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 δ$^{15}$N values of natural NO$_3^-$. An ~10 000 year record of paleorecharge from the regionally extensive High Plains aquifer indicates that δ$^{15}$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 δ$^{15}$N values spans the range that might be interpreted as evidence for fertilizer and animal-waste sources of NO$_3^-$; however, the δ$^{15}$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 δ$^{15}$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 in the 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 δ$^{15}$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 range in δ$^{15}$N values of NO$_3^-$ derived from natural N. Values of δ$^{15}$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 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 km$^2$ 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 ($^1$H, $^2$H[HI], $^18$O[HO], $^13$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 δ$^{15}$N and δ$^{18}$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-
concentrations and $\delta^{15}\text{N}[\text{NO}_3^-]$ 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 $^3\text{H}$ content. Modern recharge was defined as water containing $>0.5$ TU of $^3\text{H}$ (<50 years old). Paleorecharge was further characterized by using the $^{14}\text{C}$ 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 $^3\text{H}$ isotopic composition of the groundwater $\text{NO}_3^-$ and must be accounted for to compare the isotopic composition of $\text{NO}_3^-$ from different sources. For the transect wells, denitrification in the saturated zone was estimated from analyses of Ne–Ar recharge temperatures and $\text{N}_2$ concentrations (21). Both the initial concentration and the initial isotopic composition of $\text{NO}_3^-$ in recharge were reconstructed by combining data for reactant $\text{NO}_3^-$ and product excess $\text{N}_2$ gas in denitrified groundwater samples (12, 29). Samples from the agricultural water-table wells contained $>60$ nM ($>2$ mg/L) $\text{O}_2$, 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 $\text{NO}_3^-$ concentrations and $\delta^{15}\text{N}$ values in paleorecharge. Most of the samples of paleorecharge contained $<0.3$ TU of $^3\text{H}$ and had radiocarbon ages $>1000$ years; therefore, $\text{NO}_3^-$ in those samples was assumed to be derived from natural sources. Initial $\text{NO}_3^-$ concentrations in paleorecharge ranged from about 30 to 300 nM, with a median of 155 nM and were significantly different only between the CHP and the SHP (at $\alpha = 0.05$, Tukey–Kramer multiple comparison test). The median precision estimate for initial $\text{NO}_3^-$ concentrations is $\pm 14$ nM (22). The median concentration of excess $\text{N}_2$–$\text{N}$ from denitrification, 22 nM, represents about 15% of the median initial $\text{NO}_3^-$ concentration, indicating that denitrification effects in groundwater generally were small.

Initial $\delta^{15}\text{N}$ values for $\text{NO}_3^-$ in paleorecharge ranged from 3.4 to 12.3‰ (Figure 2A). The median precision estimate for initial $\delta^{15}\text{N}$ values is $\pm 0.8$‰ (23). The $\delta^{15}\text{N}$ values were significantly different among the three regions and increased systematically from north to south. Median $\delta^{15}\text{N}$ values for the NHP, CHP, and SHP are 3.5, 7.0, and 11.7‰, respectively. Regional isotopic gradients in natural $\text{NO}_3^-$ such as these have not previously been recognized in groundwater, yet they might have important implications with respect to the identification of anthropogenic $\text{NO}_3^-$ 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 nM (Figure 3), with a median of 506 nM. In each region, $\text{NO}_3^-$ concentrations in modern recharge were significantly larger than the concentrations in paleorecharge. Substantial amounts of $\text{NO}_3^-$, 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 $\text{NO}_3^-$ reservoirs by irrigation
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%o, 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 have been 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%o 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$_2$O−O (−11 to −5%o) and atmospheric O$_2$−O (+23.8%o) 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 (4, 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%o) are equal to or higher than expected for atmospheric N deposition or N$_2$ fixation, which typically have average values around 0 ± 4%o (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 δ^{18}O values of NO\textsubscript{3} in groundwater as a function of the (A) measured δ^{18}O values of groundwater and (B) measured δ^{18}O values of NO\textsubscript{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 δ^{18}O(NO\textsubscript{3}) = δ^{18}O(O\textsubscript{2}−air), line 2 is defined as δ^{18}O(NO\textsubscript{3}) = δ^{18}O(H\textsubscript{2}O) + δ^{18}O(O\textsubscript{2}−air), and line 3 is defined as δ^{18}O(NO\textsubscript{3}) = δ^{18}O(H\textsubscript{2}O). (B) The lines indicate the range of fractionation trends reported for NO\textsubscript{3} reduction (46, 46).

