



USE OF NITROGEN-15 NATURAL ABUNDANCE METHOD TO IDENTIFY NITRATE SOURCES IN KANSAS GROUNDWATER

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ABSTRACT

Nitrogen isotopes have been used as a tool for identifying sources of nitrate contamination in groundwater for almost 30 years. The method is used most successfully in areas with permeable vadose zones with a shallow groundwater table and in rock units such as fractured limestone, where travel times and/or distances from the source(s) are short. The hydrogeology of Kansas is variable – groundwater is present in aquifers ranging from shallow alluvial systems to deeper formations where the water table is hundreds of feet deep. Geochemical and biogeochemical processes that occur in the vadose zone can alter nitrate concentrations and nitrogen-15 signatures, complicating source identification.

Known ranges of $\delta^{15}\text{N}$ in ground water are associated with different sources: fertilizer from -2 to +8 per mil (‰) and animal waste greater than +10‰ (Heaton, 1986). However several processes such as denitrification, nitrification, and volatilization can alter the $\delta^{15}\text{N}$ signature.

Complete water chemistry analyses (major ions plus iron and manganese, dissolved oxygen, and dissolved organic carbon), soil-core descriptions, and site and land-use assessments may be necessary to apply the method in a useful manner. Case studies from Kansas are used to demonstrate the strengths, weaknesses, and caveats associated with the method.

Key words: nitrogen, groundwater, nitrogen-15 isotope, sources, Kansas

INTRODUCTION

Nitrate is a common contaminant of groundwater found throughout the United States and the world. A survey of groundwater samples collected between 1990 and 1998 from municipal, irrigation, domestic, and monitoring wells in Kansas showed that 50% of the samples had nitrate-nitrogen (nitrate in this paper) concentrations between 2 and 10 mg/L (Townsend and Young, 2000; Townsend et al., 2001). A greater than 2 mg/L nitrate concentration in groundwater indicates possible anthropogenic sources (Mueller and Helsel, 1996). The National Primary Drinking Water Standard for nitrate is 10 mg/L (U.S. EPA, 2002).

Agriculture is the predominant industry in Kansas. Irrigated agriculture is the primary consumer of water and a source of agricultural chemicals, including nitrogen fertilizers (Figure 1). Potential non-point sources of nitrate-contaminated groundwater include soil nitrogen, fertilizer, and animal waste. Point sources include leaky septic systems, spills or leaks, container disposal sites, and animal waste storage areas.



Figure 1. Nitrogen fertilizer sold and cumulative irrigation water rights issued in Kansas, 1945 to 2001. Data are from Kansas Department of Agriculture (2002) and Wilson (1998).

Identifying sources of nitrate in groundwater is an important step toward correcting the problem. The nitrogen-15 abundance method has been used for more than 30 years to identify both point and non-point sources of nitrate. Work by Kreitler (1975, 1979), Kreitler and Jones (1975), Shearer et al. (1978), Kohl et al. (1971), Heaton (1986), Mariotti et al. (1988), Korom (1992), and Kendall (1998) has contributed to the development and use of the method. Examples of a few studies that have illustrated the usefulness of the method include Gormly and Spalding (1979) in Nebraska, Mariotti et al. (1988) in France, and Townsend et al. (1994) in Kansas.

OBJECTIVES

The purpose of this paper is to provide background on the nitrogen-15 natural abundance method, and ancillary information that complements the method and enhances the accuracy of source identification. Advantages and disadvantages of the method will be illustrated in two case studies in Kansas: one in an area of permeable sand overlying a shallow aquifer, and one in an area where silty clay loam and loess overlie a shallow alluvial aquifer.

METHODS

Procedures that aid in determining the source of nitrate in groundwater include site visits and evaluation of possible point sources near wells. Photographs; historical land-use information; crop histories; fertilizer application rates; changes in irrigation practices; and locations of old farmsteads, latrines, septic systems, barnyards, feedlots, manure storage sites; and disposal sites for agrichemical containers are a few

of the site characteristics that should be examined. Information on soil type, geology, depth to groundwater, groundwater flow direction, historic water-quality data, and location of surface-water streams or lakes in the area should be acquired. Much of this information is available from federal agencies such as the National Resource Conservation Service (USDA, 2002) and USGS (2002), or state agencies such as the Kansas Geological Survey (KGS, 2002).

In addition to evaluating nitrogen-15 (^{15}N) data, complete water-quality analyses are a great asset in nitrate source identification. The complete analyses should include major cations and anions, iron, manganese, and ammonium. Specific conductance, temperature, pH, and dissolved oxygen measurements should be collected in the field if at all possible. Other isotope analyses that can assist are oxygen-18 and deuterium of the water and oxygen-18 on the nitrate itself (Kendall, 1998). The additional isotopes are useful for delineating a possible specific source when there are several source possibilities.

NITROGEN-15 ISOTOPE METHOD

Natural abundance, nitrogen isotope analysis is a frequently used method to assist in determining sources of nitrogen in groundwater. The isotope analysis involves establishing the ratio of nitrogen-15 (^{15}N) to nitrogen-14 (^{14}N) in nitrate in the sample of interest compared to the ratio observed in the standard, atmospheric nitrogen (air). Comparison of these ratios indicates 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 ^{15}N with respect to a standard.

Isotopic values are reported as $\delta^{15}\text{N}$ (delta nitrogen-15) in units of per mil (‰) (Hoefs, 2001):

$$\delta^{15}\text{N} (\text{‰}) = \left(\frac{\left(\frac{^{15}\text{N}}{^{14}\text{N}} \right)_{\text{sample}} - \left(\frac{^{15}\text{N}}{^{14}\text{N}} \right)_{\text{standard}}}{\left(\frac{^{15}\text{N}}{^{14}\text{N}} \right)_{\text{standard}}} \right) \times 1000 \quad (1)$$

Figure 2 illustrates the range of groundwater $\delta^{15}\text{N}$ values observed for various sources of nitrogen and enrichment processes (Heaton, 1986). Nitrate from commercial fertilizer sources has $\delta^{15}\text{N}$ values of -2 to +8‰, from soil nitrogen a range of +5 to +7‰, and from animal waste generally greater than +10‰ (Kreitler, 1975; Heaton, 1986; Herbel and Spalding, 1993).

