

# SOURCE IDENTIFICATION OF SODIUM AND CHLORIDE CONTAMINATION IN NATURAL WATERS: PRELIMINARY RESULTS

S.V. Panno, K.C. Hackley, H.H. Hwang,  
S. Greenberg, I.G. Krapac, S. Landsberger and D.J. O'Kelly

## ABSTRACT

Sodium-chloride ( $\text{Na}^+$ -  $\text{Cl}^-$ ) contamination in groundwater and surface water in rural and urban areas of Illinois and the U.S. is widespread. The input of  $\text{Na}^+$  and  $\text{Cl}^-$  from road salt in the northern U.S., seawater intrusion along coastal areas, animal and human waste in rural areas, leaking landfills and natural saline seeps in other areas has created progressively worsening problems with water quality in some municipal and private wells. In addition, elevated concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$  have adversely affected the biodiversity of wetland areas and waterways. These problems are especially acute in areas of the U.S. that are experiencing rapid growth.

Water samples collected (primarily in Illinois) from streams, springs and wells containing elevated  $\text{Na}^+$  and  $\text{Cl}^-$ , and from likely sources of  $\text{Na}^+$  and  $\text{Cl}^-$  contamination were analyzed for a variety of parameters. The data from these analyses were examined graphically and scrutinized for trends and clustering in order to characterize likely sources of contamination of affected waters. The halides,  $\text{Br}^-$ ,  $\text{Cl}^-$  and  $\text{I}^-$ , in conjunction with cations and other anions, total N, dissolved organic carbon, stable isotopes (including  $\delta\text{D}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of the  $\text{NO}_3^-$  ion), tritium and their ratios were found to be effective in connecting most of the contaminant sources with their affected waters. The use of mixing curves proved to be an effective means of identifying sources of  $\text{Na}^+$  and  $\text{Cl}^-$  when applied to specific study areas. Thus, the methods applied in this investigation may make it possible to identify the sources of  $\text{Na}^+$  and  $\text{Cl}^-$  contamination in natural waters.

## INTRODUCTION

Contamination of groundwater and surface water by  $\text{Na}^+$  and  $\text{Cl}^-$  is a common occurrence in growing urban areas (Mason et al. 1999; Buttle and Labadia, 1999; Naftz and Spangler, 1994) and adversely affects municipal and private water supplies in Illinois and other states (Moyland, 1980; Cleary, 1978; Richard Rice, ISGS, personal communication, 1999). Removal of  $\text{Cl}^-$  from a water supply is usually not an option because of the expense of desalination. Increasing concentrations of these ions in groundwater and surface water can adversely affect environmentally-sensitive areas such as wetlands. Sodium and  $\text{Cl}^-$  contamination within a wetland's watershed and recharge areas can destroy rare and endangered plant species (Wilcox 1986a, b; Grootjans et al. 1988; Panno et al. 1998, 1999b, 2000).

Sources for these ions related to human activities include road salt, effluent from industrial facilities, leachate from municipal landfills, effluent from private and municipal septic systems, and some agricultural chemicals. Natural sources include rock-water interactions, saline seeps, and minor atmospheric contributions. While the identification and quantification of  $\text{Na}^+$  and  $\text{Cl}^-$  in water is a simple matter, the determination of the source or sources of  $\text{Na}^+$  and  $\text{Cl}^-$  as contaminants in surface water and groundwater is problematic. It is first necessary to identify the source(s) of a

contamination problem in order to solve it. Several approaches have been used to help identify the sources of  $\text{Na}^+$  and  $\text{Cl}^-$  in natural waters (e.g., Whittemore, 1995; Davis et al. 1998), but these techniques are not always definitive. The  $\text{Cl}/\text{Br}$  ratio has been used successfully to study the formation of saline groundwater and brines from relatively deep geologic formations, and to characterize atmospheric precipitation, shallow groundwater, and domestic sewage (Davis et al. 1998). The conservation of  $\text{Br}^-$  and  $\text{Cl}^-$  during transport in groundwater make these halides and their ratios especially useful in determining surface water and groundwater movement under most circumstances. Characterization of a natural water may indicate its origin and evolution (e.g., Appelo and Postma, 1994). Analyses of radioactive and stable isotopes are excellent indicators of the history and evolution of surface water and groundwater. For example, tritium, and potentially  $^{37}\text{Cl}$ ,  $\delta^{18}\text{O}$ , and  $\delta^{13}\text{C}$ , are useful indicators of the evolution of groundwater and surface water, and may also be useful for fingerprinting contaminants (Clark and Fritz, 1997). Panno et al. (2000) used these techniques to identify the likely sources of  $\text{Na}^+$  and  $\text{Cl}^-$  contamination entering a fen in Illinois.

### **Objectives**

The purpose of this investigation was to determine which geochemical and isotopic analysis techniques used alone, together, and/or in conjunction with basic geologic and hydrologic data, and land-use information, could definitively indicate the source(s) of  $\text{Na}^+$  and  $\text{Cl}^-$  contamination in surface water and groundwater. The results presented are preliminary because samples are still being collected and analyzed for a variety of parameters, and additional samples need to be collected.

## **METHODS**

To find indicators for the sources of  $\text{Na}^+$  and  $\text{Cl}^-$  in groundwater and surface water, several end members were chemically and isotopically characterized. The term “end member”, as used here, refers to selected recognized sources of concentrated  $\text{Na}^+$ - $\text{Cl}^-$  and uncontaminated waters. Stream water and/or groundwater known to have been contaminated by a  $\text{Na}^+$ - $\text{Cl}^-$  source were collected and analyzed for comparison.

### **Analytical Procedures**

Sixty three water samples were either collected or retrieved from the ISGS Isotope Geochemistry Section’s sample archives (Table 1). Forty water samples collected by the authors were analyzed in the field for temperature, pH, Eh and specific conductance using meters that allow temperature compensation in accordance with field techniques as described in Wood (1981). Samples collected for cations and anions were passed through 0.45- $\mu\text{m}$  high-capacity filters and stored in polyethylene bottles. Cation samples were acidified in the field with ultra-pure nitric acid to a pH of  $< 2$ . All samples were transported to the laboratory in ice-filled coolers, and kept refrigerated at approximately  $4^\circ\text{C}$  until analyzed. Twenty-three archived samples had been collected in the same manner as described above, and had received partial analysis prior to retrieval. Previous analyses were conducted under the same protocols as the samples collected for this investigation.

Table 1. End members, affected water samples, and pristine water samples collected for this investigation. Upper case IDs, here and on the figures, indicate background samples and end

members; lower case IDs indicate groundwater or surface water that has been affected by contamination with a Na<sup>+</sup>-Cl<sup>-</sup> source.

<b>Sample Numbers</b>	<b>Location</b>	<b>Date of Sampling</b>
<b>Rainwater and Snow melt</b>		
P1	East Central IL rainfall	08/31/01
P2	East Central IL rainfall and snow melt	11/31/01
<b>Surface Streams</b>		
R1	Miss. River, Davenport, IA	08/14/01
R2	Miss. River, Quincy, IL	08/14/01
R3	Miss. River, Chester, IL	08/14/01
R5	Miss. River, Louisiana	08/06/01
R6	Miss. River, Chester, IL	11/15/01
R7	Miss. River, Quincy, IL	11/15/01
R9	Miss. River, Davenport, IA	11/15/01
<b>Uncontaminated Aquifers</b>		
A1	Ceiling seep, Mammoth Cave (KY) dome	08/15/01
A2	Ceiling seep, Mammoth Cave (KY) dome	08/15/01
A3	Private well, Hampshire, IL	01/17/01
A4	IDOT well, Hampshire, IL	01/17/01
A5	Background monitoring well near landfill, Kane Co.	11/05/01
A7	Weldon Spring, Weldon, IL	10/03/00
A8	Well CHM96B, Mahomet aquifer, Champaign, Co.	02/16/99
A9	Well Staff-99, Wedron aquifer, Champaign, Co.	06/15/99
A10	Well CHM94B, Glasford aquifer, Champaign, Co.	10/26/98
A11	Well CHM94A-2, Mahomet aquifer, Champaign, Co.	04/14/99
A12	Ceiling seep, Fogelpole Cave (IL) flowstone	09/13/00
<b>Fertilizers</b>		
f1	Tile water from east-central IL	10/18/01
f2	Tile water from east-central IL	04/25/00
f3	Tile water from east-central IL	04/25/00
f4	Tile water from east-central IL	02/28/02
F5	Urea fertilizer	03/21/01
F6	Solution 28 fertilizer	03/21/01
f7	Field runoff from southwestern Illinois	06/29/01
<b>Road Salt</b>		
s1	Hampshire, IL subdivision contaminated well	10/17/01
s2	Hampshire, IL subdivision contaminated well	10/17/01
s3	South Elgin, IL contaminated monitoring well	11/02/99
s4	South Elgin, IL contaminated monitoring well	01/18/00
S5	Road salt - deionized water solution	11/02/99
<b>Landfills</b>		
L1	Northeastern Illinois unidentified landfill leachate	09/03/92
L2	Northeastern Illinois unidentified landfill leachate	11/20/92