FIGURE 5. (A) Measured Br\textsuperscript{-} and Cl\textsuperscript{-} concentrations in samples from the transect wells and (B) initial δ^{15}N(NO\textsubscript{3}) values as a function of initial NO\textsubscript{3}/Cl\textsuperscript{-} 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\textsuperscript{-}/Cl\textsuperscript{-} mole ratios in modern wet deposition in the three High Plains regions. The dashed lines in (B) represent the range of median [NO\textsubscript{3}+ NH\textsubscript{4}]/Cl\textsuperscript{-} mole ratios in modern wet deposition (High Plains) (37) or average bulk deposition in central New Mexico (NM) (32).

and NO\textsubscript{3}/Cl\textsuperscript{-} 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\textsubscript{3}/Cl\textsuperscript{-} ratios also was reported for old groundwater from central New Mexico (32) (Figure 5B). In contrast, Edmunds and Gaye (14) reported that NO\textsubscript{3}/Cl\textsuperscript{-} 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\textsubscript{3}− in that aquifer resulted from NO\textsubscript{3}− production in the soil zone, possibly related to the growth of leguminous plants. Our comparison of NO\textsubscript{3}/Cl\textsuperscript{-} ratios and the contribution of N\textsubscript{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\textsubscript{3} volatilization, having contributed to fractionating losses of N prior to recharge. Seasonally flooded playas are important recharge areas in the SHP (38), and

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, 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\textsubscript{3}− + NH\textsubscript{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\textsubscript{3}/Cl− mole ratios in paleorecharge are less than the [NO\textsubscript{3}− + NH\textsubscript{4}]/Cl− ratios for modern atmospheric deposition (Figure 5B: NH\textsubscript{4}+ concentrations in groundwater were below detection, <5 μM). Furthermore, there is an inverse relation between the δ^{15}N[NO\textsubscript{3}−] values and NO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{3}− in that aquifer resulted from NO\textsubscript{3}− production in the soil zone, possibly related to the growth of leguminous plants. Our comparison of NO\textsubscript{3}/Cl− ratios and the contribution of N\textsubscript{2} fixation to soils in the High Plains during the Holocene.
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 δ¹⁵N values from north to south were generally accompanied by increased recharge 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 δ¹⁵N and NO₃⁻/Cl⁻ in Figure 5B would be approximately −10 to −2‰. These enrichment factors are smaller than those commonly reported for NH₃ 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 subsi, even though unsaturated zones at the transect sites attained thicknesses of 70 m. Numerical simulations of N₂O production in thick unsaturated zones at nine sites in the High Plains indicated that production in the subsi 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 N₂O 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 NO₃⁻ in Figure 5B can be rationalized on the basis of climate and soil processes, it is not clear from this limited data set if the patterns really reflect regional climate or if they also include local effects in each of the three areas. Densoke and Bühke (10) report variations of δ¹⁵N from about +8 to +15‰ in natural soil NO₃⁻ from ridges, slopes, and playa bottoms in a small area of the western Mojave Desert, consistent with an overall enrichment of ¹⁵N 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 δ¹⁴N from about +1 to +8‰ in natural NO₃⁻ 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 δ¹⁵N 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 N₂ fixation (resulting in larger inputs of N with relatively low δ¹⁵N values) and isotopic fractionation during nitrification (yielding relatively low δ¹⁵N values for NO₃⁻ where excess NH₄⁺ is present).

Although the δ¹⁴N values of modern anthropogenic NO₃⁻ are highly variable, they do not exhibit the same systematic regional variation as the Holocene NO₃⁻. The relative absence of regional variation in the anthropogenic NO₃⁻ 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.

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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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