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Late-Quaternary Recharge Determined from Chloride in Shallow Groundwater in the Central Great Plains

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An extensive suite of isotopic and geochemical tracers in groundwater has been used to provide hydrologic assessments of the hierarchy of flow systems in aquifers underlying the central Great Plains (southeastern Colorado and western Kansas) of the United States and to determine the late Pleistocene and Holocene paleotemperature and paleorecharge record. Hydrogeologic and geochemical tracer data permit classification of the samples into late Holocene, late Pleistocene–early Holocene, and much older Pleistocene groups. Paleorecharge rates calculated from the Cl concentration in the samples show that recharge rates were at least twice the late Holocene rate during late Pleistocene–early Holocene time, which is consistent with their relative depletion in ^{16}O and *D*. Noble gas (Ne, Ar, Kr, Xe) temperature calculations confirm that these older samples represent a recharge environment approximately 5°C cooler than late Holocene values. These results are consistent with the global climate models that show a trend toward a warmer, more arid climate during the Holocene. © 2000 University of Washington.

Key Words: isotope hydrology; paleoclimate; regional flow system; Dakota aquifer; central Great Plains.

INTRODUCTION

Estimates of natural recharge form the basis of many groundwater-management plans in the Great Plains region of the United States. The projected changes in climate from global warming are expected to have significant consequences for agriculture, including changes in the timing and amounts of precipitation and of recharge to sources of irrigation water in shallow aquifers (Vaccaro, 1992; Easterling, 1997). An understanding of the effects of past climate change on precipitation and recharge may provide insight into how management policies may need to adjust in response to a warmer climate. The transition from the cool, moist conditions of the late Pleistocene to a progressively warmer and more arid environment in the mid-Holocene (Kutzbach, 1987; COHMAP, 1988; Bartlein *et al.,* 1998) suggests a significant decrease in recharge rates in the central and southern Great Plains (Holliday, 1989; Fredlund, 1995).

Recent work has focused on using naturally occurring geochemical tracers in groundwater to determine modern and older Quaternary recharge records. Recharge rates to shallow, unconfined aquifers can be calculated using simple budget models of a conservative tracer, such as Cl (Eriksson and Khunakasem, 1969; Allison and Hughes, 1978). Recharge is assumed to be the net difference between precipitation and evapotranspiration (effective moisture). Assuming no other source, the Cl concentration in groundwater depends only on the deposition rate from precipitation and on the recharge rate. The recharge rate can then be calculated as

Recharge Rate (L/T)

$$= \frac{\text{Cl Deposition Rate } (M/L^2T)}{\text{Cl Concentration } (M/L^3) \text{ in Groundwater}}.$$

Because of the dispersive properties of porous media, the signal preserved in the aquifer is one of long-term trends in

annual recharge rate and not one of individual pulses of recharge. Using this method, Stone and McGurk (1985) and Wood and Sanford (1995) estimated modern recharge rates using the Cl mass-balance method in eastern New Mexico and the Texas Panhandle. Late Pleistocene and Holocene paleorecharge has also been estimated from ^{14}C dated groundwater samples from the Carrizo aquifer near the Texas Gulf Coast (Stute *et al.,* 1993).

Present Study

The investigation reported in this paper is part of a pilot study that was conducted cooperatively by the Kansas Geological Survey and the Lawrence Livermore National Laboratory. The purpose of this study was to use the major, minor, and trace constituent groundwater geochemistry to determine likely recharge sources, groundwater residence times, and the extent of mixing between groundwater masses of differing residence times in southeastern Colorado and central and western Kansas (Fig. 1). The earlier results from this work were presented in a paper by Clark *et al.* (1999), and details concerning analytical methods, procedures, and results can be found there. The objectives of the part of the pilot investigation reported on here were to use the geochemical-tracer data to (1) discern the pattern of recharge fluctuations in the late Quaternary and (2) develop an understanding of the paleoclimate influences on recharge.

Regional Climate and Hydrogeology

The study area is located in southeastern Colorado and adjacent western Kansas (Fig. 1). The region is in a warm, semiarid, continental environment where the mean annual temperature and rainfall range from 12.2°C and 373 mm near sample site 55 to 11.4°C and 434 mm at sample site 69. Annual evapotranspiration is much higher than annual rainfall; annual lake evaporation ranges from 1470 mm near sample site 55 to 1570 mm at sample site 69 (Farnesworth *et al.,* 1982).

The shallow aquifer units sampled in this study are the High Plains, Dakota, and Morrison-Dockum. The High Plains aquifer consists of the Pliocene Ogallala Formation and associated unconsolidated Quaternary sediments, whereas the Dakota and Morrison-Dockum bedrock aquifers consist of Cretaceous and Jurassic–Triassic sandstones, respectively. The bedrock aquifers are hydraulically connected to the overlying High Plains aquifer over much of the study area, except where thin, leaky remnants of confining units are present. Regional groundwater flow in all three aquifer units is to the east or northeast following the regional topographic gradient (Macfarlane, 1995; Fig. 1).

