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Radiocarbon Ages, Denitrification, and Paleorecharge Conditions in the Central High Plains Aquifer

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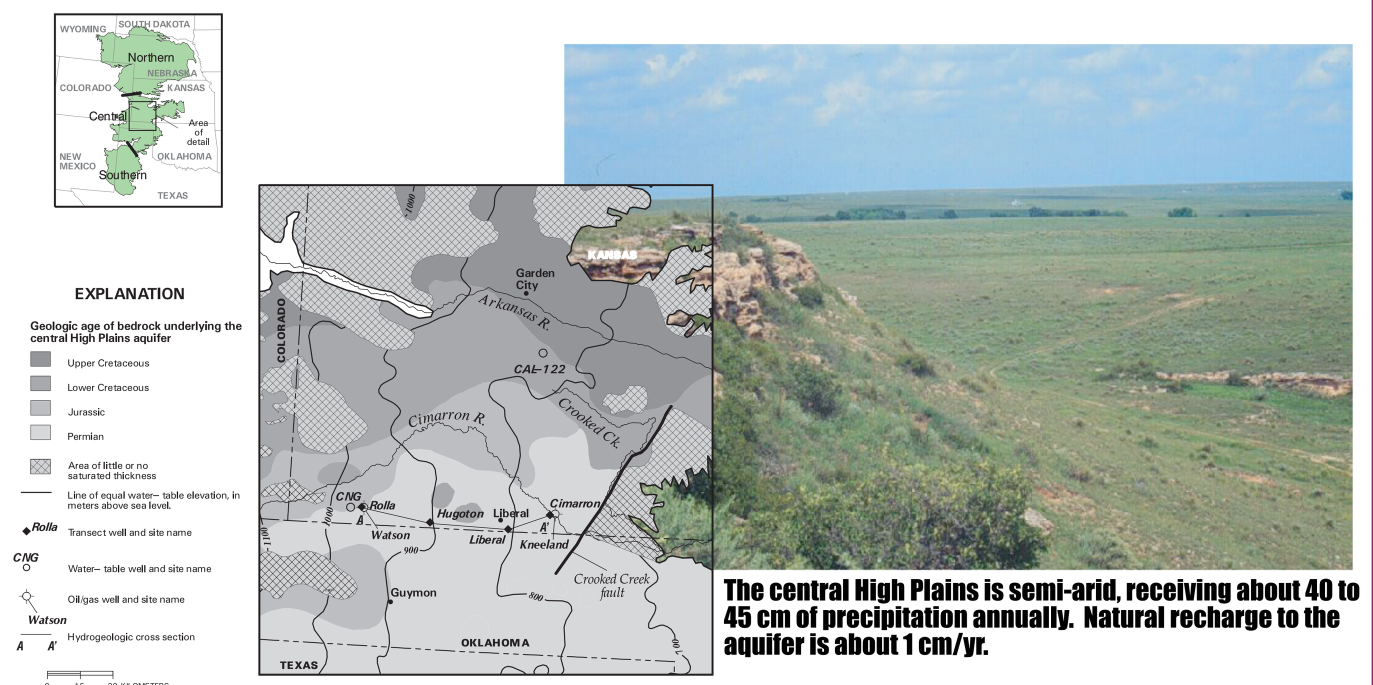
Introduction

The High Plains aquifer underlies an area of about 450,000 km2 in parts of eight western states. The aquifer supplies drinking water to 82 percent of the people who live within the aquifer boundary and about 30 percent of the ground water used for irrigation in the United States.

