Journal of the Minnesota Academy of Science

Volume 55 | Number 1 Article 8

1989

Residence Times of Minnesota Groundwaters

Scott C. Alexander
University of Minnesota

E. Calvin Alexander Jr.

Recommended Citation

Alexander, S. C., & Alexander, E. C. (1989). Residence Times of Minnesota Groundwaters. *Journal of the Minnesota Academy of Science, Vol. 55 No.1*, 48-52.
Retrieved from https://digitalcommons.morris.umn.edu/jmas/vol55/iss1/8

Residence Times of Minnesota Groundwaters

SCOTT C. ALEXANDER and E. CALVIN ALEXANDER, JR.

ABSTRACT—Tritium, ^{14}C, and nitrate analyses for eighty groundwater samples from selected Minnesota aquifers indicate a range of residence times from a few days or weeks to tens of thousands of years. The presence of significant nitrate contamination in groundwater is confined to recent or mixed groundwaters. Isotopic studies can yield information that will be useful in the design of effective groundwater protection plans in Minnesota.

Introduction

Ninty-four percent of the public water supply systems and seventy-five percent of the people in Minnesota depend on groundwater for their domestic water supply (1). The public, along with its elected and appointed officials, has grown increasingly aware of the threats pollution and overpumping pose to the continued availability of safe groundwater resources. In Minnesota, human activities on or near the land surface are responsible for most of the groundwater contamination. This surface-derived contamination moves down through the aquifers to wells. The susceptibility of a given well to contamination is largely a function of its distance from the recharge zone and the length of time required for the water to move from the recharge zone to the well. Recharge can occur naturally or be artificially induced by excessive pumpage or by the creation of artificial flow paths, such as abandoned wells or multi-aquifer wells.

Our goal has been to demonstrate reliable methods to define groundwater flow systems and their susceptibility to contamination. Currently, our studies employ an assortment of isotopic and chemical techniques. These techniques include analyses for carbon isotopes, tritium, stable isotopes, uranium isotopes, and radon as well as major cations and anions. Tritium (^{3}H) and ^{14}C have proven to be the isotopes with the broadest applications for residence-time studies of Minnesota groundwaters.

Over the past two decades ^{14}C and tritium have been successfully used to determine the age of groundwaters around the world. The age or residence time of groundwater is the time the water spent underground or the time since it infiltrated from the surface. For example, Pearson and White (2) used ^{14}C to date waters in the Carrizo Sand of Texas; tritium and ^{14}C have been used by Smith *et al.* to date waters in chalk and limestone in England (3, 4). Isotopic studies have applications across much of hydrogeology (5). Hendry's (6) recent guest editorial in *Ground Water* is an excellent, concise exposition of the utility of isotopic techniques in hydrogeology. Surprisingly few isotopic studies have been done on Minnesota waters (7, 8).

This paper reports initial results from a series of chemical and isotopic analyses of groundwater from a variety of sites in Minnesota.

Materials and Methods

Fourteen principal aquifers are currently utilized in Minnesota (1). This paper is a summary of results obtained as parts of several different projects and reflects data from nine of the fourteen principal aquifers. In most cases clusters of wells were selected in a particular region to look for vertical gradients between some of the local aquifers and to gain a general overview of the chemical and isotopic characteristics of the area. Figure 1 shows the general locations of the study areas. The detailed location of each well sampled was identified and referenced by its Minnesota Geological Survey unique number, when available. The well locations were independently confirmed during sampling. The aquifer, depth, construction, and producing level for each well came from public files of various agencies.