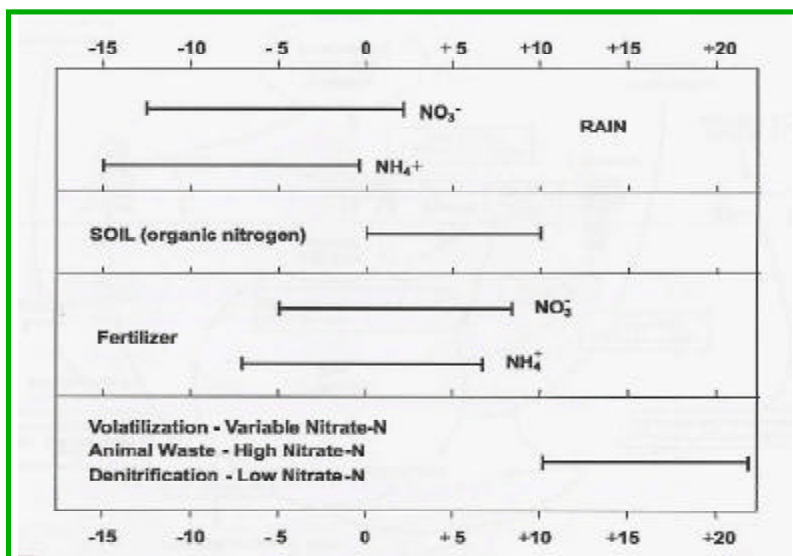


Figure 2. Range of $\delta^{15}\text{N}$ values associated with identified sources of groundwater nitrate and enrichment process. Data are from a previous compilation (Heaton, 1986) and studies in Kansas (Townsend et al., 1994; Townsend, 2001) and Nebraska (Gormley and Spalding, 1979; Herbel and Spalding, 1993; Macko and Ostrom, 1994).

CHEMICAL REACTIONS AFFECTING NITROGEN-15 SIGNATURE

Chemical reactions that can alter the $\delta^{15}\text{N}$ signature include nitrification, denitrification, and volatilization. Nitrification and denitrification are both biologically mediated. Requirements for these reactions generally include the presence of the appropriate bacteria and a source to provide fuel for the bacteria to break the nitrogen bonds. Kendall (1998) presents the reactions for these processes.

Figure 3 illustrates the effects of processes in the nitrogen cycle on the resulting $\delta^{15}\text{N}$ values. Generally, biological activities use ^{14}N preferentially, resulting in an increased $\delta^{15}\text{N}$ value in the remaining nitrogen. Legumes generally have very light initial $\delta^{15}\text{N}$ signatures (-2 to +2‰), because the $\delta^{15}\text{N}$ is close to zero (as in air) and legumes use atmospheric nitrogen with little isotope fractionation (Kendall, 1998). Legume sources generally produce low nitrate concentrations because the nitrogen is tied up in an organic form and the plant matter needs to degrade before the nitrogen is released.

Fertilizer sources have a wide range of values (see Figure 2) because of the variety of source materials used to create the fertilizers. Two examples are anhydrous ammonia manufactured from air, natural gas, and steam, and urea-based mixtures. Groundwater impacted by fertilizer frequently has measurable nitrate (generally greater than 2 mg/L in Kansas). Ammonium-based fertilizers can be converted to nitrate by the bacterially mediated process of nitrification (Kendall, 1998). This reaction preferentially uses ^{14}N , resulting in an increase of ^{15}N in the remaining nitrogen. Another mechanism for increased ^{15}N values is

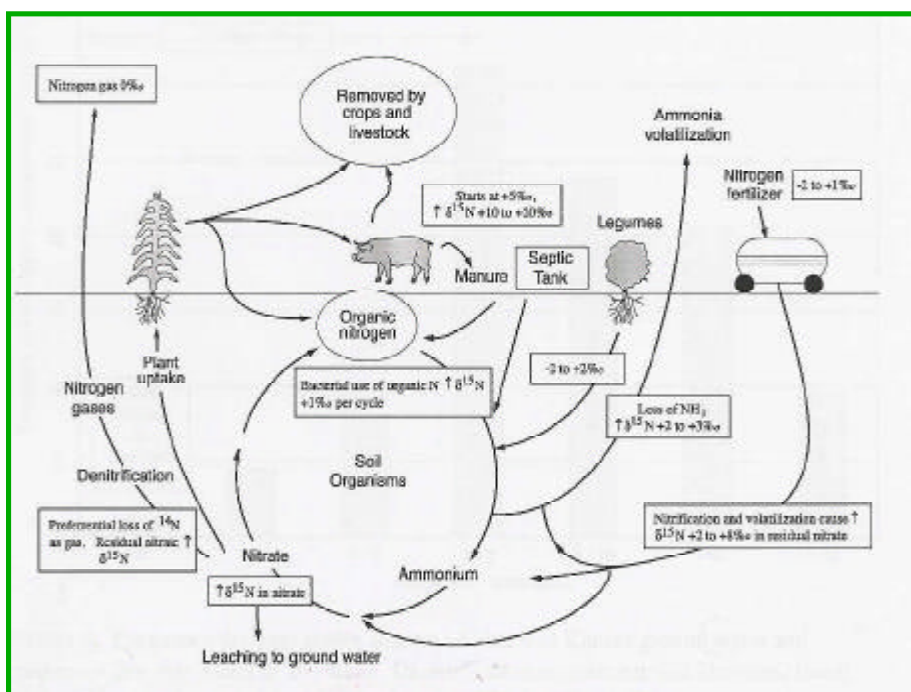


Figure 3. Nitrogen cycle with nitrogen-15 enrichment processes superimposed. Most biological processes preferentially use ^{14}N resulting in increased residual ^{15}N in the remaining nitrogen. Values given in boxes indicate starting values or amount of enrichment due to volatilization, nitrification, or denitrification processes.

volatilization of ammonia when ammonium-based fertilizers such as manure or anhydrous-ammonia are surface applied (especially to calcareous soils). The resulting $\delta^{15}\text{N}$ values are frequently enriched to the +2 to +8 ‰ range.

Other nitrogen sources such as human septic waste or animal waste (pig in Figure 3) have starting $\delta^{15}\text{N}$ values around +5 ‰ (Kreitler, 1975). Because animal waste has a high ammonium-N component, the volatilization of ammonia gas causes the loss of ^{14}N with a resulting enrichment of ^{15}N in the remaining nitrogen, which is converted to nitrate. Consequently, the $\delta^{15}\text{N}$ of the nitrate is +10 ‰ or more.

