Kansas Geological Survey

IDENTIFICATION OF NITRATE AND CHLORIDE SOURCES AFFECTING MUNICIPAL WELL WATERS OF THE CITY OF McPHERSON, KANSAS

By

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INTRODUCTION

The City of McPherson, Kansas, requested the consulting firm Burns and McDonnell to investigate the cause of increasing nitrate-N concentration in several of the city wells. The City also asked the Kansas Geological Survey (KGS) to contribute to the study by identifying the sources of nitrate. The KGS used nitrogen-15 isotope analyses to determine the nitrate origin. In addition, the KGS used bromide and chloride analyses to identify sources of salinity as an additional means to trace the the nitrate origin.

CHEMICAL DATA FOR WATERS

Sample Collection

Water samples were collected from six municipal wells in the city of McPherson, Kansas, on March 1, 2005. Wells 2, 3, and 4 were turned on for approximately 10 minutes prior to collection of samples for specific conductance and temperature readings. Samples were collected at five-minute intervals until the specific conductance and temperature readings were constant. The wells usually ran for a minimum of 20 minutes before a sample was collected.

Samples were collected in a bucket, that was cleaned with deionized water between wells, and then poured into sample bottles: a 500-ml non-preserved sample for cations (calcium, magnesium, potassium, sodium), and a 200-ml sample with 2 ml 10% HCl preservative for nitrate and anions (chloride, bicarbonate, and sulfate). Samples for nitrogen-15 analysis were collected in 100-ml bottles. All samples were kept on ice until return to the KGS. Samples for isotopes were frozen until sent for analysis at the University of Virginia. The samples were stored on ice until delivered to the laboratory at the KGS in Lawrence. Samples were refrigerated in the laboratory until analyses were performed.

A Garmin geographic positioning system (GPS) was used to take latitude and longitude location readings for each well. Notes and pictures were taken concerning the land use surrounding each well.

Water samples were also collected at the wastewater treatment plant. A bucket was used to retrieve a sample from the influent intake area to the plant. The wastewater was poured into sample bottles. A sample of the treated wastewater was collected in a bucket inside the plant from the pipe exiting the plant. The wastewater was then poured into sample bottles. Additional samples of untreated and treated wastewater were collected in 1-liter polyethylene bottles on March 7, 2005, by personnel at the wastewater treatment plant. Samples were sent with ice packs via Federal Express to the KGS where the samples were frozen for isotope analyses. An additional set of samples were sent to Servi-Tech laboratory in Dodge City, Kansas, for complete analyses.

Samples for determination of nitrogen-15 and oxygen-18 in dissolved nitrate were frozen at the KGS until they were sent by Federal Express to the University of Virginia for analysis. Samples were kept frozen at the University until analyzed. Sample analysis for oxygen-18 in nitrate has not yet been done because the method setup has not been completed.

Sample Analysis

The KGS filtered the water samples through 0.45 µm membrane filter paper before analysis. Specific conductance was measured to estimate chloride concentrations and determine dilution factors for the optimum concentration range of the analytical method. Chloride, sulfate, bromide, total inorganic iodine, and iodate concentrations were determined using automated colorimetric methods on a Technicon AutoAnalyzer II. Dissolved iodide was computed from the total inorganic iodine and iodate concentrations and used to correct for its effect on the measured bromide in the analytical method. Nitrate content was determined on the AutoAnalyzer using an ultraviolet spectrophotometric method. Bicarbonate content was computed from an alkalinity determination using an automated titrimeter. Cation concentrations were measured using an inductively-coupled argon plasma spectrometer. Only conductance, chloride, and bromide (along with iodine species for bromide correction) were determined in the untreated and treated wastewater samples. Charge balance errors calculated for the well waters, for which measurements of all major and substantial minor constituents were completed, were all <2% and averaged 1.0%. As a part of its quality assurance steps, the KGS participates in the standard reference water program of the U.S. Geological Survey.

Laboratory information and chemical data for the ground water and wastewater samples are listed in Table 1. The table includes the total dissolved solids (TDS) content calculated from the major and minor constituent concentration. In the TDS computation, the bicarbonate was multiplied by 0.4917 to approximate the carbonate that would be left in the residual solids after evaporating to dryness, and 25 mg/L was added to represent the average concentration of dissolved silica in ground water in the Equus Beds aquifer.

Nitrogen-15 Analytical Methods

The nitrogen-15 isotopic composition in the waters was determined at the Department of Environmental Sciences, University of Virginia. Samples of the dried nitrate-containing salts dissolved in the waters were combusted at high temperature to nitrogen gas for analysis of their isotopic compositions. The $\delta^{15}N$ was determined on a Micromass Optima isotope ratio mass spectrometer (IRMS) coupled with an elemental analyzer (EA), with an overall precision better than 0.5 ‰. The data are reported relative to a standard (atmospheric N_2) defined to be 0 ‰, and expressed in δ notation as:

$$\delta_{\text{sample}}(‰) = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000$$

Table 1. Sample location and chemical data for ground waters and wastewaters sampled for this study and analyzed by the Kansas Geological Survey.

Sample description	KGS lab number	Legal location	Lab pH	Sp.C. µS/cm	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	HCO_3 mg/L	SO_4 mg/L	Cl mg/L	NO_3-N mg/L	B mg/L	Br mg/L	TDS mg/L	δ^{15}N ‰
Well 2	050042	19-03W-29DBAA	7.75	1003	157	14.0	32.9	3.6	360	46.2	103	7.21	0.056	0.25	599	27.9
Well 3	050043	19-03W-29DBDA	7.6	1140	185	16.4	26.7	5.2	368	38.1	142	8.81	0.047	0.43	668	28.5
Well 4	050044	19-03W-29DCDD	7.8	1013	162	14.0	24.7	2.8	337	33.2	121	7.03	0.047	0.36	588	20.3
Well 5	050045	19-03W-29ACAD	7.8	923	150	13.5	24.4	2.6	367	38.9	81.5	5.53	0.051	0.27	547	21.7
Well 8	050046	19-03W-20CAAB	7.6	775	120	13.1	20.4	2.5	316	18.9	69.6	4.36	0.039	0.16	449	22.6
Well 10	050047	19-03W-31ADDA	7.6	780	123	10.7	21.9	2.4	330	37.7	61.4	2.39	0.035	0.12	458	17.8
Untreated wastewater	050048	19-03W-33DBAB		2620						58.3	578			0.30		6.3
Treated wastewater	050049	19-03W-33DBAB		2050						59.2	434			0.17		21.3
Manure	ServiTech	18- 04W-20DBBA	7.4	7700	160	90	450	1448	2624	209	1223	330 Total N	1			22.3
Untreated	ServiTech	19-03W-33DBAB	7.60	2600	150	16.0	300	19.0	480	69.0	630	24.0 NH_4-N				7
Treated	ServiTech	19-03W-33DBAB	8.2	2050	130	12	230	11.0	330	72	420					24.5

where δ_{sample} represents $\delta^{15}N$, and R is the molar ratio of the heavier to the lighter isotope for the standard or sample (Hoefs, 1997). The analyses were run on nitrate in all samples except the untreated wastewater sample, which has ammonium as the dominant nitrogen form.

Historical Data

Analytical data are available from the Kansas Department of Health and Environment for samples collected from selected municipal wells in 1988, 1995, and 1997 (Table 2).

Table 2. Historical chemical analyses of samples from McPherson water-supply wells. Data are from the Kansas Department of Health and Environment.

