GROUND-WATER AGE DATING AND OTHER TOOLS USED TO ASSESS LAND-USE EFFECTS ON WATER QUALITY

By J.D. Stoner, T.K. Cowdery, *and* L.J. Puckett

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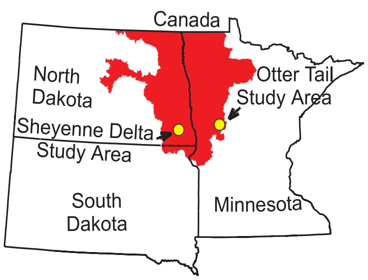
A relatively new method for age dating recent ground water along with other investigative tools improve our understanding of land-use effects on the water quality in a surficial aquifer and adjacent streams in the Red River of the North Basin:

- **Ground water commonly takes more than 20 years to reach depths in the surficial aquifer where it is withdrawn for use.**
- **Water withdrawn from most drinking-water wells was recharged through land areas greater than 1 mile upgradient.**
- **Because of these long travel times and distances, land-management practices on the land and aquifer-protection strategies may take as much as 50 years to produce measurable improvement in water quality.**
- **The amount of fertilizer and some herbicides used to enhance crop growth in this study area can be related to the distribution and trends of nitrate and herbicides found in the surficial aquifer.**



RELATING LAND USE TO WATER QUALITY

This report analyzes the use of chlorofluorocarbons (man-made freons used mainly as refrigerants) as environmental tracers in conjunction with geologic and hydrologic information to provide a better understanding of the link between land use and the water quality in an underlying surficial sand and gravel aquifer. The time for water to travel from the water-table surface of the aquifer to a well is one of several pieces of information needed to understand how the movement and fate of contaminants in a surficial aquifer relates to the history of agricultural practices (crop types, chemical use, irrigation, and tillage practices). Water withdrawn from wells using long screens likely is a mixture of water that has a broad range of ages and possible chemical compositions (fig. 1). Hydraulic data and mathematical models can be used to estimate travel times and direction of water movement, but until recently scientists have not had a reliable method to directly measure the travel time of ground water. By establishing the time water entered the aquifer (recharge), scientists can determine the age and travel time within the aquifer. The age of ground water can be used to evaluate the relative importance of other factors, such as the history of agricultural practices and physical and chemical transformations that affect the movement of contaminants from the land surface through the surficial aquifer.

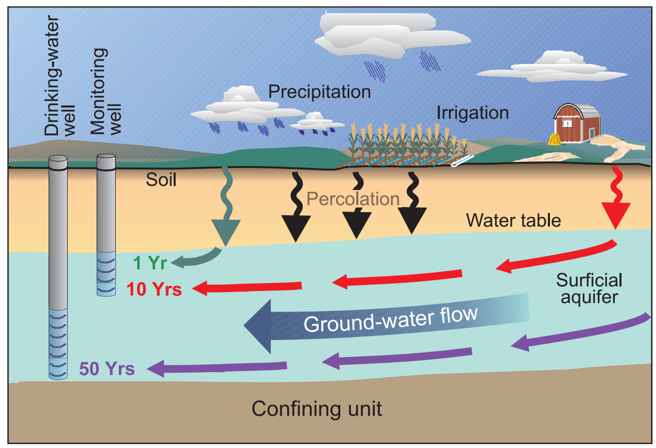


Figure 1. Schematic section showing water seepage through soil, the unsaturated zone, and a surficial aquifer and possible differences in ground-water age with depth into the aquifer.

Research at two surficial aquifers in the Red River of the North (Red River) Basin statistically showed the effects of land use (cropland) on the quality of water reaching the water table. In the Otter Tail study area (fig. 2), agricultural fertilizers, herbicides, and irrigation water applied to crops of mostly corn, hay, soybeans, small grains, and some potatoes were related to elevated concentrations of nitrate and herbicides reaching the surficial aquifer. This area has well-drained, sandy soils and hydrologic conditions that make shallow ground water susceptible to contamination from land-use activities. Although results of that research (Cowdery, 1995, 1997) showed ground-water contamination at shallow depths in one aquifer, additional work was needed to assess the effects of land use on the water resource in the entire thickness of the aquifer. In subsequent studies, we installed deeper monitoring wells to obtain water samples for chemical analysis. Water samples were collected

