) is approximate. The vertical exaggeration of 15 causes the dips of many features and the topography to appear much steeper than they really are. Reflections that are either very light or very dark in the GPR images indicate subhorizontal features. The banding in the top 1 m of each image is caused by near-field interference of the 300-MHz radar wave and is not due to subsurface reflections.

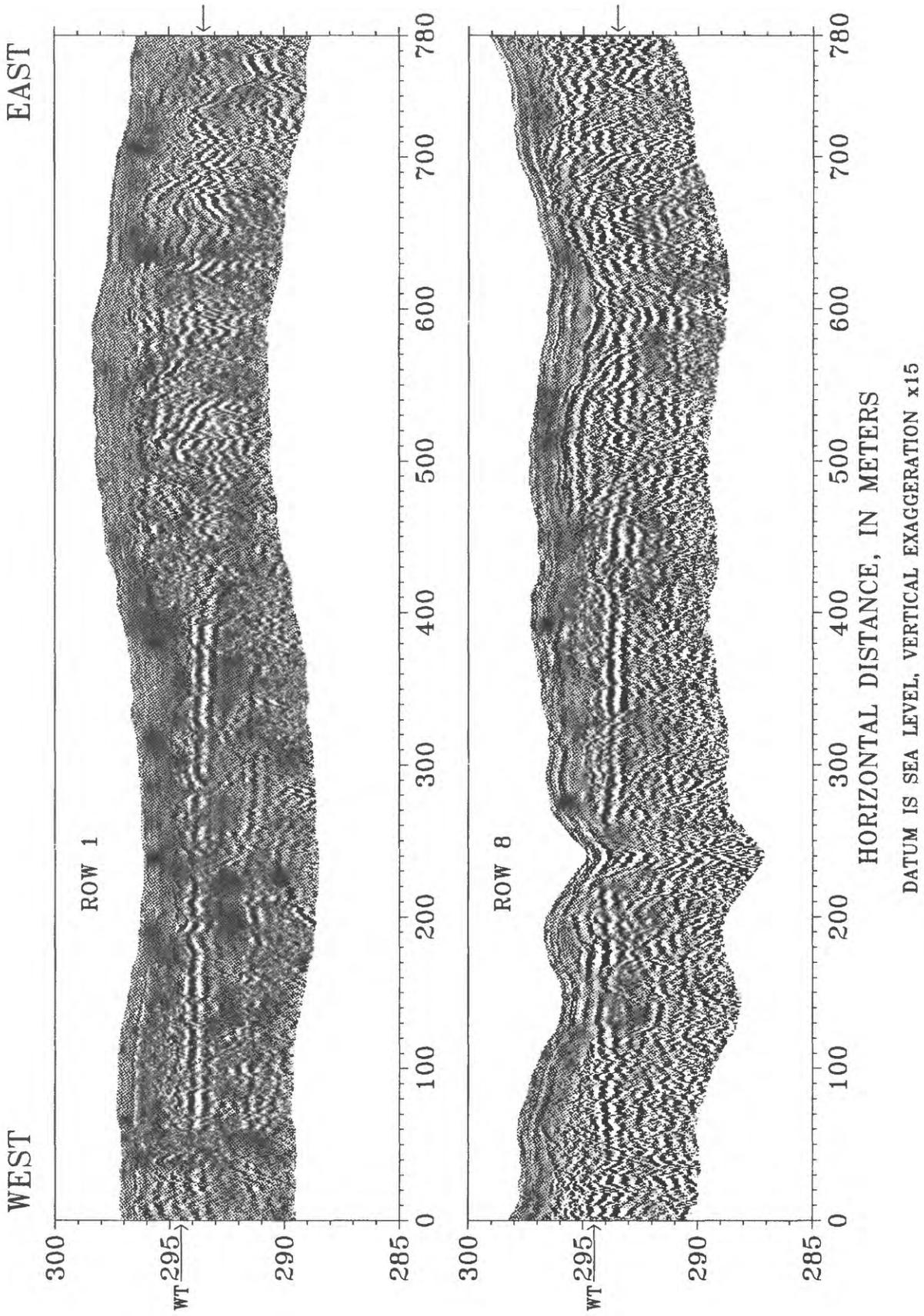


Figure 2. Gray-scale images of computer-processed 300-MHz ground penetrating radar data along west-to-east traverses, rows 1 and 8, at the Princeton, Minnesota, Management Systems Evaluation Area. (Locations are shown in fig. 1.)

The strongest and most continuous reflector in these two images is from the water table, located at about 294.5 m above sea level. The water-table reflector is easy to identify in the image of row 1 between 70 to 400 m horizontal distance and in the image of row 8 between 50 and 470 m horizontal distance. This suggests the capillary fringe is thin and that sediments near the water table are coarse-grained. East of these areas in both images, the water-table reflector becomes harder to identify because the relatively thick capillary fringe in fine-grained sediment causes a gradual transition in dielectric properties and reduces the clarity of the reflection.

The remaining reflections in these two images are generated by small changes in water content above the water table and by changes in lithology and bulk density below the water table. Analysis of reflection facies (see, for example, Sangree and Widmier, 1979; Beres and Haeni, 1991) can be applied to these images. The area west of 400 m horizontal distance in row 1 is dominated by simple, layered reflections of moderate amplitude and low spatial frequency. This indicates thin to moderately thick, horizontally layered, coarse sand and gravel with only slight contrasts in electrical properties. East of 400 m, the reflections are more chaotic, having higher amplitude and spatial frequency, suggesting the presence of mixed layers of sand, silt, and gravel of variable thickness and extent.

For row 8, the water-table reflector between 160 and 320 m horizontal distance, at an elevation of about 294 m, appears to bulge upward near the low area at 240 m horizontal distance, indicating this low area might be a source of enhanced or focused recharge. Delin and Landon (1993) have discovered this to be true for one lowland area on the site and indicate that focused recharge could be occurring at other lowland areas. These areas might contribute to focused transport of agricultural chemicals to the ground water. At 600 m horizontal distance, there appears to be a "depression" in the layering 2 m below the surface. The solid gray area above the reflector indicates homogeneous deposition, perhaps the result of eolian deposition of fine-grained material in low-lying areas. Eolian silt and sand are found at the surface over several areas on the site.