L3	Northeastern Illinois unidentified landfill leachate	12/04/91
14	Unidentified landfill mon. well (contaminated), South Elgin, IL	01/18/00
15	Unidentified landfill mon. well (contaminated), South Elgin, IL	01/18/00
L6	Northeastern Illinois unidentified landfill leachate	11/05/01
L7	Northeastern Illinois unidentified landfill leachate	11/05/01
<b>Septic Systems</b>		
E1	Septic tank effluent: flushing of ion-X resin, Kane Co.	11/02/99
E2	Septic tank effluent, Kane Co.	01/18/00
E3	Septic tank effluent, Monroe Co.	03/21/01
E4	Septic tank effluent, Monroe Co.	03/21/01
E5	Septic tank effluent, Monroe Co.	03/21/01
E6	Culligan water softening pellets	02/08/00
E7	Septic tank effluent, Monroe Co.	11/18/99
E8	Morton Salt water softening pellets	12/18/01
e11	Septic tank monitoring well (contaminated), NY	12/18/01
e12	Septic tank monitoring well (contaminated), NY	12/18/01
<b>Animal Waste</b>		
W1	Hog waste lagoon effluent	03/21/01
W2	Hog waste effluent-affected well	11/17/99
W3	Hog waste effluent (Site A)	09/05/01
W4	Hog waste effluent (Site E)	12/21/01
w5	Site A monitoring well (contaminated)	01/10/02
w6	Site A monitoring well (contaminated)	01/10/02
w7	Site A monitoring well (uncontaminated)	01/10/02
<b>Saline Seeps</b>		
B1	Villa Grove, IL saline well	07/10/97
b2	Mahomet aquifer, saline seep-affected well	10/03/00
b3	Mahomet aquifer, saline seep-affected well	10/19/00
B4	Columbia, IL saline spring	06/28/01
B5	Equality, IL saline spring	02/28/02
b6	Well BY99, Mahomet aquifer, saline seep-affected well	
<b>Published Data</b>		
SW	Seawater composition from Krauskopf (1979)	-----

---

Cation concentrations in water samples were determined at the ISGS with a Thermo-Jarrell Ash Model ICAP 61e Inductively Coupled Argon Plasma Spectrometer. Instrument operation, inter-element interference correction, background correction, and data collection were controlled using ThermoSPEC/AE 6.20 software. Blanks, calibration check standards, and reference standards were analyzed with each sample set. Solution concentrations of anions also were determined at the ISGS using a Dionex 211i ion chromatograph with Ionpac AG14 Guard Column, Ionpac AS14 Analytical Column, and Anion Self-Regenerating Suppressor-11 (4 mm) following U.S. EPA Method 300.0 (Pfaff, 1993). Analytes were measured with a CDM-3 conductivity detector cell with a DS4 detection stabilizer. The eluent was treated with 3.5 mM sodium carbonate and 1.0 mM sodium

bicarbonate. Instrument operations and data collection were controlled using PeakNet 5.01 software. A calibration check standard and blank were run with each sample set.

Nitrogen and oxygen isotopic concentrations were determined at the ISGS using methods similar to those described by Silva et al. (1994 and 2000) and Wassenaar (1995), with some modifications by Hwang et al. (1999). Briefly, water samples collected for analysis of the  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of the  $\text{NO}_3^-$  ion were placed into two-liter bottles and acidified with hydrochloric acid to a pH of  $< 2$ . The samples were first boiled under acidification to remove bicarbonate and dissolved  $\text{CO}_2$ . The dissolved organic matter and  $\text{SO}_4^{2-}$  ions were removed to minimize contamination of the  $\delta^{18}\text{O}$  in the  $\text{NO}_3^-$  ion by the oxygen in the  $\text{SO}_4^{2-}$  ions and dissolved organic matter. Removal of the  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$  ions also helped eliminate anion interference during the ion-exchange step for  $\text{NO}_3^-$  extraction. The dissolved organic matter was removed using a silicalite molecular sieve, and the  $\text{SO}_4^{2-}$  ions were removed by precipitation as  $\text{BaSO}_4$ . After the removal of  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ , and dissolved organic carbon, the  $\text{NO}_3^-$  was extracted using an anion-exchange column packed with BioRad AG 1-X8 resin, similar to that described by Silva et al. (2000). Nitrate collected on the anion-exchange column was eluted with HBr solution (Hwang et al. 1999) and converted to  $\text{AgNO}_3$  by adding silver oxide. The  $\text{AgNO}_3$  was precipitated by freeze-drying the sample in a vacuum system. The dried  $\text{AgNO}_3$  was converted to  $\text{CO}_2$  and  $\text{N}_2$  for  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  analysis, respectively, by combustion techniques described by Silva et al. (2000) and Hwang et al. (1999). Both gases were analyzed on a Finnigan Mat Delta-E Isotope Ratio Mass Spectrometer (IRMS). International isotope standards IAEA-N1, IAEA-N2, USGS25, and USGS26 were used for  $\delta^{15}\text{N}$  calibration. International standard IAEA-N3 was used for  $\delta^{18}\text{O}$  calibration. Reproducibility of duplicate analyses was usually equal to or better than 0.5 ‰ for both  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ .

Ammonia was determined at the Illinois Natural History Survey using the Berthelot Reaction, which involves the formation of a blue-colored indophenol compound in a solution of ammonia salt, sodium phenoxide and sodium hypochloride. Following enhancement of the color using sodium nitroprusside, the color intensity was measured by a Bran & Luebbe TRAACS 2000 colorimeter at 660 nm. Total Kjeldhal Nitrogen (TKN) was determined by oxidation of organic material in water, followed by digestion by NaOH to convert all organic nitrogen compounds to  $\text{NH}_3$ . The  $\text{NH}_3$  was then analyzed as above. A separate analysis of  $\text{NO}_2$  and  $\text{NO}_3$  yielded TKN by difference (Raveh and Avnemelech, 1979).

Neutron Activation Analysis (NAA) was used for the analysis of the halides  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  in the water samples. NAA was used because of the relatively small concentrations of the latter two ions. Analyses were conducted at the University of Texas at Austin using standard NAA techniques involving liquid samples as described in Strellis et al. (1996).

Isotopes of chlorine ( $^{37}\text{Cl}$ ), hydrogen (deuterium (D) and tritium), oxygen ( $^{18}\text{O}$ ), and carbon ( $^{13}\text{C}$ ) were determined on selected samples. The samples for chlorine isotope analysis were sent to the University of Waterloo, Canada. Briefly, the dissolved chloride was converted to methylchloride, purified, and analyzed using an isotope ratio mass spectrometer. The techniques used for chlorine isotope determination were developed by Kaufmann et al. (1984) and Long et al. (1993). The  $\delta^{18}\text{O}$  of the water samples was determined at the ISGS using a modified  $\text{CO}_2$ - $\text{H}_2\text{O}$  equilibration method as originally described by Epstein and Mayeda (1953), with modifications described in Hackley et al. (1999). The  $\delta\text{D}$  of water was determined using Zn-reduction methods (Coleman et al.

1982; Vennemann and O'Neil, 1993) with modifications described in Hackley et al. (1999). The  $\delta^{13}\text{C}$  of dissolved inorganic carbon was determined by a gas evolution technique that was similar to that described in Atekwana and Krishnamurthy (1998).

Brine solutions were made from road salt collected at Illinois Department of Transportation salt storage facilities and from water softener salts. Solutions of approximately 100,000 mg/L of total dissolved solids were made from each salt type using approximately 100 grams of salt dissolved in one liter of deionized water. These brines were analyzed for halides to determine their ratios.

All surface water samples were from the Mississippi River and were collected at the intakes of the city water companies in Davenport, IA, Quincy, IL and Chester, IL . Each plant treats millions of liters of water per day for these cities. The intakes facilitated the collection of a composite water sample from of a relatively large area of the river that should be more representative of the river's composition than a grab sample at a selected point.

## **RESULTS**

Because this is an ongoing project, not all data were available at this writing, and continued sampling of contaminated groundwater and surface water is underway. For this reason, the results of this investigation are preliminary and data tables were not included. However, descriptive statistics on the  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations of some background, end member and contaminated samples are presented in Table 2.

Single parameters, pairs of parameters, or combinations involving ratios for all samples were plotted on scatter plots to see if the different sources showed clustering. It is hoped that clustering of the samples will provide a means of separating and identifying contaminant sources. At this stage of the investigation, this technique cannot provide definitive information about the origin of the  $\text{Na}^+$  and  $\text{Cl}^-$  in all of the end member and contaminated water samples collected. However, it was found that the use of several pairs and ratios of the parameters, and mixing curves identified in this investigation appeared to be very promising techniques for determining the sources of  $\text{Na}^+$  and  $\text{Cl}^-$  contamination. Parameters that have been found to be potentially useful as indicators of  $\text{Na}^+$  and  $\text{Cl}^-$  contamination are discussed below.

Table 2. Descriptive statistics of background samples and sources, plus contaminated surface and groundwater samples. Data are for completely analyzed samples only, and are in milligrams per liter (\*Complete analysis from only one fertilizer-contaminated sample has been received).

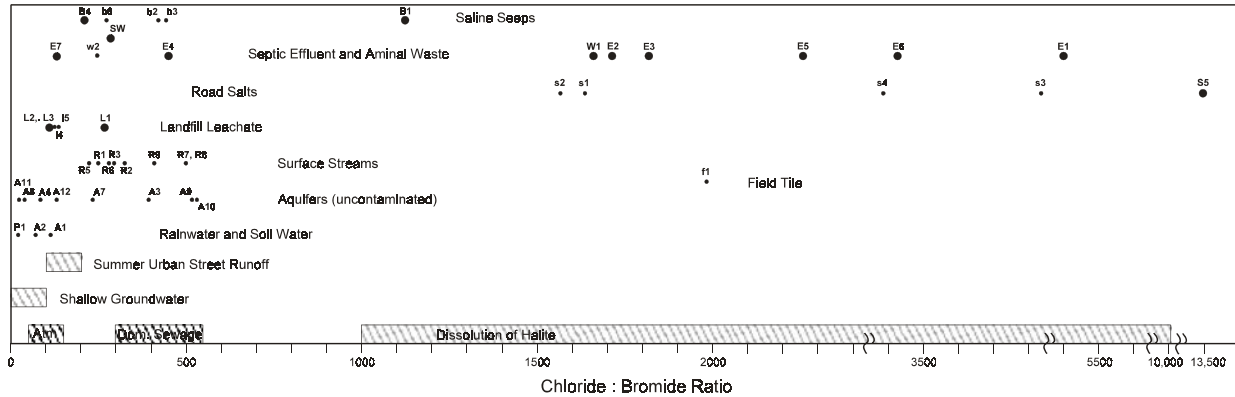
Sources of Water Samples	n	Na <sup>+</sup> mean	Na <sup>+</sup> median	Na <sup>+</sup> range	Cl <sup>-</sup> mean	Cl <sup>-</sup> median	Cl <sup>-</sup> range
Precipitation	2	0.25	0.25	0.2 - 0.3	0.15	0.15	0.1 - 0.2
Surface Stream	9	18.8	14.5	10.9 - 30.5	22.6	20.2	12.5-50.4
Uncon. Aquifer	6	36.0	37.0	8.1 - 70.0	6.9	7.0	0.8 - 16
Fertilizer	1	---	---	5.4*	---	---	30.2*
Road Salt	5	146	218	7.0 - 224	264	352	12.0 - 416
Landfill	7	1740	1370	75.2 - 4420	2310	838	86.5-6170
Septic Effluent	9	509	243	50.6 - 2740	886	186	91- 5620
Animal Waste	7	327	113	11.9 - 1190	609	280	9.3 - 1980
Saline Seep	7	1250	220	19.4 - 4520	3460	292	25.2-8360