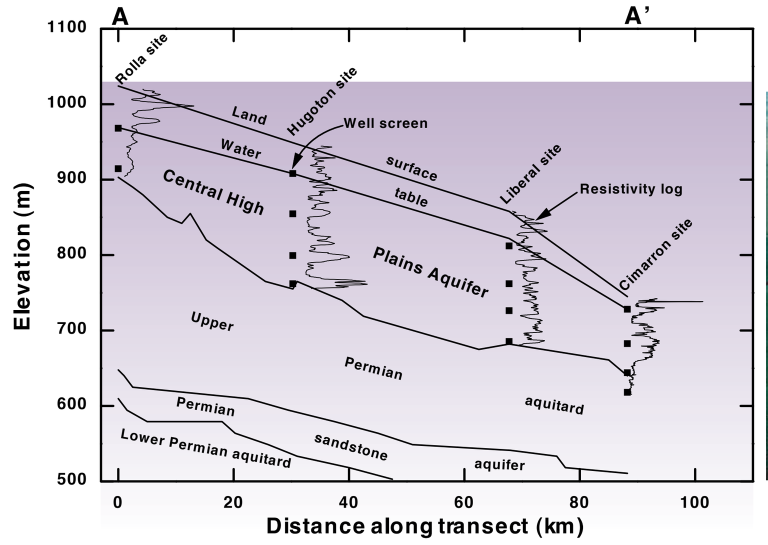
The Ogallala Formation, which is Pliocene in age, is the largest geologic unit in the central High Plains aquifer. The aquifer consists primarily of unconsolidated clay, silt, sand, and gravel with scattered consolidated zones cemented with calcium carbonate. The aquifer is regionally unconfined; however, thick clays of limited aerial extent cause locally confined conditions in the aquifer. Natural recharge to the aquifer occurs at a rate of about 1 cm/yr. The maximum saturated thickness of the aquifer is about 170 m. The aquifer in the study area is underlain by interbedded shale, siltstone, sandstone, dolomite, gypsum, anhydrite, and halite of Permian age.

Nitrate is a primary contaminant in the central High Plains aquifer and its occurrence in the aquifer is of concern because of the aquifer's importance as a drinking water supply. Nitrate concentrations in the aquifer decrease with depth below the water table. However, it is not known whether the decrease is the result of denitrification along flow paths, changes in nitrate concentrations in recharge over time, or both. Different land-use management practices may be required to reduce the impact of nitrate contamination in the aquifer, depending on the answers to these questions.



The central High Plains is semi-arid, receiving about 40 to 45 cm of precipitation annually. Natural recharge to the aquifer is about 1 cm/yr.

The study area is located in the central High Plains aquifer in southwestern Kansas. Multi-level monitoring wells (Rolla, Hugoton, Liberal, and Cimarron transect well sites) are located along the flow path aligned with cross section A-A'.



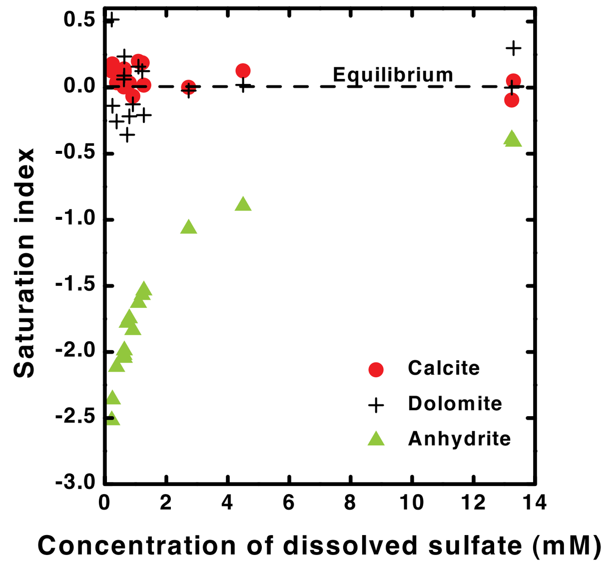
Hydrogeologic cross section A-A' (location shown on map). Monitoring wells with 3-m-long screens were installed at various depths in the aquifer at four locations and at one depth in the upper Permian aquitard at the Cimarron site.