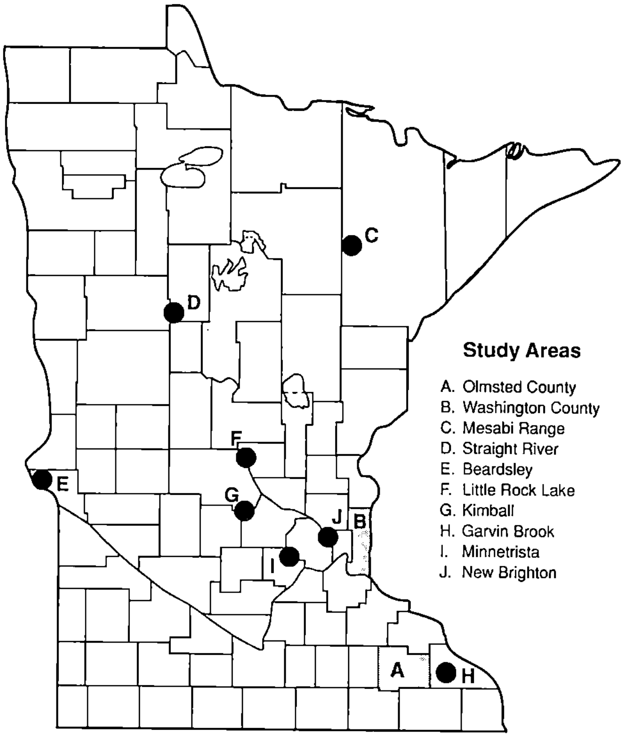

Figure 1. Locations of study areas. The dots represent well clusters. The Washington and Olmsted County studies involved wells distributed across the counties.

Calvin Alexander is a professor in the Department of Geology and Geophysics at the University of Minnesota and Scott Alexander is a technician in Professor Alexander's laboratory.

Field Sampling

The wells generally were pumped until the water reached a constant temperature as measured with an ASTM 63C mercury thermometer calibrated to 0.1°C. The pH of the water was measured using an Orion SA 210 field pH meter. Each measurement was calibrated with pH 7 and 10 buffers. Samples were collected for the various chemical and isotopic analyses.

Chemical Analyses

The major and minor dissolved species in the water samples were determined by: 1) alkalinity titrations for bicarbonate ion concentration; 2) ion chromatography for chloride, nitrate, sulfate, and other minor anions, and 3) AES/DCP for a suite of 12 metals. The precision of these measurements was always better than ± 10% and was usually better than ± 5%. The accuracy of the data as judged by interlaboratory comparisons of the chemical analyses of split-samples was better than ± 5%.

Carbon and Tritium Isotopic Analyses

The procedure used to extract the dissolved carbonate species was designed to avoid contamination during sampling with recent atmospheric CO_2 which contains relatively large amounts of ^{14}C. Samples of 120 to 200 L were collected in large plastic bags supported in 30 or 55 gallon drums. While the water was pumped into the bag 500 mL of concentrated NH_4OH was added to raise the pH to about 10. The increased pH converted the dissolved HCO_3^- to CO_3^{-2}. The NH_4OH was pretreated with $BaCl_2{\cdot}2H_2O$ to precipitate all the dissolved carbon including any recent atmospheric ^{14}C and was filtered immediately before use. About 200 g of $BaCl_2{\cdot}2H_2O$ was added to the water as the bags filled. The barium reacted with the carbonate ions to precipitate $BaCO_3$. The drums of water were allowed to sit overnight as the precipitate settled to the bottom. All but one or two liters were then siphoned off and the remaining slurry was transferred to plastic bottles for storage and shipping.

The barium carbonate slurry was shipped to a commercial lab for ^{14}C and $\delta\,^{13}C$ analyses. The analyses were done by Beta Analytic in Coral Gables, Florida using analytical techniques described in (9). The ^{14}C data are reported as the fraction of modern (1950) biospheric content. The reported errors of the ^{14}C data are one standard deviation counting errors. The δ 13C data are reported as the per mil (parts per thousand) deviation from the PDB-1 international standard.

Samples for tritium analyses were collected in 500 mL amber colored glass bottles. These bottles were filled without rinsing and without air bubbles to minimize any contamination by tritium in the air. The tritium bottles are then shipped to a commercial laboratory for enriched tritium analyses. The Environmental Isotope Laboratory of the University of Waterloo, Ontario, Canada, performed the analyses using analytical techniques described in (10). Tritium is reported in TUs (TUs = Tritium Units = 1 atom of ^3H per 10^{18} atoms of ^1H = about 3.2 pCi/L.) The detection limit of Waterloo's enriched tritium analyses is about 0.8 TUs. The reported errors are one standard deviation counting errors.

Determination of Groundwater Residence Times

A cautionary note is necessary. Groundwater systems inevitably involve mixing of water from different reservoirs and mixing of water of varying ages within the same reservoir. The concept of a groundwater age or residence time will rarely be as specific as that of an artifact or a piece of charcoal. The numerical values of the following "ages" are at best averages and are strongly model dependent. Nevertheless, useful insights result from these model-dependent ages.