Gray-scale images of processed 80-MHz data along a west-to-east traverse are shown in figure 3. The location of the traverse is shown in figure 1. The vertical exaggeration is 10 in the upper image. The lower image shows part of the traverse between 140 and 280 m horizontal distance without vertical exaggeration. The band-

ing caused by near-field interference of the 80-MHz radar wave covers about 3 m at the top of each radar image, effectively concealing the water-table reflector at 294.5-m elevation. The lowest strong reflector in each image is from the glacial till underlying the outwash sands and gravels. Undulations of the till surface are apparent. Comparing the upper and lower images also shows how vertical exaggeration distorts the GPR reflectors. The reflectors in the lower image indicate the structural complexity in the depositional sequence on this part of the Anoka glacial outwash plain.

CORRELATION OF REFLECTORS AND LITHOLOGY LOGS

Several of the GPR traverses were near USGS sampling wells. The driller's lithology logs were examined to determine how well they correlated with the GPR images. An example for well MC-11 near the start of GPR traverse row 16 is shown in figure 4 (see fig. 1 for locations). A possible correlation of the log to the GPR reflectors is indicated by the lines connecting the log to the GPR image. "WT" is the water-table reflector. Ground surface at MC-11 is slightly higher than it is at the western end of Row 16. In general, the logs do not correlate well with the GPR image, in part, because the sediments are mixed by the power auger used to drill the wells and can only be approximately located. Beres and Haeni (1991) note that correlation commonly improves when the core is a continuous sample. There can be several other causes for the poor correlation. Variations in porosity, which change the water content and, therefore, the electrical properties, may be not be uniquely related to variations in lithology. In addition, constructive and destructive interference of the reflected GPR waves may hide closely spaced layers, create "false" layers, and/or combine several layers to appear as only one.

DISCUSSION

There are several scales of investigation in the MSEA program: core sample, small, field, and regional scales. The resolution and sampling of the GPR system are probably too coarse to be useful at the scale of a core sample (millimeters to several centimeters), and the size of the field site is too small for regional-scale investigations (several kilometers). However, GPR data can be useful at small-scale (less than 1 m) and field-scale (tens to hundreds of meters) investigations,

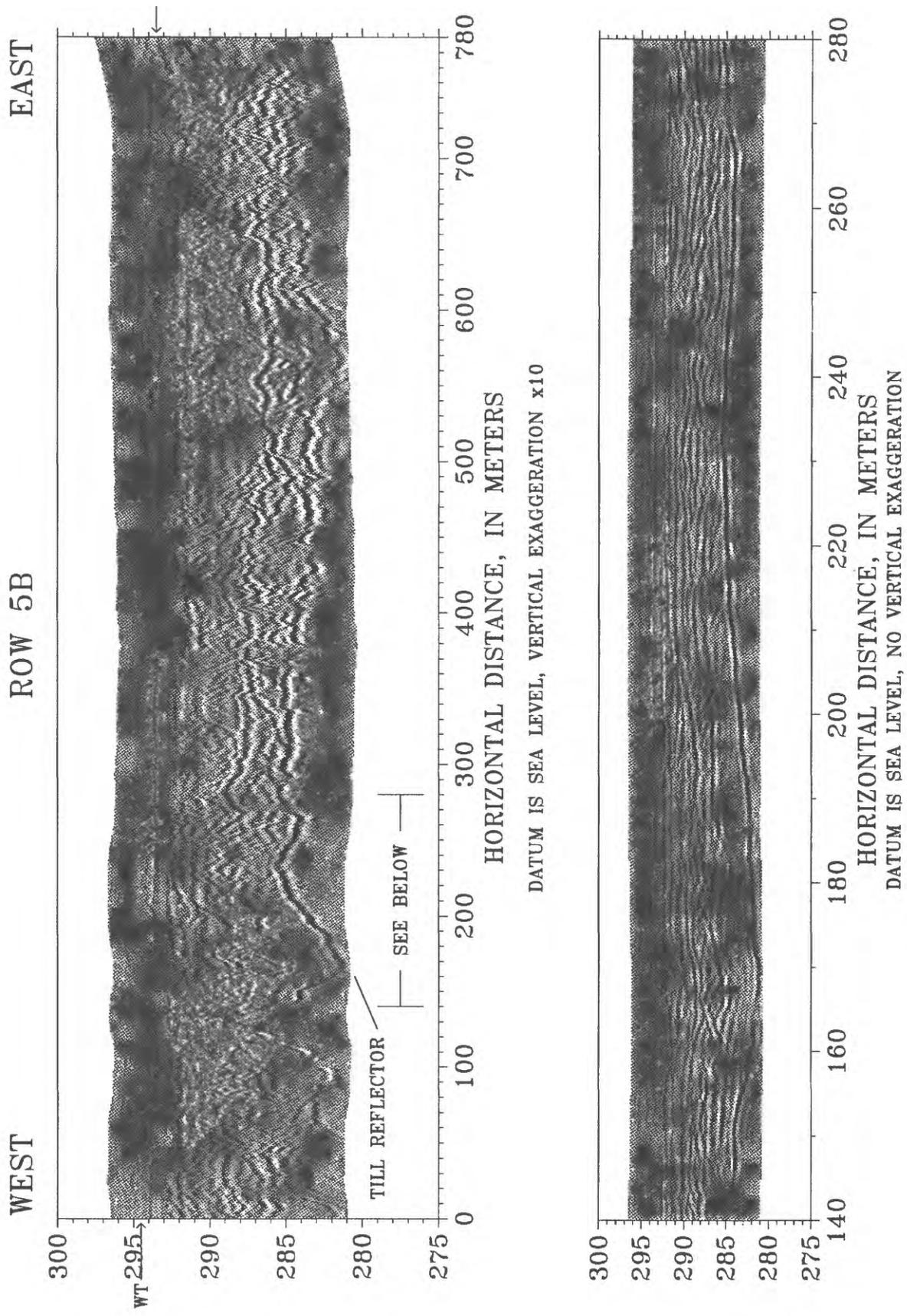


Figure 3. Gray-scale images of computer-processed 80-MHz ground penetrating radar data along west-to-east traverses, row 5B, at the Princeton, Minnesota, Management Systems Evaluation Area. (Location is shown in fig. 1.)

