

SOURCES OF NITRATE IN GROUNDWATER BELOW A MAJOR AGRICULTURAL AREA: THE HIGH PLAINS IN MID-WEST UNITED STATES

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Location:

The High Plains are located in the mid-west United States. The High Plains aquifer is unconfined and underlies eight states: South Dakota, Nebraska, Wyoming, Colorado, Kansas, Oklahoma, New Mexico and Texas. The aquifer spans an area of 450,000 km² and supports “one of the largest agricultural economies in the United States” (Mc Mahon).

Main problem illustrated:

- What is the source and age of nitrate in groundwater?
- What are the main processes affecting the concentration of nitrate?

Summary:

Nitrate is a common contaminant of groundwater. Groundwaters under areas of extensive agricultural practices are particularly prone to nitrate contamination. To address the situation, it is important to determine what the sources of the nitrate are and what processes affect its concentration. Using isotopic techniques, we can determine the age (³H, ¹⁴C) and the recharge temperature (Ne-Ar) of groundwaters, in order to determine the initial N₂ concentration and isotopic signature. This in turn can help to quantify the extent of denitrification in the aquifer system. The isotopic signatures of nitrogen and oxygen in nitrates are useful to distinguish the nitrate sources between fertilizers and manure in modern samples. The samples older than 50 years are assumed to represent the natural sources of nitrates in groundwater (atmospheric). Using oxygen isotopes and chlorine concentrations, we can further determine if nitrification was significant and whether the atmospheric nitrogen was directly deposited in groundwater or if it was recycled in the soil zone before recharge.

Tracers used:

³H, ¹⁴C, [Ne], [Ar], [N₂], δ²H_{H₂O}, δ¹⁸O_{H₂O}, δ¹⁸O_{NO₃}, δ¹⁵N_{NO₃}, δ¹⁵N_{N₂}, δ¹³C_{DIC}

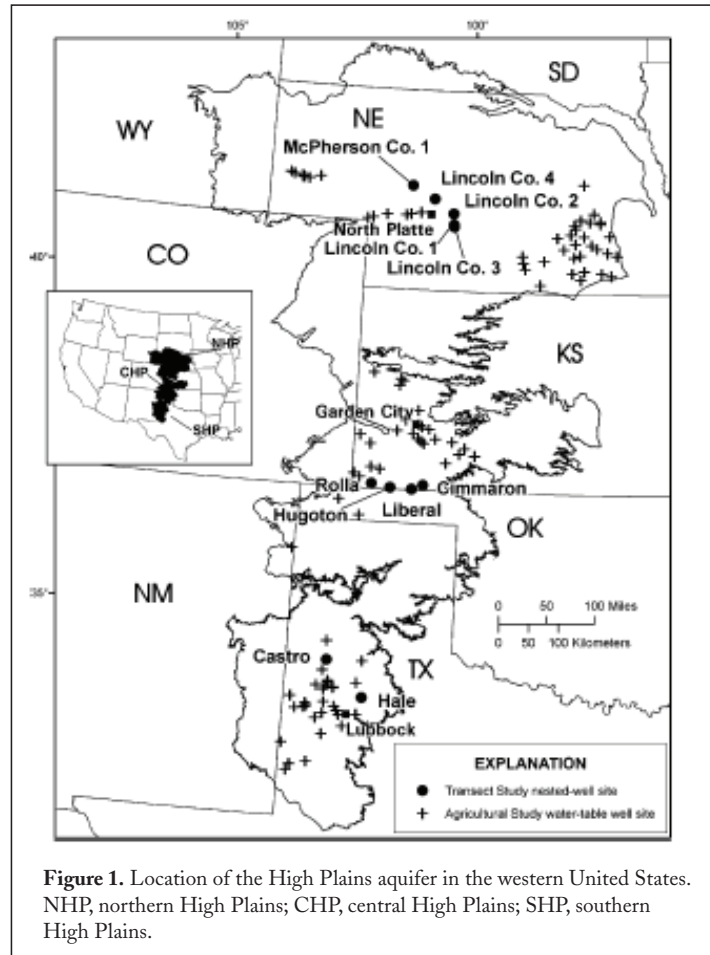


Figure 1. Location of the High Plains aquifer in the western United States. NHP, northern High Plains; CHP, central High Plains; SHP, southern High Plains.

