Regional Patterns in the Isotopic Composition of Natural and Anthropogenic Nitrate in Groundwater, High Plains, U.S.A.

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Mobilization of natural nitrate (NO_3^-) deposits in the subsoil by irrigation water in arid and semiarid regions has the potential to produce large groundwater NO_3^- concentrations. The use of isotopes to distinguish between natural and anthropogenic NO_3^- sources in these settings could be complicated by the wide range in $\delta^{15}N$ values of natural NO_3^-. An ~10 000 year record of paleorecharge from the regionally extensive High Plains aquifer indicates that $\delta^{15}N$ values for NO_3^- derived from natural sources ranged from 1.3 to 12.3‰ and increased systematically from the northern to the southern High Plains. This collective range in $\delta^{15}N$ values spans the range that might be interpreted as evidence for fertilizer and animal-waste sources of NO_3^-; however, the $\delta^{15}N$ values for NO_3^- in modern recharge (<50 years) under irrigated fields were, for the most part, distinctly different from those of paleorecharge when viewed in the overall regional context. An inverse relation was observed between the $\delta^{15}N[NO_3^-]$ values and the NO_3^-/Cl^- ratios in paleorecharge that is qualitatively consistent with fractionating losses of N increasing from north to south in the High Plains. N and O isotope data for NO_3^- are consistent with both NH_3 volatilization and denitrification, having contributed to fractionating losses of N prior to recharge. The relative importance of different isotope fractionating processes may be influenced by regional climate patterns as well as by local variation in soils, vegetation, topography, and moisture conditions.

Introduction

Nitrate (NO_3^-) is one of the most common groundwater contaminants in the world and its presence in the environment at elevated concentrations poses well-known human-health and ecological risks (*1, 2*). Identifying sources of NO_3^- in groundwater is fundamental to developing effective management plans intended to reduce nitrogen (N) inputs to the environment. Measurements of $^{15}N/^{14}N$ ratios are widely used to infer sources of NO_3^- in groundwater, such as fertilizer, soil, and manure (*3–6*).

Fertilizer and manure sources of NO_3^- commonly can be distinguished from each other on the basis of their $\delta^{15}N$ values. Distinguishing between fertilizer and natural (soil or geologic) sources of NO_3^-, or between natural and manure sources, is more complicated because of the potentially wide

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range in $\delta^{15}N$ values of NO_3^- derived from natural N. Values of $\delta^{15}N$ for soil and groundwater NO_3^- derived from natural sources range from at least −5 to +15‰ or higher (*4, 7–10*) and extend well into the range of values considered to be characteristic of fertilizer and manure N. In general, concentrations of natural NO_3^- in groundwater are less than about 140 μM (*11*), which is much smaller than the United States drinking-water standard of 714 μM (10 mg/L as N), but concentrations as large as 1500 to 7000 μM have been noted in some arid and semiarid regions (*7, 12*). A further complicating factor is the presence of large natural NO_3^- deposits in the soil and subsoil of some arid and semiarid areas (*13–15*). These NO_3^- deposits can be mobilized by irrigation water, making it difficult to distinguish between anthropogenic and natural NO_3^- sources (*16, 17*).

The regionally extensive High Plains aquifer is located in the western United States. About 30% of the groundwater used for irrigation in the United States is pumped from this aquifer (*18*), thus supporting one of the largest agricultural economies in the country. Large natural NO_3^- deposits in the unsaturated zone are known to be mobilized by irrigation return flows (*16, 19*). In addition, about 10^9 kg of fertilizer N are applied to High Plains cropland on an annual basis (*20*). These conditions could result in uncertainty as to the primary sources of NO_3^- contamination in the aquifer. The purpose of this study was to characterize regional patterns in the isotopic composition of natural and anthropogenic NO_3^- in the High Plains aquifer to make more accurate source assessments of groundwater NO_3^- contamination in this semiarid region.