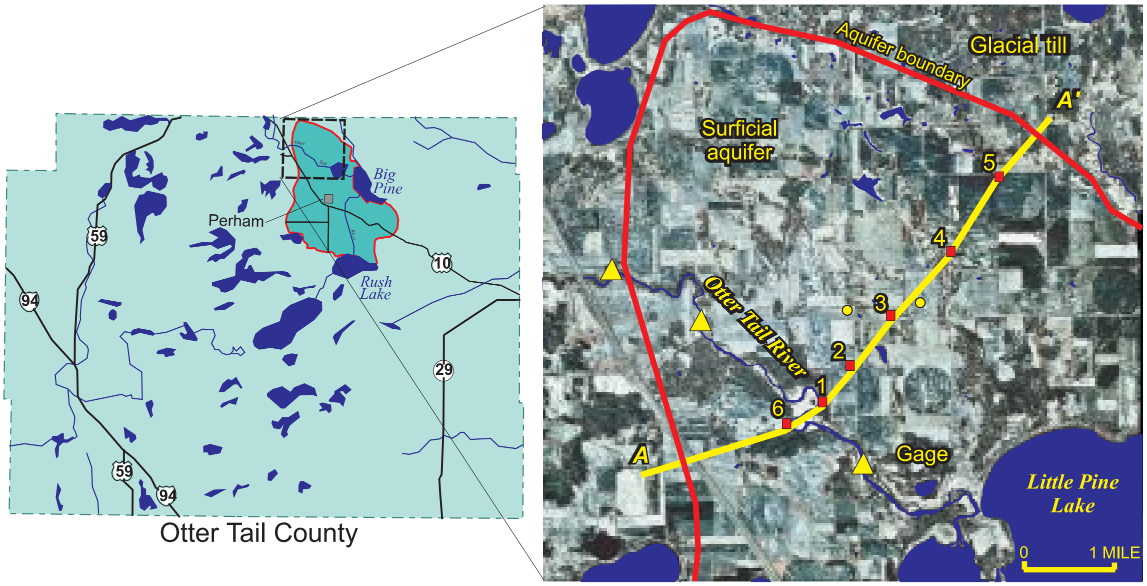


Figure 2. Study area. *A-A'* is line of section through monitoring well sites 1-6 indicated by ■ ; ○ indicates well with geologic log; △ indicates streamflow-measurement site.

along expected paths of ground-water flow from cropland areas (where ground water recharges) to a nearby stream (where ground water discharges).

MEASURING GROUND-WATER AGE

Many studies have indicated that land-use practices can affect the quality of shallow ground water. Studies that have incorporated a relatively new and accurate method of age dating ground water that recharged as long ago as the 1940's have helped scientists relate ground-water contamination to the history of land use. This improved understanding can help land and water managers make informed decisions about management practices to protect the quality of shallow ground water.

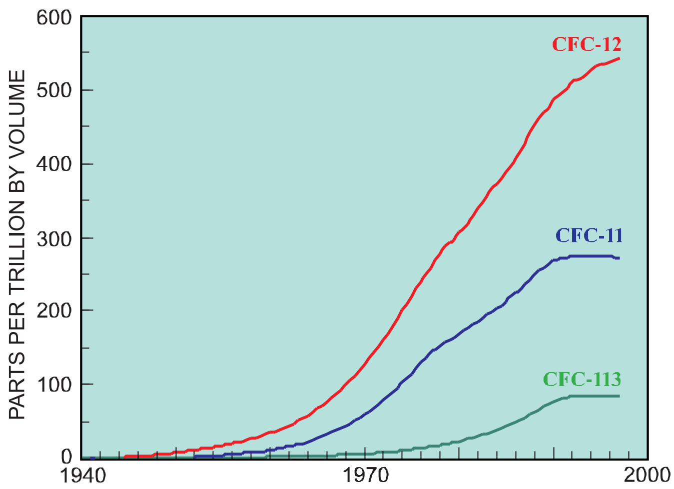


Figure 3. Chlorofluorocarbon concentrations in the atmosphere have increased over time (Cook and others, 1995, and E. Busenberg, U.S. Geological Survey, written commun.,1997).

Small atmospheric concentrations of man-made chlorofluorocarbons (CFC's), specifically CFC-113 ($C_2F_3Cl_3$), CFC-11 ($CFCl_3$), and CFC-12 (CF_2Cl_2), have been increasing steadily between the 1940's and the early 1990's, based on background data from different studies in the United States (fig. 3). These compounds are soluble in water and are relatively stable once in ground water. Therefore, CFC concentrations in ground water can be used to estimate the age of the ground water (Plummer and others, 1993).