Hydrogeological setting:

The High Plains aquifer contains unconsolidated units of interbedded sand, gravel, silt, and clay deposited by fluvial and aeolian processes. Mainly composed of the Ogallala Formation of Miocene age, the High Plains aquifer is underlain by bedrock that range in age between Tertiary and Permian and overlain by Quaternary-age deposits. Water flows an average of approximately 1 foot per day in response to the hydraulic gradient of 10 to 15 feet per mile. The aquifer is between 50 and 400 feet deep and its thickness is as great as 600 feet. The thickness has been declining at average rates of 0.33 feet per year before 1980, and 0.44 feet per year between 1980 and 1990 due to extensive agricultural development.

People affected, environmental, ecological impacts:

Groundwater accounts for 93% of all the water used in the High Plains, including domestic, agricultural and industrial. Therefore, the livelihood of communities in the High Plains is highly dependent on groundwater. Nitrate is a common contaminant in groundwater. High-nitrate water has been known to cause the blue-baby disease (methemoglobinemia) and can cause eutrophication, killing wildlife in rivers and lakes.

Water sampling and analysis summary:

Water samples were collected from 38 monitoring wells along regional transects of the Northern High Plains (NHP), Central High Plains (CHP) and Southern High Plains (SHP). The water was analyzed for dissolved NO_3 , Cl, and Br, dissolved gases (Ne, Ar, O_2 , N_2), and the following isotopes: ^3H , $\delta^2\text{H}_{\text{H}_2\text{O}}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, $\delta^{18}\text{O}_{\text{NO}_3}$, $\delta^{15}\text{N}_{\text{NO}_3}$, $\delta^{15}\text{N}_{\text{N}_2}$, $\delta^{13}\text{C}_{\text{DIC}}$, and ^{14}C . Nitrate concentrations and isotopes were also measured in areas unaffected by agricultural practices.

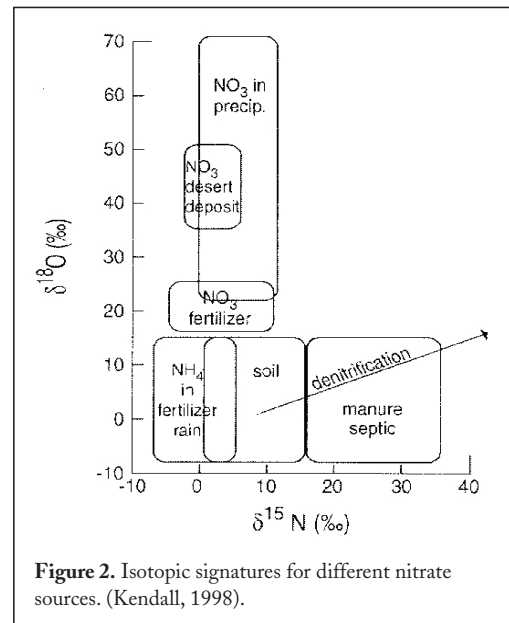
Results of tracer studies:

Based on the distinct isotopic signatures of N in NO_3 , it is easier to distinguish sources of nitrates between fertilizers and animal wastes (Figure 2). The challenge is to distinguish between anthropogenic and natural sources.

Tritium was used to determine which samples represented modern recharge (younger than 50 years) and carbon-14 was used to determine those samples having residence times of thousands of years (paleorecharge). The Ne, Ar, and N_2 concentrations were used to determine the temperature and NO_3 concentrations of paleorecharge.

The nitrate concentrations of paleorecharge ranged between 30 and 300 μM with $\delta^{15}\text{N}$ values between 1.3 and 12.3‰, and were set to be the natural range. The modern recharge samples had significantly higher NO_3 concentrations, from 46 to 7570 μM , indicating that fertilizers and animal wastes represent significant nitrate inputs to the groundwater. Unlike in NHP, there was a significant difference in $\delta^{15}\text{N}_{\text{NO}_3}$ between paleorecharge and modern waters in CHP and SHP groundwater.