Experimental Section

Study Area. The unconfined High Plains aquifer underlies an area of about 450 000 km² in parts of eight western States (Figure 1). Grassland became dominant in the High Plains during the Holocene (last 10 000 years) as the climate shifted toward warmer, drier conditions. Today, the High Plains climate is semiarid and supports short- and mixed-grass prairie as well as one of the largest agricultural economies in the United States.

Materials and Methods. In 1999–2004, water samples for chemical and isotopic analyses were collected from 38 nested monitoring wells with 3-m-long screens installed along regional transects in the northern High Plains aquifer of Nebraska (NHP), central High Plains aquifer of Kansas (CHP), and southern High Plains aquifer of Texas (SHP; Figure 1). The wells are located along transects ranging in length from about 90 to 100 km that represent multiple flow paths in the aquifer. Unsaturated-zone thicknesses along the transects ranged from about 2 to 70 m and aquifer thicknesses ranged from about 50 to 230 m. Well water was analyzed for numerous chemical and isotopic parameters including dissolved NO_3^-, Cl^-, and Br^-; dissolved gases (Ne, Ar, O_2, N_2); and multiple isotopes (^3H, $\delta^2H[H_2O]$, $\delta^{18}O[H_2O]$, $\delta^{15}N[NO_3^-]$, $\delta^{18}O[NO_3^-]$, $\delta^{15}N[N_2]$, $\delta^{13}C[DIC]$, and $^{14}C[DIC]$). Parameters and methods for sample collection and analysis are described in McMahon et al. (*21*). For NO_3^-, the N and O isotopic compositions were analyzed using a bacterial reduction method with typical reproducibilities of 0.3 and 0.6‰ (2σ) for $\delta^{15}N$ and $\delta^{18}O$, respectively (*22–24*). Nitrate concentrations were analyzed using a cadmium-reduction method with a detection limit of 4 μM (0.06 mg/L as N) (*25*) and a reproducibility of 6 percent (2σ) based on analyses of replicate samples. Chemical and isotopic data for transect wells analyzed in this paper are listed in the Supporting Information. These transect data are compared with NO_3^- concen-
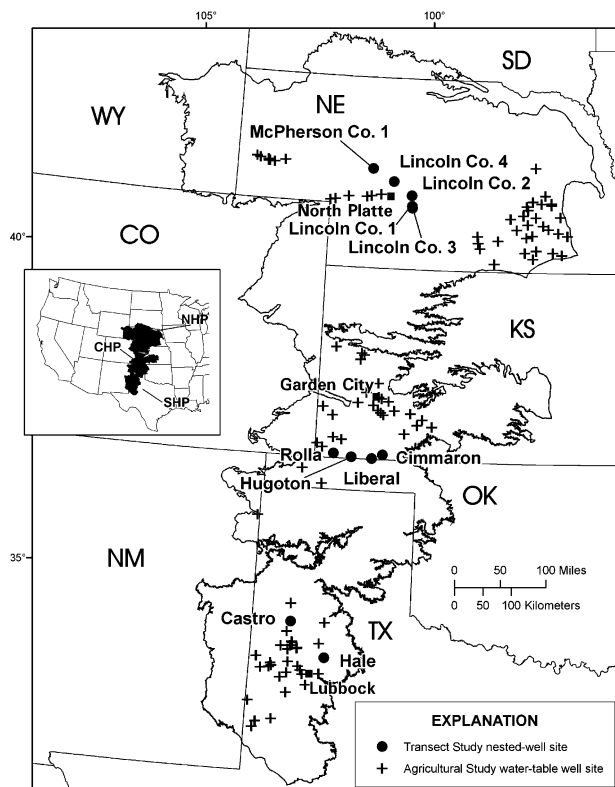
FIGURE 1. Location of the High Plains aquifer in the western United States. NHP, northern High Plains; CHP, central High Plains; SHP, southern High Plains.