GROUNDWATER-SAMPLE COLLECTION, ANALYSIS, AND RESULTS

Groundwater samples were collected from 13 wells that tap sources of water in the High Plains, Dakota, and Morrison-
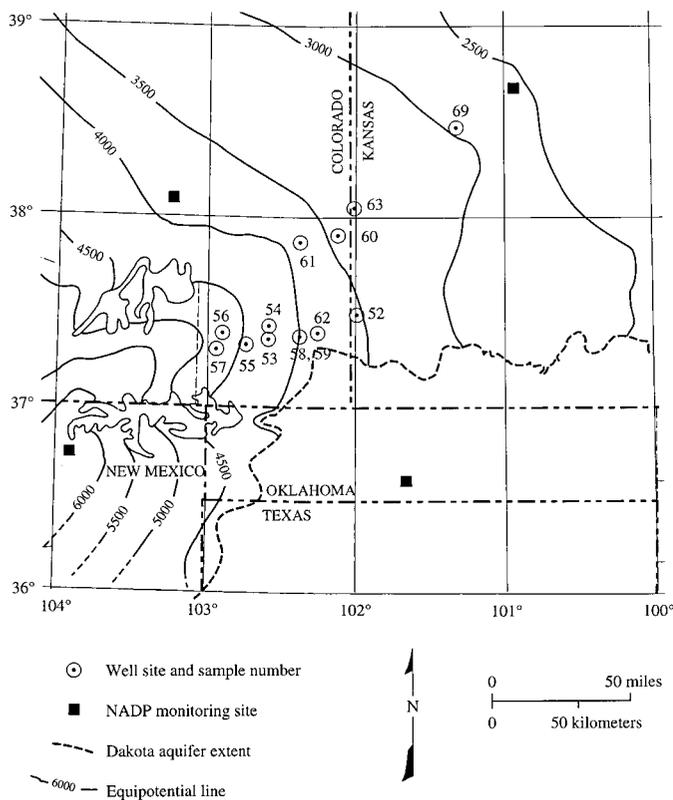
FIG. 1. Map showing hydrogeologic setting in southeastern Colorado and western Kansas, wells that produced the Group 1 and 2 groundwater samples, and the monitoring sites in the National Atmospheric Deposition Program. The equipotential contours indicate groundwater flow to the north and east in the Dakota aquifer of southeastern Colorado and western Kansas.

Dockum aquifers. The wells selected for sampling were chosen to characterize changes in groundwater geochemical composition along the direction of regional flow (Fig. 1). These changes occur in response to changes in the geochemical environment, mixing with other groundwater masses, and rock–water chemical interactions.

The analytical results pertinent to this part of the investigation are presented in Table 1. The ^{18}O and *D* were reported in the standard δ (‰) notation representing per mil deviations from the SMOW (Standard Mean Ocean Water; Craig, 1961). Reproducibilities for the δ^{18}O and the δ*D* analyses are ±0.1‰ and ±1.0‰, respectively. The ^{3}H was reported as tritium units (TU) with a reproducibility of ±1 TU. The ^{13}C is reported relative to the PDB standard and has a reproducibility of ±0.3‰. The ^{14}C was reported as percent modern carbon (pmc) and has a reproducibility of ±1%.

DISCUSSION OF THE ANALYTICAL RESULTS

^{14}C Ages of Water Samples

Numerical ^{14}C ages were difficult to calculate for the samples using standard correction methods because of the δ^{13}C

TABLE 1
Geochemical Tracer Data in Groundwater Samples from Southeastern Colorado and Western Kansas,
Modified from Clark *et al.* (1999)

Sample no.	Aquifer units[a]	Elevation (m a.l.s.)[b]	$\delta^{13}C$ (‰)	^{14}C (PMC)	^{14}C model age (yr B.P.)	δ^2H (‰)	$\delta^{18}O$ (‰)	^3H (TU)	NO_3–N (mg/L)	NO_4–N (mg/L)	Cl (mg/L)
Group 1											
53	H, D	1344	−3.0	81.1	400	−85	−11.4	4.0	3.25	<0.08	25.0
54	D	1325	−5.4	74.4	1100	−75	−10.7	4.8	3.25	<0.08	20.4
57	D	1509	−5.2	75.0	1000	−67	−9.8	0	2.96	<0.08	7.7
58	D	1208	−7.4	72.4	1300	−68	−9.4	0.1	4.99	<0.08	49.1
59	D	1206	−6.2	68.2	1800	−66	−9.7	3.0	1.58	<0.08	22.2
69	H	1007	−8.1	70.9	1500	−61	−8.9	3.1	3.12	<0.08	30.8
Average				73.7					3.19	<0.08	25.9
Group 2											
52	M	1087	−6.6	17.9	12,900	−79	−10.9	1.0	0.20	0.08	20.3
55	D	1422	−4.9	27.8	9200	−104	−14.1	0	<0.02	0.23	23.6
56	D	1455	−5.7	40.6	6100	−80	−11.5	0	<0.02	<0.08	2.6
60	D	1104	−7.7	37.5	6800	−60	−9.2	0	2.48	<0.08	7.5
61	D	1184	−8.6	44.6	5300	−69	−10.0	0	<0.02	<0.08	9.2
62	D, M	1268	−6.3	21.6	11,300	−88	−12.2	—	<0.02	<0.08	5.4
63	D	1031	−4.5	35.7	7200	−93	−13.0	0	<0.02	<0.08	11.9
Average				32.2					0.38	<0.08	11.5