About 17% of the central High Plains is irrigated. Recharge rates under irrigated lands may be as large as 10 to 20 cm/yr.

Objectives

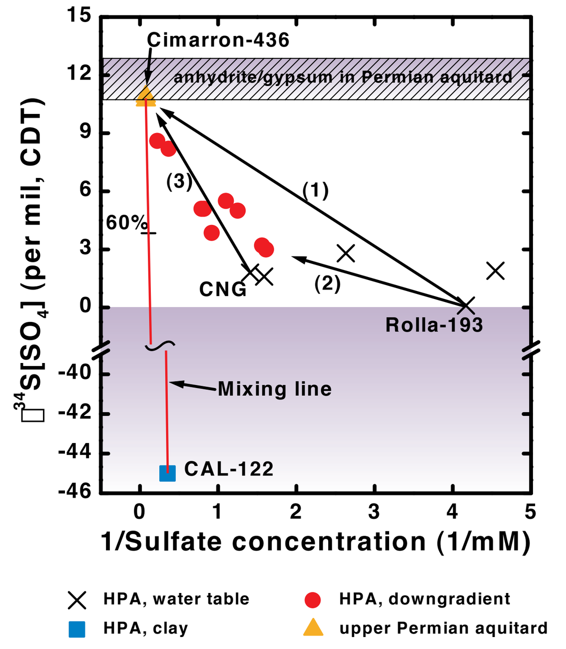
- Determine vertical gradients in nitrate concentrations and ground-water ages in the central High Plains aquifer
- Estimate extent and rates of denitrification in the aquifer
- Reconstruct records of nitrate concentrations and water temperatures in paleorecharge

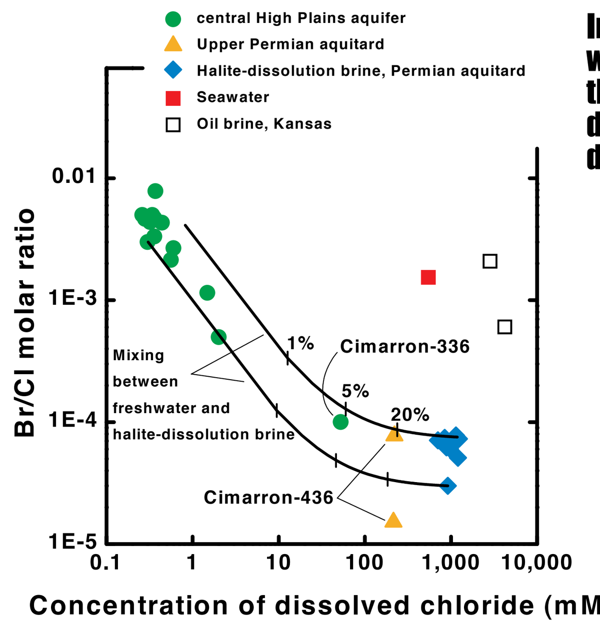
Geochemistry & Radiocarbon Ages



Dedolomitization (dolomite dissolution and calcite precipitation driven by anhydrite dissolution) and cation exchange (Ca^{2+} + Mg^{2+} for Na^{+}) are the primary geochemical reactions that produced the observed water chemistry in the aquifer. Small amounts of oxygen reduction and denitrification also occurred. The chemical composition of water in the upper Permian aquitard at the Cimarron site can be accounted for by the same reactions plus halite dissolution.