The age or residence time of groundwater can be estimated from the water's content of tritium and ^{14}C. Both tritium and ^{14}C are radioactive isotopes. Tritium has a half-life of 12.43 years; for ^{14}C it is 5,730 years. Both isotopes are produced naturally by cosmic rays in the earth's atmosphere. Prior to the 1950s, the natural atmospheric concentration of the two isotopes was a few TUs for tritium and about 13.5 disintegrations/min-g carbon for ^{14}C. The atmospheric concentration of both isotopes was significantly increased in the late 1950s and 1960s by the atmospheric testing of nuclear weapons. The ^{14}C content of the atmosphere peaked in 1964 at about 188 percent of its 1950 value (11). The 1950 value is defined as the "modern" value. The atmospheric tritium content peaked in 1954, 1959, and 1962-64 at between one and two thousand TUs (12).

Given the relatively short half-life of tritium and the enormous fallout spikes, tritium is a very sensitive indicator of water that has entered groundwater systems since 1954 or conversely, a solid indicator of the absence of such recent water. The following tritium groundwater age divisions are modified from those listed in (6). If a water sample contains more than about 10 TU of tritium, that water probably entered the ground since 1954 and will be referred to as "recent" water. If a water sample contains less than about one TU of tritium, that water entered the ground before 1954 and will be referred to as "vintage" water. Water samples containing between one and ten TUs of tritium are of either mixtures or recent and older waters or are of intermediate age and will be referred to as "mixed" water.

High levels of ^{14}C in groundwater are also indicative of recent (post-1954) recharge. Given its 5,730 year half-life, ^{14}C can be used to determine residence times or ages back to 30,000 to 40,000 years before the present. The ^{14}C system is complicated by the presence of numerous potential carbon sources in addition to the atmospheric reservoir. These non-atmospheric carbon sources must be taken into account, through various model-dependent schemes, in order to calculate an age (see (13) for a recent review). Nevertheless, the presence of high levels of tritium and ^{14}C clearly indicate a groundwater system dominated by recent recharge. Water samples with no detectable tritium and low levels of ^{14}C have been isolated from the atmosphere for long periods of time. Intermediate cases are rare and probably indicate mixing of two or more different groundwater reservoirs.

Results

This paper is based on the analyses of 80 groundwater samples from a wide variety of Minnesota aquifers. The complete data compilation, showing the location, aquifer, depth, carbon isotope, tritium and nitrate data from the 80 wells, is available on request from E.C.A., Jr. The data compilation has also been deposited in the National Technical Information Service, Springfield, VA 22161, and may be ordered as document # PB90-117045.

The major cation and anion data for these wells reveal a range of chemical types of groundwater. Most of the waters are calcium magnesium bicarbonate waters. Some samples, however, contain significant sodium chloride, calcium sulfate, sodium bicarbonate, and/or magnesium components. In some of the areas such as Washington and Olmsted Counties waters from wells producing from different aquifers show very similar chemical compositions. In other areas such as Hibbing and Beardsley the waters in a small area show a wide range of chemical composition. This variation in the scale of homogeneity presents many challenges in the interpretation of existing data and for the design of new groundwater studies.

Thirty-one of the wells contain vintage water with no detectable tritium (<0.8 TU). This water entered the ground before 1954. Twelve of the 31 water samples contain ^{14}C contents of less than 0.5 of modern, and it is possible to calculate numerical ages for these samples. As noted above, the age calculated from a groundwater ^{14}C content is very model dependent (13). One of the simplest models is to assume that the chemical reaction:

$$CaCO_3 + H_2O + CO^2 \Rightarrow Ca^{+2}\ 2\ HCO_3^- \quad (1)$$

is an adequate model of the dissolved carbonate geochemistry. In this model half of the dissolved bicarbonate comes from limestone and half comes from carbon dioxide in the soil zone. The latter component was derived from the decay of biological material in the soil and thereby contained biospheric levels of ^{14}C when the water passed through the soil.

Within the context of this model the measured ^{14}C is simply doubled to correct for dilution by "dead" rock carbon. An age can be calculated from the equation:

$$\text{age} = -\ (t_{1/2} / \ln 2) \cdot \ln(2 \cdot {}^{14}C) \quad (2)$$

where $t_{1/2}$ is the half-life of ^{14}C or 5,730 years and ^{14}C is the measured value from the barium carbonate slurry analysis.