Well No.	Well location	Date	Ca mg/L	Mg mg/L	Na mg/L	SO_4 mg/L	Cl mg/L	NO_3-N mg/L
2	19S-3W-29DBAA	11/28/1988	145	12.8	25.9	44.0	77.6	8.80
3	19S-3W-29DACB	11/28/1988	132	11.9	24.6	37.0	68.8	6.45
4	19S-3W-29DDCB	11/28/1988	114	9.5	23.9	26.0	55.8	4.37
4	19S-3W-29DDCB	3/22/1995	146	10.5	16.4	24.0	48.9	5.21
4	19S-3W-29DDCB	2/10/1997	121	10.5	20.5	28.5	49.9	3.33
5	19S-3W-29ACAD	11/28/1988	116	10.5	20.5	24.0	61.8	3.92
7	19S-3W-31AAAA	3/22/1995	149	12.4	23.7	46.7	46.6	2.31
7	19S-3W-31AAAA	2/10/1997	127	11.4	25.4	47.7	49.7	2.63
8	19S-3W-20CAAB	3/22/1995	131	12.4	14.9	15.9	40.0	3.41
8	19S-3W-20CAAB	2/10/1997	106	11.6	17.6	16.2	41.9	3.29
9	19S-3W-20CCDC	3/22/1995	137	11.4	18.4	21.3	51.0	3.31
9	19S-3W-20CCDC	2/10/1997	122	11.1	19.2	21.6	48.7	3.40
10	19S-3W-31ADDA	3/22/1995	126	10.2	19.7	29.4	40.9	1.29
10	19S-3W-31ADDA	2/10/1997	114	10	19.4	30.3	42.6	1.53
11	19S-3W-31DCCC	3/22/1995	98.3	9.9	17.3	20.2	20.9	0.55
11	19S-3W-31DCCC	2/10/1997	93.3	9.3	16.2	17.5	21.5	0.68
12	20S-3W-06BBBB	3/22/1995	102	8.9	17.7	24.2	26.6	0.62
12	20S-3W-06BBBB	2/10/1997	98.9	9.1	17.8	25.9	31.0	0.87
13	20S-4W-01DAAA	3/22/1995	101	8.5	19.8	23.5	34.7	0.81
13	20S-4W-01DAAA	2/10/1997	103	9.3	19.0	25.2	36.1	0.95
14	20S-4W-01DDDD	3/22/1995	94.4	8.2	18.9	20.6	34.0	0.93
14	20S-4W-01DDDD	2/10/1997	100	9.0	18.3	21.3	35.5	1.15

HYDROGEOLOGY OF THE STUDY AREA

Unconsolidated sediments, including clay, silt, sand, and gravel, primarily of Quaternary age, underlie the study area. The saturated sediments compose part of the Equus Beds aquifer. The bedrock underlying the unconsolidated sediments is the upper part of the Permian Wellington Formation, which consists of shale and thin beds of limestone, dolomite, siltstone, gypsum, and anhydrite. The bedrock surface underlying the Equus Beds part of the High Plains aquifer in the McPherson area slopes to the west to the paleochannel known as the McPherson channel. The thickness of the Equus Beds aquifer increases as the bedrock surface deepens towards the McPherson channel. The saturated thickness of the Equus Beds aquifer in the vicinity of the sampled wells is approximately 100 - 200 ft (Schloss and Buddemeier, 2000). Depth of the wells ranges from 127 to 147 ft (Wilson, 1998). Maps of the water-level surface in the aquifer for the region show a generally westward slope in the McPherson area. The water-table divide between ground-water flow to the Smoky Hill River valley and to the Little Arkansas River valley is south of McPherson (Williams and Lohman, 1949; Leonard and Kleinschmidt, 1976; Gogel, 1981). Depths to water at the sampled wells ranges from 78 to 96 ft as of January 2004. The saturated thickness in the study area is thinner than existed before development of the aquifer for ground-water supply due to the decline in the water-table level (based on comparison with water levels in Williams and Lohman, 1949).

Soils in the area are predominantly Crete silty clay loam of loess origin (Rott,1983). The soils in the area are approximately 50-70 ft thick (KGS, 2005,). The description of the soil includes no mention of measurable carbonate or caliche formation within the profile. The predominant clay is montmorillonite with mica and kaolinite also being present.

GENERAL WATER QUALITY

Figure 1 is a Piper trilinear diagram that shows points for the sampled waters relative to the percentage of major dissolved constituents in the water. Points for the city wells (2, 3, 4, and 5) fall in the region of calcium -bicarbonate, chloride type waters. These are hard waters with relatively high calcium, moderate chloride, and lower magnesium, sodium, and sulfate concentrations. Wells 8 and 10 have somewhat higher percentages of bicarbonate than the other well waters because the other anions are relatively lower. The wastewater influent and treated wastewater (cross and red box), show the impact of the water softeners to substantially increase both the concentration and percentage of sodium and chloride relative to the other major cations and anions. The manure (feedlot lagoon) sample shows the combined impact of use of some constituents and concentration of other constituents in the waste from transpiration. The addition of constituents in the animal diets, including salt licks, is also expected to affect the animal wastewater composition, such as an increase in sodium and chloride content.

The piper diagram illustrates the general chemical character of the water but is not particularly useful for determining potential sources of contamination to the city wells. This is partly because we do not have analyses of uncontaminated water from the city wells, which would help determine if the current city well samples (triangles on graph) are a mixture of uncontaminated ground water and wastewater or other sources such as animal waste.

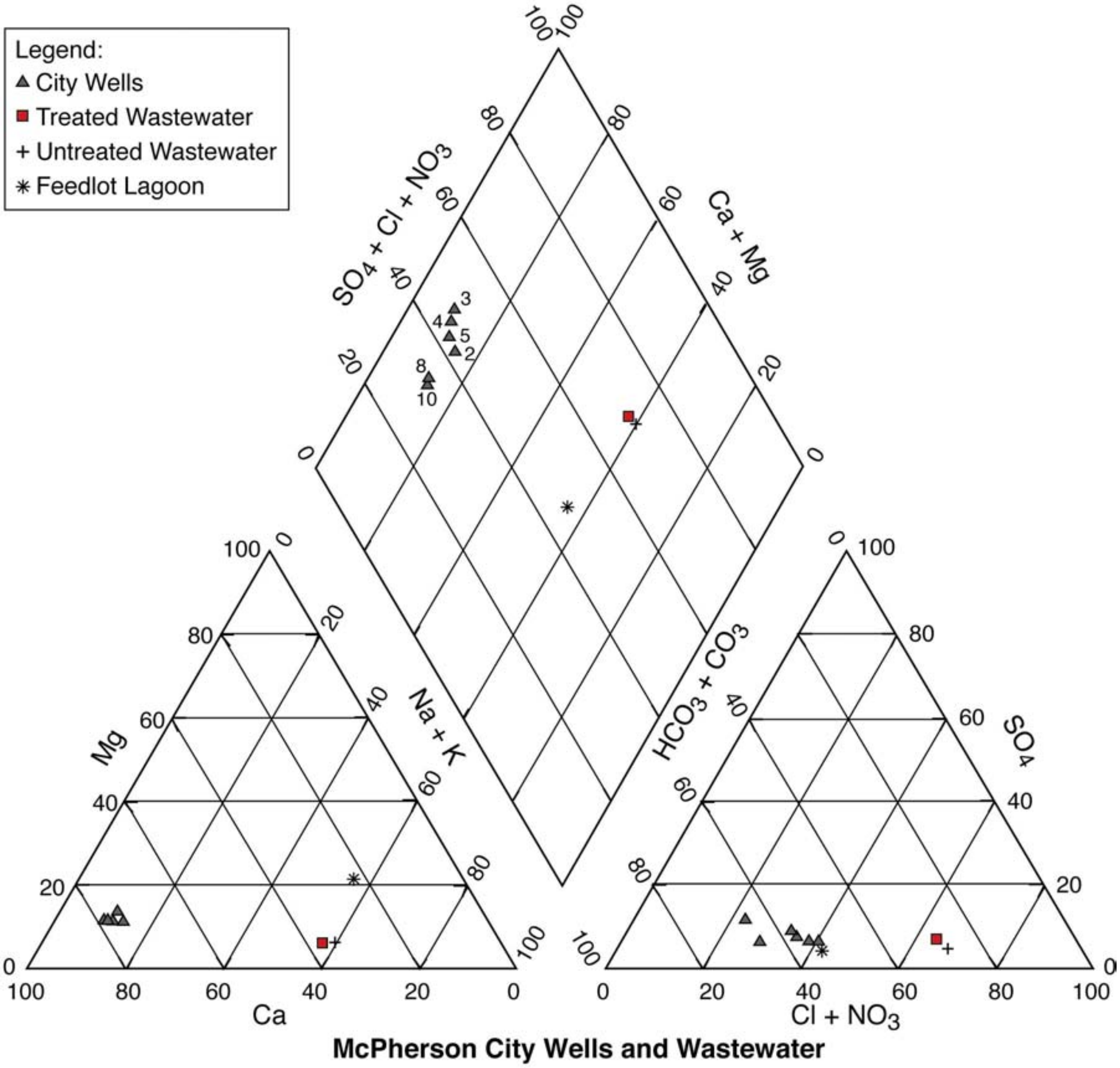

Figure 1. Piper trilinear diagram for City of McPherson sampled waters (after Piper, 1944).