Volatilization also can occur in soils and rocks with carbonate zones. Dissolution of soil 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 in ^{15}N . This process most frequently occurs when fertilizer or manure are applied to calcareous soils. In addition, this process can occur at depths where the soil pH exceeds 8 (Herbel and Spalding, 1993).

Another process that can result in an enriched $\delta^{15}\text{N}$ 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

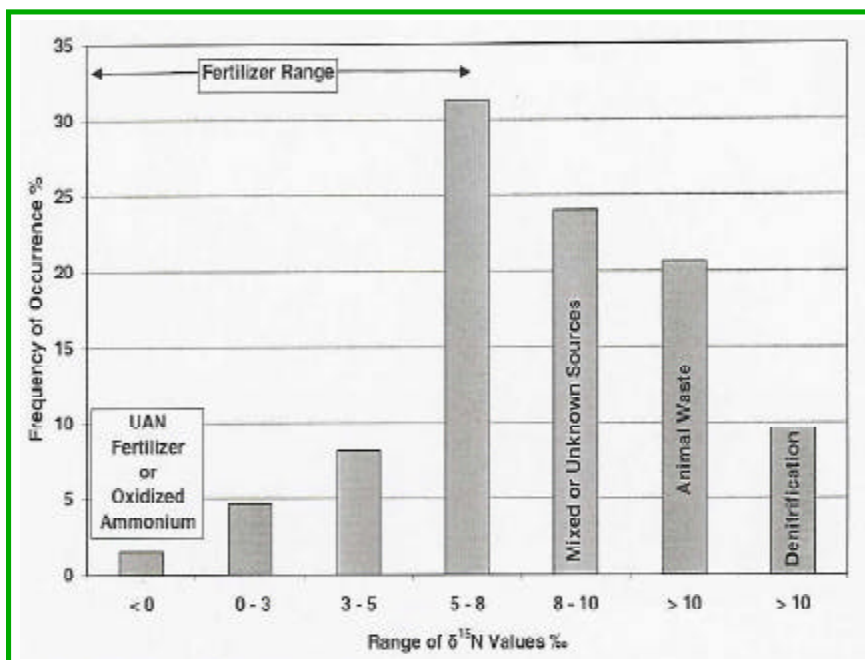


Figure 4. Frequency diagram shows sources of nitrate in Kansas groundwater and processes that may affect $\delta^{15}\text{N}$ values. Denitrification enrichment was identified based on low nitrate values, enriched $\delta^{15}\text{N}$ values ($> +10\text{‰}$), and reducing water chemistry. Data are from Young (1992), Dealey, (1995), KDHE (1996), and Townsend (2002 unpublished data).

utilized resulting in an enriched $\delta^{15}\text{N}$ in the remaining nitrate. Indicators of possible denitrification are low nitrate values (commonly $< 1 \text{ mg/L}$) (Korom, 1992) and enriched $\delta^{15}\text{N}$ values.

NITROGEN-15 IN KANSAS GROUNDWATER

The nitrogen-15 natural abundance isotope method (^{15}N) has been used for the study of contaminated groundwater in Kansas for at least 10 years. The method has been used primarily to assist various cities, counties, and agencies in identification of sources of high nitrate concentration found in the various aquifers in Kansas.

The method has been reasonably successful in terms of assisting groups that require information to protect municipal and regional water supplies. The method has also been used to evaluate areas where increasing nitrate trends were observed over a period of time.

Figure 4 illustrates the range of $\delta^{15}\text{N}$ values found during the many site studies done in Kansas. The majority of samples (45%) fall into the fertilizer range. Animal waste sources were identified in 21% of the samples. About 24% of the samples had unidentifiable mixed sources, and denitrification enrichment affected 10% of the samples. The majority of samples identified are from non-point sources such as fertilizer or manure use in fields.

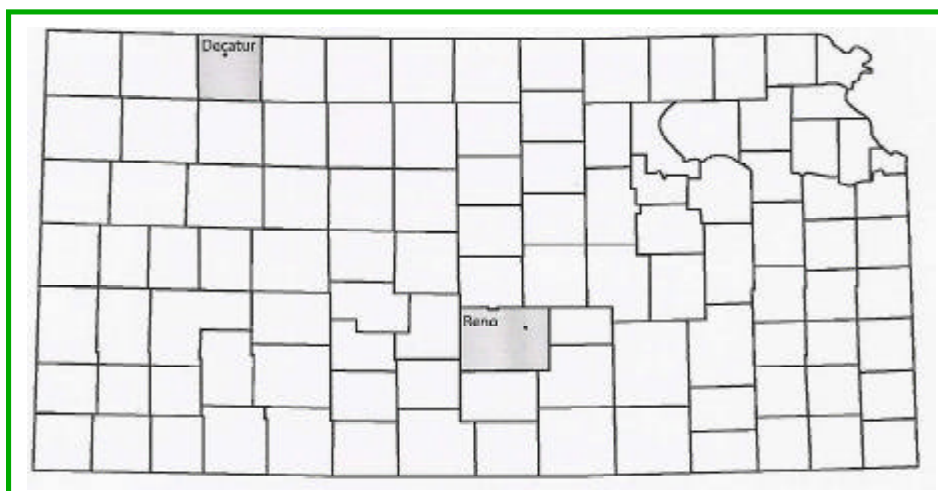


Figure 5. Location of two study sites in Kansas. Reno County is the site of a hog facility in south-central Kansas. The city of Oberlin, Kan., is located in Decatur County in northwestern Kansas.

Classification of the data used in Figure 4 is based on the $\delta^{15}\text{N}$ and nitrate values, site descriptions and land use evaluations for crop type, fertilizer use, soil types, and geology of the area. General water chemistry is evaluated to determine if the ground water has reducing water chemistry, or unusual bicarbonate or pH values that might be related to denitrification processes.

The ^{15}N method is most successful where the unsaturated zone and aquifer are permeable, such as sandy soils and sand and gravel aquifers. The method works best in these types of situations because of rapid recharge of water to the aquifer with limited time for enrichment processes to occur from bacteria or from chemical enrichment processes, which are enhanced by long travel time and exposure to soils of variable permeability or chemistry (such as silt loams, loess, clay, or caliche layers).

Two case studies will be presented in this paper: one from Reno County and one from Decatur County (Figure 5). These two counties are of contrasting geology and general land use. The site in Reno County is a hog facility surrounded by dry land and irrigated farming. The municipal wells in Decatur County are surrounded by a variety of land uses including dry land and irrigated farming, calf-feeder pens, sewage-treatment areas, a golf course, and small industry.