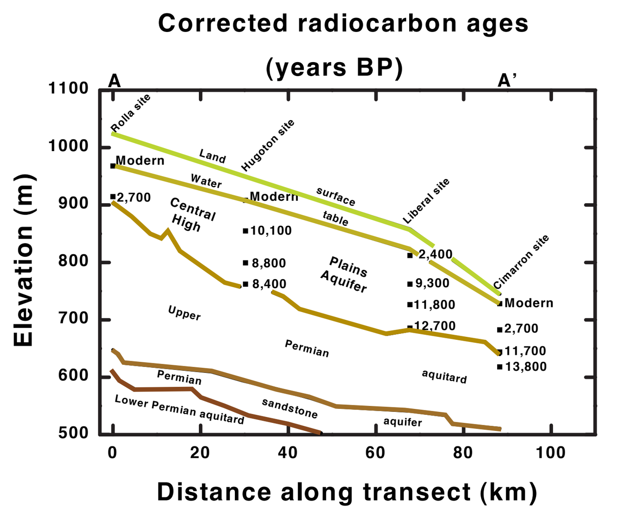
Water samples collected from the water table (x) represent recent recharge in the central High Plains aquifer (HPA). Those samples had the smallest sulfate concentrations and $\delta^{34}SO_4$ values ranging from 0 to 3 per mil. As that water moved downgradient in the aquifer (•), its dissolved sulfate concentrations increased and $\delta^{34}SO_4$ values approached values characteristic of anhydrite in the Permian aquitard (10.5 to 13 per mil). Dissolved sulfate produced along flow paths in the aquifer could be derived from Permian anhydrite incorporated in aquifer sediments during deposition and isotopically depleted (-45 per mil) sulfate from clays in the aquifer, in mixtures ranging from 100/0% (pathways (1) and (3)) to 60/40% (pathway (2)).



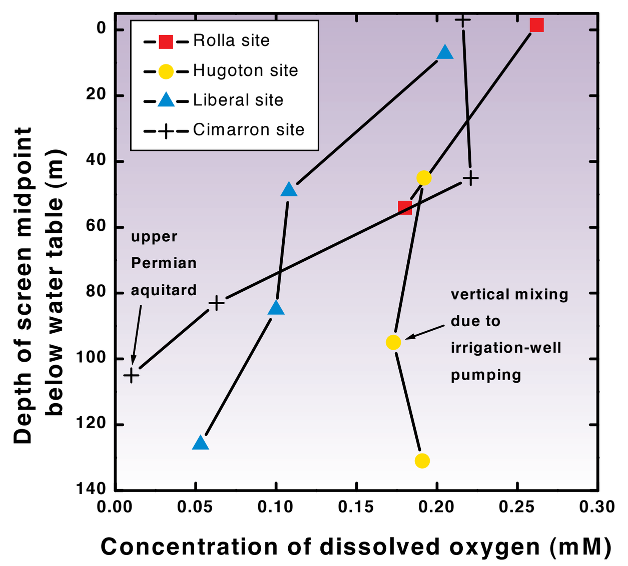


Increases in chloride concentrations along flow paths in the aquifer were generally accounted for by mixing with less than 1% water from the upper Permian aquitard. Dissolved chloride in the aquitard was derived from the dissolution of halite in the Permian sediments by deeply circulating meteoric water.

Vertical gradients in ground-water age along hydrogeologic cross section A-A' (location shown on map). Modern water was defined as water containing more than 0.3 TU of tritium. All other ages were based on radiocarbon dates corrected for geochemical reactions involving carbon. Note that the age gradient at the Hugoton site was affected by vertical mixing due to irrigation-well pumping.