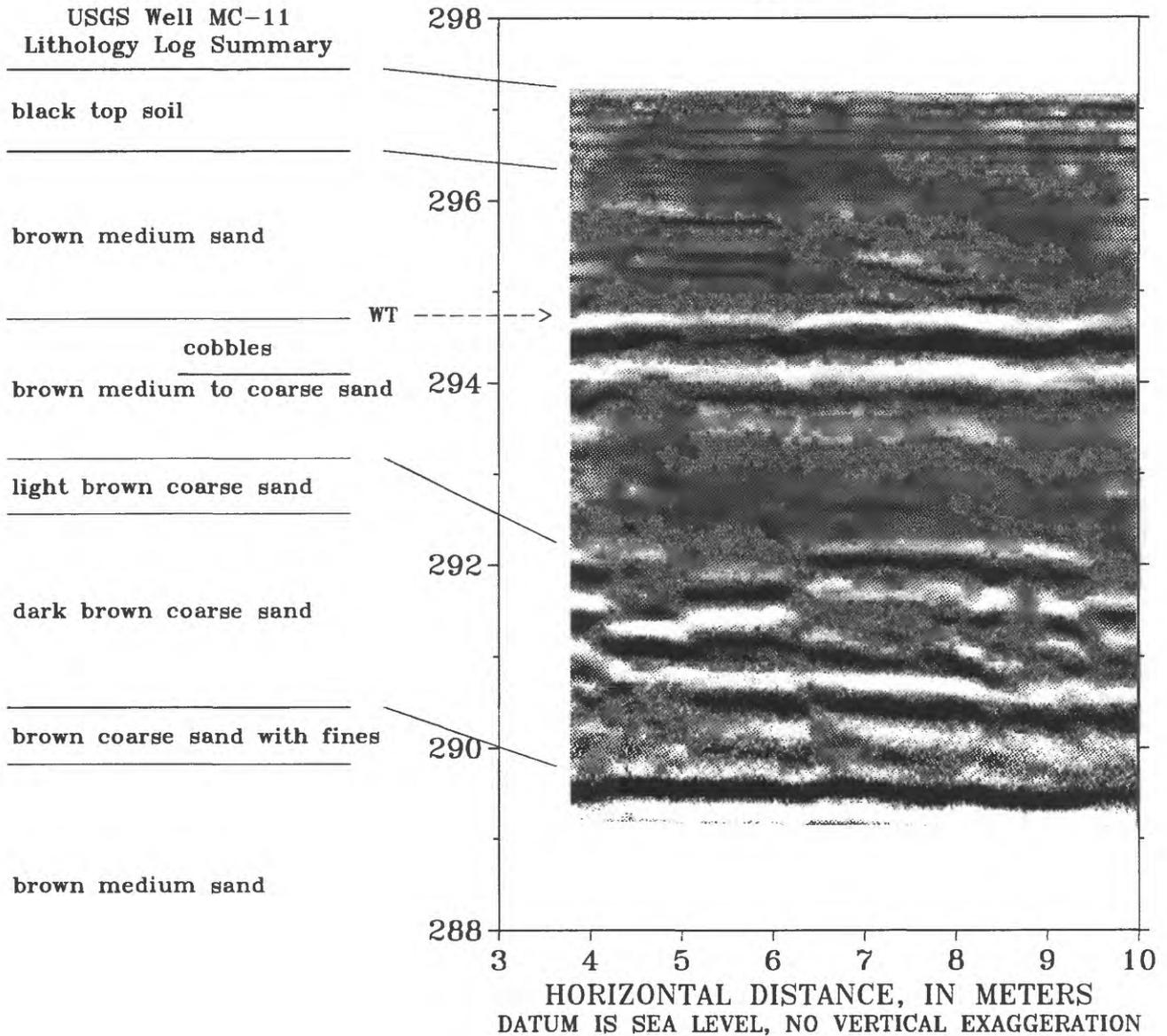


Figure 4. Summary of lithologic log for USGS well MC-11 near the start of ground penetrating radar traverse row 16 at the Princeton, Minnesota, Management Systems Evaluation Area. (Locations are shown in fig. 1.)

depending on antenna frequency and spacing of traverses.

At all scales, hydraulic-flow patterns are observed to be three dimensional and controlled by hydrogeologic heterogeneity. Uncertainties caused by the spatial variability of hydraulic properties, such as unsaturated hydraulic conductivity, affect the ability to model and forecast flow and transport of solutes in porous media. GPR can provide the additional information required to extend hydrologic information obtained at test holes

and wells to much larger areas. In some cases, GPR data can directly provide hydrologic information such as moisture content (Duke, 1990; Sutinen and others, 1992) or transmissivity (by repeated measurements across time to track the position of moving fluids or wetting fronts; Sander and others, 1992).

GPR measurements record signals that are interpreted as reflections from boundaries of hydrogeologic units with contrasting electrical properties (relative dielectric permittivity and electrical conductivity)

controlled by water content, bulk density, lithology, and grain-size distribution. Because the signals are reflected by contrasts between layers, the processed images give good structural and geometric information, whereas information about absolute properties must be deduced by modeling individual signals (Duke, 1990; Powers and others, 1992). The relation between GPR measurements and hydraulic properties is complex. However, an empirical relation between relative dielectric permittivity and volumetric water content for glacial materials can be determined (Sutinen and others, 1992). An infiltration test has been planned so that the GPR system can be used repetitively over an area to determine the progressive movement of the wetting front and thereby infer vertical hydraulic conductivity (see Olhoeft, 1985; Sander and others, 1992).

The GPR system may prove extremely helpful to hydrologists in characterizing a new site. However, in an agricultural setting, the GPR system cannot directly detect very low concentrations of pesticides or fertilizers in the subsurface. If the site is relatively free of clay minerals, GPR data can be useful in (1) determining depth and topography of bedrock or other formation (such as till); (2) measuring variations in the water table (Shih and others, 1986); (3) detecting the effects of well draw-down tests; (4) identifying perched water tables; (5) determining the lateral variations of lithologies (extent and thickness) near test wells and between wells; (6) measuring the type and thickness of soil horizons with the high-frequency antennas (Collins, 1992; Doolittle and Asmussen, 1992); and (7) detecting the presence of preferential flow paths (Donohue and others, 1992; Sander and others, 1992).

