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

P. B. McMahon*1 and J. K. Böhlke

Mobilization of natural nitrate (NO$_3^-$) deposits in the subsoil by irrigation water in arid and semi-arid 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 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 $\delta^{15}$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 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 semi-arid 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 semi-arid 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 ($^3$H, $^3$H[HI], $^3$H[HOI], $^3$H[IO$_3$], $^3$H[NO$_3$]), $^13$C[DI], $^13$C[DIC], and $^13$C[DCIC]). 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$_3^-$ concent-
and the initial isotopic composition of NO₃⁻ was further characterized by using the ¹⁴C content of dissolved concentrations and ⁰¹⁵N[NO₃⁻] 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 ¹⁴C 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 NO₃⁻ and must be accounted for to compare the isotopic composition of NO₃⁻ from different sources. For the transect wells, denitrification in the saturated zone was estimated from analyses of Ne−Ar recharge temperatures and N₂ concentrations (21). Both the initial concentration and the initial isotopic composition of NO₃⁻ in recharge were reconstructed by combining data for reactant NO₃⁻ and product excess N₂ gas in denitrified groundwater samples (12, 29). Samples from the agricultural water-table wells contained >60 μM (>2 mg/L) O₂, 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 NO₃⁻ concentrations and ⁰¹⁵N values in paleorecharge. Most of the samples of paleorecharge contained <0.3 TU ³H and had radiocarbon ages >1000 years; therefore, NO₃⁻ in those samples was assumed to be derived from natural sources. Initial NO₃⁻ 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 NO₃⁻ concentrations is ±14 μM (2o). The median concentration of excess N₂−N from denitrification, 22 μM, represents about 15% of the median initial NO₃⁻ concentration, indicating that denitrification effects in groundwater generally were small.

Initial ⁰¹⁵N values for NO₃⁻ in paleorecharge ranged from 1.3 to 12.3‰ (Figure 2A). The median precision estimate for initial ⁰¹⁵N values is ±0.8‰ (2o). The ⁰¹⁵N values were significantly different among the three regions and increased systematically from north to south. Median ⁰¹⁵N values for the NHP, CHP, and SHP are 3.5, 7.0, and 11.7‰, respectively. Regional isotopic gradients in natural NO₃⁻ such as these have not previously been recognized in groundwater, yet they might have important implications with respect to the identification of anthropogenic NO₃⁻ 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, NO₃⁻ concentrations in modern recharge were significantly larger than the concentrations in paleorecharge. Substantial amounts of NO₃⁻, 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 NO₃⁻ 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‰, 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 typically have average values around 0 ‰ (expected for atmospheric N deposition or N$_2$ fixation, which normally have substantially larger $\delta^{15}$N values (8, 16), 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,
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 [NO₃⁻ + NH₄⁺]/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 NO₃⁻/Cl⁻ mole ratios in paleorecharge are less than the [NO₃⁻ + NH₄⁺]/Cl⁻ ratios for modern atmospheric deposition (Figure 5B; NH₄⁺ concentrations in groundwater were below detection, <5 μM). Furthermore, there is an inverse relation between the δ¹⁵N[NO₃⁻] values and NO₃⁻/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 NO₃⁻/Cl⁻ ratios also was reported for old groundwater from central New Mexico (32) (Figure 5B). In contrast, Edmunds and Gaye (14) reported that NO₃⁻/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 NO₃⁻ in that aquifer resulted from NO₃⁻ production in the soil zone, possibly related to the growth of leguminous plants. Our comparison of NO₃⁻/Cl⁻ ratios in groundwater to [NO₃⁻ + NH₄⁺]/Cl⁻ ratios in atmospheric deposition assumes that ratios in wet deposition were similar to those in bulk deposition. Data from New Mexico indicate that [NO₃⁻ + NH₄⁺]/Cl⁻ ratios in bulk deposition may have been about 20% smaller than the ratios in wet deposition (32). Nevertheless, most of the NO₃⁻/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 [NO₃⁻ + NH₄⁺]/Cl⁻ ratios and the contribution of N₂ 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 NH₃ volatilization, having contributed to fractionating losses of N prior to recharge. Seasonally flooded playas are important recharge areas in the SHP (38), and...
saturation of the unsaturated zone were more active in the soil zone than in the subsoil, 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 N₂O 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). 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 to 0.015), 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 dataset if the patterns really reflect regional climate gradients or if they also include local effects in each of the three areas. Denso and Böhle (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 Sl-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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