FIGURE 2. Initial $\delta^{15}N$ values of NO_3^- in recharge as a function of (A) radiocarbon age and (B) Ne–Ar recharge temperature. Initial $\delta^{15}N$ values were obtained by correcting measured $\delta^{15}N$ values in samples from the transect wells for denitrification effects produced in the aquifer (12, 21, 29). Solid circles, stars, and triangles represent the NHP, CHP, and SHP, respectively. The lines in (A) are LOWESS smooths of the data. Median precision (2σ) estimates for the variables are: radiocarbon age (±1800 ^{14}C years), $\delta^{15}N$ (±0.8‰), and Ne–Ar recharge temperature (±1.0 °C).

trations and $\delta^{15}N[NO_3^-]$ values from 103 monitoring wells with 3- to 6-m-long screens near the water table that were installed for investigations of agricultural effects on groundwater quality in the High Plains (26, 27).

Results and Discussion

Samples from the transect and water-table wells were characterized as modern recharge or paleorecharge, according to their ^3H content. Modern recharge was defined as water containing >0.5 TU of ^3H (<50 years old). Paleorecharge was further characterized by using the ^{14}C content of dissolved inorganic carbon in groundwater to estimate its radiocarbon age. Radiocarbon ages were adjusted for carbon sources and sinks along flow paths by using chemical and isotopic data from the wells, as previously reported for the High Plains aquifer (21, 28).

Regional Isotopic Patterns. Denitrification in the saturated zone could affect the N isotopic composition of the groundwater NO_3^- and must be accounted for to compare the isotopic composition of NO_3^- from different sources. For the transect wells, denitrification in the saturated zone was estimated from analyses of Ne–Ar recharge temperatures and N_2 concentrations (21). Both the initial concentration and the initial isotopic composition of NO_3^- in recharge were reconstructed by combining data for reactant NO_3^- and product excess N_2 gas in denitrified groundwater samples (12, 29). Samples from the agricultural water-table wells contained >60 μM (>2 mg/L) O_2, so they are not expected to have undergone substantial denitrification (21, 29, 30).

The SHP contained an ~6000-year record, and the CHP and NHP each contained ~12 000-year records of NO_3^- concentrations and $\delta^{15}N$ values in paleorecharge. Most of the samples of paleorecharge contained <0.3 TU ^3H and had radiocarbon ages >1000 years; therefore, NO_3^- in those samples was assumed to be derived from natural sources. Initial NO_3^- concentrations in paleorecharge ranged from
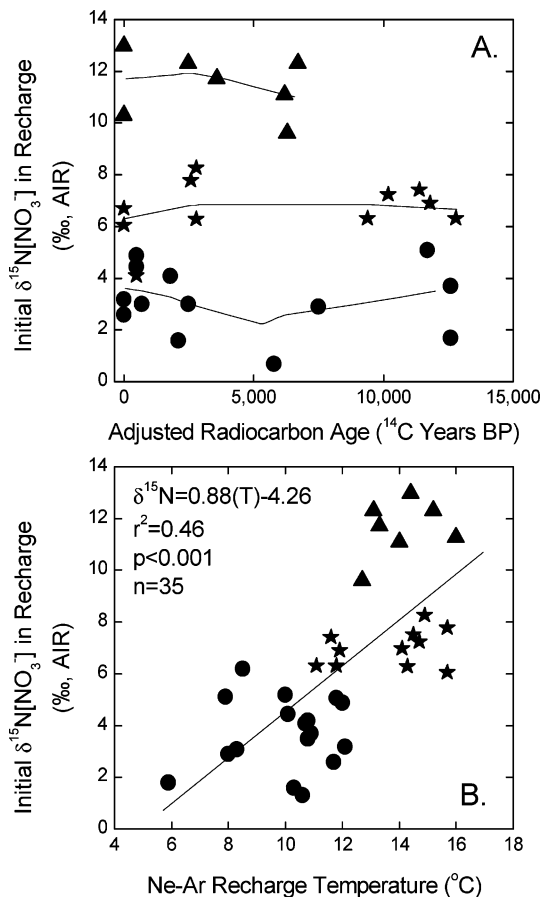
about 30 to 300 μM, with a median of 155 μM and were significantly different only between the CHP and the SHP (at α = 0.05, Tukey–Kramer multiple comparison test). The median precision estimate for initial NO_3^- concentrations is $\pm14\,\mu$M (2σ). The median concentration of excess N_2–N from denitrification, 22 μM, represents about 15% of the median initial NO_3^- concentration, indicating that denitrification effects in groundwater generally were small.