GPR-data collection and processing is relatively fast and cost effective in comparison to other methods that might collect near-continuous data, such as close-spaced drilling or trenching. The GPR system also has the advantage of being noninvasive. For each of the 780-m-long GPR traverses, approximately 15 minutes were needed to collect the GPR data using a pickup truck and three people. The 80 to 110 topographic stations along a traverse took about 1 hour to survey using an electronic total station connected to a pocket computer. Processing GPR data in a computer is not necessary in all applications, as some problems do not require any enhancement or geometric correction of the data. A 780-m traverse of GPR data required 1 to 2 hours to process (using software developed by the authors) and produce an image (stored on disk as an

Encapsulated PostScript (EPS) file) such as those shown in the figures.

CONCLUSIONS

Understanding the hydrogeology of a site is integral to determining the potential for ground water contamination by surface-applied agricultural chemicals. Analysis of the geometrically corrected GPR images shows that reflector continuity, amplitude, configuration, and spatial frequency reveal details of the subsurface unavailable by point-source measurements provided by drilling. Lithologic structure, depositional processes, moisture content, stratification patterns, and grain-size distributions can all be interpreted from GPR data using antennas of appropriate frequency and images displayed at appropriate scale. Ground penetrating radar offers a fast, cost-effective, high-resolution method for extending information acquired at test wells and for presenting a comprehensive view of subsurface structure. With the addition of computer processing, GPR data can also produce information about hydrologic properties. GPR does not work at all sites, but for areas with very little or no clay near the surface, it should be considered as a preliminary study tool and as a geophysical technique to provide better understanding of geologic and hydrologic information.

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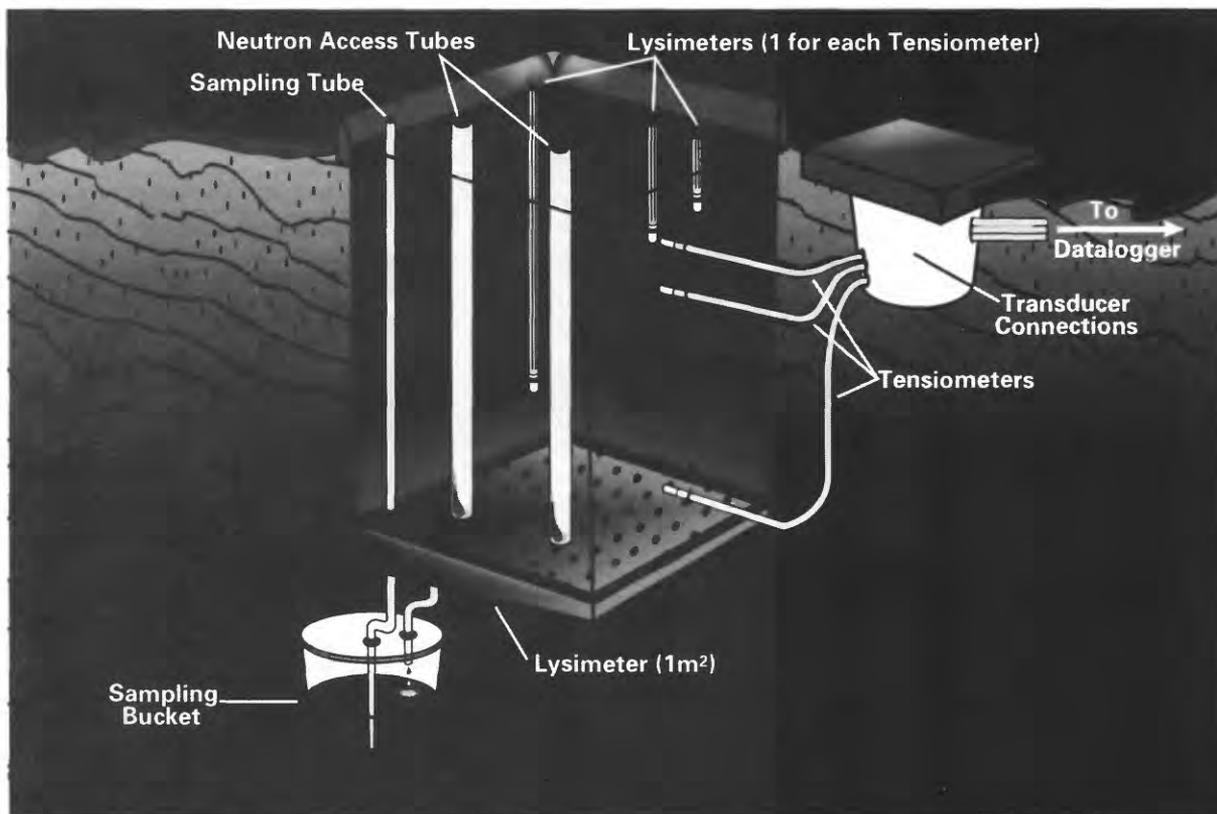


Figure 2. Diagram of plot instrumentation (not to scale).

The herbicide atrazine was applied on May 18, 1992 at a rate of 1.4 kg ha^{-1} . Six hours after application, an infiltrometer was used to apply 5 cm of water to each plot (1.5 cm hr^{-1}). Water samples were extracted from suction and pan lysimeters monthly (June through November) and analyzed for atrazine on a high-precision liquid chromatograph (hplc) with a 25-mm by 4.6-mm column and an 80:20 volume-per-volume methanol-to-water ratio (adjusted to pH 7.4 with 0.05 M ammonium acetate). Wavelength was set at 222 nm with a retention time of 9.5 minutes and a flow rate of 8 mL minute^{-1} . All samples were maintained at 0°C until analysis and filtered through a 0.45- μm syringe filter prior to analysis. Atrazine concentrations were determined from standards and a linear regression curve ($r^2 = 0.991$). Standards as well as blank samples were inserted at frequent (blind) intervals to insure quality control. Soil samples also were extracted and analyzed by hplc. A 20-g sample of soil was cored from each depth increment, and atrazine was extracted by adding 42 mL of 90 percent methanol and 10 percent hplc-grade water, shaking for 2 hours, and centrifuging. The supernatant was collected, filtered, and analyzed.