Reno County Hog Facility

The hog facility in Reno County is sited in an area where sandy soil and a thin unsaturated zone overlie the sand and gravel Quaternary High Plains Aquifer. Depth to groundwater is 3.5 m (10 ft), and depth to bedrock is approximately 10.6 m (35 ft; Bayne, 1956). Figure 6 shows the location of the swine lagoon, the

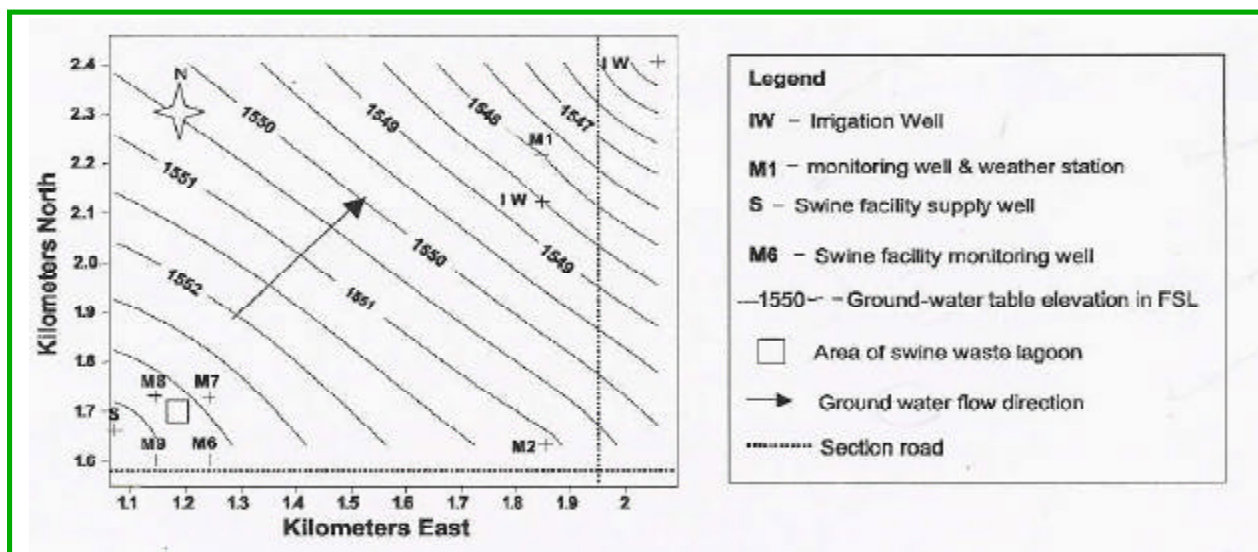


Figure 6. Location of swine facility, supply and monitoring wells, and irrigation wells near the site. Groundwater flow direction is to the northeast.

monitoring and facility supply wells, site irrigation well, and adjacent irrigation well. Also shown are ground water table contours in feet above sea level.

The lagoon is approximately 9000 m² (96,000 ft²) in surface area by 1.2 m (4 ft) deep with a 0.6 m (2 ft) thick bentonite liner (Townsend, 2000). Measured leakage from the lagoon is 0.0794 cm/day (0.03125 in./day; Ham et al., 2000) or 7.1 m³/day over the area of the lagoon (Townsend, 2001). Figure 7 shows the precipitation for the period of study (approximately 76 cm/yr; 30 in./yr) and the rapid response of the shallow water table because of the very permeable unsaturated zone.

The vertical cross-sectional area of the sand and gravel aquifer in the direction of groundwater flow under the lagoon is approximately 1180 m² (12,700 ft²). The estimated hydraulic conductivity value ranges from 6.3 m/day (20.8 ft/day; Bayne, 1956) to 7.9 m/day (26 ft/day; Ham et al., 2000). The hydraulic gradient is estimated at 2.4 m/km (12.6 ft/mi; Kansas Groundwater Management District GMD 2 staff, personal communication, 2000) to the northeast. Flow through the aquifer under the area of the lagoon is estimated at 17.8 m³/day (627 ft³/day).

Water Chemistry

Regionally, groundwater is calcium-bicarbonate-type water with low chloride concentrations (generally less than 15 mg/L) and high nitrate concentrations (generally greater than 10 mg/L). The chemistry of the supply and monitoring wells upgradient of the lagoon (Figure 6, wells 6, 8, and 9 and supply well) all show high nitrate values (mean of 18 mg/L) but low chloride (mean value of 3 mg/L). Well 7, downgradient

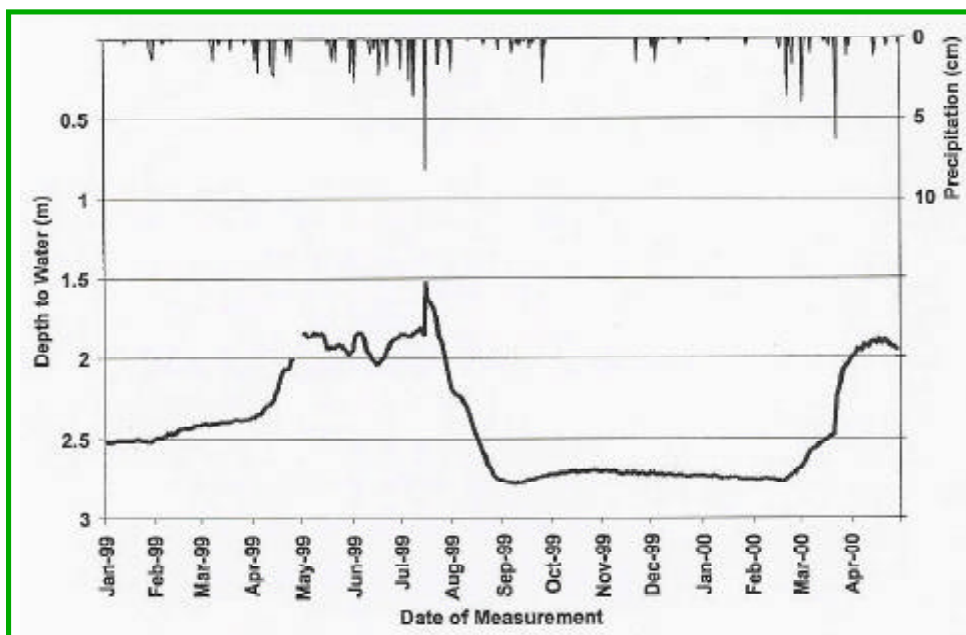


Figure 7. Groundwater table shows rapid response to precipitation events (Townsend, 2000).

of the lagoon (Figure 6), has a nitrate concentration of 4.6 mg/L and a chloride value 159 mg/L. The lagoon has an ammonium-N value of 1484 mg/L and chloride value of 547 mg/L.