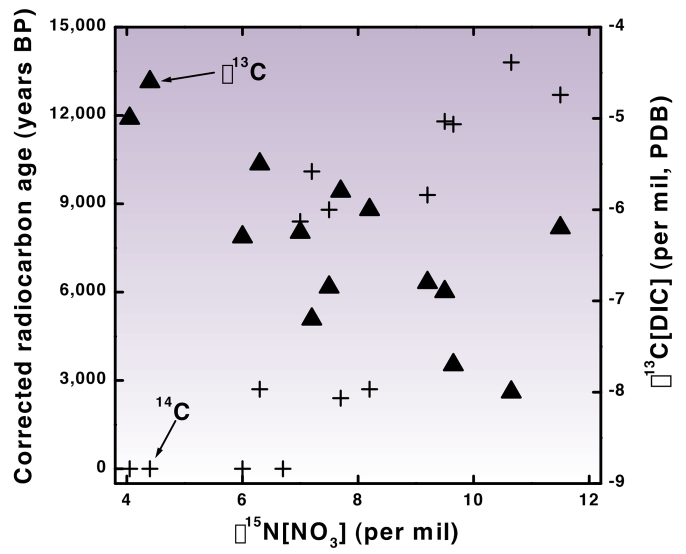


Evidence for Denitrification



Concentrations of O_2 exhibited gradual decreases with depth below the water table. However, none of the samples contained less than 0.01 mM O_2, considered by some (Skerman and MacRae, 1957) to be the largest O_2 concentration at which denitrification can occur. More recent studies indicate that some strains of bacteria can actively denitrify at O_2 concentrations up to 0.22 mM (Frette et al., 1997), well within the range of measured O_2 concentrations. The persistence of O_2 in the aquifer reflects the limited supply of organic carbon to support microbial metabolism.

Dissolved nitrate became enriched in ^{15}N with increasing age of the ground water. That trend could result from denitrification of nitrate along flow paths and/or a change in the $\delta^{15}N$ composition of nitrate in recharge over time. The fact that ^{13}C depletion in DIC accompanied the ^{15}N enrichment in nitrate suggests that oxidation of organic carbon (a source of ^{13}C-depleted carbon) was coupled with denitrification in the aquifer.



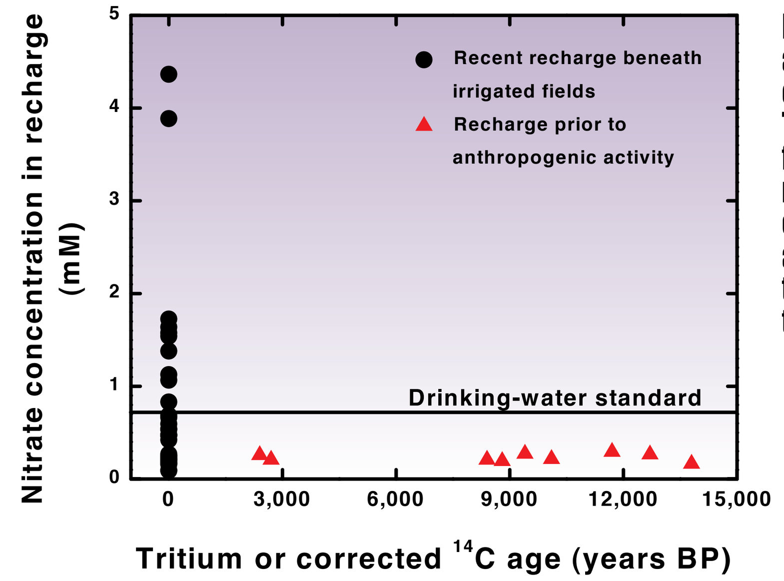
Well name	Depth of screen top below water table (m)	Initial [a] NO_3 (mM)	Excess N_2-N (mM)	$\delta^{15}N[N_2]$ (per mil)	Fraction of NO3 that reacted	Corrected ^{14}C age (years BP)	Denitrification rate (mM yr^{-1})
Rolla-193	-1.6	0.408[b]	--	0.52	--	modern	--
Rolla-366	54.4	0.206	0.035± .011	0.64± .06	0.17	2,700	1.3E-05
Hugoton-140	-1.4	0.160[b]	--	--	--	modern	--
Hugoton-313	53.3	0.213	0.030± .013	--	0.14	10,100	3.0E-06
Hugoton-495	109.6	0.193	0.014± .008	--	0.07	8,800	1.6E-06
Hugoton-617	146.0	0.204	0.040± .003	0.53	0.20	8,400	4.8E-06
Liberal-160	6.7	0.155	0.019± .003	0.58± .02	0.12	2,400	7.9E-06
Liberal-319	51.9	0.271	0.046± .002	0.27± .03	0.17	9,300	4.9E-06
Liberal-436	87.9	0.219[b]	--	--	--	11,800	--
Liberal-570	129.2	0.261	0.093	--	0.36	12,700	7.3E-06
Cimarron-65	-3.7	0.169	0.022	0.46	0.13	modern	--
Cimarron-210	44.8	0.256	0.038± .012	0.52± .06	0.15	2,700	1.4E-05
Cimarron-336	81.9	0.293	0.128± .013	1.04± .01	0.44	11,700	1.1E-05
Cimarron-436	103.9	0.166	0.138± .010	1.66± .02	0.83	13,800	1.0E-05