A number of tracers such as naturally occurring isotopes of oxygen and carbon and man-made releases of krypton-85, tritium, and pesticides can be used to estimate the relative ages of ground water (Plummer and others, 1993). Tritium was analyzed in ground water from this study area (Cowdery, 1997), but the resulting estimates of ground-water ages were not sufficiently accurate to resolve the relation between land use and water quality. Pesticides that have reached the surficial aquifer in this area also can indicate ground-water age (organic pesticides generally were not used in this area prior to the 1960's), but uncertainties about amounts of pesticides used historically and their degradation in ground water over time make pesticides only qualitatively useful for age dating.

CFC's have been used to measure ground-water age because this method gives more accurate estimates of age (plus or minus 2 years) and can resolve better the dates of recharge of younger ground water (early 1990's), which is needed to study water-quality problems in relatively shallow aquifers (Busenberg and Plummer, 1992; Dunkle and others, 1993; Boehlke and others, 1994; Reilly and others, 1994; Cook and others, 1995; Boehlke and Denver, 1996). Many of the conditions for successful use of the CFC age-dating method existed at the Otter Tail study area, such as limited possibility of nonatmospheric sources of CFC's; very low carbon content in the soils and aquifer, which could sorb CFC's; relatively few high-capacity wells with large, sustained pumping rates, which could cause vertical mixing of ground water; and few areas within the aquifer with low oxygen concentrations, which is conducive to CFC degradation. In addition, the 2-inch-diameter monitoring wells sampled had relatively short screen intervals (3 to 5 feet), effectively reducing the age-dating errors caused by mixing ground water of several ages during sampling.

We studied specifically the variation of ground-water chemistry with depth and along paths of ground-water flow. The general flowpath in the northern part of the Otter Tail surficial aquifer is from areas of recharge, mostly through cropland, to discharge into the Otter Tail River (fig. 2). The soils are generally well drained to excessively well drained sandy loam. The underlying aquifer material is composed of as much as 60 feet of medium sand to fine gravel (fig. 4). Glacial till and ice contact deposits, which have limited ability to transmit ground water, form the bottom and edges of this surficial aquifer. Average annual net recharge (considering losses from evaporation and plant transpiration) is estimated to range from 4 to 7 inches per year, based on analysis of water-level hydrographs and ground-water-model simulations (Cowdery, 1997). During the winter of 1994, streamflow measurements along a 5.2-mile reach of the Otter Tail River (fig. 2) indicated that the river gained 20 percent of its flow from ground water (about 3 cubic feet per second per river mile). Both the soil and aquifer material have low (0 to 1.5 percent) organic carbon content with the exception of wetland areas, which contain organic-rich peat and clay. More details about the hydrologic and chemical characteristics of the study area are available from published reports (Cowdery, 1995, 1997).

Monitoring wells were installed along an estimated direction of flow (figs. 1, 2) from the northeastern edge of the aquifer (well 5) to the river valley (wells 1 and 6 on each side of the Otter Tail River). Each well was grouted to ensure that water could be sampled from specific depth intervals within the surficial aquifer. Wells were pumped at rates less than 0.5 gallon per minute to minimize vertical mixing of ground water during sampling. Sampling incorporated consistent procedures (Menheer and Brigham, 1997) designed to ensure that the water collected was chemically the same as the water in the aquifer. All samples were analyzed by U.S. Geological Survey (USGS) laboratories. A sample set collected during summer 1994 was analyzed for nutrients (nitrogen and phosphorus), major ions, and 80 pesticides. Other samples were collected for analysis of nitrogen isotopes and dissolved argon and nitrogen gases to help interpret CFC data and nitrogen cycling. The temperature of recharge water also was needed for the determination of age. We used a recharge temperature of 6 degrees Celsius based on mean annual air temperature. Most of the wells were sampled for CFC's during August 1995. CFC samples were collected and sealed in borosilicate glass ampoules (vials) using a system (Busenberg and Plummer, 1992) that prevented contact of water samples with air because "modern" air CFC concentrations could change the concentrations in samples of older ground water. Sampling for nutrients and major ions was repeated several times at some wells during 1994–95 to evaluate seasonal variability.