Chloride as a Tracer

Chloride is a conservative tracer, which means the concentrations are generally not impacted by biological or chemical processes. In addition, it has been observed that movement of negative ions such as chloride through clay liners can occur, whereas positive ions such as ammonium will be retained in the clays due to adsorption onto the clays (Drever, 1982).

Evaluation of chloride concentration for the regional groundwater showed a mean value of 3 mg/L. The lagoon had a measured chloride of 547 mg/L and well 7 had 159 mg/L. Because of the low regional chloride value, it was assumed that the source of the well 7 chloride was from the lagoon.

The dilution model of Hem (1985) (Equation 2) was used to determine if mixing and dilution were the sole cause of the observed chloride and nitrate values in well 7. The dilution model assumes there is a constant solute input from upgradient (C_1) at a constant rate (Q_1), and the observed solute value downgradient (C_3) is due to dilution by another source of water with a second input (C_2) at a constant rate (Q_2).

$$\frac{C_1 Q_1 + C_2 Q_2}{Q_1 + Q_2} = C_3 \quad (2)$$

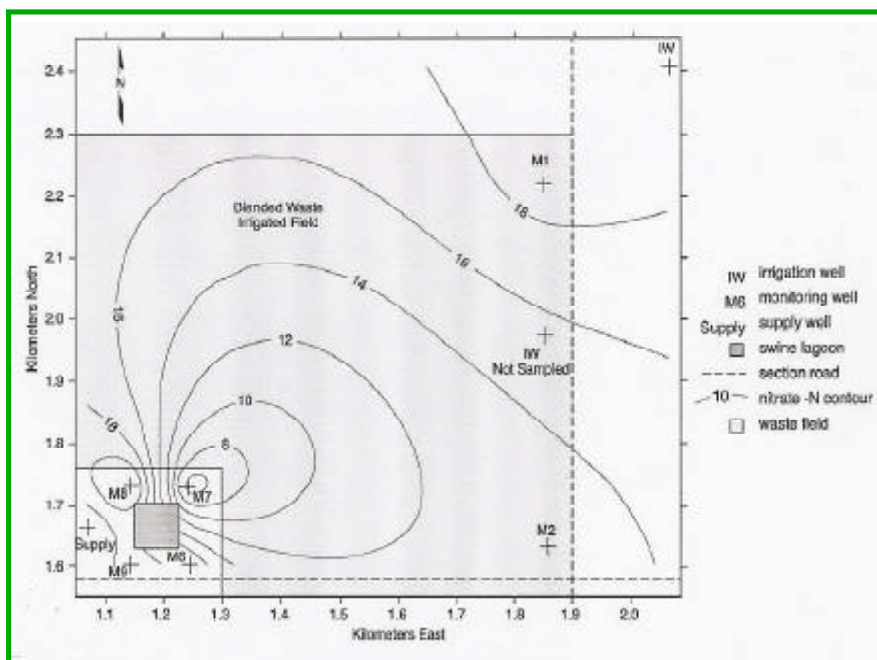


Figure 8. Contour map of nitrate values in the study area. Gray square is the lagoon. Lagoon waste is blended with regional groundwater and sprayed on field north and east of lagoon area. Note low nitrate value at M7 on northeast corner of site.

Where:

C_1 = Regional groundwater values (mean chloride 3 mg/L and mean nitrate 18 mg/L)

C_2 = Lagoon concentration (chloride 547 mg/L or nitrate 0.28 mg/L)

C_3 = Calculated values in downgradient well 7

Q_1 = Calculated volume of flow through the aquifer ($17.6 \text{ m}^3/\text{day}$) before mixing with lagoon water

Q_2 = Leakage from lagoon ($7.1 \text{ m}^3/\text{day}$)

Using Equation 2, the calculated chloride value at well 7 (C_3) was 158 mg/L, and the actual concentration was 159 mg/L, indicating that dilution of the lagoon water by regional groundwater had occurred.

Using Equation 2 for nitrate, the calculated value was 12.9 mg/L. The observed value was 4.6 mg/L. The difference in these values suggests that dilution is not the sole process associated with the observed nitrate value. This will be discussed further in the next section.

Nitrogen-15 Results at Reno County Site

The nitrogen-15 natural abundance method was used to determine if contamination in the area was from regional non-point sources, point sources, or more specifically, was the swine facility lagoon contributing to high groundwater nitrate.