[a]Initial NO_3 = measured NO_3 + excess N_2-N
[b]Does not include excess N_2

The oldest ground water contained the largest concentrations of excess N_2 and fractions of reacted nitrate. Measurements of $\delta^{15}N[N_2]$ indicate that excess N_2 in those samples was non-atmospheric in origin, supporting the hypothesis that denitrification did occur in the aquifer. Younger ground water contained small concentrations of excess N_2 and $\delta^{15}N[N_2]$ measurements indicate that excess N_2 in those samples could be from trace amounts of denitrification or excess air. Ongoing analyses should resolve the source of that excess N_2 as well as the $\delta^{15}N[NO_3]$ composition of the initial nitrate.

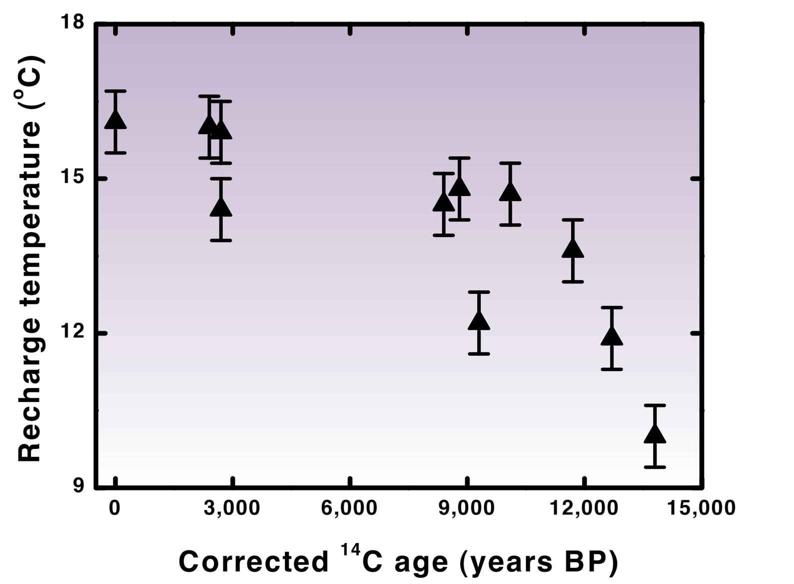
Denitrification rates calculated on the basis of excess N_2 and radiocarbon ages were very low and relatively constant throughout the aquifer. Those rates were similar to denitrification rates in the aquifer containing Pleistocene aged recharge in the Kalahari Desert (3×10^{-5} mM yr-1) (Vogel et al., 1981). In contrast, denitrification rates commonly are >1 mM yr-1 in shallow aquifers containing recent recharge with anthropogenic nitrate (Korom, 1992). The slow rates of denitrification in the central High Plains aquifer reflect the limited supply of organic carbon in the aquifer to support microbial metabolism