EXPERIMENTAL RESULTS AND DISCUSSION

The zero-tension pan lysimeters were designed to intercept all water flowing vertically through each plot so that total flux (volume basis) could be determined. Concentrations of atrazine at depths of 60 to 135 cm (plot 1; fig. 3A) and 90 to 105 cm (plot 6; fig. 3B) 1 month after application are greater than would be expected if flow and chemical transport were through the soil matrix alone, because atrazine would normally be diffused within the soil matrix, allowing for little if any transport below 15- to 30-cm depths. Plots 1 and 6 (figs. 3A and 3B) were selected for illustration because they are representative of each of the six plots. In plots 4-6, the pan lysimeter was just below a claypan that exhibited severe cracking with slight decreases in water content (claypan cracks were observed on separate, adjacent plots). Cracking that was evident on the surface was likely caused by the development of cleavage planes at points of high-water content. As the soil dried, the cleavage planes separated, causing large cracks. Several surface cracks were 2 cm wide by about 20 m long; these cracks did not follow cultivation planes. Cracking of the claypan was probably the cause of the rapid transport of atrazine through the soil profile.

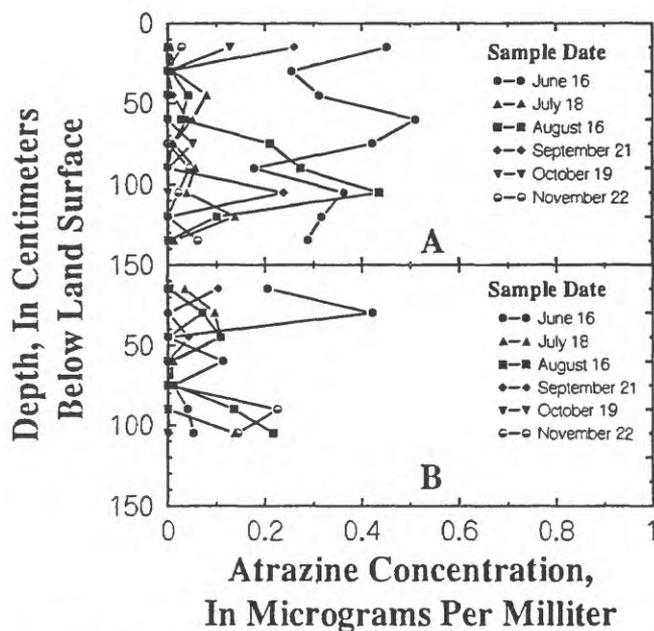


Figure 3. (A) Atrazine concentrations in ground water from suction and pan lysimeters (plot 1).; and (B) Atrazine concentrations in ground water from suction and pan lysimeters (plot 6).

A companion laboratory study on undisturbed, unsaturated soil cores (28 cm diameter by 40 cm height) that were extracted by the method of Tindall and others (1992) and analyzed by the method of Green and others (1990), showed that the claypan, which is 40 to 80 cm below land surface, had anomalously high saturated hydraulic conductivity (K_s) values greater than 30 cm d^{-1} . After staining the cores in the laboratory study with crimson-red dye, large numbers of macropores were found in the claypan cores compared to cores collected from above and below the claypan, where K_s averaged about 10 cm d^{-1} . Because of high clay content, K_s values for claypan sediments are generally in the range of 3 to 4 orders of magnitude less than 30 cm d^{-1} . Thus, the high K_s values are likely a result of the macroporosity of the claypan cleavage planes. Unsaturated hydraulic conductivities of the laboratory cores were in the same range as those which had been measured in the field plots (10^{-1} to $10^{-3} \text{ cm d}^{-1}$) at the same relative water content ($\theta \approx 0.23$). Therefore, rapid transport of atrazine probably occurred under saturated conditions during times of large recharge events and, as the atrazine moved from the soil surface through the top 15-cm, it was able to move quickly through the claypan to the water table at a depth of about 1.5 m below land surface. The high K_s values for the claypan probably account for the high peak concentrations of atrazine collected in the zero-tension pan lysimeters.

Generally, atrazine concentrations decreased with depth; however, large concentration peaks were observed at various depths and times within all plots. These peaks confirm that atrazine was being transported to a depth below 15 cm relatively quickly. Although the concentrations were lower with depth than those at the time of application, however, considerable amounts of atrazine were still being transported within the soil profile, as evidenced by the high peaks in August 16 samples (figs. 3A and 3B).

During the 6 month sampling period, 52-cm of rainfall was recorded. At the end of July 1992, the plots received about 15 cm rainfall just prior to the August 16 sampling. The atrazine concentrations in the 60- to 120-cm depth interval (fig. 3A) and 90- to 105-cm depth interval at plot 6 (fig. 3B) in August were much higher than atrazine concentrations near land surface. Prior to the November 22 sampling, about 7 cm of rainfall was recorded and similar, but smaller increases in atrazine concentration with depth occurred at the 90- and 135-cm depth interval at plot 1 (fig. 3A) and at the 90-cm and 105-cm depth interval at plot 6 (fig. 3B). High atrazine concentrations observed as late as August and November may reflect entrapment and partial desorption of atrazine from soil within the macropore system where it remained in immobile pockets until it was later flushed by recharging water.

Compared to concentrations in the water samples (fig. 4) extracted from the suction and pan lysimeters, the concentrations in the soil samples are greater near the surface but decrease with depth, as would be expected for bulk soil. At the surface (fig. 4), atrazine concentrations collected in cores in June are similar to applied concentrations, but soil samples collected in November indicate that large rainfall events caused fluctuations in atrazine concentrations in the soil matrix similar to fluctuations in the lysimeter extracts. The same trends are quite noticeable in soil and extract samples.