### Background Samples

Background samples were collected to identify end member concentrations and ion ratios for the mixing models. The background concentrations of Na<sup>+</sup> and Cl<sup>-</sup>, and other constituents in surface water and shallow groundwater resulting from soil-water and rock-water interactions can be estimated using statistical methods and from historical records. Panno et al. (1999b) used a probability technique and chemical data from 160 groundwater samples to determine Na<sup>+</sup> and Cl<sup>-</sup> background concentrations in a wetland complex in northeastern Illinois. The thresholds for background concentrations (points between background and anomalous concentrations) for Na<sup>+</sup> and Cl<sup>-</sup> in a shallow sand and gravel aquifer were estimated to be 10 and 45 mg/L, respectively. Kelly (2002) showed that background concentrations for Cl<sup>-</sup> in two counties in northeastern Illinois (DuPage and McHenry), using historic groundwater chemistry data for wells in shallow sand and gravel aquifers, were between 10 and 20 mg/L. Our data suggest that surface water concentrations of Na<sup>+</sup> and Cl<sup>-</sup> are probably similar (Table 2).

**Rainwater and Snow Melt.** The annual average concentration of Na<sup>+</sup> and Cl<sup>-</sup> in rain and snow melt in Illinois was 0.05 and 0.28 mg/L, respectively in 1998 (NADP, 1998). The Cl/Br ratio in precipitation in the Midwestern U.S. was approximately 50, which is somewhat smaller than the Cl/Br ratio of 250 determined in coastal areas (the results from our August composite rainfall sample were similar to values from the Midwestern U.S.). The larger ratio near the coasts reflects the influence of ocean spray on local precipitation (Davis et al. 1998). Because of the very small concentrations of Na<sup>+</sup> and Cl<sup>-</sup> in precipitation, addition of NaCl from any source will easily modify the Cl/Br ratio of the precipitation (Figure 1).

Figure 1. Cl/Br ratios of water samples collected for this investigation relative to the domains identified by Davis et al. (1998). The large dots represent end member samples and the smaller dots represent precipitation, surface water, uncontaminated groundwater, and end member-affected water samples. Sample IDs are keyed to Table 1.



**Groundwater.** Groundwater from sand and gravel aquifers was collected from the Mahomet aquifer, smaller aquifers overlying the Mahomet, and several small, but locally productive, aquifers in northeastern Illinois. All samples were collected from wells screened tens of meters to several hundred meters below land surface and plotted within the  $\text{Ca-HCO}_3^-$  water type (Figure 2). In addition, several samples were collected from ceiling seeps in Mammoth Cave (KY) and Fogelpole Cave (IL) and represent soil water.  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations in the aquifers typically did not exceed background levels. Radiocarbon ages of groundwater samples from the Mahomet and associated aquifers (Panno et al. 1994; Hackley, 2002) were in the thousands of years BP range, suggesting a minimum of anthropogenic contamination (Table 2).

**Surface Water.** Water samples collected under low-flow conditions from the Mississippi River were of the  $\text{Ca-HCO}_3^-$  type and cluster tightly on a trilinear diagram (ID numbers starting with “R” on Figure 2). The water sample from Chester, IL (R2) had slightly elevated  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations relative to the other samples; however, the source of the  $\text{Na}^+$ - $\text{Cl}^-$  is unknown at this point. Potential sources of  $\text{Na}^+$  and  $\text{Cl}^-$  contamination in these waterways include road salt, septic effluent (private and municipal), animal waste, and agrichemicals.

### Naturally-Saline Water

**Saline Groundwater.** Naturally-occurring saline groundwater in Illinois, in the form of springs and underground seeps, discharge to streams and groundwater (e.g., Habermeyer, 1940; Panno et al. 1994). Upwelling of basin brines into shallow groundwater can influence water quality such that it too saline for human consumption. Two saline springs, one saline well, and three private wells affected by saline water seeping into the base of the Mahomet aquifer (Panno et al. 1994) were sampled. The saline spring near Columbia, IL (B4) is located along the Waterloo-Dupo Anticline, and is associated with oil and natural gas deposits. The saline spring near Equality, IL



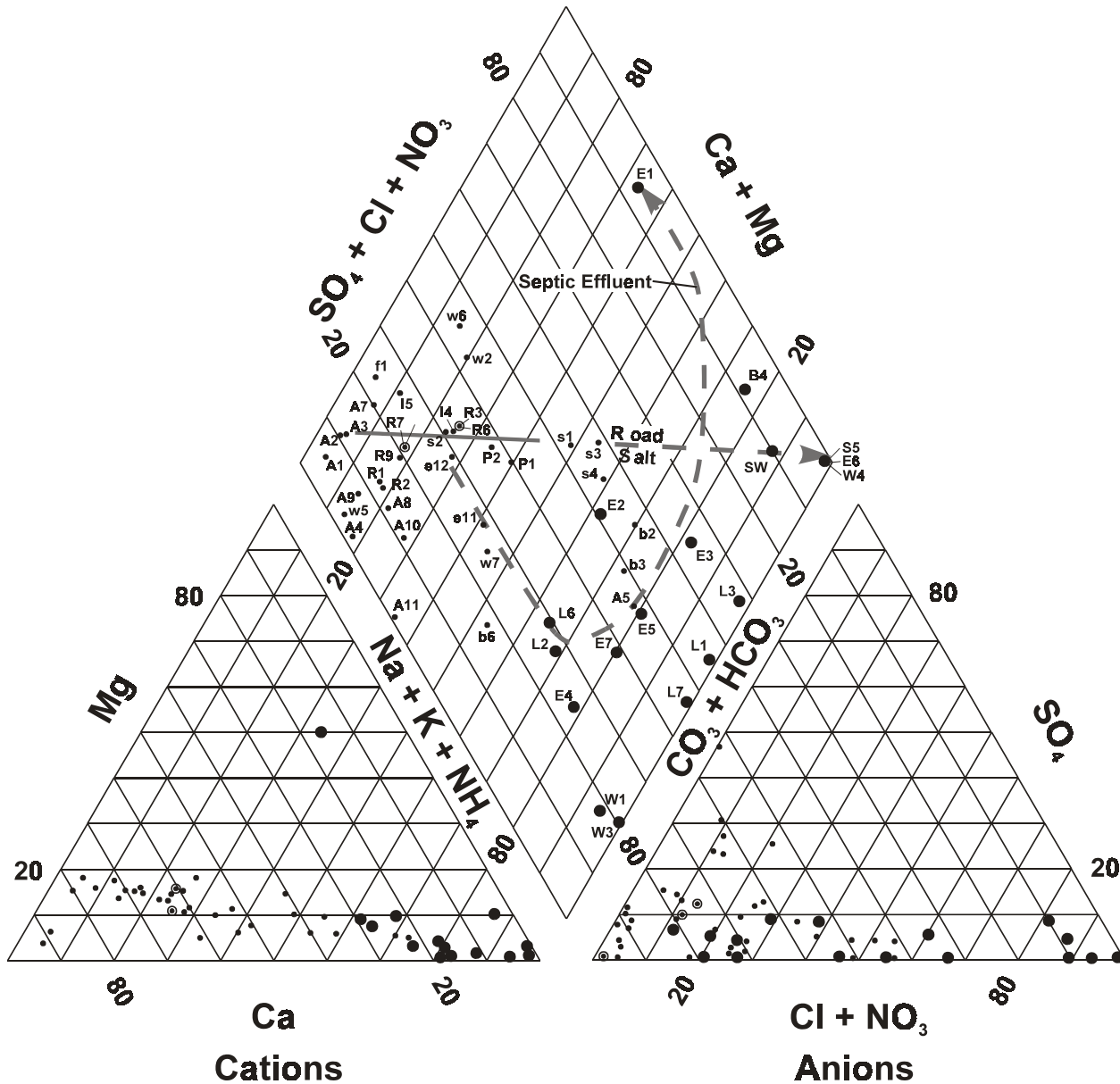


Figure 2. Trilinear diagram showing water samples of various degrees of salinity. The large dots represent Na<sup>+</sup>-Cl<sup>-</sup> sources, whereas the smaller dots represent precipitation, stream water, uncontaminated groundwater, and water samples contaminated with Na<sup>+</sup>-Cl<sup>-</sup> sources. Sample IDs are keyed to Table 1.

(B5) is associated with the Wabash Valley Fault System. The Villa Grove well (B1) was drilled to a depth of 111 m in Pennsylvanian-age sandstone in 1997 (Tim Young, ISGS, personal communication, 1997). Preliminary results by the ISGS (Panno et al. 2000) initially suggested that δ<sup>37</sup>Cl may be useful in identifying these sources; however, further work has shown this technique to yield ambiguous results.