Initial $\delta^{15}N$ values for NO_3^- in paleorecharge ranged from 1.3 to 12.3‰ (Figure 2A). The median precision estimate for initial $\delta^{15}N$ values is ±0.8‰ (2σ). The $\delta^{15}N$ values were significantly different among the three regions and increased systematically from north to south. Median $\delta^{15}N$ values for the NHP, CHP, and SHP are 3.5, 7.0, and 11.7‰, respectively. Regional isotopic gradients in natural NO_3^- such as these have not previously been recognized in groundwater, yet they might have important implications with respect to the identification of anthropogenic NO_3^- in the hydrologic cycle in the High Plains by isotope techniques.

Nitrate concentrations in modern recharge under the irrigated fields ranged from 46 to 7570 μM (Figure 3), with a median of 506 μM. In each region, NO_3^- concentrations in modern recharge were significantly larger than the concentrations in paleorecharge. Substantial amounts of NO_3^-, presumably leached from the soil zone during the Holocene, still reside in the subsoil in parts of the High Plains (15, 16). Mobilization of those subsoil NO_3^- reservoirs by irrigation
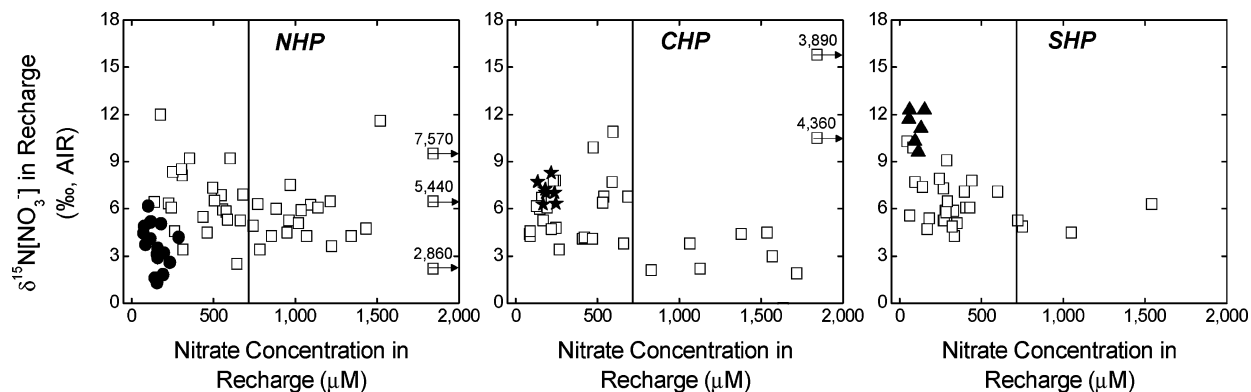
FIGURE 3. Initial NO_3^- concentrations and $\delta^{15}N$ values in paleorecharge (solid symbols) and measured NO_3^- concentrations and $\delta^{15}N$ values in modern recharge under irrigated fields (open squares) in the NHP, CHP, and SHP. Initial concentration and isotope values were obtained by correcting measured values in samples from the transect wells for denitrification effects produced in the aquifer (*12, 21, 29*). Modern recharge (<50 years) samples were not corrected for denitrification effects because they contained dissolved O_2 concentrations >60 μM (>2 mg/L). Vertical lines indicate the U.S. Environmental Protection Agency drinking water standard for NO_3^-—N. Data for modern recharge from Bruce et al. (*26*) and U.S. Geological Survey (*27*).