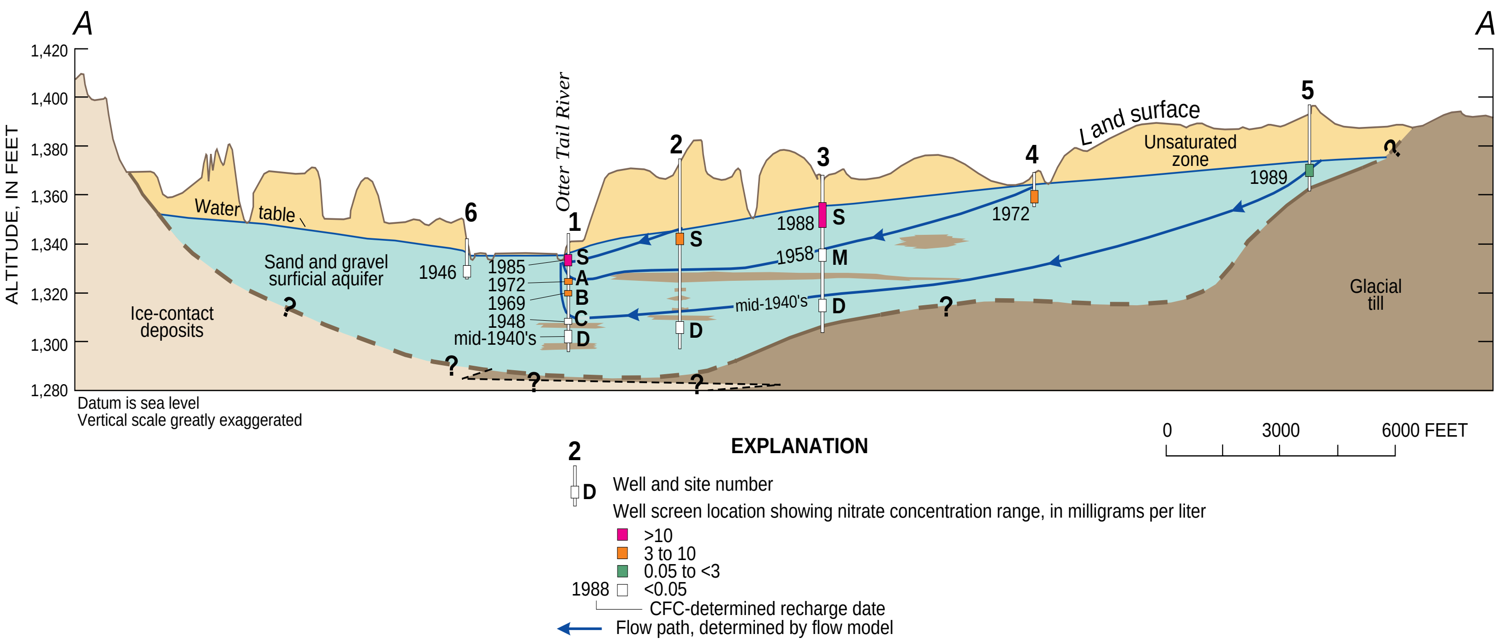


Figure 4. Cross section *A-A'* (line of section on fig. 2) along ground-water flowpath and nitrate concentrations and age date next to well screen symbols (modified from Cowdery, 1997).

A steady-state ground-water-flow model (mathematical simulation) was calibrated to measured water levels and ground-water discharge to the Otter Tail River. The model was used to estimate ground-water travel time through the study area and compared to CFC-determined age dates. Figure 4 shows the distribution of some of the chemicals and the CFC-determined age measured along the section of the aquifer. For most sampling sites, the CFC ages compared closely to ages estimated by flow modeling (table 1). This comparison assumed that CFC's move conservatively with ground water, effects from high-capacity production wells were small, annual recharge was fairly uniform, and CFC's did not degrade over time. The CFC ages generally were 2 to 7 years older than those computed by the flow model, which can be explained by the oversimplifying assumptions of the model. Larger age discrepancies occurred at wells 4, 3M, and 3D (fig. 4). Well 4 probably receives recharge through a local wetland, which has bottom sediments rich in organic carbon that can sorb CFC. This sorption would result in overestimating ground-water age dates. The CFC ages of water from wells 3M and 3D were 29 and 26 years older, respectively, than those computed by the flow model. These differences cannot be explained from what we know about the ground-water flow system and chemistry.