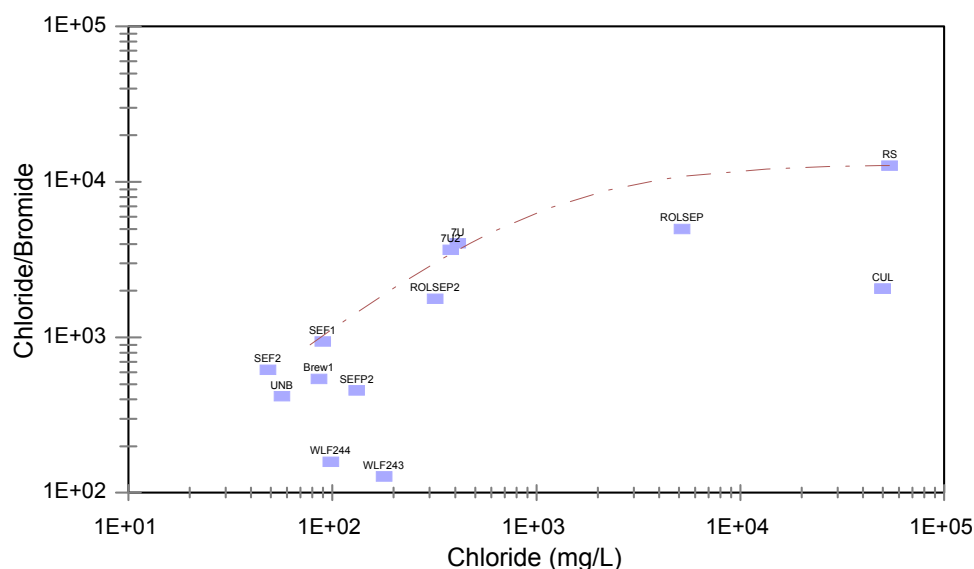


Figure 3. Mixing curve from Panno et al. (2000) for water samples collected near South Elgin Fen. Samples SEF1 (near-pristine groundwater discharging to the fen) and RS (road salt solution) were used as end members. A mixing line between the two samples intersect water samples collected from monitoring well 7U (samples s3 and s4 from this study;  $\text{Cl}^-$  concentration = 352 and 392 mg/L) strongly suggesting that the monitoring well was affected by road salt.

Chloride/Br ratios from most of our saline water samples were typical of basin brines (Davis et al. 1998). However, sample B1 had a Cl/Br ratio of 1122 (Figure 1). The elevated ratio for this sample may indicate the dissolution of NaCl at some point in the evolution of this water (as opposed to rock-water interactions with nonevaporites). For comparison, saline spring sample B4 had a Cl/Br ratios of several hundred (Figure 1).

Saline groundwater seeping from bedrock into the Mahomet aquifer at a depth of about 100 m near the Piatt-Champaign County line is represented by samples b2 and b3. The greatest  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations were found to be coincident with a thermal anomaly (Cartwright, 1970) and the Osman Monocline (Panno et al. 1994). The Cl/Br ratios ranged from 272 to 441 in the samples and were similar to those of the saline springs.

### Urban Sources

**Road Deicers.** Rock salt, made up predominantly of halite (NaCl) with trace amounts of sylvite (KCl) and other minor constituents, was first used on roads after World War II. Rock salt is the primary road deicer used by counties in northeastern Illinois. Little, if any,  $\text{CaCl}_2$  is used as a deicing agent in Illinois because of its higher cost (IDOT, personal communications, 2002). Road deicer constitutes a significant mass of  $\text{Na}^+$  and  $\text{Cl}^-$  that enters streams and groundwater in northeastern Illinois where the municipalities may apply as much as 20 tons of salt per lane mile per season (Field et al. 1973).

Samples s1 through s4 were identified as containing NaCl contamination from road salt (Table 1) and had Cl/Br ratios in the range defined by Davis et al. (1998) for waters containing dissolved halite (Figure 1). These samples are from shallow sand and gravel aquifers in northeastern Illinois that geologically, geographically and chemically exhibit very strong evidence of being contaminated with road salt. The addition of road salt to stream water and shallow groundwater results in a linear mixing line, across a trilinear diagram, extending from uncontaminated groundwater to the road salt end member (Figure 2). This was in contrast to the apparently curved mixing line of samples containing septic effluent (discussed below).

Groundwater from a site in South Elgin, IL (s3 and s4 are the same as 7U and 7U2 of Panno et al., 2000) had elevated  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations that were determined to be from road salt (Panno et al. 1999a) through the use of a mixing curve (suggested by Whittemore, 1995). A mixing curve based on the Cl/Br ratio and the  $\text{Cl}^-$  concentration, using near-pristine fen groundwater samples and a brine solution made from road salt as a  $\text{Na}^+$  and  $\text{Cl}^-$  source (Figure 3), suggested that the road salt was primarily responsible for the elevated  $\text{Na}^+$  and  $\text{Cl}^-$  in the monitoring well up gradient of a fen complex (Panno et al. 2000).

### **Rural Sources**

**Septic Effluent.** Effluent discharged from both municipal septic and private septic systems in Illinois contained anomalously high concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$  and  $\text{PO}_4^{3-}$  with maximum concentrations of 255, 281, 29, 66, 618 and 9 mg/L, respectively (Panno et al. 2002). Even greater concentrations of  $\text{Na}^+$ ,  $\text{Cl}^-$  and other ions can result from cycling of a water softener. That is, we found that the use of brine solutions in household water softeners can result in  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations in septic system effluent in the thousands of mg/L. Residents of the United States use an average of 100 gallons of water per person per day for toilet flushing, bathing, and other household activities (US EPA, 2000). Consequently, for a family of three or four with moderately hard water, a water softening system uses about 1.8 kg of NaCl per day (per manufacturer's recommended use) and thus, can contribute up to 660 kg/year of dissolved halite to surface and groundwater resources.

Davis et al. (1998) concluded that Cl/Br ratios can be useful in identifying septic effluent that has entered the environment. Some of the largest Cl/Br ratios in this investigation are associated with septic effluent; however, they overlap with the ratios of saline waters where halite dissolution is the mechanism for large  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations. Panno et al. (1999a, 2001) found that Cl/Br fingerprinting of septic effluent and impacted waters can be complemented by using  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ , alkalinity concentrations, and  $\text{NO}_3^-$  isotopes.

The groundwater from two monitoring wells (e11 and e12) adjacent to the septic leach field of a large teaching/day-care facility in Verona, New York was sampled for us by the New York State Department of Environmental Conservation (NYSDEC). The monitoring wells, located adjacent to the leach field, were screened in about 1 meter of sand located beneath about 1 meter of topsoil and red silty clay-rich loam. The NYSDEC reported that the initial  $\text{Cl}^-$  and  $\text{NO}_3^-$  concentrations for the three monitoring wells ranged from 3.8 to 28 mg/L and 0.23 to 0.53 mg/L,

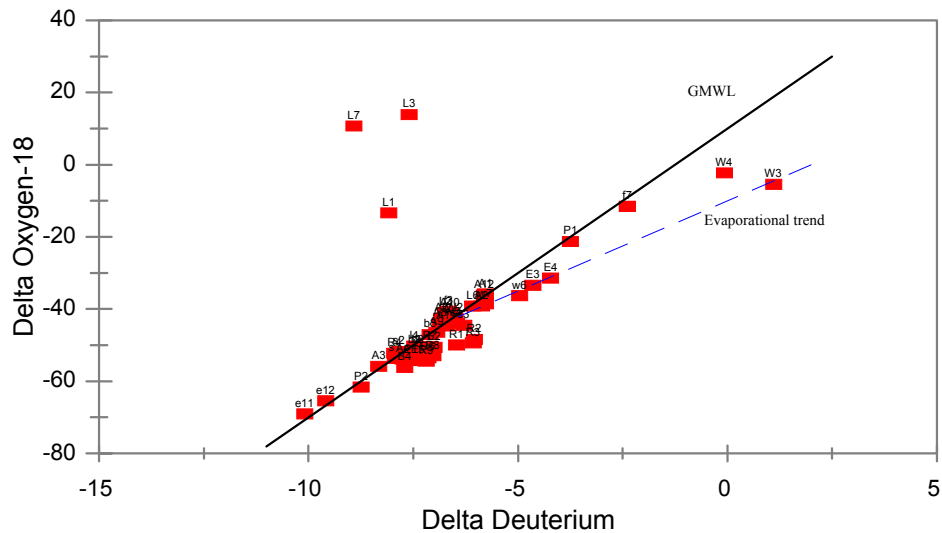


Figure 4.  $\delta D$  vs  $\delta^{18}O$  plot showing the meteoric relationship between these two isotopes. Most samples plotted on the global meteoric water line (GMWL) with the exception of landfill leachate that typically contains elevated  $\delta^{18}O$  values, and septic effluent and animal waste (and affected) samples that plotted along an evaporational trend. River water sample plotted along a similar evaporational trend. Landfill leachate tends to plot well above the GMWL because of isotopic fractionation within the landfill. Sample IDs are keyed to Table 1.

respectively. Following the installation of the leach field and its use from 1990 to 1998, the  $Cl^-$  and  $NO_3^-$  concentrations in the monitoring wells increased to as great as 16,400 mg/L  $Cl^-$  and 487 mg/L  $NO_3^-$ -N (A. Ash, NYSDEC, personal communications, 2001). The occurrence of very large  $Cl^-$  concentrations in the groundwater near a leach field is almost certainly the result of the use of a water softener at the facility. About 270 kg of water-softener salt was consumed at the facility per month, or 3240 kg per year (A. Ash, personal communications, 2001). Probably all of the saline water discharging from the septic system entered the underlying sand.