WATER-QUALITY CHANGES

Nitrate and chloride concentrations have generally increased with time from 1988 to 2005 for ground waters pumped from municipal supply wells numbers 2-5, 8, and 10 of the City of McPherson (Figures 2 and 3). The nitrate and chloride contents are generally correlated (Figure 4), suggesting that the concentration increases could be related.

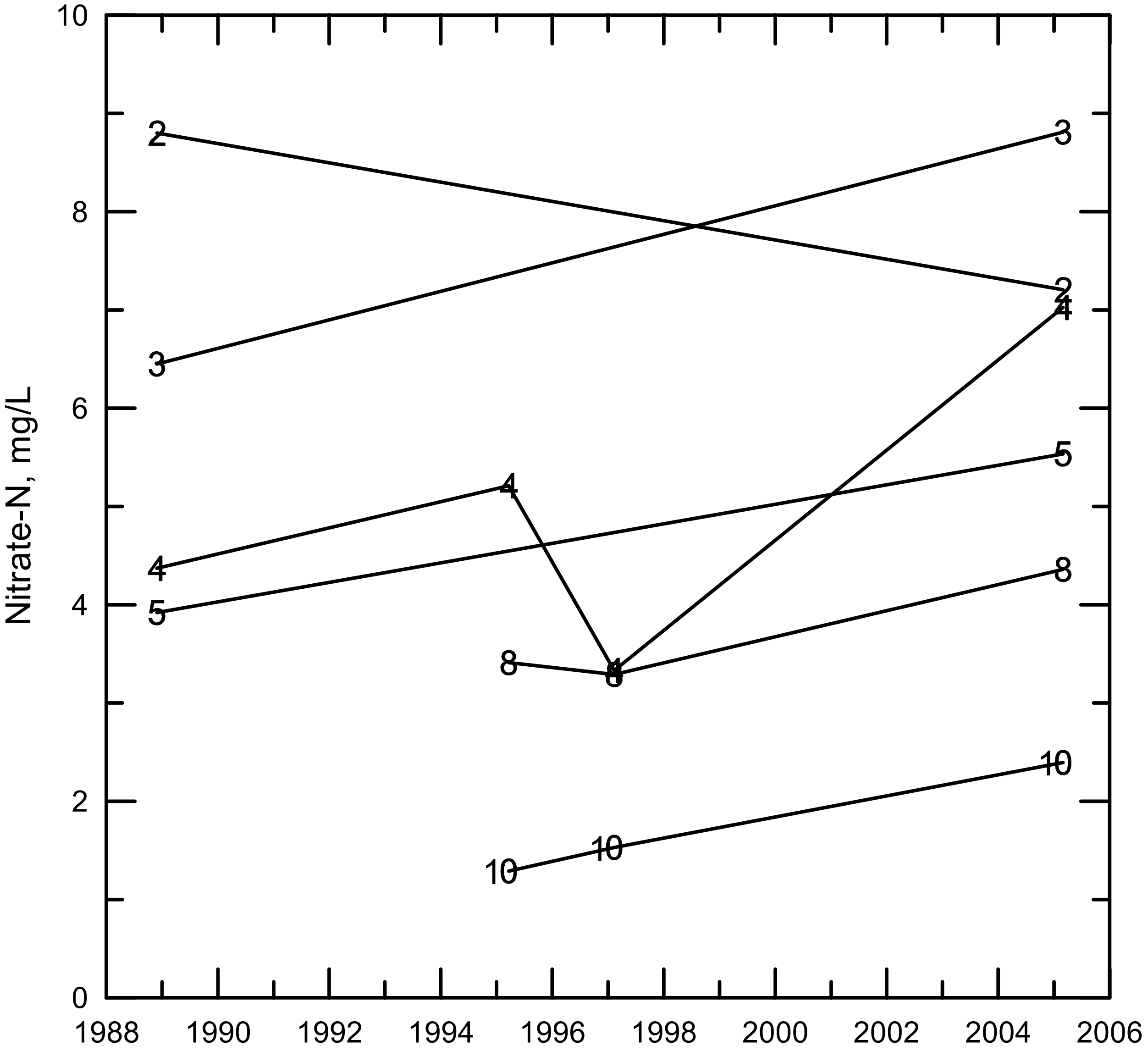

Figure 2. Change in nitrate concentration with time for municipal well waters of McPherson. The numbers in the figure refer to the supply well numbers.

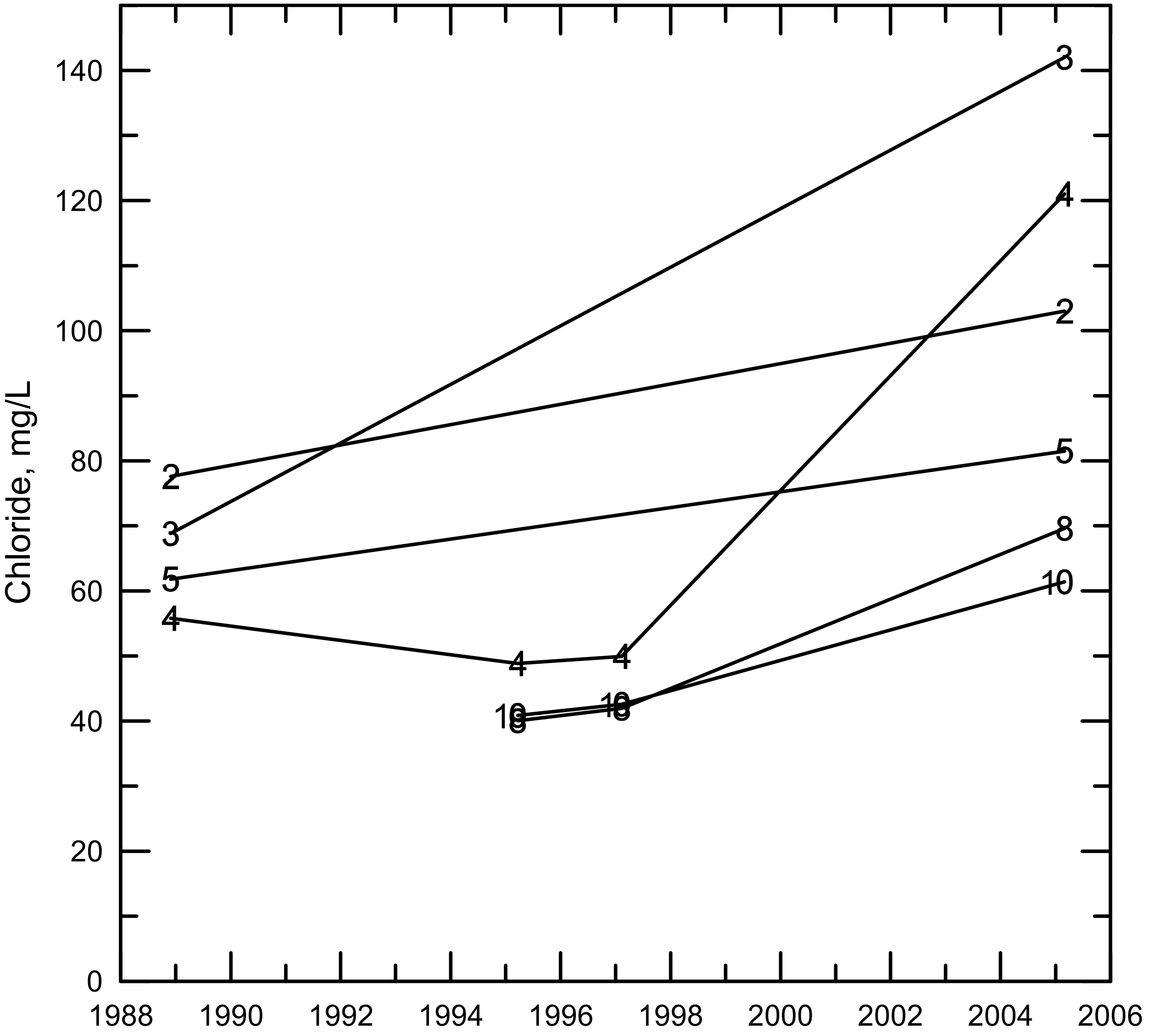

Figure 3. Change in chloride concentration with time for municipal well waters of McPherson. The numbers in the figure refer to the supply well numbers.