A check on the applicability of the model is provided by the measured $\delta\ ^{13}C$ in the dissolved bicarbonate. Limestones normally have $\delta\ ^{13}C$ values of about 0, while the $\delta\ ^{13}C$ values of soil CO_2 vary from about -18 to -25 depending on the source of the biological carbon. If the measured $\delta\ ^{13}C$ is between -9 and -12.5, then the model above may be applicable. If the measured $\delta\ ^{13}C$ is outside this range the model is clearly an oversimplification. The numerical ages given in the data compilation for those samples with <0.8 TU and ^{14}C <0.5 of modern were calculated with equation (2). The ages are given to only one significant figure in view of the model uncertainties.

Figure 2 shows the nitrate contents of the water samples sorted according to their tritium contents. Thirty-one samples contain vintage water with no detectable tritium. One of these samples contains 0.11 ± 0.01 mg/L of nitrate-N. None of the other samples contain more than 0.1 mg/L, and most have no detectable nitrate, <0.01-0.02 mg/L.

Twelve samples contain mixed water with 0.8 to 10 TUs of tritium. It is interesting to note that nine of these twelve wells are producing water from the Jordan aquifer. Apparently, the Jordan is particularly prone to the mixing of younger and older groundwaters. Of the twelve wells, seven contain <0.1 mg/L nitrate-N, four contain 0.1 to 1.0 mg/L, and one contains 1.88 ± 0.04 mg/L. No well yielded water above the 10 mg/L drinking water standard.

Thirty-four samples contain recent water with more than 10 TUs of tritium. Seven of the wells contain water with <0.1 mg/L nitrate-N. A few areas in Minnesota do not yet contaminate the recent recharge with nitrate. The samples from the Mesabi Range, where there has been very little agriculture, have very low or no detectable nitrate. Five of the recent wells contain between 0.1 and 1.0 mg/L of nitrate-N, twelve wells contain between 1.0 and 10 mg/L, and ten wells yielded water above the 10 mg/L nitrate-N drinking water standard. The high-nitrate wells are scattered all across Minnesota.

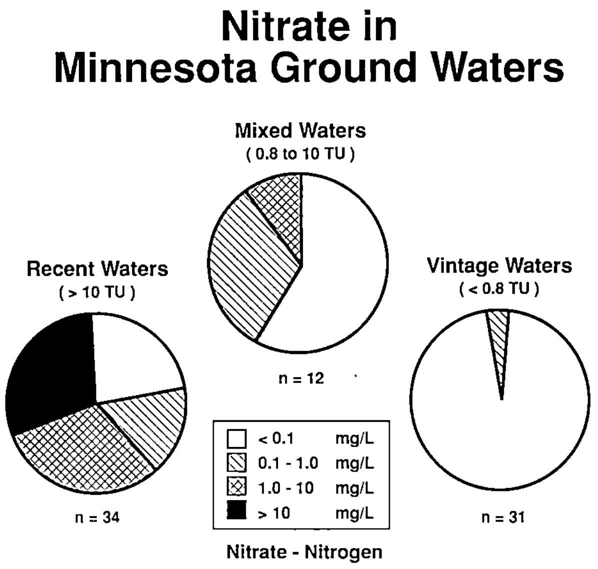

Figure 2. Nitrate/age correlation in Minnesota groundwaters.

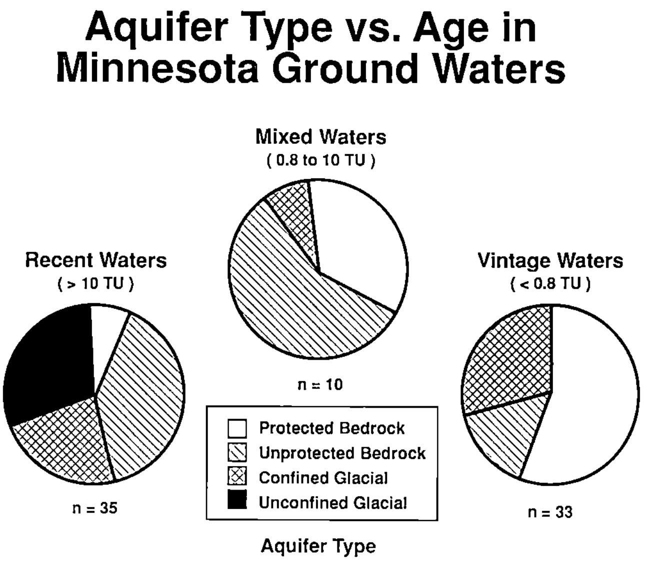

Figure 3. Aquifer catagory/age correlation in Minnesota groundwaters.