**Animal Waste.** Large animal confinement facilities can produce significant volumes of animal manure that is enriched in  $Na^+$  and  $Cl^-$ . An increase in the number and size of these facilities is an ongoing trend in Illinois and other states. While investigating the impacts of swine confinement facilities on local groundwater quality, Krapac et al. (1998, 2000) found groundwater  $Cl^-$  concentrations to be a useful indicator of the extent and magnitude of contamination from these facilities. Groundwater samples (w5, w6 and w7) and samples of the lagoon manure (W3) were collected from the swine finishing facility designated site A by Krapac et al. (1998, 2000). In addition, manure samples from other confinement facilities (W1 and W4) were collected and analyzed for use as end members. These included a background monitoring well and monitoring wells known to have been contaminated with hog waste (Larson et al. 1997; Krapac et al. 1998). In

addition, groundwater from a shallow aquifer beneath a smaller hog facility in southwestern Illinois, known to be contaminated by hog waste (W2), was analyzed.

The  $\delta^{15}\text{N}$  isotopic ratios from  $\text{NH}_4^+$  of the hog waste in these lagoons was exceptionally heavy, probably because of evaporation. The heavy  $\delta^{15}\text{N}$  ratios of the ammonia or resultant  $\text{NO}_3^-$  (if present) in animal waste lagoons may be useful as an indicator of animal waste. This is especially true for open-air waste storage where evaporation can occur (as shown by evaporational trends of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  (Figure 4)) and  $\text{NH}_4^+$  may be converted to  $\text{NO}_3^-$ , yielding a more definitive indicator of groundwater contamination.

**Artificial Fertilizers.** Work by Hamamo et al. (1995) showed that Cl concentrations in super phosphate and triple super phosphate fertilizers ranged from  $< 50$  mg/kg to 6.18% (by weight) in the solid phase, with a median concentration of 112 mg/kg. Such large concentrations of chlorine in the fertilizer may, in part, be responsible for the elevation of  $\text{Cl}^-$  in tile drainage from agricultural fields. The use of potash (KCl) on fields (applied at a rate of approximately 200 pounds per acre; P. Kremmell, U.S. Department of Agriculture, personal communications, 2000) also would be expected to increase  $\text{Cl}^-$  concentrations in soil water and underlying groundwater.

### **Industrial sources**

**Landfills.** Leachate from municipal landfills is typically enriched in  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{NH}_4^+$ , Fe and  $^3\text{H}$  (Baedecker and Back, 1979; Hackley et al. 1996). Potential sources of  $\text{Br}^-$  in landfills are not known, but  $\text{Br}^-$  is used commercially for fumigants and fire-retardant agents which could be disposed of in landfills (Hem, 1985). Elevated  $^3\text{H}$  concentrations in landfill leachate could be useful in the identification of  $\text{Na}^+$  and  $\text{Cl}^-$  contamination from these facilities. Leachate (L1 to L3) was collected from 3 landfills in northeastern Illinois (Table 1); their names and locations are confidential. In general, the  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $^3\text{H}$  concentrations in the leachate were exceptionally large relative to other end members. Tritium concentrations ranged from 61 to 2247 TU. In addition,  $\text{I}^-$  concentrations and I:Br and I:Cl ratios were elevated in leachate samples relative to other samples and end members; the source of  $\text{I}^-$  was not known.

Groundwater sampled from two monitoring wells immediately adjacent to a municipal landfill near Elgin, IL (I4 and I5) contained elevated  $^3\text{H}$  concentrations (12.8 and 23.8 TU). Background concentrations of  $^3\text{H}$  in the area ( $\approx 7.8$  TU) indicated that these values were anomalously large and probably caused by seepage from the landfill. In addition,  $\text{I}^-$  and  $\text{Na}^+$  concentrations in these samples clustered with those of landfill leachate (Figure 5).

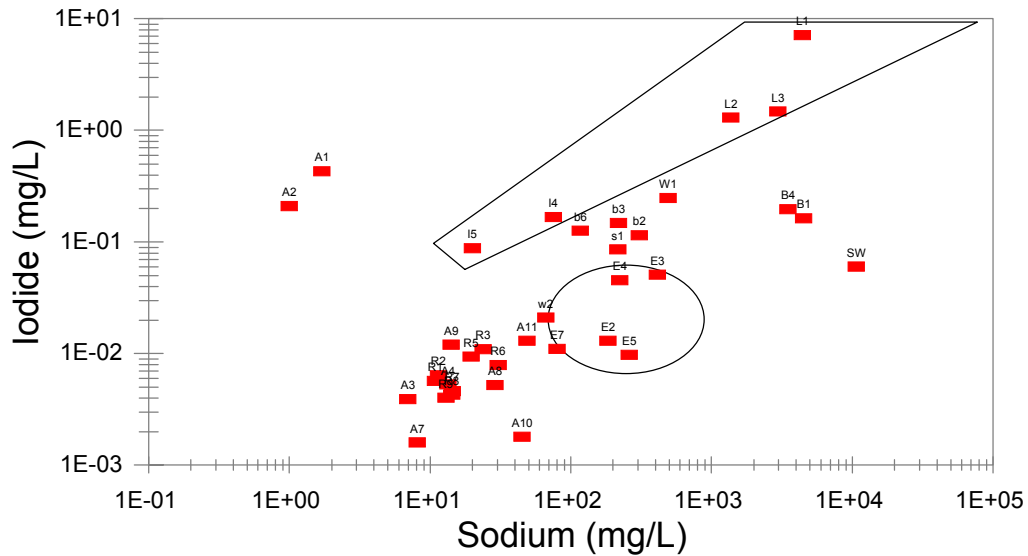


Figure 5. I<sup>-</sup> and Na<sup>+</sup> concentrations in landfill leachate (L) and leachate-affected (I) groundwater samples, as well as samples of septic effluent (E). Stream and uncontaminated aquifer samples clustered together. Sample IDs are keyed to Table 1.

## DISCUSSION

Graphical techniques were used in an attempt to relate the contaminated water samples to the possible end member sources of the contamination based on subtle differences in their trace elemental and isotopic compositions. Below is a brief discussion of each technique that appears to be useful in separating or clustering the samples based on the sources of their contaminants.

### Field Parameters, Cations and Anions

As might be expected, a scatter diagram of Na<sup>+</sup> and Cl<sup>-</sup> shows that most samples collected fall on or close to the line defined by NaCl (Figure 6). The exceptions are groundwater samples from the Mahomet aquifer, which contain little Cl<sup>-</sup> and show an enrichment of Na<sup>+</sup> because of rock-water interaction within the aquifer (Panno et al. 1994; Hackley, 2002). The plotting of cation and anion concentrations on a trilinear diagram proved useful for discriminating among sources, especially when used in conjunction with other parameters (Figure 2). Trilinear diagrams showed trends such as the evolution of pristine groundwater and soil water along a mixing line to a NaCl-brine (Figure 2), or the evolution of hard water through treatment with a water softening column that removes the Ca<sup>2+</sup> and Mg<sup>2+</sup> and replaces them with Na<sup>+</sup>. Recharging of the water softener causes enrichment of Ca<sup>2+</sup> and Mg<sup>2+</sup> in the effluent as it strips these ions from the ion exchange resins and replaces them with Na<sup>+</sup>. This results in an arcuate trend that begins with “hard”

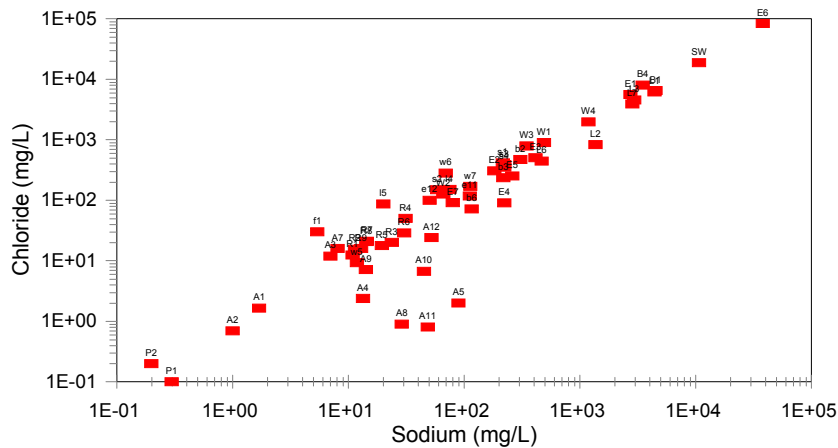


Figure 6. A scatter diagram of  $\text{Na}^+$  and  $\text{Cl}^-$ . Most water samples plotted along a line defined by  $\text{NaCl}$  showing a continuum from precipitation, uncontaminated groundwater, surface water, and end members and their affected waters. Sample IDs are keyed to Table 1.

groundwater and ends with the saline rinse water that has passed through the ion exchange column (Figure 2). Additional data may refine these trends.

### Stable and Radioactive Isotopes

On the basis of our preliminary data,  $\delta^{37}\text{Cl}$  was not useful for distinguishing among sources of  $\text{Cl}^-$  because of the similarities of  $\delta^{37}\text{Cl}$  values in all the water and salt-solution samples collected. However, the stable isotopes  $\delta\text{D}$  and  $\delta^{18}\text{O}$  were somewhat useful in that they showed the effects of evaporation on samples collected from waste lagoons and river water (Figure 4). Samples of landfill leachate and waters affected by such leachate typically plot above the meteoric water line because of partitioning of oxygen isotopes during biodegradation of the waste and methane formation within the landfill (Hackley et al. 1996). Tritium, when used in conjunction with  $\text{Cl}^-$  (Figure 7) has proved to be a useful discriminator for landfill leachate as a contamination source (Panno et al. 2000) because of the relatively large tritium concentrations typically present in seepage from municipal landfills (Hackley et al. 1996).