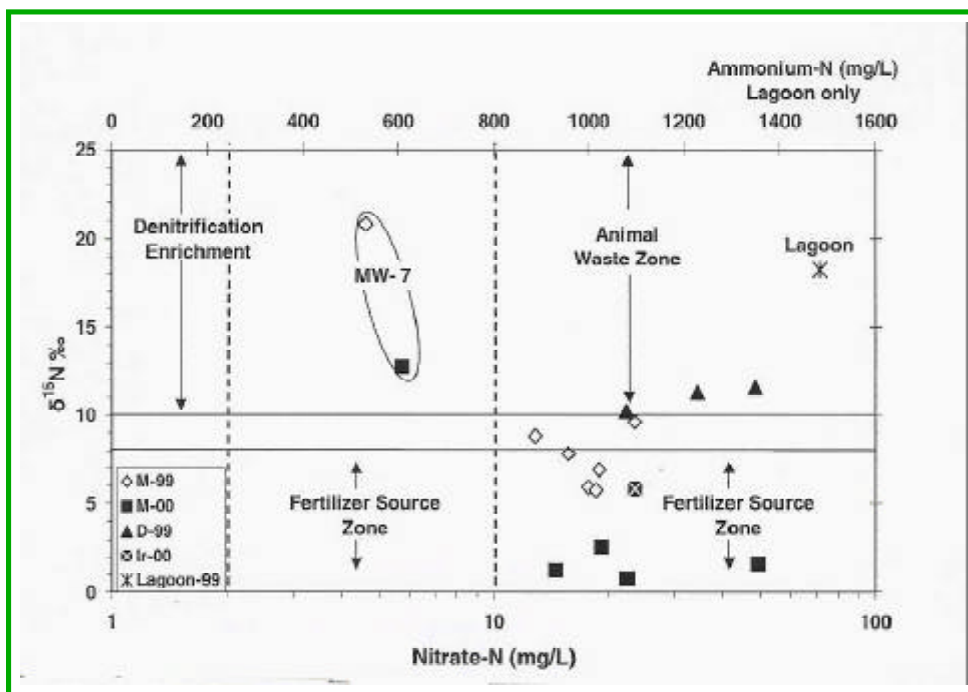


Figure 9. Diagram of $\delta^{15}\text{N}$ versus nitrate concentration with zones indicating probable sources of nitrate, and enrichment processes that can affect $\delta^{15}\text{N}$ values. Fertilizer source zone can be from +0 to +8 ‰. Animal waste zone is generally greater than +10 ‰, with nitrate above 10 mg/L. Denitrification-enrichment zone is frequently above +10 ‰ with nitrate values below 1 mg/L. Ammonium-N value for lagoon sample is on secondary x-axis. M indicates monitoring wells, D for domestic wells, and Ir for irrigation. Years of sampling indicated by 99 (1999) and 00 (2000).

Figure 8 is a contour map of nitrate concentration at the site. The overall high concentrations surrounding the lagoon site suggest a long-term, non-point source of contamination. The area surrounding the swine facility is generally dry land and irrigated agriculture. Rapid recharge of nitrified fertilizer was proposed as the primary source of contamination in the area. Movement of fertilizer from south and west of the lagoon (Figures 6 and 8) results in the high nitrate values observed at the supply and monitoring wells on the west and south sides of the lagoon.

Figure 9 is a diagram of $\delta^{15}\text{N}$ versus nitrate concentration, with zones indicating different probable sources of nitrate and enrichment processes that can affect $\delta^{15}\text{N}$ values. The fertilizer zone extends from <0 ‰ to +8 ‰. The range is large because of the variety of fertilizer source materials, as well the effects of enrichment processes discussed previously.

The animal waste zone is generally defined as greater than +10 ‰ based on the work of Kreitler (1975). In Kansas, sites that have obvious animal waste sources typically have nitrate values greater than 10 mg/L (Townsend et al., 1994; Townsend, 2001). The denitrification zone generally has $\delta^{15}\text{N}$ values greater than +10 ‰, but the nitrate concentrations are less than 1 mg/L and reducing water chemistry is observed.

Figure 9 shows the measured $\delta^{15}\text{N}$ and nitrate values for monitoring wells near the facility, irrigation wells, and three domestic wells located south and north of the site (not shown in Figure 8). Site evaluations indicated multiple possible sources of nitrate.

Likewise, $\delta^{15}\text{N}$ values for the samples are plotted in several zones of Figure 9. The domestic wells fell in the animal waste zone (nitrate > 10 mg/L and $\delta^{15}\text{N}$ values > +10‰). All three domestic samples were affected by one or more of the following: (1) old, shallow dug wells susceptible to surface inflow contamination, (2) calf-feeder pens or unused animal pens, or (3) septic systems. The lagoon sample also occurred in the animal waste zone (+18‰).

All the monitoring sites (except well 7, downgradient of the lagoon) had nitrate greater than 10 mg/L and $\delta^{15}\text{N}$ values between +3 to +8 ‰, indicating a probable fertilizer source for the nitrogen (Figure 9). There was seasonal variation to the $\delta^{15}\text{N}$ and nitrate values. The nitrate values were slightly lower in December than in March, perhaps related to mineralization or denitrification processes.

The samples collected in March 2000 had $\delta^{15}\text{N}$ values of +0.8 to +1.2‰, whereas the 1999 samples (collected in December) had values in the +5 to +9‰, suggesting that processes such as volatilization or denitrification affected the concentration and isotopic signature as groundwater moved from areas with fertilizer sources into the area influenced by the lagoon (Figures 8 and 9).

The fact that the regional water quality of high nitrate (mean 18 mg/L) and low $\delta^{15}\text{N}$ values (mean 3.8‰) was transformed into low nitrate (4.6 mg/L) and an enriched $\delta^{15}\text{N}$ value (+20 ‰) observed at well 7 strongly suggests that denitrification enrichment of the regional groundwater resulted in the decreased nitrate concentration and enriched $\delta^{15}\text{N}$ value at well 7.

City of Oberlin, Kansas

The city of Oberlin is located in Decatur County in northwestern Kansas (Figure 5). The city requested a study of possible sources of nitrate in the area because of historically high nitrate at several city wells and the observation of increasing nitrate at another city well (Townsend, 2001).

The area is generally a mix of irrigated and dry land farming with rangeland and feedlots also present. Figure 10 shows the sampling points and associated land use. Sappa Creek is the main surface drainage through the area. The shallow alluvial ground water system is not connected to deeper regional groundwater in the High Plains Aquifer. Due to groundwater pumping in the area, groundwater no longer supplies water to

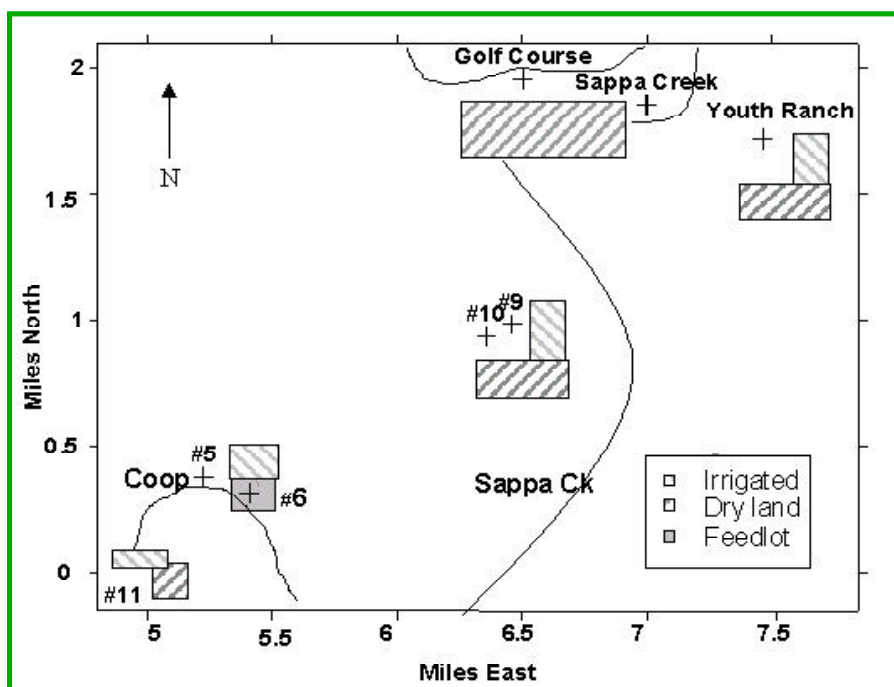


Figure 10. Site map of Oberlin city wells, golf course well, and youth ranch well with associated land use. Sampling points indicated by +. Sappa Creek flows to northeast.

most of Sappa Creek. U.S. Geological Survey streamflow records for Sappa Creek indicate little flow in the creek after the mid-1980s (USGS, 2002).