The difference in atrazine concentration in soil and extract samples at the 15-cm and other depths results from the fact that the suction lysimeters collect water that moves relatively quickly through the larger pores. As water and chemicals flow into the soil matrix, flow is retarded by the small size of the pores, which, because of capillary tension, restrict the flow of water to large conducting pores; because of these zones of restricted flow, some of the atrazine may be entrapped while additional amounts are adsorbed onto soil particles. Consequently, atrazine concentration in

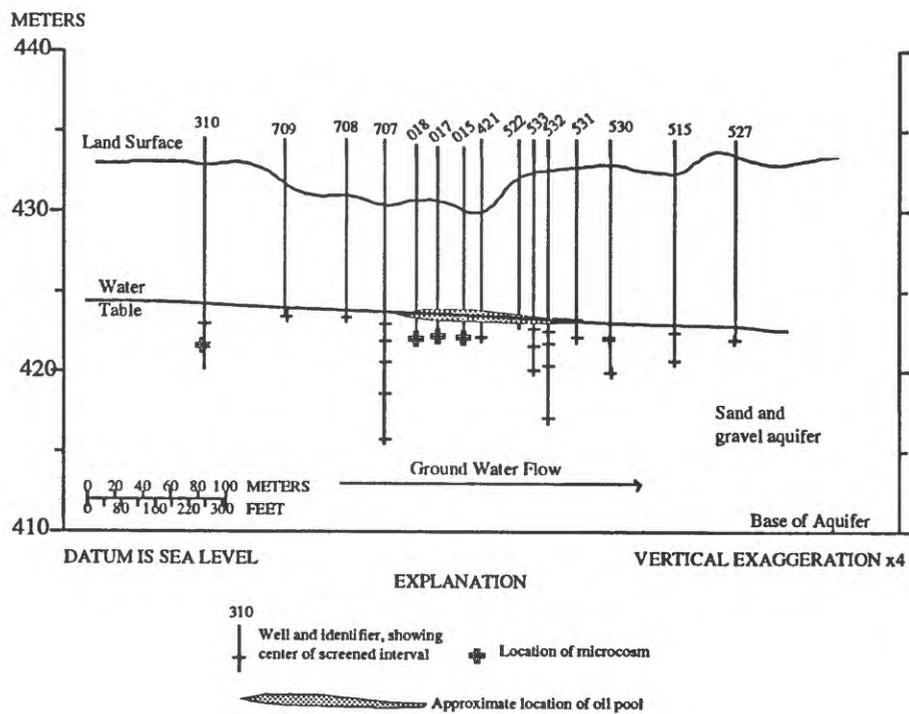


Figure 2. Hydrologic section showing microcosm placement in a well bore.

attachment, and morphology, and the mineral surface was examined for evidence of biogeochemical precipitation and dissolution. A subset of mineral fragments was sonicated to remove adhering material and was similarly examined for weathering features. The geochemistry of the silicate surfaces was examined by SEM with energy dispersive analysis of X-rays and by sequential leaching techniques (Berndt, 1987). In particular, organic carbon coatings, carbonates, and iron precipitates were examined. The current experimental series will also characterize mass loss and gain caused by dissolution and precipitation reactions, and changes in microporosity.

RESULTS TO DATE

Three years of data have been collected from a total of 24 field-reaction microcosms. Mineral surfaces were characterized for microbial colonization, microfauna morphology and attachment, surface chemistry, and diagenetic textures. Preliminary leaching experiments have also been completed to characterize the chemistry of the surface precipitates. The results to date for three mineral groups are summarized here.

Quartz

The quartz fragments from the control experiments consist of clean fractured surfaces with fine ridges and steps (fig. 3a). No evidence of chemical weathering or remnant inclusions is visible. After reaction in the contaminated aquifer, many of the surfaces had been colonized by a variety of bacteria seen as individual organisms rather than as biofilms. Much of the visible quartz surface is subtly roughened by extremely fine pitting or more extensively etched in some areas to produce distinctive triangular etch pits (fig. 3b).

Feldspars

The control feldspar surfaces are clean and unweathered, with evidence of linear steps along cleavage and very small ellipsoidal inclusion pits (fig. 4a). As with quartz, some of the reacted feldspar surfaces were colonized, while other surfaces remained uncolonized. The colonized surfaces show evidence of intense chemical weathering, with deep prismatic etch pits oriented along inferred cleavage planes (fig. 4b). The pits are several microns wide,

and over 1 μm deep, with irregular edges. Little evidence of clay mineral precipitation is seen around the etched areas except for thin strands of an unknown amorphous material (fig. 4b). Uncolonized surfaces on the same grain, however, are unetched, and support extensive aluminous clay precipitates (fig. 4c).

Calcite.

Calcite fragments used in the microcosm experiments were prepared in a manner similar to the silicates, except that the duration of the water rinses was much shorter. The clean rhombohedral crystal fragments exhibit flat surfaces with regular 100 to

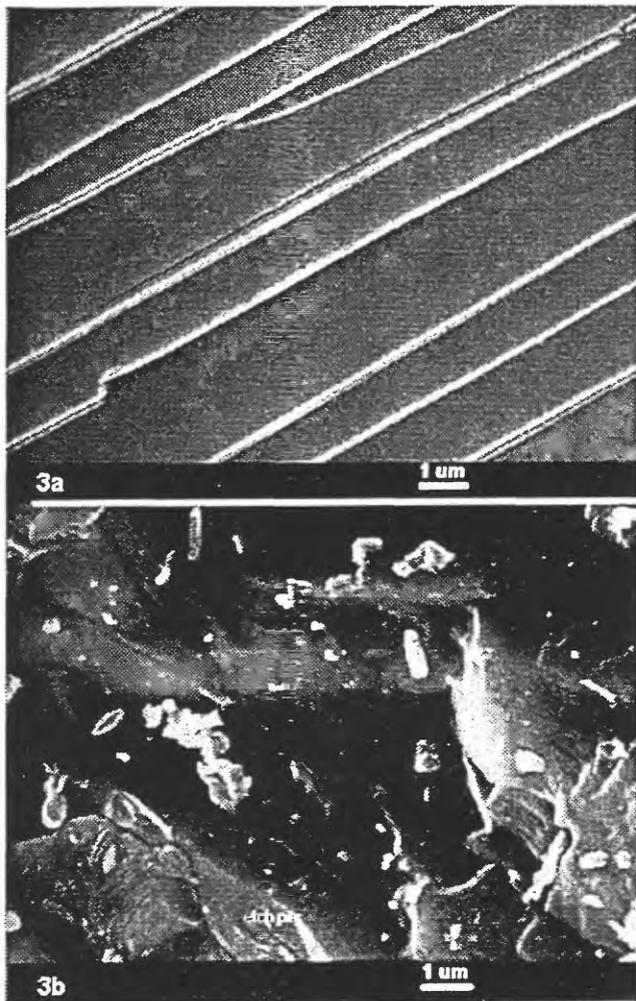


Figure 3. Scanning electron microscope micrographs of quartz fragments. (a) Clean quartz fragment from control group; (b) etched quartz fragment from the field reaction group, showing roughened surface and triangular etch pits.