CFC-determined ground-water ages do not account for the time required for water to infiltrate the soil surface and percolate to the water table. This percolation cannot begin until the soil moisture is at infiltration capacity, a condition for well-drained sandy soils that commonly occurs during heavy rains, rainfall coincident with irrigation, or spring snowmelt. A comparison of precipitation data and water-level hydrographs suggests that recharge usually occurs during the spring and occasionally during the summer (Cowdery, 1997). A reasonable estimate of the time for water to move from the soil to the water table would be 0.5 to 1 year.

In general, ground water older than 1958 contained no evidence of contamination by pesticides and little evidence of contamination by nutrients.

Table 1. Comparison between model-estimated and chlorofluorocarbon-determined ground-water ages, in years

[CFC, chlorofluorocarbon]

Well number	Model-estimated age	CFC-determined age	Difference [CFC-model] in age
1S	3	10	7
1A	18	23	5
1B	20	26	6
1C	40	47	7
1D	45	51	6
3S	5	7	2
3M	about 8	37	29
3D	about 26	about 52	26
4	3	23	20
5	2	6	4

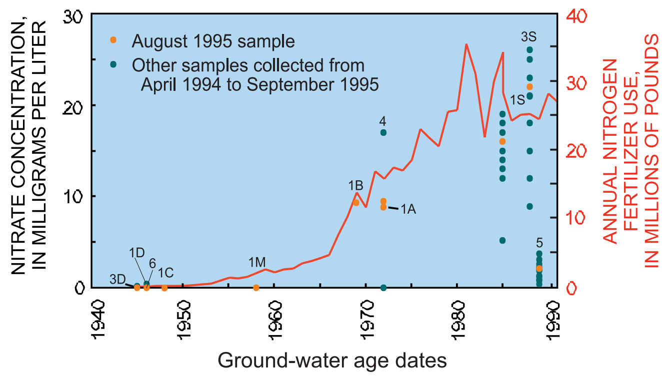


Figure 5. Relations between chlorofluorocarbon-determined ground-water age date, nitrate concentration in ground water, and reported nitrate application amounts for Otter Tail County.

Degradation of contaminants could explain this lack of detection, but it is more likely that this distribution is related to the history of application of fertilizer, pesticides, and irrigation water to the land surface over time. Figure 5 shows the increased nitrate concentrations with younger ground-water age, based on 1994 and 1995 sample analyses. Increased nitrate concentrations over time closely parallel the trend in nitrogen application estimated from State reporting of chemical fertilizer use for Otter Tail County (Alexander and Smith, 1990). Aerial photographs of the study area showed that irrigation also began to increase in the late 1960's. Increased irrigation commonly is associated with increased crop production and increased uses of fertilizer.

In two of three shallowest wells (3S and 1S) sampled repeatedly from April 1994 to September 1995 (Cowdery, 1997), nitrate concentrations varied considerably near the water table. The August 1995 nitrate concentrations, the same samples for which CFC age dating was determined, were among the highest concentrations detected at these wells. Most of the lowest nitrate concentrations from wells 3S and 1S were sampled before summer 1994 (Cowdery, 1997), and the average nitrate concentration from each well is close to the August 1995 value. All samples from well 5 show significantly lower concentrations of nitrate than water sampled from other wells screened near the water table for this study and were similar to or slightly higher than a background concentration of 3 milligrams per liter based on a national study (Madison and Brunett, 1985). Nitrate concentrations also varied much less in well 5. The area upgradient from well 5 is cropland but was not irrigated, suggesting less nitrate contamination of ground water related to smaller amounts of fertilizer use in a nonirrigated area. Low dissolved-oxygen concentrations were measured in water sampled from all of the deeper wells (wells 1C, 1D, 2D, 3M, and 3D). Low dissolved oxygen provides one of the critical conditions favorable for denitrification (reducing nitrate to other forms of nitrogen, such as nitrogen gas). Measured nitrogen gas concentrations also indicated denitrification, but this process could not account for all of the decreasing nitrate concentration with increased ground-water age.

IMPLICATIONS OF RESULTS

These data show the complexity of contaminant distribution in a surficial aquifer and are useful for describing the quality of ground water from the perspective of water use.

Many samples collected near the water table (Cowdery, 1997) had concentrations of nitrate higher than the 10 milligrams per liter drinking-water standard established by the U.S. Environmental Protection Agency (1996). However, most drinking-water supply wells are deeper in this area and may not have nitrate concentrations that exceed drinking-water standards.