return flow (*16, 19*), or by changes in climate (*15*), could theoretically produce NO_3^- concentrations at the water table that are larger than any of the concentrations measured under the irrigated fields. Furthermore, the collective range in natural $\delta^{15}N[NO_3^-]$ values in paleorecharge, 1.3 to 12.3‰, spans the range that might be interpreted as evidence for fertilizer and animal-waste sources of NO_3^- in anthropogenically disturbed areas (*3, 5*). However, $\delta^{15}N$ values for NO_3^- in modern recharge under fields that were irrigated for at least 20 years in the CHP and SHP were, for the most part, distinctly different from those of paleorecharge when viewed in the overall regional context (Figure 3). In each of those regions, NO_3^- in modern recharge with the largest concentrations apparently was derived primarily from sources other than natural N. The most likely sources are fertilizer and manure (yielding NO_3^- with relatively low and high $\delta^{15}N$ values, respectively) applied to those fields during their modern irrigation history. The data show that natural subsoil NO_3^- reservoirs, if originally present under those irrigated fields, apparently have not reached the water table yet or may have only a transient effect on groundwater quality when mobilized by infiltrating irrigation water. In the NHP, there was greater overlap in the $\delta^{15}N$ values for NO_3^- in paleorecharge and modern recharge (Figure 3). As a result, mobilization of natural subsoil NO_3^- reservoirs by irrigation return flow at some of the sites cannot be ruled out on the basis of these N isotope data. In each region, new inputs of NO_3^- from anthropogenic sources have tended to homogenize the pre-existing regional isotopic gradient, while increasing isotopic variability locally.

Sources of Natural NO_3^-. The sources of natural NO_3^- in groundwater can be quite variable and include reduced forms of N in rocks and minerals (geologic N) (*7, 31*), direct infiltration of atmospheric deposition (*8*), and atmospheric N (bulk deposition and fixed N_2) that is cycled in the unsaturated zone prior to recharge (*14, 32*). Geologic N in some glacial sediments in the North American Great Plains is known to be an important source of NO_3^- (*7, 16*), but those identified areas are outside the study area.

Geologic N in the saturated zone in the study area is not believed to be a substantial source of NO_3^-, because O_2 consumption in the groundwater can generally be accounted for by pyrite oxidation (*21, 28*), median concentrations of dissolved NH_4^+ plus organic N (<7 μM) were small compared to initial NO_3^- concentrations (155 μM), and the aquifer sediments generally contained very little organic matter (<0.02–0.6 wt % organic C) (*21, 28*). Geologic N in the unsaturated zone in the study area may not be a substantial

source of NO_3^- either on the basis of small KCl-extractable NH_4^+ concentrations (median = 0.4 μg/g as N, $n = 58$) in unsaturated-zone sediments from six High Plains sites (*19, 33*). For comparison, average KCl-extractable NH_4^+ concentrations were 20–145 μg/g as N in some Great Plains subsoil sediments that are known NO_3^- sources (*7, 16*). If these interpretations regarding geologic N are correct, then atmospheric N may be the primary source of natural groundwater NO_3^- in the study area.

Values of $\delta^{18}O[NO_3^-]$ for transect samples that were unaffected by denitrification in the aquifer ranged from about −5 to +5‰ and are equal to or slightly less than the expected values for NO_3^- produced by microbial nitrification in the soil zone, assuming the O was derived from a 2:1 proportion of unfractionated H_2O–O (−11 to −5‰) and atmospheric O_2–O (+23.8‰) in the soil zone (*34, 35*) (Figure 4A). These data indicate that NO_3^- in Holocene recharge did not come directly from NO_3^- in atmospheric deposition, which would have substantially larger $\delta^{18}O$ values (*8, 36*), but instead was formed in the soil from reduced N. Presumably, this reduced N was derived from atmospheric deposition and (or) fixed N_2 that was incorporated into the soil and plant N. This interpretation is consistent with recent work showing that directly deposited atmospheric NO_3^- dominates microbial NO_3^- in the soil zone only in extremely dry environments such as the Atacama Desert (*36*).