### Halides

The halides  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  are relatively conservative anions that migrate with surface water and groundwater with a minimum of interaction with substrates. Bromide may concentrate in brines as a result of evaporation and clay-membrane effects, and  $\text{I}^-$  tends to concentrate in marine

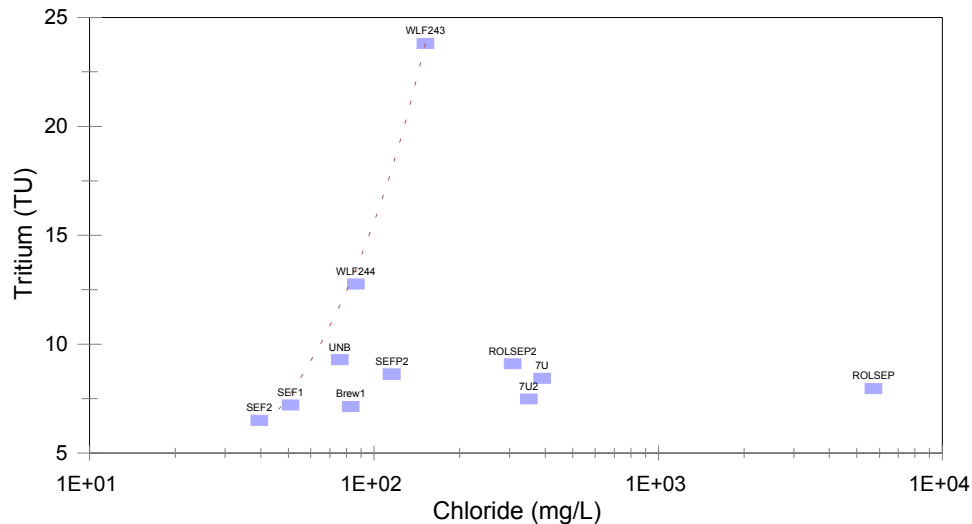


Figure 7. Mixing curve from Panno et al. (2000) for water samples collected near South Elgin. Samples SEF1 (near-pristine groundwater from a fen seep) and WLF243 (from a landfill monitoring well) were used as end members. A mixing line between the two sample intersect a water sample collected from a nearby landfill monitoring well. The elevated tritium in the landfill leachate-affected samples (WLF243 and 244) is apparent relative to other samples collected from the fen area.

vegetation and may be concentrated in some brines (Hem, 1985). Organic materials (e.g., soil organic matter) also tend to concentrate  $\text{Br}^-$  and  $\text{I}^-$  and release them upon degradation of the materials, resulting in their enrichment relative to  $\text{Cl}^-$  (Gerritse and George, 1988). Because of these tendencies,  $\text{Br}^-$  and  $\text{I}^-$  were selected as potential indicators of sources.

The  $\text{Cl}/\text{Br}$  ratio proved to be useful by showing characteristic ranges for a variety of sources (Figure 1). There were relatively low  $\text{Cl}/\text{Br}$  ratio for samples affected by landfill leachate and a spectrum of values that reflected the influence of halite dissolution on almost all water samples. Specifically, water samples with  $\text{Cl}/\text{Br}$  ratios greater than 250 to 500 appeared to have been affected by the dissolution of halite. However, these samples were mixed with samples affected by animal waste and septic effluent and were not separable by this technique alone.

The arcuate trend displayed by a  $\text{Cl}-\text{Br}$  scatter diagram for our samples appears to reflect the evolution of water from precipitation to contaminated surface water and groundwater, and seawater (Figure 8). The trend begins with precipitation (P, the most dilute of the samples), followed by groundwater from a variety of aquifers (A, as concentrations increase), then stream water (R), and finally the more concentrated saline waters that include brines (B and b), animal waste (W), septic effluent (E), and landfill leachate (L). Field tile-drain samples (f) plotted between groundwater and stream water. Road salt-affected samples plotted at the more concentrated end of the stream samples, but lower than the saline samples (S).



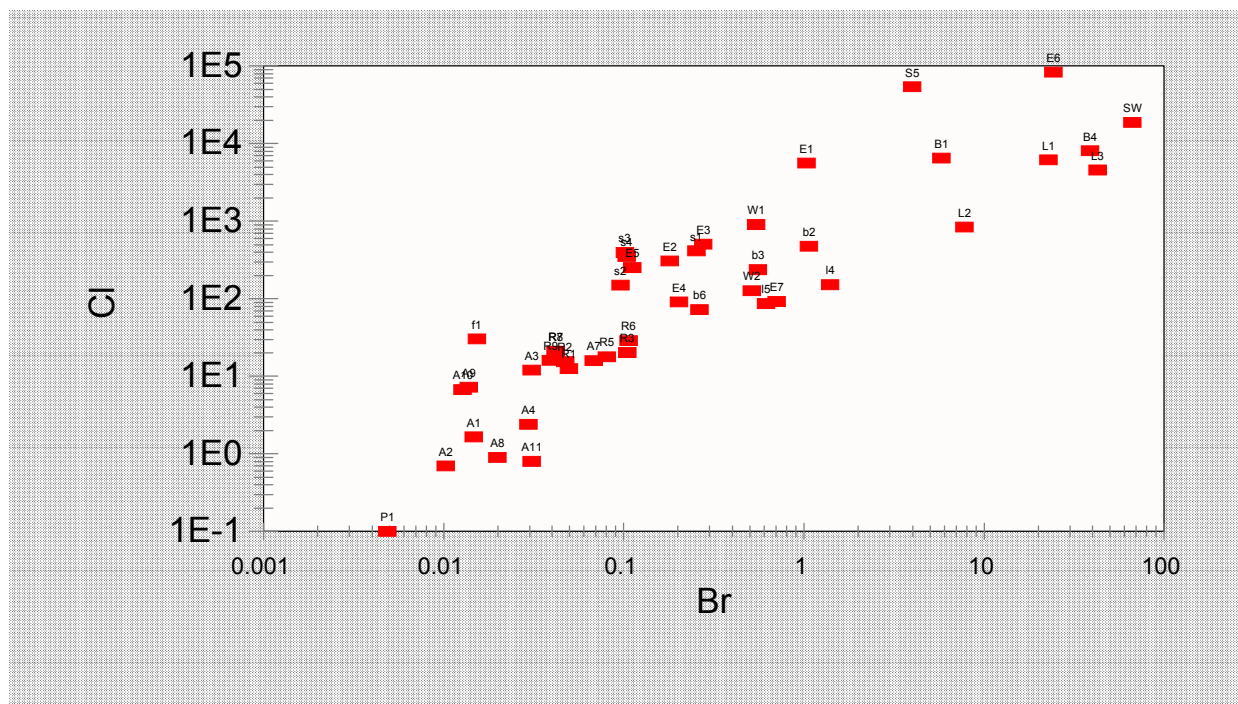


Figure 8.  $\text{Cl}^-$  and  $\text{Br}^-$  concentrations in various samples reflect the evolution of the waters, starting from precipitation (P) and ending with seawater (SW). Sample IDs are keyed to Table 1.

We found  $\text{I}^-$  concentrations to be elevated in municipal landfill leachate and brines, and  $\text{I}^-$  concentrations will probably be useful in distinguishing among some sources of  $\text{NaCl}$ . The landfill leachate, saline water, and septic effluent end members and their affected wells appear to be differentiated (as a trend) on an  $\text{I}^-/\text{Na}^+$  scatter diagram (Figure 5). Iodide tends to increase with  $\text{Na}^+$  in the landfill samples, but to a lesser extent for septic effluent samples and not at all for saline water samples. The degree of separation of these end members and their affected samples was similar, but even more distinct, on an  $\text{I}^-/\text{Na}^+$  vs  $\text{Br}^-$  scatter diagram (Figure 9). Stream water and groundwater samples tended to cluster as one group on both of these diagrams, whereas samples affected by road salt and animal waste were scattered (Figures 5 and 9).

### Total Nitrogen and Nitrogen/Nitrate Isotopes

The potential for using  $\text{NO}_3^-$  as an indicator for contamination of groundwater by sewage was discussed briefly by Marie and Vengosh (2001). We found that total N ( $\text{NO}_3^- + \text{NH}_4^+ + \text{TKN}$ ) provided a more complete and potentially more reliable indicator. Total N plotted against  $\text{Cl}^-/\text{Br}^-$  provides a means of separating samples affected by animal waste and septic effluent from those affected by road salt and from the other samples (Figure 10). Because of the enrichment of N in animal waste and septic effluent, these samples separate from the others at a total N concentration

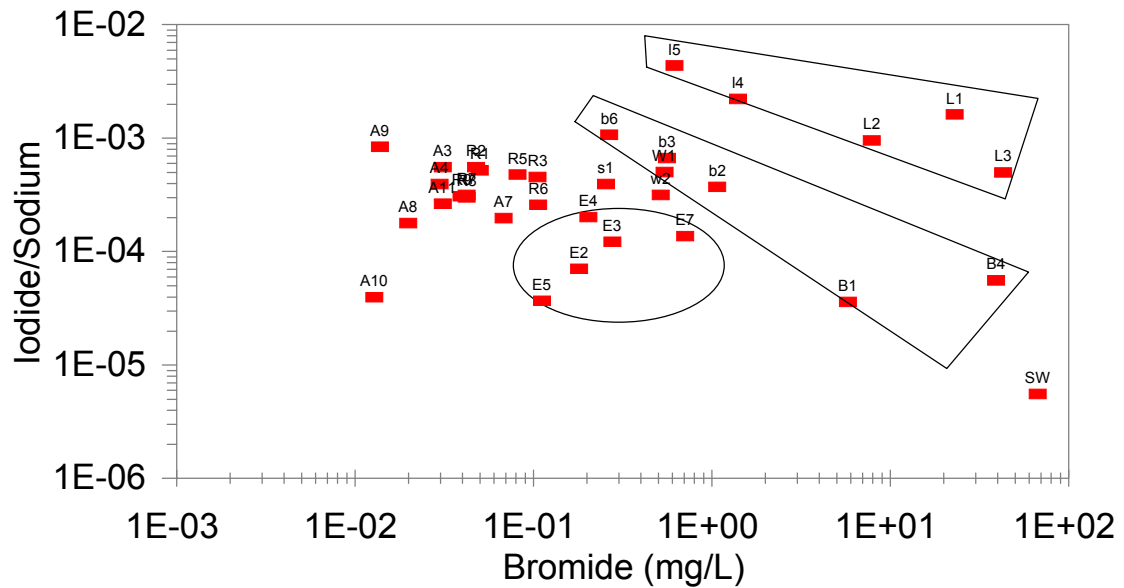


Figure 9. The I/Na ratio plotted against Br<sup>-</sup> concentrations readily clusters septic effluent, saline waters, and landfill leachate and affected groundwater. Sample IDs are keyed to Table 1.

of approximately 10 mg/L. Road salt-affected samples cluster by themselves (as opposed to Figure 1) at the higher end of the Cl/Br ratios because of the effects of the dissolution and addition of NaCl (addition of Cl<sup>-</sup>). A field tile sample plotted between the waste and road-salt clusters, suggesting that it too may have been affected by road salt.