The geology of the area consists of alluvial sediments, and the overlying Pleistocene loess deposits and the Ogallala Formation in the upland areas. In the vicinity of Oberlin, the wells are sited in the alluvial sediments of Sappa Creek. The wells range in depth from 15 to 24 m (50 to 80 feet) deep.

Soils in the area are generally alluvial in origin and consist of the Bridgeport silt loam or Holdrege silt loam soils. The Bridgeport series consists of deep, well-drained, moderately permeable soils on stream terraces and alluvial fans and is formed in calcareous, silty alluvium [(Hamilton et al., 1989; USDA (NRCS), 2002)]. The Holdrege series consists of deep, well-drained, moderately permeable soils on uplands and is formed in loess.

The soils are predominantly silt-size with variable amounts of sand and clay. Permeability is low to moderate (1.5 to 5 cm/hr, 0.6 to 2 in/hr). Field descriptions of these soils show a strong calcareous component as indicated by moderate to violent effervescence (J. McDowell, 2000, personal communication). This characteristic indicates that the soil chemistry changes with depth and becomes more basic. The implications of this will be discussed in the water chemistry and nitrogen isotope sections.

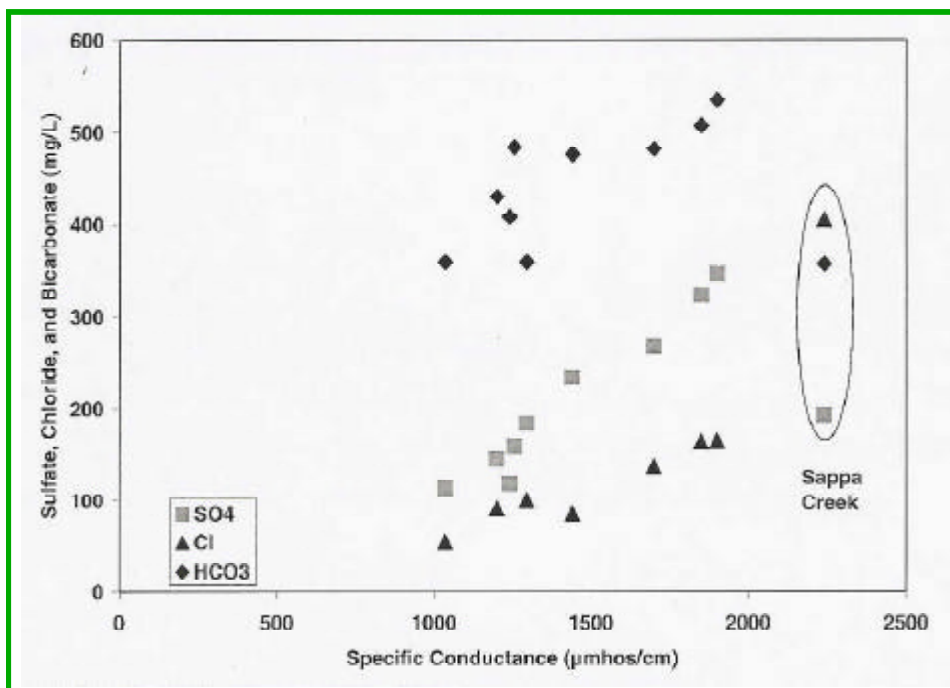


Figure 11. Concentration of sulfate, chloride, and bicarbonate versus specific conductance from sampled wells and Sappa Creek. Concentrations of chloride in Sappa Creek and high specific conductance suggest evapoconcentration of surface water runoff and possible effects of treated sewage effluent discharge to the creek.

Water Chemistry in Oberlin Area

The water in the Oberlin, Kan., area is generally a calcium-bicarbonate-sulfate water type (Townsend, 2001). All the wells have specific conductance readings greater than 833 mmhos/cm (Figure 11). Figure 11 shows the direct relationship of chloride, sulfate, and bicarbonate with increasing specific conductance. This relationship suggests that evaporation and concentration of solutes, as well as dissolution of salts within the unsaturated zone, are responsible for the high concentrations at sites near dry land and irrigated farming (Whittemore, 1995; Townsend, 2001). The higher concentrations of salts make it difficult to use the anions to assist in source identification for nitrate in this area.

The Sappa Creek sample also shows the influence of higher chloride that may be a result of evaporation concentration of surface water runoff and possibly a contribution from the sewage treatment lagoon discharge into the creek (Townsend, 2001).

Nitrogen-15 Values from Oberlin Samples

Figure 12 shows nitrate and ^{15}N values along with zones indicating different probable sources and enrichment processes. In this study the sampled values plotted all over the chart. The discussion below is based on one round of sampling in the area. Another set of samples should be collected and evaluated to verify the $\delta^{15}\text{N}$ values observed in this study.