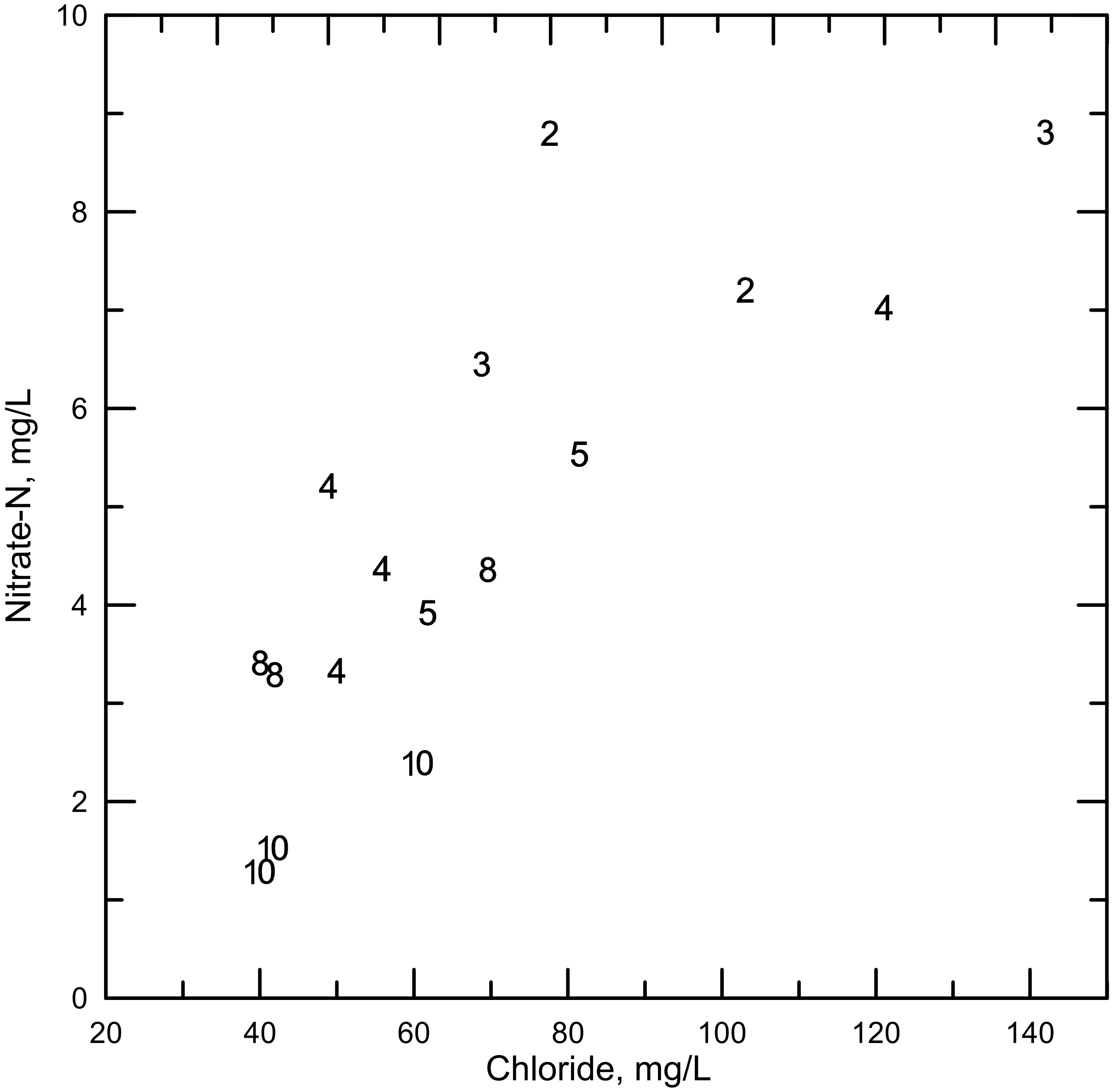

Figure 4. Relationship of nitrate and chloride concentrations for municipal well waters of McPherson collected from 1988 to 2005. The numbers in the figure refer to the supply well numbers.

IDENTIFICATION OF SALINITY SOURCES

The sources contributing to chloride in the ground waters were identified using the geochemical methods of Whittemore (1984, 1988, 1995). These methods primarily involve plots of the constituent mass ratios bromide/chloride and sulfate/chloride versus chloride concentration, with points for the water sample data and curves for the mixing of different source waters. Each mixing curve is generated using an algebraic equation for conservative mixing of two end-member waters. Conservative mixing refers to the simple mixing of waters without chemical reactions, such as mineral precipitation or adsorption, which could alter the concentrations of one or both of the constituents. The bromide/chloride ratio is multiplied by 10,000 for graphical display to give numbers that range from about one upwards (the lowest mass ratios are near 0.0001 for halite or rock salt dissolution). Logarithmic scales are used in the graphs because they produce a more even distribution (separation) of points for large ranges in concentration and ratios than linear scales. The mixing curves bend in different directions depending on the relative difference in the ratios compared to the difference in the chloride concentrations for the end points.

Figure 5 is a bromide/chloride versus chloride concentration plot containing points for the well waters and wastewater samples from the study area, ground waters from monitoring wells screened in the middle or lower portion of the Equus Beds aquifer in southern McPherson County, northwestern Harvey County, and northeastern Reno County, and oil brines from the Johnson and Ritz-Canton oil fields east of the study area. Data for the monitoring wells are KGS analyses of samples collected by Groundwater Management District No. 2 within the rectangular area of T. 21-23 S., R. 3-4 W. Data for the oil brines are reported in Whittemore (2003).

The two long-dashed curves in Figure 5 enclose a zone representing the mixing of freshwater with natural Permian saltwater. The freshwater end members for the dashed curves are based on fresh ground waters from the Equus Beds area of the High Plains aquifer (Whittemore, 1984; and data for the Equus Beds Aquifer Mineral Intrusion Study, Young et al., 1998). The saltwater end members for the dashed curves are for saltwaters from the Wellington Formation in the Smoky Hill River valley (Whittemore et al., 1981) and from the saltwater intrusion area in the western Equus Bed aquifer (Young et al., 1998). The two solid curves in Figure 5 represent the mixing of formation brine from the oil fields to the east of the study area with freshwater in the Equus Beds aquifer. Formation brines associated with hydrocarbons in strata not containing rock salt in Kansas have substantially higher bromide/chloride ratios than saltwater primarily derived from the dissolution of rock salt.

The untreated and treated wastewater samples collected at the treatment plant have substantially greater chloride concentrations and lower bromide/chloride ratios than for the well waters. The source of the additional chloride is attributed to the dissolution of halite (rock salt) used in conventional water softeners. The source of the rock salt is expected to be that mined from the Wellington Formation in Kansas. The City of McPherson obtains its source water from the Equus Beds but does not soften it. Many homes in the city use conventional softener units to soften the water. Saltwater produced from dissolution of rock salt is used to regenerate the exchange medium in the water softeners. The saltwater from the regeneration process is disposed into the sewer system, thereby increasing the chloride concentration of the City wastewater. The treated wastewater is discharged into Dry Turkey Creek. Whittemore (1997, 2003) previously noted the water-softener source of salinity in Dry Turkey Creek downstream of the effluent discharge from the wastewater treatment plant.

If the main source of the chloride concentration in the 2005 samples from the McPherson water-supply wells was untreated wastewater leaking from sewer lines, then the bromide/chloride ratios for the samples would have been lower and the points on Figure 5 would have fallen within the mixing zone of freshwater with halite-dissolution brine. Thus, wastewater from the sewerage system does not appear to be the source of the increased chloride concentration in the ground waters pumped by the municipal wells.

The additional wastewater samples collected from the sewer system near the sampled city wells have chloride concentrations and bromide/chloride ratios that generally plot on Figure 5 between those for the city well waters and the wastewaters collected at the treatment plant. The sewer system waters fit the mixing of city well waters with brine discharged from the regeneration of water softeners. The lower bromide/chloride ratios for the sewer system samples in comparison to the 2005 well water samples is further evidence that the increased chloride content in the well waters is not derived from the seepage of recent sewage water into the underlying aquifer.