The isotopes of the nitrate and ammonium ions may be useful in separating tile drain samples from animal waste and septic effluent and related samples. The typically heavy  $\delta^{15}\text{N}$  values for the animal waste and effluent, when coupled with  $\delta^{18}\text{O}$  values (either measured or calculated from groundwater), could provide a distinctive indicator to distinguish among the sources of elevated concentrations of Na<sup>+</sup> and Cl<sup>-</sup>.

### Dissolved Organic Carbon

Dissolved organic carbon (DOC) is expected to be useful in differentiating sources that typically contain elevated concentrations of DOC from those that do not. Specifically, landfill leachate and animal waste (including septic systems) are expected to have elevated concentrations of DOC and, on that basis, should be distinguishable from waters contaminated with road salt and natural saline seeps. However, at this point in the investigation, few data are available.

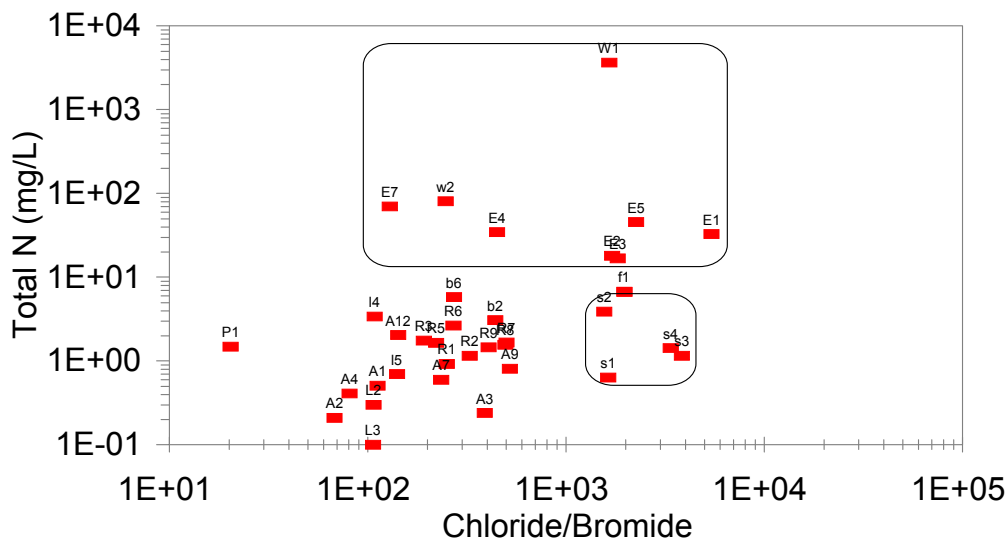


Figure 10. A scatter diagram of total N and Cl/Br effectively clusters animal waste (W) and septic effluent (E) together above a N concentration of 10 mg/L. Road salt affected samples (s) also cluster well in this diagram, away from the remaining mix of samples. The presence of one of the field tile samples (f) between the road salt and animal waste/septic effluent clusters suggests that road salt may have contaminated the tile water. Sample IDs are keyed to Table 1.

## CONCLUSIONS

The results of our investigation indicate that chemical and isotopic analyses may be effective in identifying most and possibly all of the end-member sources of  $\text{Na}^+$  and  $\text{Cl}^-$  and waters contaminated by them. If the relationships observed so far remain consistent, they should provide a set of powerful tools for determining the sources of  $\text{Na}^+$  and  $\text{Cl}^-$  in groundwater and stream water in urban, as well as rural areas (especially near animal-confinement facilities). Because identification is the first step in reducing emissions from roadways, municipal landfills, septic systems, and industrial sites, these results should be useful in the protection of groundwater resources in rural and growing urban areas in Illinois, the U.S., and in other countries.

Scatter plots of parameters, their ratios, and isotopes that proved most useful in identifying one or more end-member samples and waters affected by the end members include Cl/Br ratios (line plot),  $\delta\text{D}$  vs  $\delta^{18}\text{O}$ ,  $^3\text{H}$  vs  $\text{I}^-$ ,  $\text{I}^-$  vs  $\text{Na}^+$ ,  $\text{Cl}^-$  vs  $\text{Br}^-$ ,  $\text{I}/\text{Na}$  vs  $\text{Br}^-$ , and total N vs Cl/Br. The usefulness of isotopes of  $\text{NO}_3^-$  is still being evaluated. The overall chemical composition of the samples (as

plotted on a trilinear diagram) yielded information useful in the general interpretation of the sources and evolution of the water. Specifically, the trilinear diagram revealed trends developed from the addition of road salt to groundwater and the evolution of waste water as it flowed through the ion exchange column of a standard water softener. As did the trilinear diagram, a line plot of Cl/Br ratios yielded a first approximation of some types of contaminant source (i.e., road salt and septic effluent). Mixing curves using Cl/Br ratios or tritium, when plotted against Cl<sup>-</sup>, can reveal likely source(s) of Na<sup>+</sup> and Cl<sup>-</sup>, and worked especially well for road salt and septic systems at a wetland area. The stable isotopes δD and δ<sup>18</sup>O, when plotted on a meteoric water line, revealed separate evaporational trends for stream water and animal waste. Because <sup>3</sup>H and I<sup>-</sup> are enriched in landfill leachate, a scatter plot of these two parameters readily separates landfill leachate and leachate-affected water from other samples and sources. Similarly, I<sup>-</sup> and Na<sup>+</sup> plotted against one another or as I/Na ratios plotted against Br<sup>-</sup> separates landfill effluent and affected waters, but also isolates naturally-saline waters and septic effluent. Finally, because many of the Na<sup>+</sup>-Cl<sup>-</sup> sources contain N compounds, total N plotted against Cl/Br separates source and affected waters with N compounds from those without. Thus, road salt-affected waters are separated from most of the other contaminant sources and affected waters as in the Cl/Br line plot; however, total N successfully separates the road salt-affected waters from animal waste and septic effluent and their affected waters.

Further work with isotopes of N and NO<sub>3</sub><sup>-</sup> will be done to explore potential for identifying sources with elevated concentrations of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>, such as N-fertilizers, septic effluent and animal wastes.

## ACKNOWLEDGMENTS

The authors thank Rick Rice for his assistance in the field and for identifying contaminated wells in Kane County that were used for this investigation, and Pam Carrillo and Jackie Hannah for assistance with the figure preparation. We also thank the Iowa-American Water Co., Quincy, IL Water Co., and the Chester, IL Water Co. for allowing us to sample their intakes along the Mississippi River, and Albert Ash of the New York State Department of Environmental Conservation for collecting septic effluent-contaminated water samples for us. This investigation was funded by a grant from the U.S. Department of Agriculture through the Illinois Groundwater Consortium at Southern Illinois University at Carbondale, and by state funds from the Department of Natural Resources, Illinois State Geological Survey Division. Publication of this article has been authorized by the Chief of the Illinois State Geological Survey.

## REFERENCES

Appelo, C.A.J. and D. Postma. 1994. *Geochemistry, groundwater and pollution*, Rotterdam: A.A. Balkema. 536 pp.

Atekwana, E.A. and R.V. Krishnamurthy. 1998. Seasonal variations of dissolved inorganic carbon and  $\delta^{13}\text{C}$  of surface water: application of a modified gas evolution technique. *Journal of Hydrology*, v. 205. pp. 265-278.

Baedecker, M.J. and W. Back. 1979. Hydrogeological processes and chemical reactions at a landfill. *Ground Water*, v. 17. pp. 429-437.

Buttle, J.M. and C.F. Labadia. 1999. Deicing salt accumulation and loss in highway snowbanks. *Journal of Environmental Quality*, v. 28. pp. 155-164.

Cartwright, K. 1970. Groundwater discharge in the Illinois Basin as suggested by temperature anomalies. *Water Resources Research*, v. 6, no. 3. pp. 912-918.

Clark, I.D. and P. Fritz. 1997. Environmental isotopes in hydrogeology. Lewis Press, New York. 328 pp.

Cleary, R.W. 1978. Pollution of groundwater. In Water Problems of Urbanizing Areas, Proceedings of the Research Conference, New England College, Henniker, New Hampshire, July 16-21, 1978. The American Society of Civil Engineers, New York. pp. 134-142.

Coleman, M.L., T.J. Shepard, J.J. Rouse, and G.R. Moore. 1982. Reduction of water with zinc for hydrogen isotope analysis. *Analytical Chemistry*, v. 54. pp. 993-995.

Davis, S.N., D.O. Whittemore and J. Fabryka-Martin. 1998. Uses of chloride/bromide ratios in studies of potable water. *Ground Water*, v. 36, no. 2. pp. 338-350.

Epstein, S. and T. Mayeda. 1953. Variation of  $^{18}\text{O}$  content of waters from natural sources. *Geochemica et Cosmochemica Acta*, v. 4. pp. 213-224.

Field, R., E.J. Struzeski, Jr., H.E. Masters and A.N. Tafuri. 1973. Water pollution and associated effects from street salting. U.S. Environmental Protection Agency Research Report EPA-R2-73-257. 48 pp.