Based on the well logs we have sorted the aquifers into four catagories: protected bedrock, unprotected bedrock, confined glacial, and unconfined glacial. Figure 3 shows the aquifer catagories sorted according to the wells' tritium content. The unconfined glacial aquifers contain only recent water. The confined glacial aquifers contain about equal numbers of recent and vintage water. Most of the protected bedrock aquifers contain vintage water but examples were found of recent and mixed water in the protected bedrock aquifers.

We have enough data to discuss the tritium age distribution within the Prairie du Chien and Jordan aquifers. Figure 4 shows the tritium contents of the water from these two aquifers. The Prairie du Chien and Jordan both contain roughly equal numbers of recent and vintage water. The mixed waters appear to be concentrated in the Jordan aquifer.

Although the data in the study are from a variety of areas and aquifers, the samples may not be representative of all the groundwater in Minnesota. The wells were selected to study recharge in areas with previously identified pollution problems. In most areas we also attempted to sample a few nearby, properly constructed wells in protected aquifers. The data should delimit the best and worst cases — but are not a statistically valid sample of wells in Minnesota.

Discussion

The ages, chemistries, and contaminant levels of Minnesota groundwaters vary enormously over small distances. Groundwater residence times range from days (14) or weeks to tens of thousands of years. Adjacent wells can have very different properties. Deep wells do not always yield older or better quality water than nearby shallow wells.

These observations have important implications for well head protection and management of groundwater resources. The design of an effective well head protection and resource management plan is dependent on knowledge of when and where an aquifer is recharged. Wells in aquifers with short residence times are very prone to contamination from local recharge. Point-source pollution such as leaky underground storage tanks and chemical spills or non-point sources such as agricultural chemicals or drainfield effluents are the major threats to such wells. Wells in aquifers with long residence times and which are protected by effective aquitards or long flow paths from distant recharge zones are most vulnerable to contamination via improperly constructed or abandoned wells. This threat can arise either from the production well or from a nearby well. Isotopic analyses permit a resource manager to separate short residence-time wells from long-residence time wells and thereby concentrate on effective well head protection strategies on a well-by-well basis. The costs of isotopic analyses are comparable to those of pesticide or VOC scans and are much less than the costs of full scale Priority Pollutant scans.

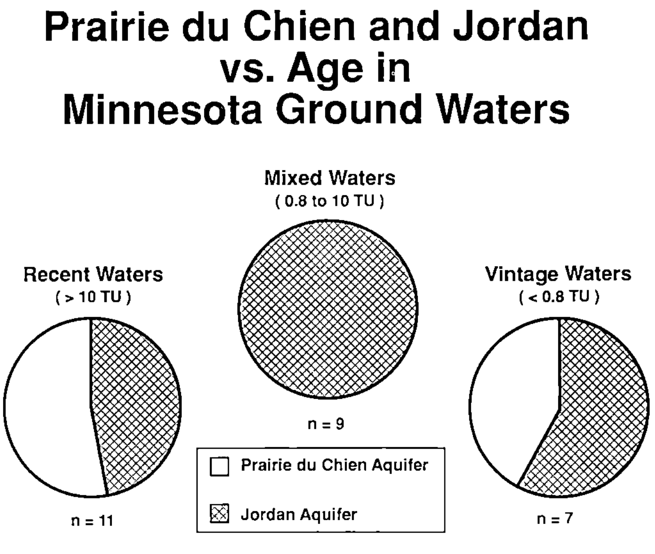

Figure 4. Distribution of tritium ages in the Prairie du Chien and Jordan aquifers in Minnesota.

In Minnesota, and particularly in the Twin Cities area, several aquifers are separated by aquitards of varying effectiveness and lateral extent. In this complex geologic setting there are many potential short residence-time contaminant pathways. Isotopic studies may not be able to identify individual pathways but can ascertain if a fast pathway is affecting any particular well.

The age/nitrate correlations in Figure 2 are remarkably good. Vintage groundwaters contain little if any nitrate. Recent groundwaters usually contain nitrate. Mixed waters yield intermediate nitrate contents. The lack of nitrate in vintage waters suggests that there is either no significant natural background of nitrate in the areas sampled or that there is some chemical/biological process that removes nitrate on the time scale of decades.