N Isotopic Fractionation. The initial $\delta^{15}N$ values for Holocene recharge (1.3–12.3‰) are equal to or higher than expected for atmospheric N deposition or N_2 fixation, which typically have average values around 0 ± 4‰ (*4, 5*). The apparent isotopic enrichment in some of the samples might result from fractionating losses of N from the soil prior to recharge, which could vary in relation to climate, soils, vegetation, topography, seasonal timing of recharge, and other factors. Alternatively, the apparent isotopic enrichment might reflect systematic regional differences in the isotopic composition of atmospheric N inputs, in which case fractionating N losses would be relatively less important. The N/Cl ratios in groundwater and atmospheric deposition have been used to examine NO_3^- production (*14*) and N loss (*32*) in soils. This approach assumes that Cl^- is a conservative indicator of atmospheric deposition; therefore, it only applies to those groundwater samples that did not have deep Cl^- sources and that have atmospheric Br^-/Cl^- ratios.

Median Cl^- concentrations in modern (1984–2004) wet deposition collected at nine National Atmospheric Deposition Program (NADP) sites in or near the NHP, CHP, and SHP are 1.92, 2.74, and 3.12 μM, respectively (NADP sites SD08, WY99,
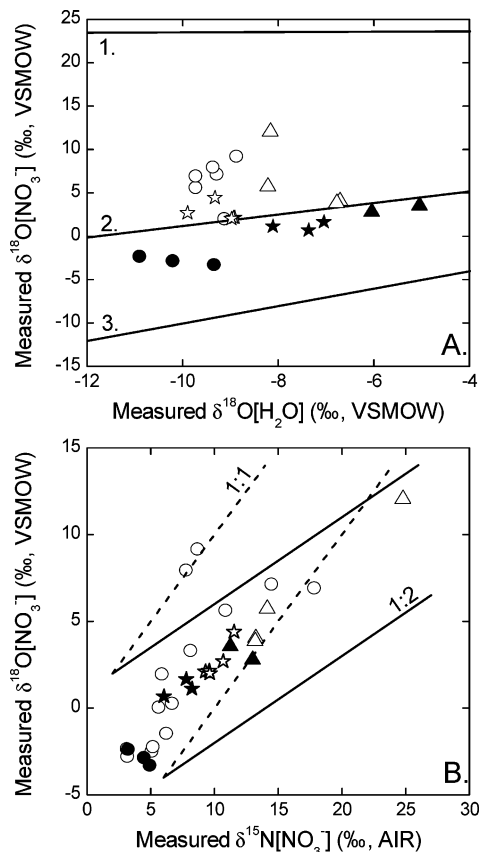
FIGURE 4. Measured $\delta^{18}O$ values of NO_3^- in groundwater as a function of the (A) measured $\delta^{18}O$ values of groundwater and (B) measured $\delta^{15}N$ values of NO_3^- in groundwater. Circles, stars, and triangles represent the NHP, CHP, and SHP, respectively. Solid symbols represent samples unaffected by denitrification in the aquifer, and open symbols represent samples affected by denitrification in the aquifer. (A) Line 1 is defined as $\delta^{18}O[NO_3^-] = \delta^{18}O[O_2-air]$, line 2 is defined as $\delta^{18}O[NO_3^-] = \frac{2}{3}\delta^{18}O[H_2O] + \frac{1}{3}\delta^{18}O[O_2-air]$, and line 3 is defined as $\delta^{18}O[NO_3^-] = \delta^{18}O[H_2O]$. (B) The lines indicate the range of fractionation trends reported for NO_3^- reduction (45, 46).

NE99, CO01, KS32, OK29, TX02, TX04, TX22) (37). Bromide was not measured in the NADP samples, but median Br^-/Cl^- mole ratios in meteoric groundwater containing <425 μM (<15 mg/L) Cl^- in each High Plains region ranged from 0.0039 to 0.0053 μM (27), which correspond to median Br^- concentrations in wet deposition of 0.010 to 0.013 μM. Most of the samples from the transect wells have Br^-/Cl^- ratios similar to those in modern atmospheric deposition (Figure 5A). Three samples containing Cl^- concentrations >50 000 μM plot well below the curves for modern atmospheric deposition, indicating that those samples were enriched in Cl^- from deep saline sources (21, 28).