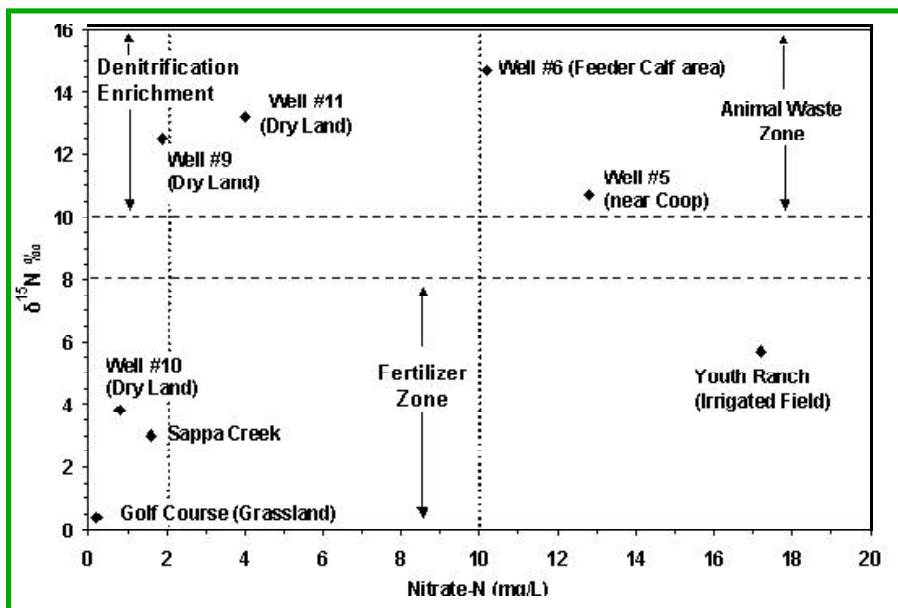


Figure 12. Nitrate and $\delta^{15}\text{N}$ values for samples from Oberlin, Kan. Fertilizer source zone can be from +0 to +8 ‰. Animal waste zone is generally greater than +10 ‰ with nitrate above 10 mg/L. Denitrification enrichment zone is frequently above +10 ‰ with nitrate values below 1 mg/L. Very low $\delta^{15}\text{N}$ values (golf course well) are related to chemical oxidation of ammonium from clays with no resulting enrichment of nitrogen-15.

The general conclusion from this study is that fertilizer is the probable major source of nitrate in the area. However, different processes have affected the $\delta^{15}\text{N}$ signatures for each site. The Youth Ranch well is impacted by irrigation and may retain the fertilizer signature because of permeable soils and a source of reliable recharge from irrigation water that pushes the nitrate through the soil profile relatively quickly. The dry land sites have enriched $\delta^{15}\text{N}$ values that may be related to long travel times. Long travel times could permit volatilization reactions to occur near the observed caliche zones found in all the collected soil cores, thus resulting in low nitrate and enriched $\delta^{15}\text{N}$ values. It is also possible that denitrification reactions are contributing to the enriched $\delta^{15}\text{N}$ values.

Some mixing of water between municipal wells and irrigation wells in the area could be happening. Wells #10 and #11 are used most consistently, so long-term pumping may result in an increased area of influence from the well that might intersect the area from an irrigated field and pull nitrate to the well.

Well #11 is next to a field that was used for alfalfa in the past. Decay of legume nodules over time results in a release of nitrate (R. Raymond, KSU, personal communication, 1999). Slow movement through the unsaturated zone and possible volatilization or denitrification reactions would result in low nitrate but enriched $\delta^{15}\text{N}$.

Wells #5 and #6 are most impacted by probable point sources. Location of well #5 near the local farm cooperative and lack of use of this well suggest that past fertilizer spills provided the source of nitrate and denitrification or volatilization reactions with the caliche zones are responsible for the enrichment. No source of animal waste was found near this well. Well #6 is located in a calf feeder area (with obvious cow pies). Because of the enriched $\delta^{15}\text{N}$ value, high nitrate, and lack of use of the well, it is likely that the animal waste with possible volatilization enrichment in the soil profile has resulted in the enriched $\delta^{15}\text{N}$ value.

The golf course well has the lowest nitrate and $\delta^{15}\text{N}$ values. Location of the well is in a non-irrigated area with native grass cover sited in silt loam soil near an abandoned oxbow portion of the creek. This site had reducing water chemistry as suggested by measurable iron and manganese. The low nitrate value may be due to slow release of ammonium-N from mineralized organic matter. The low $\delta^{15}\text{N}$ value may be due to chemical oxidation of this ammonium in a reducing environment (R. Spalding, UNL, unpublished data, 1995). This would result in low nitrate and low $\delta^{15}\text{N}$ values.

The Oberlin, Kan., site illustrates some of the difficulties in using the ^{15}N natural abundance method. Site-soil stratigraphy adds a level of complication in that volatilization and/or denitrification enrichment can occur because of long travel times in the unsaturated zone, and also the presence of caliche layers can permit chemical changes in the water and result in changes in the nitrogen-15 signature. A mixture of possible point and non-point sources also complicates the picture. The area around each well needed to be evaluated in a fairly detailed manner to try to determine possible sources for contamination. To truly understand the area, it is likely that some pumping tests should be done to try to determine if well interference and possible mixing of municipal and irrigation water is occurring. Although the general source appears to be fertilizer, several more rounds of sampling with nitrogen-15 analyses would probably result in a clearer picture of the overall source(s) of the nitrate in this area.

CONCLUSIONS

Identification of sources of nitrate in groundwater is often possible using the nitrogen-15 natural abundance method. However, biological and chemical processes can alter the $\delta^{15}\text{N}$ signature resulting in erroneous source assignment. Other information, such as complete water-chemical analyses, dissolved oxygen, pH, other isotopic analyses, soil cores at the sites of interest, site evaluation around each sampling point, land use around each well (both past and present), and information on depth to groundwater and flow direction is needed to support the ^{15}N data.

Two case studies in Kansas showed potential benefits and problems of using the nitrogen-15 natural abundance method. The Reno County study illustrated that the method may work well in areas with permeable soils, shallow groundwater table, and water chemistry that has low anion concentrations (chloride, sulfate, bicarbonate) relative to the area of contamination. Use of alternative tracers such as chloride or other isotopes helps to support the nitrate-source identification from the nitrogen-15 data.

The study in Oberlin, Kan., illustrated some of the potential problems in using the nitrogen-15 natural abundance method. The soil was a silty, clay loam with low permeability and observed caliche zones. Low precipitation, a relatively thick unsaturated zone, multiple sources near sampled wells, and enriched anion concentrations due to evapoconcentration of solutes further complicated the source identification. Because of the long travel times and the presence of potentially reactive caliche zones, it was difficult to determine if volatilization or denitrification caused the enriched $\delta^{15}\text{N}$ signatures. Site examination, determination of the historical and recent land use, and obtaining the record of well use in the city assisted in assigning the most probable sources for the observed nitrate.

In summary, the nitrogen-15 natural abundance method is a useful tool for source identification of nitrate in groundwater when it is used in conjunction with other chemical and site-evaluation information. Used only by itself, the method may not provide an accurate identification of a nitrogen source to groundwater. Other factors such as seasonal variation because of land-use practices (such as application of fertilizer in the spring) or irrigation effects (such as evapoconcentration) need to be considered and evaluated in order to maximize the accuracy of the method.

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