Acknowledgements

The initial development of the techniques was done under a grant from the Legislative Commission on Minnesota Resources which deserves special thanks for its foresight. Parts of the work were funded by the cites of Rochester, New Brighton, and Minnetrista; Olmsted and Washington Counties; the Iron Range Resource and Rehabilitation Board; the Minnesota Department of Natural Resources and Pollution Control Agency; the Minnesota Geological Survey; and the U.S. Geological Survey. We also thank the well owners, agency personnel, and utility workers who have assisted us in many ways. This is publication # 1123 of the N.H. Winchell School of Earth Sciences, Department of Geology and Geophysics, University of Minnesota.

References

1. Woodward, D.G. 1985. Minnesota ground-water resources. U.S. Geol. Survey Water-Supply Paper 2275, pp. 261-268.
2. Pearson, F.J., Jr., and White, D.E. 1967. Carbon 14 ages and flow rates of water in Carrizo Sand, Atoscosa County, Texas. *Water Resour. Res.* 3:251-261.
3. Smith, D.B., Downing, R.A., Monkhouse, R.A., Otlet, R.L., and Pearson, F.J. 1976. The age of groundwater in the chalk of the London Basin. *Water Resour. Res.* 12:392-404.
4. Downing, R.A., Smith, D.B., Pearson, F.J., Monkhouse, R.A., and Otlet, R.L. 1977. The age of groundwater in the Lincolnshire Limestone, England, and its relevance to the flow mechanism. *Jour. Hydro.* 33:201-216.
5. Fritz, P., and Fontes, J.Ch. 1980. *Handbook of Environmental Isotope Geochemistry.* Vol. 1, New York, Elsevier, 545 pp.
6. Hendry, M.J. 1988. Do isotopes have a place in groundwater studies? *Ground Water.* 26:410-415.
7. Alexander, E.C., Jr., Siegel, D.I., and Milske, J.I. 1983. Isotopic studies of the Mt. Simon Aquifer, Southern Minnesota [abs.]. *EOS.* 64:225. Alexander, E.C., Jr., and Lively, R.S. 1987. Isotopic investigation of glacial sand aquifer near Park Rapids, Minnesota [abs.]. *Abstracts with Programs, 1987 North-Central Section, Geol. Soc. Amer. Meeting, St. Paul, Minn., April 30 - May 1, 1987.* p. 185. Alexander, E.C., Jr., Alexander, S.C., and Lively, R.S. 1987 Recharge of the Mt. Simon/Hinckley Aquifer: Responses to climate change and water use [abs.]. *EOS.* 68:1270.

8. Siegel, D.I., and Mandle, R.J. 1984. Isotopic evidence for glacial melt-water recharge to the Cambrian-Ordovician aquifer, north-central United States. *Quaternary Res.* 22:328-335.
9. Tammers, M.A. 1975. Chemical yield optimization of the ben-zene synthesis for radiocarbon dating. *Internatl. Jour. Appl. Rad. & Isotopes.* 26:676-682.
10. Environmental Isotope Laboratory, Univ. of Waterloo. 1989. Technical Procedure 1.0: Tritium Analyses. Revision: 01, 3/5/89. 25 pp.
11. Swan, J.T., Krueger, H.W., and Sullivan, C.H. 1983. Radiocarbon activities in agricultural products: 1950 thru 1982. unpublished manuscript orginally submitted to *J. Assoc. Official Anal. Chem.* (manuscript available from H. Krueger, Geochron Labs, 24 Blackstone St., Cambridge, MA 02139).
12. Gat, J.R. 1980. The isotopes of hydrogen and oxygen in pre-cipitation. In P. Fritz and J.Ch. Fontes [eds.] *Handbook of Environmental Isotope Geochemistry,* Vol. 1, pp. 21-47. New York, Elsevier.
13. Mook, W.G. 1980. Carbon-14 in hydrogeological studies. In P. Fritz, and J.Ch. Fontes [eds.] *Handbook of Environmental Isotope Geochemistry,* Vol. 1, pp. 49-74. New York, Elsevier.
14. Mohring, E., and Alexander, E. 1986. Quantitative tracing of karst groundwater flow: Southeastern Minnesota, North Central U.S.A. Proc. 5th Internat. Symp. on Underground Water Tracing. Instit. of Geol. and Min. Expl., Athens, Greece, pp. 215-227.