The Ne, Ar and O_2 data was used to determine whether denitrification was significant or not. The $\delta^{18}\text{O}_{\text{NO}_3}$ data showed that in samples unaffected by denitrification, the O was produced with 2/3 coming from H_2O and 1/3 from the atmosphere, which is consistent with microbial nitrification. This test showed that microbial nitrification was a significant process.



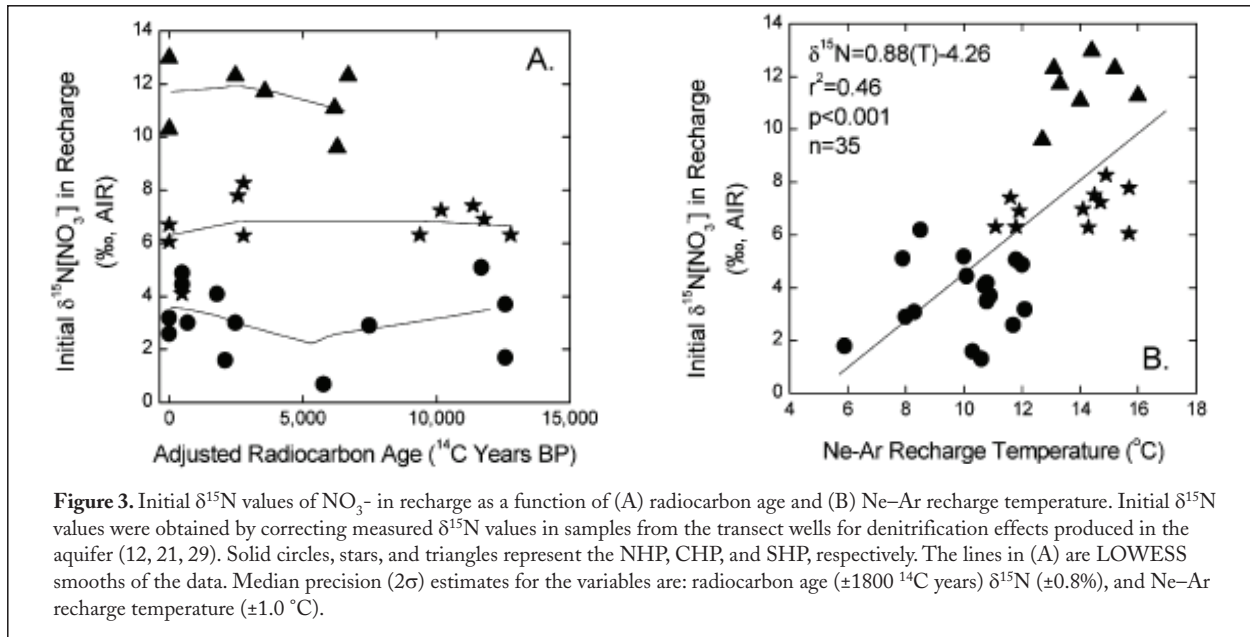


Figure 3. Initial $\delta^{15}\text{N}$ values of NO_3^- in recharge as a function of (A) radiocarbon age and (B) Ne–Ar recharge temperature. Initial $\delta^{15}\text{N}$ values were obtained by correcting measured $\delta^{15}\text{N}$ values in samples from the transect wells for denitrification effects 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) $\delta^{15}\text{N}$ ($\pm 0.8\%$), and Ne–Ar recharge temperature (± 1.0 $^\circ\text{C}$).