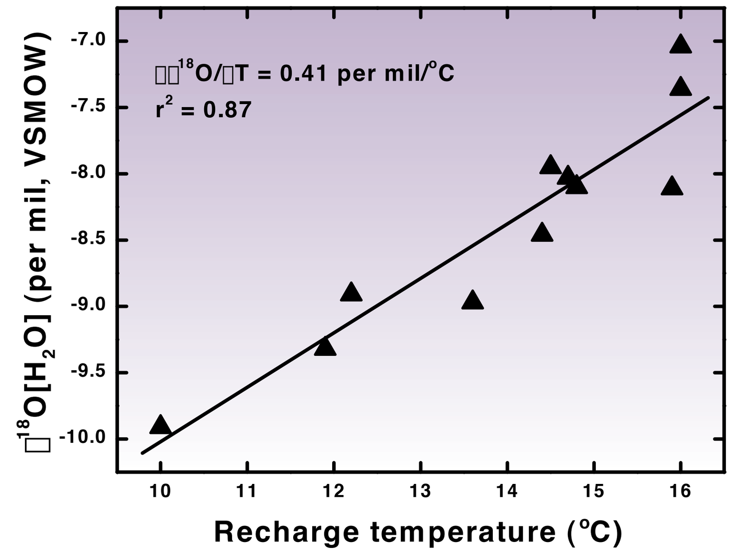
Paleorecharge Conditions



Nitrate concentrations in recharge to the central High Plains aquifer appeared to be relatively constant from about 14,000 years BP to the onset of large-scale irrigated agriculture during the last 50 years. The median concentration of nitrate in recent recharge under irrigated fields (0.464 mM) was more than twice the median concentration of nitrate in paleorecharge (0.214 mM). That difference in median nitrate concentrations is not surprising given the increased amounts of water and nitrogen applied to irrigated fields relative to natural grasslands in the High Plains. The slow rates of denitrification in the aquifer indicate that nitrate contamination in the aquifer will likely persist.

Recharge temperatures estimated from measured concentrations of dissolved Ne and Ar ranged from about 16 °C for recent water to 10 °C for the oldest water. The 6.0±0.6 °C temperature difference between recent water and the water recharged 13,800 years B.P. in this stratified unconfined aquifer is similar to the temperature differences reported between waters recharged during Holocene times and the last glacial maximum in confined aquifers in southern Texas (Stute et al., 1992), northwestern New Mexico (Stute et al., 1995), and west-central Kansas (Clark et al., 1998), further indicating that the southwestern United States was cooler during the last glacial maximum.





$\delta^{18}O[H_2O]$ was positively correlated with recharge temperatures in the central High Plains aquifer, as would be expected for ground waters that were recharged during a period of time spanning the cooler climatic conditions of the Late Pleistocene to the warmer climatic conditions of the Holocene. However, that trend is the opposite of what was observed in the northern High Plains aquifer, where Pleistocene-age ground water was enriched in 180 relative to recent recharge (Dutton, 1995). The patterns of atmospheric moisture transport in the High Plains needed to explain those differences in $\delta^{18}O$ trends require further study.

Conclusions

Water in the central High Plains aquifer ranged in age from modern to about 12,700 years BP. Dissolved oxygen and nitrate were detected throughout the saturated thickness of the aquifer, indicating that the aquifer contained limited amounts of organic carbon to support microbial metabolism. Denitrification rates in the aquifer were measurable, but very low because of the carbon limitation. Concentrations of nitrate in paleorecharge, reconstructed using measurements of nitrate and excess N_2, had a median value of 0.214 mM. In contrast, recent recharge under irrigated fields had a median nitrate concentration of 0.464 mM. The recent increase in nitrate concentrations in recharge, combined with the limited denitrifying activity in the aquifer, indicates that nitrate contamination in the aquifer will increase. The slow movement of ground water indicated by the radiocarbon ages and the fact that most production wells in the aquifer are screened far below the water table should limit the impact of recent nitrate contamination on drinking-water supplies. However, it is possible that nitrate-contaminated ground water could be rapidly transported downward along the annular spaces of improperly sealed wells or by drawdown caused by long-term pumping of large-capacity wells.