Oil-field brine has contaminated ground water in the Equus Beds aquifer south of McPherson (Whittemore, 1997, 2003, 2004). A plume of saline water is migrating from the Johnson oil field, which is located to the southeast of McPherson, in a westward direction into the area of the National Cooperative Refinery Association south of the City. The locations of the points for the 2005 samples of municipal well waters in Figure 5 appear to fit an oil-brine source of the chloride concentration greater than 50 mg/L in the samples. Oil brine could be a possible source of the additional chloride because there are oil fields to the east of the City that have operated for a long time. The early practices of brine disposal in the oil fields typically included surface disposal in ponds that could allow seepage of the brine into the underlying Equus Beds aquifer.

The association of nitrate and chloride (Figure 4), however, suggest that the chloride source could also be from a source other than oil-brine contamination. Evaporation and transpiration consumption of water, which concentrates the levels of conservative dissolved solids in the residual water, would increase both chloride and bromide contents without changing the bromide/chloride ratio. For example, transpiration of water vapor from animals (including humans) concentrates dissolved solids in the animal wastewater. Assuming that the animal uptake in bromide and chloride are not substantially different and that the addition of chloride and bromide in the animal diets do not greatly change the bromide/chloride ratio, the ratio would be in a similar range as for the intake water. The result would be a shift towards higher chloride concentrations while the bromide/chloride ratio remained in the same general range. This shift could also explain the distribution of points for the municipal well waters on Figure 5. A sample of manure (Table 1) from a location west of the study area contained high chloride concentration (1,225 mg/L), indicating that animal waste could be a source of chloride. The bromide content was not measured in this sample.

Sulfate/chloride versus chloride plots and mixing curves often can be used to assist salinity identification. Figure 6 is a plot of sulfate/chloride mass ratio versus chloride concentration with points for the municipal well waters collected during 1988-1997 and in 2005, the untreated and treated city wastewater samples, irrigation well samples collected in 1980 (Hathaway et al., 1981), the manure sample (Table 1), and oil brines to the east of the study area. The solid curves in the figure bound the freshwaters from the irrigation and municipal supply wells and the oil brines to form a zone of mixing of fresh ground water with oil brine. The mixing zone bounded by solid lines could also represent the mixing of fresh ground water with high-purity salt used in water softeners. The dashed curves represent conservative mixing of the fresh ground waters with the composition of the manure sample. The distribution of the points for the 2005 samples from the McPherson municipal wells relative to the points for earlier well waters and potential salinity sources indicates that both or either of the oil brine or manure waste could be (a) possible source(s) of the additional chloride in the well waters. The water-softener salt source is ruled out by the bromide/chloride relationships described earlier (Figure 5). No significant nitrate would be expected to be associated with oil-brine pollution. If the nitrate and chloride increases shown in Figure 4 are related to the same source, then the manure source fits better as the origin of chloride increases than oil brine. However, the primary contributors to the elevated nitrate and chloride concentrations could be a combination of these different sources.

Sodium/chloride ratios in the 2005 and earlier samples of municipal well waters relative to irrigation waters from the Equus Beds aquifer suggest that the source of increasing chloride is contamination that is being affected by cation exchange as it passes through or into the aquifer (Figure 7). The decrease in the sodium/chloride ratio with increasing chloride is similar to that in the slightly saline front of the oil-brine plume to the south of McPherson. However, a similar result would be expected for animal wastewater passing through the unsaturated zone to the water table in the study area, as well as migration from the shallow to the deeper parts of the aquifer where the wells are screened. The significance of this observation is that the increase in chloride concentration represents the front of a contamination source that is expected to contain higher concentrations of the contaminants behind the front.

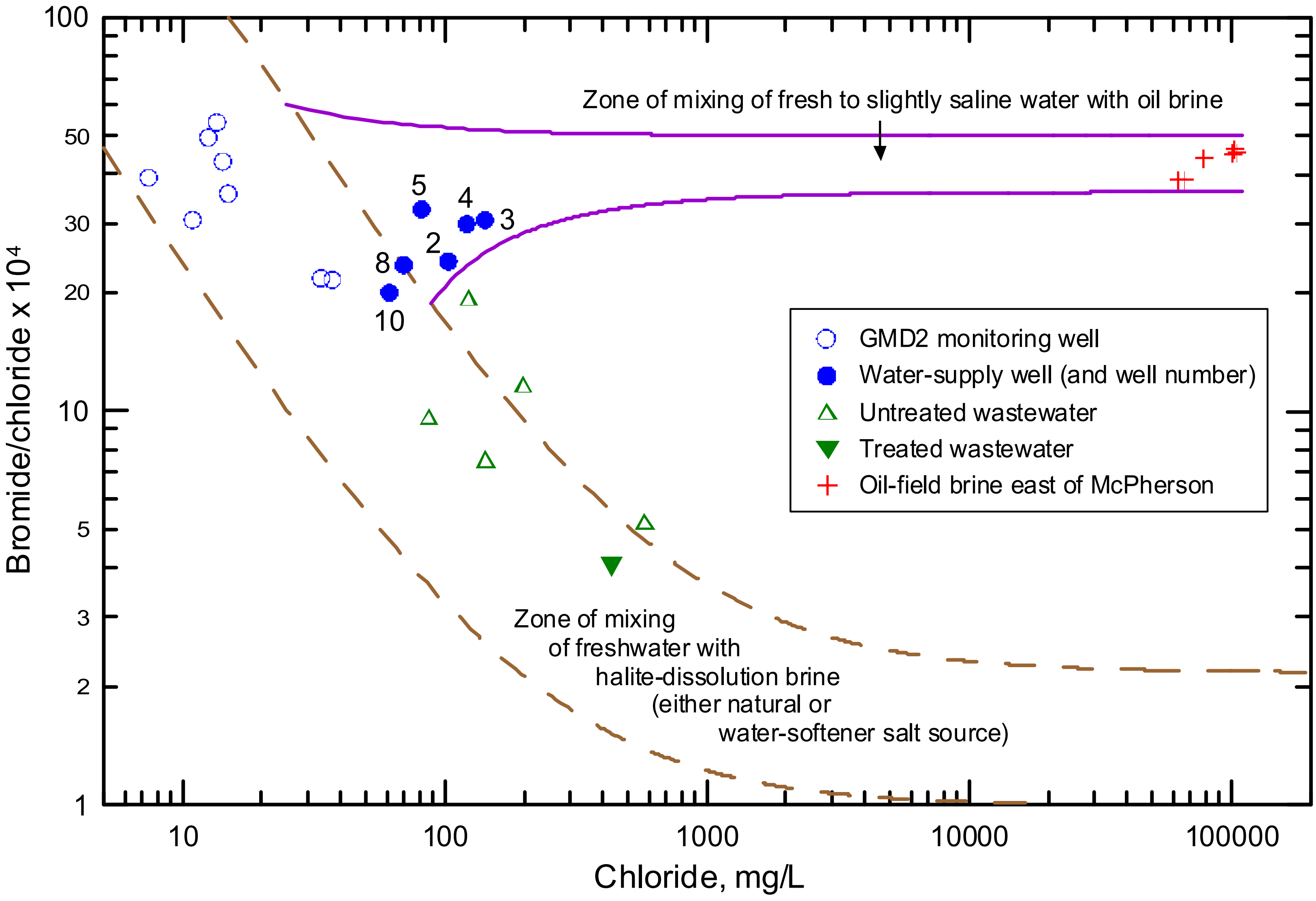

Figure 5. Bromide/chloride mass ratio versus chloride concentration, and conservative mixing curves bounding mixing zones.