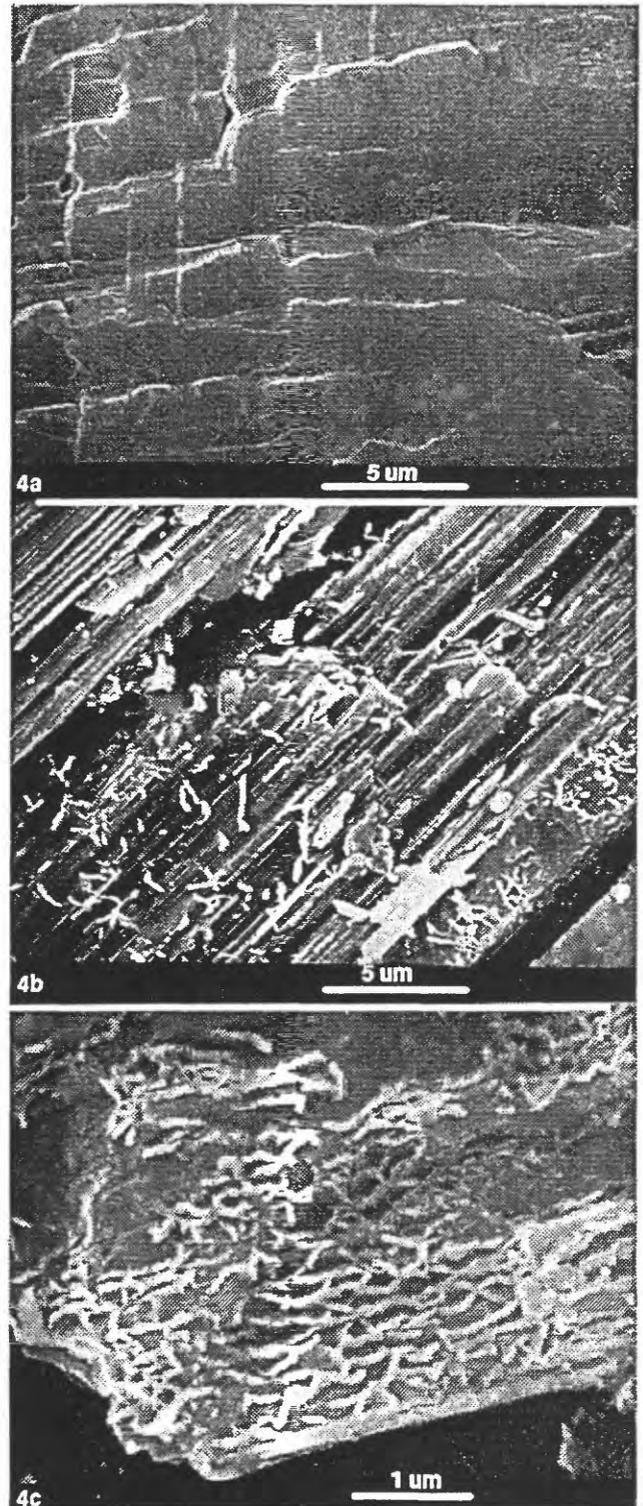


Figure 4. Scanning electron microscope micrographs of microcline fragments. (a) Clean microcline surface from control group showing cleavage and remnant inclusion features; (b) etched feldspar surface from field-reaction group; (c) unetched surface from field-reaction group showing precipitated kaolins.

500 nm high steps where cleavage planes have been fractured during crushing (fig. 5a). After reaction for ~1 year, only very sparse microbial colonization was found, and the amount of colonization was much less than that on the silicate surfaces. Where bacterial colonization was observed, etching of the mineral surface was evident, and was characterized by deep irregular prismatic dissolution pits along cleavage planes (fig. 5b).

The most common surface alteration of calcite was precipitation of calcite overgrowths. Growth of 500-nm-thick tabular calcite on the previously clean surfaces was recorded on almost all crystal faces examined. A hypothesized crystal-growth progression begins with 100- to 500-n-high individual spikes extending upward from a flat background surface (fig. 5c). The spikes form straight rows and rhombohedral enclosures uniformly 1000 nm across. The open enclosures of calcite spikes fill to form isolated plateaus 500 nm high that apparently coalesce into sheets of smooth calcite, thus adding a new layer to the original calcite grain (fig. 5c).

DISCUSSION

Previous research into silicate and carbonate weathering at the Bemidji site relied on geochemical characterization of ground water and examination of native sand grains collected from contaminated and pristine locations (Bennett and others, 1993; Baedecker and others, 1993; Bennett and Siegel, 1987). This approach suggested that silicates are weathering, but the rate and extent of dissolution of a specific silicate type is obscured by lack of knowledge of the starting condition of the mineral surface. Similarly, the carbon mass-balance calculations suggest that a carbonate mineral may be precipitating in the anoxic region under the oil (see, for example, Baedecker and others, 1993), but the composition of the mineral and the rate of precipitation were unclear. In both cases, the role of microbes was unknown and initially was thought to be primarily as net producers of carbonic and organic acids released directly into the bulk ground water.