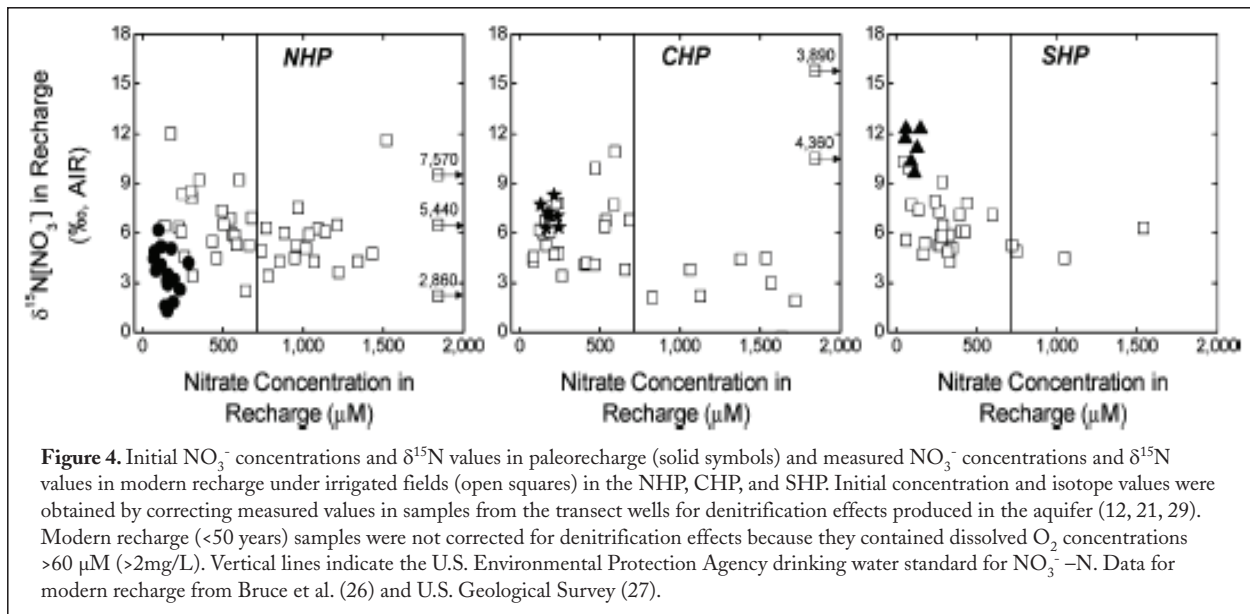
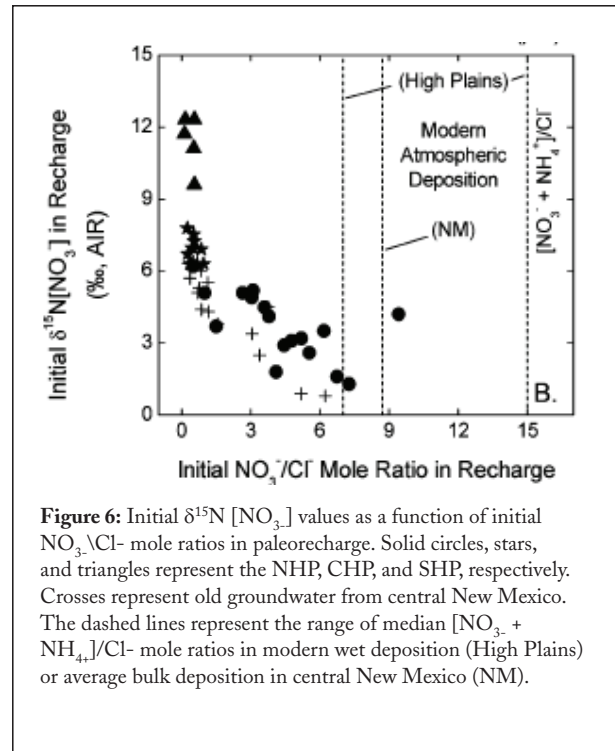
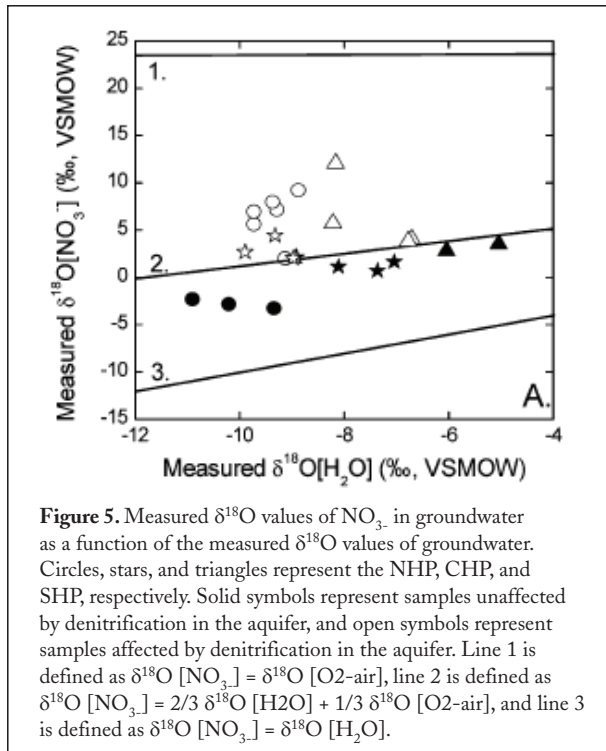