The $[NO_3^- + NH_4^+]/Cl^-$ mole ratios in atmospheric deposition collected at the nine NADP sites were relatively small and constant during the first five years of sample collection, beginning in 1984, and ranged from about 7 to 15. Subsequently, the ratios at some of the sites increased so that by 2004 they ranged from about 7 to 45. Thus, the ratios during the early time period were used to characterize modern atmospheric deposition with relatively small impacts from anthropogenic N inputs.

Almost all of the NO_3^-/Cl^- mole ratios in paleorecharge are less than the $[NO_3^- + NH_4^+]/Cl^-$ ratios for modern atmospheric deposition (Figure 5B; NH_4^+ concentrations in groundwater were below detection, <5 μM). Furthermore, there is an inverse relation between the $\delta^{15}N[NO_3^-]$ values
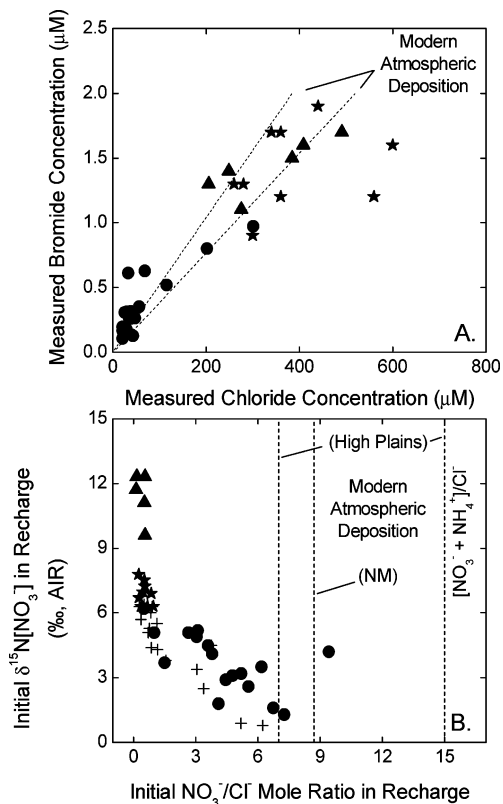

FIGURE 5. (A) Measured Br^- and Cl^- concentrations in samples from the transect wells and (B) initial $\delta^{15}N[NO_3^-]$ values as a function of initial NO_3^-/Cl^- mole ratios in paleorecharge. Solid circles, stars, and triangles represent the NHP, CHP, and SHP, respectively. Crosses represent old groundwater from central New Mexico (32). The dashed lines in (A) represent the range of median Br^-/Cl^- mole ratios in modern wet deposition in the three High Plains regions. The dashed lines in (B) represent the range of median $[NO_3^- + NH_4^+]/Cl^-$ mole ratios in modern wet deposition (High Plains) (37) or average bulk deposition in central New Mexico (NM) (32).

and NO_3^-/Cl^- ratios in paleorecharge that is qualitatively consistent with fractionating losses of N increasing from north to south in the High Plains (Figure 5B). Nitrogen isotopic enrichment with decreasing NO_3^-/Cl^- ratios also was reported for old groundwater from central New Mexico (32) (Figure 5B). In contrast, Edmunds and Gaye (14) reported that NO_3^-/Cl^- ratios in groundwater from an aquifer in Senegal were substantially larger than those for modern atmospheric deposition and concluded that large concentrations of natural NO_3^- in that aquifer resulted from NO_3^- production in the soil zone, possibly related to the growth of leguminous plants. Our comparison of NO_3^-/Cl^- ratios in groundwater to $[NO_3^- + NH_4^+]/Cl^-$ ratios in atmospheric deposition assumes that ratios in wet deposition were similar to those in bulk deposition. Data from New Mexico indicate that $[NO_3^- + NH_4^+]/Cl^-$ ratios in bulk deposition may have been about 20% smaller than the ratios in wet deposition (32). Nevertheless, most of the NO_3^-/Cl^- ratios in High Plains groundwater still would be less than those for atmospheric deposition if they were smaller by 20%. Our analysis also is limited by a lack of information on the temporal variability in atmospheric $[NO_3^- + NH_4^+]/Cl^-$ ratios and the contribution of N_2 fixation to soils in the High Plains during the Holocene.