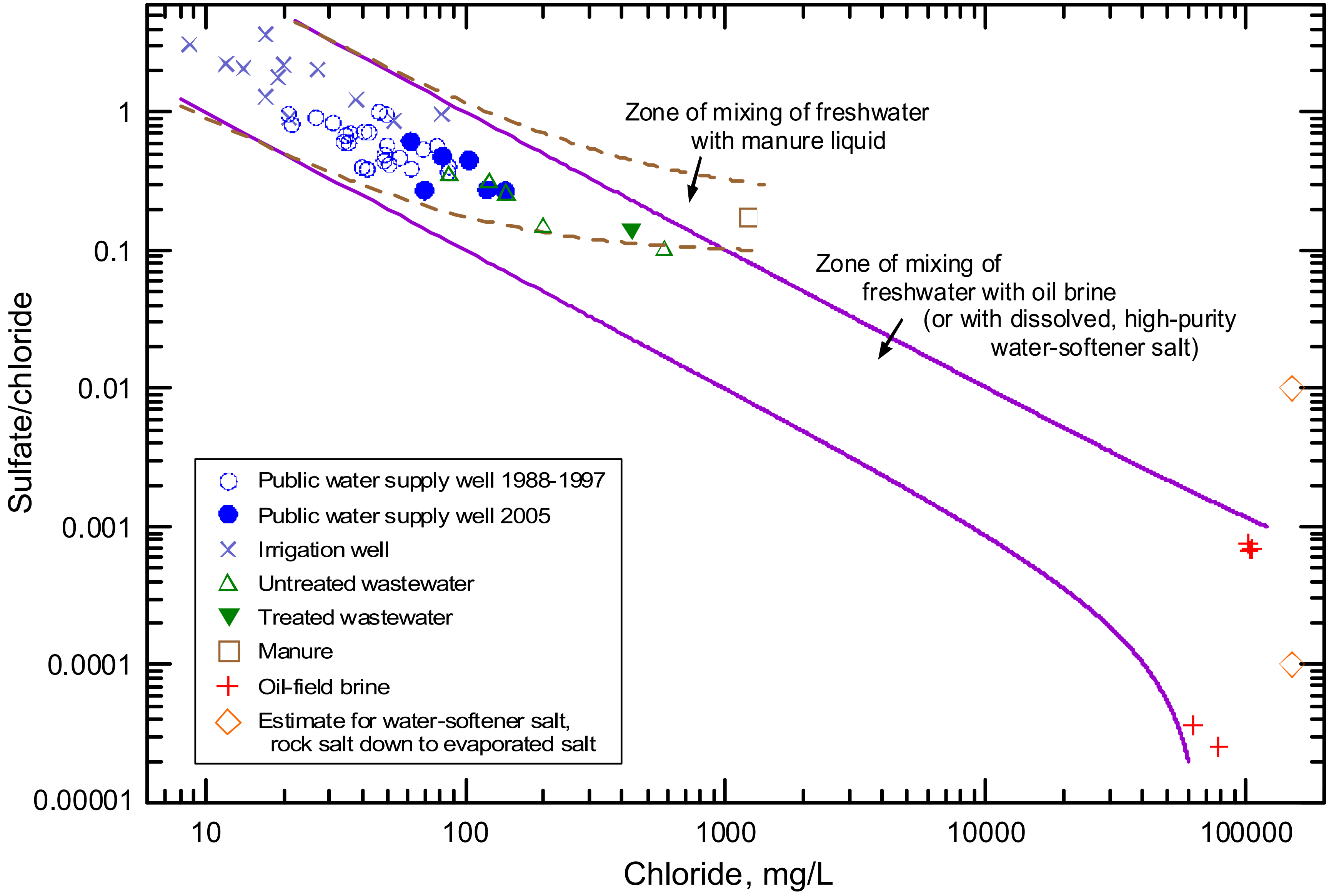

Figure 6. Sulfate/chloride mass ratio versus chloride concentration, and conservative mixing curves bounding mixing zones.

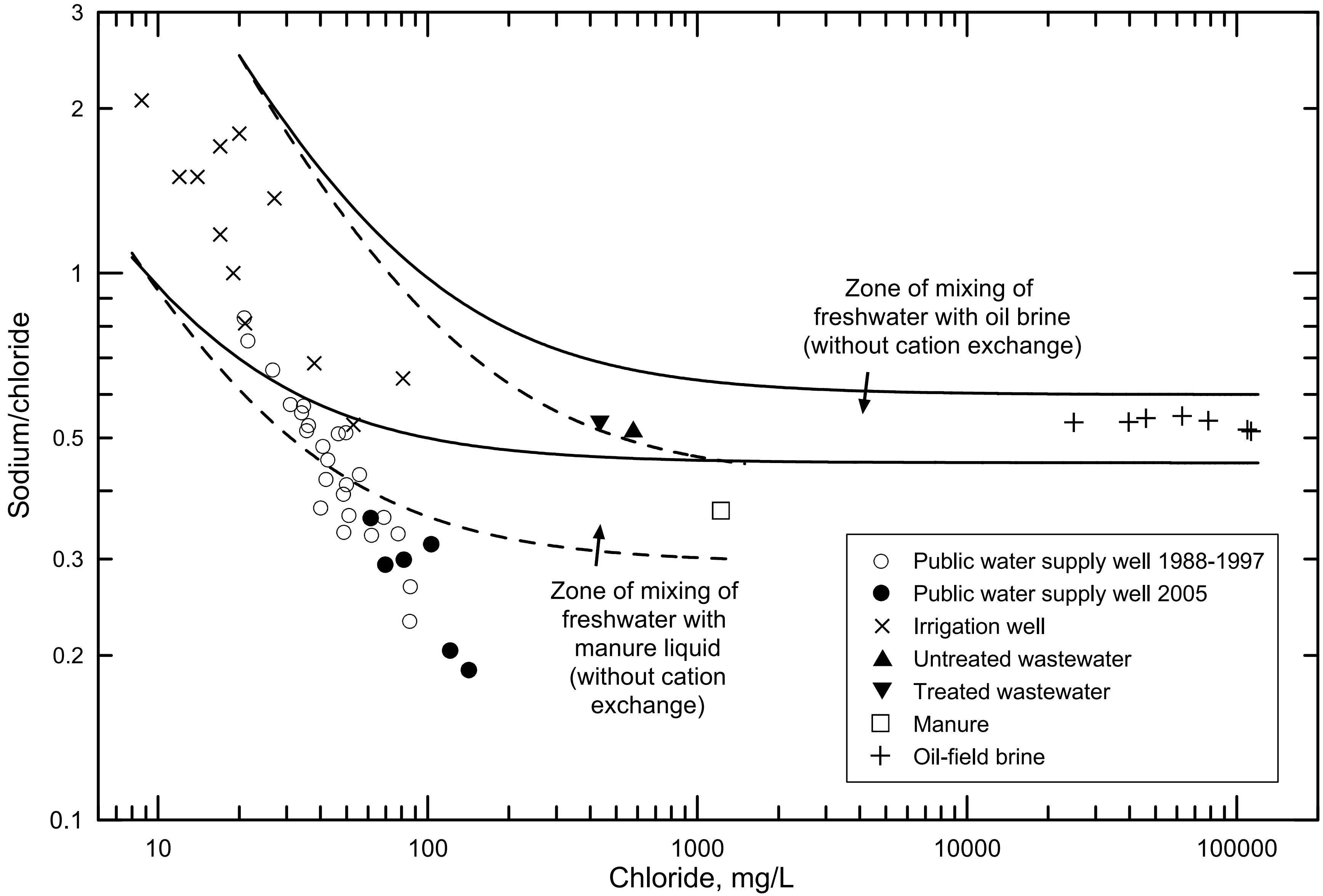

Figure 7. Sodium/chloride mass ratio versus chloride concentration, and conservative mixing curves bounding mixing zones.

Identification of Nitrate Sources Using Nitrogen-15 Natural Abundance Method

Natural abundance nitrogen isotope analysis is a frequently used method to assist in determining sources of nitrogen to ground water. The isotope analysis involves establishing the ratio of nitrogen-15 (^{15}N) to nitrogen-14 (^{14}N) on the nitrogen in nitrate compared to the ratio observed in the standard, atmospheric nitrogen (air). Comparisons of these values indicate if there is more (positive) or less (negative) ^{15}N in the sample. The values thus indicate whether the sample is enriched (+) or depleted (-) in relation to the standard.

Isotopic values are reported as δ^{15}N in per mil (‰) (Hoefs, 2001):

$$\delta^{15}N(‰) = \left(\frac{\left({}^{15}N/{}^{14}N\right)_{sample} - \left({}^{15}N/{}^{14}N\right)_{s\tan dard}}{\left({}^{15}N/{}^{14}N\right)_{s\tan dard}} \right) \times 1000 \qquad (1)$$

Figure 8 illustrates the range of δ^{15}N values for various sources of nitrogen and associated processes affecting the ^{15}N abundance (Heaton, 1986). Generally, biological activities use ^{14}N preferentially, resulting in an increased δ^{15}N value in the remaining nitrogen. Previous work has shown that δ^{15}N values in nitrate from commercial fertilizer sources range from -2 to +8‰, from soil nitrogen are in the range of +5 to +7‰, and from animal waste are generally greater than +10‰ (Heaton, 1986, Herbel and Spalding 1993). Other information, such as dissolved oxygen, salinity, iron, and manganese concentrations, and proximity to potential sources, aid in source determination.