Gerritse, R.G. and R.J. George. 1988. The role of soil organic matter in the geochemical cycling of chloride and bromide. *Journal of Hydrology*, v. 120. pp. 83-95.

Grootjans, A.P., R. van Diggelen, M.J. Wassen, and W.A. Wiesinga. 1988. The effects of drainage on groundwater quality and plant species distribution in stream valley meadows. *Vegetation*, v. 75. pp. 37-48.

Habermeyer, G.C., 1940. Public ground-water supplies in Illinois. Illinois State Water Survey Bulletin no. 21, Supplement II. pp. 1091-1135.

Hackley, K.C., C.L. Liu and D.D. Coleman. 1996. Environmental isotope characteristics of landfill leachates and gases. *Ground Water*, v. 34, no. 5. pp. 827-836.

Hackley, K.C., C.L. Liu and D.Trainor. 1999. Isotopic identification of the source of methane in subsurface sediments of an area surrounded by waste disposal facilities. *Applied Geochemistry*, v. 14. pp. 119-131.

Hackley, K. C., 2002, A Chemical and Isotopic Investigation of the Groundwater in the Mahomet Bedrock Valley Aquifer: Age, Recharge and Geochemical Evolution of the Groundwater. Ph.D. Thesis, University of Illinois, Urbana-Champaign, Illinois. 152 pp.

Hamamo, H., S. Landsberger, G. Harbottle and S. Panno. 1995. Studies of radioactivity and heavy metals in phosphate fertilizer. *Journal of Radioanalytical and Nuclear Chemistry*, v. 194, no. 2. pp. 331-336.

Hem, J.D. 1985. Study and interpretation of the chemical characteristics of natural water (Water-Supply Paper 2254, 3rd ed.). Washington, DC: U.S. Geological Survey. 263 pp.

Hwang, H.H., C-L. Liu, and K.C. Hackley. 1999. Method improvement for oxygen isotope analysis in nitrates. Geological Society of America, Abstracts with Programs, North-Central Section, vol. 31, No. 5, April 22-23, Champaign, Illinois. pp. A-23.

Kaufmann, R.S., A. Long, H.W. Bentley, and S.W. Davis. 1984. Natural chlorine isotope variations. *Nature*, v. 309. pp. 338-340.

Kelly, W.R. 2002. Temporal changes in shallow ground-water quality in northeastern Illinois: Preliminary results. In Proceedings of the 11<sup>th</sup> Annual Research Conference of the Illinois Groundwater Consortium. Research on Agrichemicals in Illinois, Groundwater Status and Future Directions XI. Carbondale, IL. [www.siu.edu/worda/igc/](http://www.siu.edu/worda/igc/). April 22, 2001. 18 pp.

Krapac, I.G., W. S. Dey, C. A. Smyth, W. R. Roy, 1998. Impacts of bacteria, metals, and nutrients on groundwater at two hog confinement facilities, Proceedings of the National Ground Water Association Animal Feeding Operations and Groundwater: Issues, Impacts, and Solutions- A Conference for the Future, November 4-5, St. Louis, Mo. pp. 29-50.

Krapac, I.G., W. S. Dey, W.R. Roy, B.G. Jellerichs, C. Smyth, 2000. Groundwater quality near livestock manure pits, Proceedings of the 8<sup>th</sup> International Symposium on Animal, Agricultural and Food Processing Wastes, October 9-11, 2000 Des Moines, IA ASAE Publication 701P0002. pp. 710-718.

Krauskopf, K.B., 1979. Introduction to Geochemistry. McGraw-Hill, NY. 617 pp.

Larson, T.H., I.G. Krapac, W.S. Dey, and C.J. Suchomski, 1997. Electromagnetic terrain conductivity surveys used to screen swine confinement facilities for groundwater contamination. Proceedings of the Symposium on the Application of Geophysics to Engineering and Environmental Problems. Reno, Nevada, March 23-26. pp. 271-279.

- Long, A., C.J. Eastoe, R.S. Kaufmann, J.G. Martin, L. Wirt, and J.B. Finely. 1993. High-precision measurements of chlorine stable isotope ratios. *Geochimica et Cosmochimica Acta*, v. 57. pp. 2907-2912.
- Marie, A., and A. Vengosh. 2001. Sources of salinity in ground water from Jericho Area, Jordan Valley. *Ground Water*, v. 39, no. 2. pp. 240-248.
- Mason, C.F., S.A. Norton, I.J. Fernandez, and L.E. Katz. 1999. Deconstruction of the chemical effects of road salt on stream water chemistry. *Journal of Environmental Quality*, v. 28. pp. 82-91.
- Moyland, R.L. 1980. City examines effects of road salting on its water supply. City of Worcester, Massachusetts Public Works, v. 111, no. 8. pp. 59-60.
- NADP. 1998. National Atmospheric Deposition Program (NRSP-3)/National Trends Network. NADP Program Office, Illinois State Water Survey, 2204 Griffith Dr., Champaign, IL 61820.
- Naftz, D.L. and L.E. Spangler. 1994. Salinity increases in the Navajo Aquifer in southeastern Utah. *Water Resources Bulletin*, v. 30, no. 6. pp. 1119-1135.
- Panno, S.V., K.C. Hackley, C-L. Liu, and K. Cartwright. 1994. Hydrochemistry of the Mahomet Bedrock Valley Aquifer, east-central Illinois: Indicators of recharge and ground-water flow. *Ground Water*, v. 32, no. 4. pp. 591-604.
- Panno, S.V., K.C. Hackley, and V.A. Nuzzo. 1998. Teaching of multidisciplinary environmental science in a wetland setting. *Journal of Geological Education*, v. 46, no. 2. pp. 157-163.
- Panno, S.V., K.C. Hackley, and S.E. Greenberg. 1999a. A possible technique for determining the origin of sodium and chloride in natural waters: Preliminary results from a site in northeastern Illinois. [Abstract] in *Environmental Horizons 2000, Conference Proceedings*, March 27-28, 2000. pp. 57.
- Panno, S.V., V.A. Nuzzo, K. Cartwright, B.R. Hensel, and I.G. Krapac. 1999b. Changes to the chemical composition of groundwater in a fen-wetland complex caused by urban development. *Wetlands*, v. 19, no. 1. pp. 236-245.
- Panno, S.V., K.C. Hackley, and S.E. Greenberg. 2000. An exploration of techniques for determining the origin of sodium and chloride in groundwater feeding South Elgin Fen. Unpublished report to Kane County Illinois. 23 pp.

Panno, S.V., K.C. Hackley, H.H. Hwang, and W.R. Kelly. 2001. Determination of the sources of nitrate contamination in karst springs using isotopic and chemical indicators. *Chemical Geology*, v. 179. pp. 113-128.

Panno, S.V., K.C. Hackley, and H.H. Hwang. 2002. Distribution and sources of heterotrophic bacteria in wells, caves and springs of a karst aquifer in the Midwestern US. *In Hydrogeology and Biology of Post-Paleozoic Carbonate Aquifers, Proceedings of the symposium Karst Frontiers: Florida and Related Environments, March 6-10, 2002, Gainesville, FL.* pp. 92-95.

Pfaff, J.D., 1993. Method 300.0: Determination of inorganic anions in water by ion chromatography, Revision 2.1. U.S. Environmental Protection Agency, Cincinnati, OH. 30 pp.

Raveh, A., and Y. Avnemelech, 1979. Total nitrogen analysis in water, soil and plant material with persulfate oxidation. *Water Research*, v. 13. pp. 911.

Silva, S.R., C. Kendall, C.C. Chang, J.C. Radyk and D.H. Wilkinson. 1994. A new method of preparing dissolved nitrate for nitrogen and oxygen isotopic analysis. *EOS Transactions, American Geophysical Union* 75. pp. 280.

Silva, S.R., C. Kendall, D.H. Wilkinson, C.C.Y. Chang, A.C. Zeigler, and R. Avanzino. 2000. A new method for collection of nitrate from fresh water and the analysis of nitrogen and oxygen ratios. *Journal of Hydrology*, v. 228. pp. 22-36.

Strellis, D.A., H.H. Hwang, T.F. Anderson and S. Landsberger, 1996. A comparative study of IC, ICP-AES and NAA measurements of chlorine, bromine and sodium in natural waters. *Journal of Radioanalytical Nuclear Chemistry*, v. 211. pp. 473-484.

U.S. Environmental Protection Agency (US EPA), 2000. How much drinking water do we use in our homes? [www.epa.gov/safewater/wot/howmuch.html](http://www.epa.gov/safewater/wot/howmuch.html). US EPA Office of Ground Water and Drinking Water.

Vennemann, T.W. and J.R. O'Neil. 1993. A simple and inexpensive method of hydrogen isotope and water analyses of minerals and rocks based on zinc reagent. *Chemical Geology*, v. 103. pp. 227-234.

Wassenaar, L.I. 1995. Evaluation of the origin and fate of nitrate in the Abbotsford Aquifer using the isotopes of  $^{15}\text{N}$  and  $^{18}\text{O}$  in  $\text{NO}_3^-$ . *Applied Geochemistry*, v. 10. pp. 391-405.

Whittemore, D.O. 1995. Geochemical differentiation of oil and gas brine from other saltwater sources contaminating water resources: Case studies from Kansas and Oklahoma. *Environmental Geosciences*, v. 2, no. 1. pp. 15-31.



Wilcox, D.A. 1986a. The effects of deicing salts on vegetation in Pinhook Bog, Indiana. *Canadian Journal of Botany*, v. 64. pp. 865-874.

Wilcox, D.A. 1986b. The effects of deicing salts on water chemistry in Pinhook Bog, Indiana. *Water Resources Bulletin*, v. 22. pp. 57-65.

Wood, W.W. 1981. Guidelines for collection and field analysis of ground-water samples for selected unstable constituents. in *Techniques of Water-Resources Investigations of the U.S. Geological Survey*, Book 1, Chap. D2. 24 pp.