Other ground-water studies in the Otter Tail surficial aquifer corroborate that nitrate concentrations are lower at depth (Ruhl, 1997). This is not to say that future water quality from the lower portion of this surficial aquifer is completely safe from land-use effects. Water recharged to the water table could eventually reach the lower portion of the aquifer, and in the absence of chemical and biological degradation, contaminants could migrate deeper and affect drinking water in a timeframe of decades.

Additional research also explained why the nitrate-enriched ground water has limited effects on the water quality in the hydraulically connected Otter Tail River (Cowdery, 1997). Two processes in the riparian area between the aquifer and the stream decreased nitrate concentration of ground water before it discharged to the Otter Tail River. These processes were denitrification and mixing of the younger, nitrate-rich ground water with older ground water having nondetachable concentrations of nitrate (Puckett and others, 1995). The ground-water age data indirectly will help us estimate the relative significance of these two processes in future research. This information in turn will be useful for predicting the effects of nutrients in ground water on the concentrations and loads of nutrients in stream water.

PRECAUTIONS USING CFC AGE DATING

Under optimal conditions, researchers can expect a 2-year accuracy for ground-water age determination using CFC's. Conditions were favorable for using this method at the Otter Tail surficial aquifer. Important in our analysis was the use of a basic understanding of ground-water flow in conjunction with the CFC-determined ground-water age. The large variability of nitrate concentrations over time near the water table also reflected dynamic land-use and recharge conditions that must be considered when evaluating CFC-determined recharge dates and water-quality data.

The CFC method may have some limitations in other surficial aquifers in the region. For example, the conditions at the Sheyenne Delta aquifer in North Dakota (Cowdery, 1997) might not be ideal for using the CFC method of dating ground water. Greater care, at least, would be needed to use the CFC method in that environment because (1) the depth to water is shallow (mean depth was 5 feet), (2) lignite (organic substances) in the aquifer materials and low dissolved oxygen may result in falsely old CFC age dates, and (3) there are steep gradients in ground-water age over short distances due to slow ground-water flow in that aquifer, which could result in ages extending beyond the 55-year limit of the CFC method.

Uncertainty of age estimates increases with age because older recharge waters have lower CFC concentrations (Busenberg and Plummer, 1992) and a greater possibility for CFC degradation (leading to falsely older estimates of ages). In the future, the CFC technique will become less sensitive for estimating ages of relatively young ground water because with decreasing production of CFC's, their concentrations in the atmosphere will decrease (Oster and others, 1996).

ABOUT THE NAWQA PROGRAM

During the past two decades, all levels of government and industry have made large financial investments in the protection of water quality across the Nation. Current and future expenditures are anticipated to abate and control water pollution. These challenges are being addressed by Federal, State, interstate, and local water-resources agencies and many academic institutions. The study described in this report was part of the USGS National Water-Quality Assessment (NAWQA) program implemented in 1991 to enhance the base of scientifically sound and consistent information for managing water resources. The purpose of this program is to assess the quality of a large, representative part of the Nation's water. The Red River of the North Basin was one of the first 20 study areas. The study began in 1991, and intensive data collection was completed in 1995. The NAWQA program also assesses the quality of surface water and the health of aquatic biota (Lorenz and Stoner, 1996).

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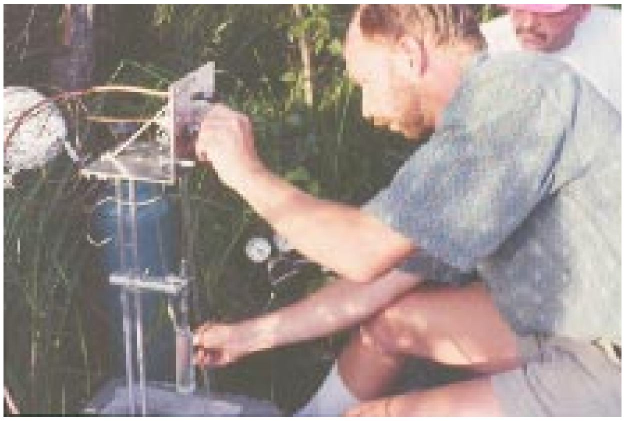

Water samples were collected and sealed to avoid contact with air.

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For more information, contact:

Red River NAWQA Coordinator
U.S. Geological Survey
2280 Woodale Drive
Mounds View, MN 55112
Phone: (612) 783-3100

Internet address:
http://wwwmn.cr.usgs.gov/redn/index.html

Study area looking from Otter Tail River to the northeast.