The experimental results described here suggest that microbes in this aquifer colonize fresh mineral surfaces, resulting in a non-uniform pattern of attached biologic material. In the vicinity of attached microbes, feldspar and quartz dissolve, even in waters greatly supersaturated with respect to quartz. We hypothesize that attached microbes on the surface create a microreaction zone, where extremely high

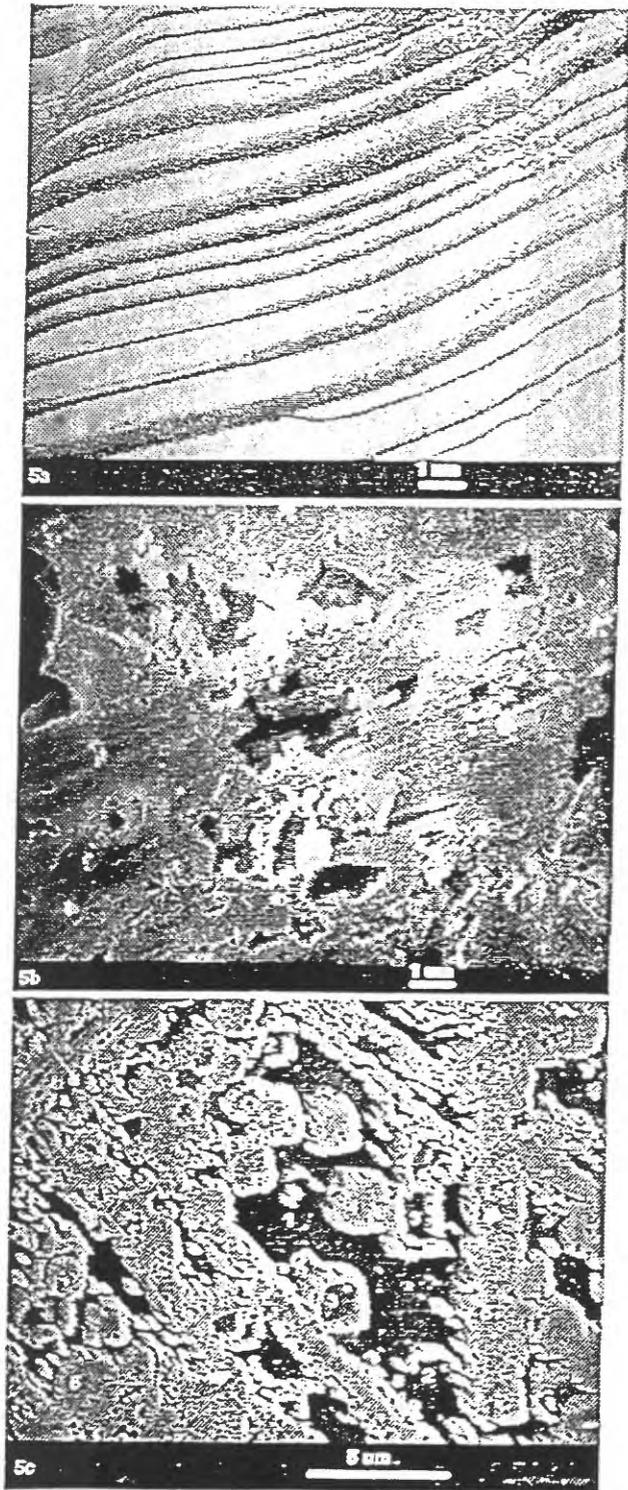


Figure 5. Scanning electron microscope micrographs of calcite fragments. (a) Clean calcite surface from control group showing 500 nm cleavage steps; (b) calcite surface from field-reaction group showing etch-pitting associated with attached bacteria; (c) precipitated calcite overgrowth showing inferred progression of growth from 1 to 5: 1. initial calcite spike; 2. linear group of spikes forming enclosure; 3. fully formed enclosure consisting of individual spikes; 4. filled enclosure forming 500-nm-high plateau; 5. coalesced plateaus forming a nascent 500-nm-high step.

concentrations of extracellular organic ligands accumulate (Hiebert and Bennett, 1992). In this small area, silicate weathering is greatly enhanced, increasing both the dissolution *rate* due to ligand-promoted mechanisms and the *solubility* due to solution complexes. The rate of feldspar dissolution, inferred from an estimate of mineral volume removed, is many times faster than that predicted from inorganic experimental systems (Bennett and others, 1991; Hiebert and Bennett, 1992).

Uncolonized silicate surfaces, in contrast, are unweathered or show evidence of clay precipitation. Away from the microbial microreaction zone, the reactive ligands and chelated products of dissolution mix with the bulk aquifer water, possibly shifting equilibria from that established at the dissolving surface. This water may be greatly supersaturated with respect to kaolin-group minerals, thus precipitating aluminum as a kaolinite or halloysite and leaving excess silica in solution. This hypothesis is supported by the chemical composition of the ground water, where silica concentration increases greatly, but aluminum concentration never exceeds 2 μM (Bennett and others, 1993). We are currently investigating the possibility that microbes preferentially colonize the upstream side of a fragment, where microfauna will first attach and where nutrients are supplied by flowing ground water.

In the carbonate system, the microbial use of iron oxide as an electron acceptor for carbon metabolism may shift the carbonate geochemistry toward calcite supersaturation by increasing pH and producing bicarbonate (Bennett and others, 1993). Calcite precipitates, forming the distinctive overgrowth morphologies seen on the cleaved calcite fragments. The form of the carbonate precipitate and results of EDAX analysis of the individual spikes suggest that the calcite is nearly pure, with no detectable iron or magnesium. We are presently investigating the controls on the geometry of calcite overgrowth spikes, and overgrowth step height.

CONCLUSIONS

This ongoing study of microbial processes in an oil-contaminated aquifer suggests that native microfauna have a significant effect on mineral-weathering mechanisms and rate. Where microbes attach to silicate surfaces, microenvironments produced by metabolic processes greatly enhance silicate dissolution. The rate and extent of dissolution

cannot be evaluated from the bulk chemical composition of the water, because this is a dilute reflection of the environment immediately adjacent to a metabolizing microbe. The nature of this microenvironment and the types and concentrations of reactive ligands are expected to be affected by the biogeochemical environment, the nature of the carbon substrate, and the availability of nutrients. In the nutrient-poor, anoxic, and carbon-rich environment of the Bemidji aquifer, the microbial microenvironment apparently is very aggressive toward silicate minerals. The carbonate system, in contrast, is apparently perturbed by the overall biogeochemical reactions that consume the carbon in petroleum, resulting in calcite precipitation.

The *in situ* microcosm approach allows for the direct examination of the form and rate of both silicate dissolution and calcite precipitation in low-temperature systems using well-characterized starting surfaces. By combining surface-texture examination with long-term geochemical characterization, rock-water reactions can be demonstrated directly.

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