The N and O isotope data for samples from the transect wells that were unaffected by denitrification in the aquifer (Figure 4, solid symbols) are consistent with both denitrification and NH_3 volatilization, having contributed to fractionating losses of N prior to recharge. Seasonally flooded playas are important recharge areas in the SHP (38), and

saturated playa sediments can promote denitrification (39). Denitrification could have been relatively less important in the NHP recharge areas if well-drained soils in the Nebraska Sand Hills (40), where most of the NHP wells are located, maintained low soil−water contents. Because much of the variation in $\delta^{18}O[NO_3^-]$ can be related to variation in $\delta^{18}O[H_2O]$ during nitrification (Figure 4A, solid symbols), it appears that NH_3 volatilization may have been at least as important as soil denitrification in contributing to fractionating N losses. The possible importance of NH_3 volatilization is consistent with the observation that increases in $\delta^{15}N$ values from north to south were generally accompanied by increased recharge temperatures (Figure 2B) and carbonate content of High Plains soils. Warm temperatures and calcareous soils promote NH_3 volatilization (3). Volatilization may have been relatively less important in the NHP because of lower temperatures (Figure 2B) and slightly acidic soils (40) in the NHP recharge areas. The apparent enrichment factors that would be consistent with the inverse relation between $\delta^{15}N$ and NO_3^-/Cl^- in Figure 5B would be approximately −10 to −2‰. These enrichment factors are smaller than those commonly reported for NH_3 volatilization and denitrification in closed systems (about −30 to −20‰) but within the range of possibilities in heterogeneous open systems (41, 42), such as partially or intermittently saturated soils.

Presumably, fractionating processes in the unsaturated zone were more active in the soil zone than in the subsoil, even though unsaturated zones at the transect sites attained thicknesses of 70 m. Numerical simulations of N_2O production in thick unsaturated zones at nine sites in the High Plains indicated that production in the subsoil was negligible compared to production in the soil zone (top 2 m) (43). Nitrous oxide can be produced by nitrification and denitrification. Furthermore, measurements of unsaturated-zone gases in the High Plains showed that Ar/N_2 ratios in the deep unsaturated zone were similar to atmospheric values (0.012) (33, 44), indicating that subsoil denitrification may not have been substantial.

Although the regional differences in the isotopic composition of NO_3^- in Figure 5B can be rationalized on the basis of climate and soil processes, it is not clear from this limited dataset if the patterns really reflect regional climate gradients or if they also include local effects in each of the three areas. Densmore and Böhlke (10) report variations of $\delta^{15}N$ from about +8 to +15‰ in natural soil NO_3^- from ridges, slopes, and playa bottoms in a small area of the western Mojave Desert, consistent with an overall enrichment of ^{15}N in warm dry environments but indicating variability that may be related locally to topographic variations in moisture or ecosystems. Plummer et al. (32) report variations of $\delta^{15}N$ from about +1 to +8‰ in natural NO_3^- in old groundwater from central New Mexico (Figure 5B), apparently related to varying degrees of N depletion and isotopic fractionation in subregions with different vegetation prior to recharge. In these cases, the highest $\delta^{15}N$ values are in areas more likely to have been wetted more frequently or to have more vegetation. Alternative causes of N isotopic differences also could include varying amounts of N_2 fixation (resulting in larger inputs of N with relatively low $\delta^{15}N$ values) and isotopic fractionation during nitrification (yielding relatively low $\delta^{15}N$ values for NO_3^- where excess NH_4^+ is present).

Although the $\delta^{15}N$ values of modern anthropogenic NO_3^- are highly variable, they do not exhibit the same systematic regional variation as the Holocene NO_3^-. The relative absence of regional variation in the anthropogenic NO_3^- may be related to the much higher leaching fluxes that result from higher N loads and higher recharge rates, especially from irrigation (19), effects from cultivation, or differences in vegetation types and density between natural grasslands and irrigated cropland.

Supporting Information Available

Table SI-1 contains the chemical and isotopic data used in the study. This material is available free of charge via the Internet at http://pubs.acs.org.

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