Figure 8 also illustrates the effects of processes in the nitrogen cycle on the resulting δ^{15}N values. Sources such as fertilizer and legumes have very light δ ^{15}N signatures (-2 to +2 ‰). Ground water impacted by fertilizer frequently has measurable nitrate as well (generally greater than 2 mg/L in Kansas). Because of possible volatilization of anhydrous ammonia by bacteria, the δ ^{15}N values frequently are in the range +2 to +8 ‰. Legume sources generally have low nitrate concentrations because the nitrogen is often tied up in an organic form and the plant nodules need to degrade before the nitrogen is released.

Other sources such as human-septic waste or animal waste (pig in figure 8) have starting δ^{15}N values around +5 ‰. Animal waste has a high ammonia component, and the release of the ammonia when the waste is produced causes an immediate enrichment of the δ^{15}N because the δ^{14}N in the waste is released by volatilization. As a result, the δ^{15}N of the remaining nitrogen is much higher, in the range of +10 ‰ or more. Generally with animal-waste sources, nitrate-N values are high (commonly more than 10 mg/L) as well.

Volatilization also can occur in soils and rocks with carbonate zones. Carbonates can increase the pH of water towards 8.5, which means the water is more basic. In this range nitrate can be converted to ammonia gas. The lighter ^{14}N isotope is released with the gas. The remaining nitrogen becomes enriched with δ^{15}N of a higher value.

Another process that can result in an enriched $\delta^{15}N$ value is denitrification. In this process, bacteria degrade nitrate to nitrogen gases that are released to the atmosphere. The ^{14}N of the nitrate is preferentially utilized, resulting with an enriched $\delta^{15}N$ occurring in the remaining nitrate. Signs of possible denitrification are low nitrate values, enriched $\delta^{15}N$ values, and high levels of bicarbonate, which is a byproduct of the denitrification process.

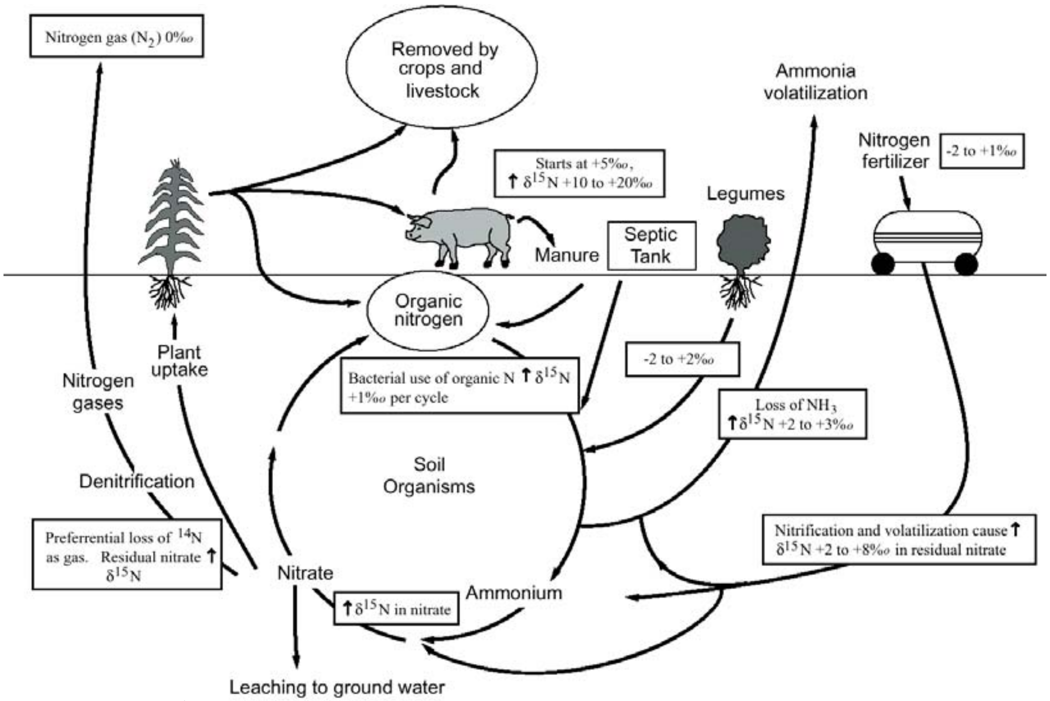

Figure 8. Range of $\delta^{15}N$ values for various sources of nitrogen and the enrichment effects of denitrification and volatilization processes. Ranges of $\delta^{15}N$ values from Heaton (1986) and site studies in Kansas (Townsend et al., 1996).

Figure 9 is a plot of the nitrogen-15 isotope and nitrogen values for the City of McPherson water samples and for some comparison samples: UAN fertilizer, city of Haven in-line sewer influent (Townsend, 1997), and a manure lagoon sample from a feedlot. Points for McPherson water samples fall within the animal waste zone. The source of the waste is unknown at this time. It could be related to prior land use such as improperly closed septic tanks, manure piles or use of manure on farm fields many years ago, the presence of stables or hotels with stable facilities in years past, or a combination of these factors.

The graph shows the enrichment of sewage from the in-line pipe (Haven –1.3 ‰) to the somewhat enriched McPherson sewage influent (+7 ‰) as a result of exposure to air where the influent enters the plant, to the very enriched sewage effluent (+24.5 ‰) due to the aeration treatment process. These values show the effect of volatilization (release of ammonia) on the resulting nitrogen-15 signature of the remaining nitrogen.

The fact that the point for the somewhat enriched McPherson sewage influent falls well below the points for the well water samples on Figure 9 indicates the unlikelihood that leaky sewer lines are the cause of the problem. The occurrence of the treated effluent in the same $\delta^{15}N$ and nitrate concentration ranges as for the well waters suggests the possibility that volatilization of the original nitrogen source resulted in an enriched signature for the well waters.

The occurrence of manure in the same $\delta^{15}N$ range as for the well water samples also helps to support the idea that animal waste (whether human or feedlot) is a potential source for the contamination.

The previous discussion of the bromide/chloride signature of the well waters also indicated that the sewer water is not a probable source for the well water contamination because the ratios for the well waters do not fall in the range where softener salt would be the expected origin (Figure 4). In addition, both the chloride and nitrate concentrations are increasing over time.

The $\delta^{15}N$ for the UAN fertilizer sample falls within the range of most fertilizers (-2.6 ‰) (Heaton, 1986; Kreitler, 1979). The fact that the McPherson water samples fall nowhere near the –2.6 to +8 ‰ range helps to support the interpretation that fertilizer is not a sole source for the present contamination.

The denitrification zone on the graph represents a process that generally occurs in water in a chemically reducing environment indicated by a low pH with measurable iron, manganese, hydrogen sulfide, and extra bicarbonate that is a by product of the process. None of the water samples have any of the features commonly found associated with water samples that have been denitrified.

Overall, the source of the nitrate-N observed in the city wells appears to be related to animal waste sources, whether the source is old septic systems (without significant influence of water-softener salt), abandoned or active feedlots, or use of manure as fertilizer. The higher chloride content, the bromide/chloride ratio, and the nitrogen-15 signature indicate that the source is not recent city wastewater but is impacted by some animal-related source that probably entered the subsurface in the past.