Figure 4. Initial NO_3^- concentrations and $\delta^{15}\text{N}$ values in paleorecharge (solid symbols) and measured NO_3^- concentrations and $\delta^{15}\text{N}$ values in modern recharge under irrigated fields (open squares) in the NHP, CHP, and SHP. Initial concentration and isotope values were 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 ($> 2\text{mg/L}$). 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).

Since chlorine is a conservative tracer, the NO_3^-/Cl ratios are used to determine the proportion of nitrate input from the atmosphere. There is an inverse relation between $\delta^{18}\text{O}_{\text{NO}_3}$ and NO_3^-/Cl ratios, showing increasing fractionating losses of $\delta^{18}\text{O}_{\text{NO}_3}$ from north to south of the High Plains. Fractionating losses can be caused by denitrification or NH_3 volatilization.

Findings and conclusions:

Fertilizers and manures are very important sources of nitrates in modern samples. A temperature gradient was measured for paleorecharge with increasing temperature from the northern to the southern well transects. Increasing fractionating losses of nitrates was observed from north to south, due to denitrification and NH_3 volatilization being more significant in warmer climates. In addition, denitrification could have been less important in NHP due to well-drained soils (low soil-water content). The atmospheric deposition of nitrate to the groundwater was



not direct. Instead nitrate was recycled in the soil zone through bacterial processes before recharge. The similar N isotopic values observed between paleorecharge and modern waters in the NHP groundwater were probably due to mixing with pockets of Holocene nitrates flushed through the unsaturated zone by irrigation flows. These pockets of nitrates have not yet reached the aquifer in CHP and SHP.

Take home message:

High nitrate concentrations measured in the High Plains aquifer are due to agricultural activity. Anthropogenic sources of nitrates are more easily distinguishable than natural sources. To better characterize the natural input in nitrate, it's important to know the climate, soil, vegetation, and seasonal timing of recharge. In addition, the contribution of nitrate from pockets of Holocene nitrates flushed through the vadose zone via irrigation flows should not be neglected.

Credits:

Work done by USGS

Further reading:

- Bruce B. W.; Becker M. F.; Pope L. M.; Gurdak J. J. *Ground-Water Quality Beneath Irrigated Agriculture in the Central High Plains Aquifer, 1999, 2000; Water Resources Investigations Report 03-4219*
- Chang C. C.; Kendall C.; Silva S. R.; Battaglin W. A.; Campbell D. H. *Nitrate stable isotopes: tools for determining nitrate sources among different land uses in the Mississippi River Basin. NRC Research Press Web site. <http://cjas.nrc.ca>. 10 January 2003*
- McMahon P. B.; Bohlke J. K. *Regional Patterns in the Isotopic Composition of Natural and Anthropogenic Nitrate in Groundwater, High Plains, USA. Environmental Science Technology 2006, 40 2965-2970.*