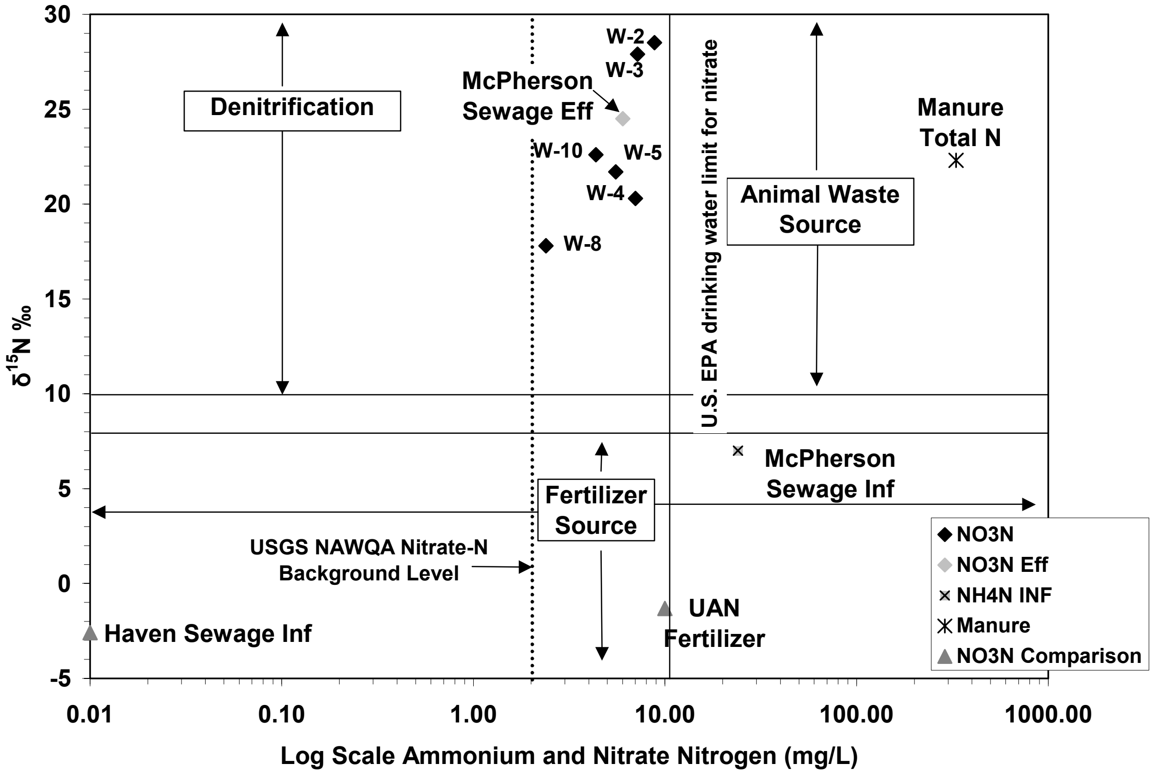

Figure 9. Nitrogen-15 and nitrogen values for McPherson water samples and UAN fertilizer, manure, and city of Haven sewage influent samples for comparison. The denitrification enrichment area is shown with low nitrogen (less than 2 mg/L). The fertilizer range (for Kansas) is generally from below 0 ‰ to around +8 ‰, depending upon the original fertilizer and length of travel time to the ground water.

Conclusions

- Nitrogen-15 isotope values in the well waters are within the range of animal waste but do not appear to be impacted by city wastewater, either treated or untreated.
- Bromide/chloride ratios in the well waters are not in the range expected for contamination by discharge of brine from water softener salt regeneration to the sewer. Therefore, the source does not fit wastewater in the current sewer system.
- Bromide/chloride ratios are in the range of mixtures of uncontaminated ground water with oil-filed brine and possibly animal waste not related to the city sewer system.
- Well water samples are outside the nitrogen-15 isotope range of fertilizer.
- Nitrogen-15 isotope values are not a result of denitrification.

This eliminates several potential sources. However, it does not positively identify the source. Potential sources of elevated nitrate concentration include:

- Old septic systems
- Old manure piles that have leached into the ground water
- Past use of manure as fertilizer in fields now incorporated into the city limits

Next Step

Based on the data presented here, the KGS recommends additional water and perhaps soil sampling in the areas surrounding the city wells. Soil sampling for nitrogen and chloride content would permit evaluation of vertical sources within the unsaturated zone. Sampling additional wells will help to identify if the source of nitrate contamination is a plume originating from a possible undiscovered point source.

Several industries in the area may need to be evaluated in terms of materials used to see if a nitrogen source is possible. Evaluation of historical land uses in the area might uncover possible sources that are only now arriving at the water table.

The KGS is assisting Equus Beds Groundwater Management District No. 2 and the Kansas Corporation Commission in studying the groundwater contamination plume emanating from past brine disposal in the Johnson oil field located southeast of McPherson. Future results from this investigation should be considered along with the impact of the pumping of the city wells on ground-water flow direction in the aquifer to determine whether part of the saline contamination plume has reached some of the city wells.

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REFERENCES

Gogel, T., 1981, Discharge of saltwater from Permian rocks to major stream-aquifer systems in central Kansas: Kansas Geological Survey Chemical Quality Ser. 9,

60 p.

Hathaway, L.R., Waugh, T.C., Galle, O.K., and Dickey, H.P., 1981, Chemical quality of irrigation waters in the Equus Beds area, south-central Kansas: Kansas Geological Survey Chemical Quality Ser. 10, 45 p.

Heaton, T. H. E., 1986, Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: a review. Chemical Geology, v. 59, p. 87-102.

Herbel, M. J., and Spalding, R. F., 1993, Vadose zone fertilizer-derived nitrate and $\delta^{15}N$ extracts: Ground Water, v. 31, no. 3, pp. 376-382.

Kansas Geological Survey (KGS), 2005), Water Well Completion Records (WWC5), http://www.kgs.ku.edu/Magellan/WaterWell/index.html.

Kreitler, C. W., 1979, Nitrogen-isotope ratio studies of soils and groundwater nitrate from alluvial fan aquifers in Texas: Journal of Hydrology, v. 42, pp. 147-170.

Leonard, R.B., and Kleinschmidt, M.K., 1976, Saline water in the Little Arkansas River basin area, south-central Kansas: Kansas Geological Survey Chemical Quality Ser. 3, 24 p.

Piper, A.M., 1944, A graphic procedure in the geochemical interpretation of water analyses: Am. Geophys. Union Trans., v. 25, p. 914-923.

Rott, D. E., 1983, Soil survey of McPherson County, Kansas: USDA NRCS Soil Conservation Service.

Schloss, J. A. and R. W. Buddemeier, R. W., 2000, Current Saturated Thickness, in An Atlas of the Kansas High Plains Aquifer, Kansas Geological Survey Open-file report 2000-29,

Townsend, M. A., 1997, Nitrate contamination of ground water in the vicinity of Haven, KS: Kansas Geological Survey Open-file Report 97-79, 28 p.

Whittemore, D.O., 1984, Geochemical identification of salinity sources, in R.H. French (ed.), Salinity in Watercourses and Reservoirs (Proceedings of the International Conference on

State-of-the-Art Control of Salinity): Ann Arbor Science, Butterworth Publishers, Stoneham, MA, p. 505-514.

Whittemore, D.O., 1988, Bromide as a tracer in ground-water studies: Geochemistry and analytical determination: Proceedings Ground Water Geochemistry Conference, National Water Well Association, Dublin, OH, p. 339-360.

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 2, 15-31.

Whittemore, D.O., 1997, Geochemical identification of sources of salinity in surface and ground waters in central McPherson County, Kansas: Kansas Geol. Survey Open-File Report 97-78, 25 p.

Whittemore, D.O., 2003, Geochemical identification of sources of salinity in ground waters of the High Plains aquifer west of the Johnson Oil Field in central McPherson County, Kansas: Kansas Geol. Survey Open File Report 2004-4, 16 p.

Whittemore, D.O., 2004, Geochemical Identification of Sources of Salinity in Ground Waters of the High Plains Aquifer South of McPherson, Kansas: Kansas Geol. Survey Open-File Report 2004-62, 21 p.

Whittemore, D.O., Basel, C.L., Galle, O.K., and Waugh, T.C., 1981, Geochemical identification of saltwater sources in the Smoky Hill River Valley, McPherson, Saline, and Dickinson counties, Kansas: Kansas Geol. Survey Open-File Report 81-6, 78 p.

Williams, C.C., and Lohman, S.W., 1949, Geology and ground-water resources of a part of south-central Kansas: Kansas Geological Survey Bull. 79, 455 p.

Wilson, B., 1998, Water information management and analysis system (WIMAS) for ArcView, v. 4: Kansas Dept. of Agriculture, Division of Water Resources (available from DASC, http://www.kansasgis.org/).

Young, D.P., Buddemeier, R.W., and Whittemore, D.O., 1998, Equus Beds mineral intrusion project report, FY 1998: Kansas Geol. Survey Open-File Report 98-24, 100 p.