[a] Aquifer units: H, High Plains; D, Dakota; M, Morrison-Dockum.
[b] a.l.s., above land surface.

range found in young (^{14}C content > 68 pmc) groundwater (Table 1). For instance, in Table 1 the isotopic composition of dissolved inorganic carbon shows that sample 53 ($\delta^{13}C = -3.0$‰ and $^{14}C = 81$ pmc) is not a simple mixture of biogenic CO_2 soil gas and aquifer-carbonate material. Rather, it indicates that the dissolved inorganic carbon has equilibrated to some extent with the atmosphere. The extent of equilibration varies significantly and cannot be predicted from other well data. For the purposes of this work, estimated ^{14}C ages were calculated using the simple model of Vogel (1970), which assumes an initial ^{14}C content of 85 pmc. Because the ranges of dissolved inorganic carbon concentrations of the Group 1 and 2 samples are similar, the adjusted ^{14}C ages should reflect relative age differences among the samples.

Natural Sample Groupings

On the basis of well construction, hydrogeology, and geochemical characteristics, the samples cluster naturally into three groups (Table 2; Clark *et al.,* 1999), the first two of which are the focus of this paper. Group 1 samples are characterized by ^{14}C contents >68 pmc and noble gas temperatures which range between 13.1° and 14.5°C. There is measurable ^3H in all but one of the samples from atmospheric thermonuclear testing, which indicates that some of this recent recharge entered the flow system during the last 40 yr. The noble gas temperatures are in good agreement with the local present mean annual temperature. The high ^{14}C content indicates that these samples entered the groundwater-flow system within the last 2000 yr.

Group 2 samples have ^{14}C contents between 45 and 17 pmc

and noble gas temperatures between 4.8° and 11.7°C (Table 2). These samples come from wells in the same region as the Group 1 wells and have overlapping depths, but with well screens that, on average, are at greater depths below surface. Presumably, these samples come from the deeper, older part of the average groundwater-flow system. The higher ^4He concentrations and lower ^{14}C content indicate that the groundwater ages of the Group 2 samples are older than those of the Group 1 samples. We believe that these samples probably entered the groundwater-flow system primarily as recharge from infiltrating precipitation 6000 to 13,000 yr ago.

The Group 3 samples come from deep wells screened only in the confined Dakota aquifer system in western and central Kansas downgradient of its recharge area and have ^{14}C contents <15 pmc (Table 2). Cl concentrations are significantly greater than those observed in either Group 1 or Group 2 samples (average Cl concentrations of 25.9 mg/L and 11.5 mg/L, respectively) and increase systematically downgradient of the recharge area (Clark *et al.,* 1999). Concomitantly, ^4He and NH_4–N concentrations in the Group 3 samples systematically increase in the downgradient direction (Fig. 2). The ^4He enrichment results from alpha-decay of U- and Th-series nuclides both within the aquifer and deeper in the crust (Torgerson and Ivey, 1985). NH_4–N is a reduced form of nitrogen that is often associated with brines from deep confined aquifer systems (White *et al.,* 1963). The concurrent buildup of Cl, NH_4–N, and ^4He along the flow path is taken as evidence of upward leakage from a deeper brine source and incomplete flushing of formation water in the confined aquifer by fresher

TABLE 2

Summary of Characteristic Tracer Compositives of the Three Sample Groups Found in Groundwater from Southeastern Colorado and Western Kansas, Modified from Clark *et al.* (1999)

Constituent or parameter value	Group 1	Group 2	Group 3
[14]C content (pmc)	>68	18 to 45	<5
[14]C model age (yr B.P.; Vogel, 1970)	<1800	6000–13,000	>20,000
Noble gas temperature (°C)	13.1 to 14.5	6.9 to 11.7	—
$\delta^{18}O$ (‰)	−9 to −11	−9 to −14	−12
Cl (mg/L)	7.7 to 49.1	2.6 to 23.6	16.6 to 1363
[4]He ($\times 10^{-8}$ ccSTP gr^{-1})	4 to 7	10 to 50	170 to 3600
NH_3–N (mg/L)	1.58 to 4.99	<0.02 to 2.48	<0.02
NH_4–N (mg/L)	<0.08	<0.08 to 0.23	0.47 to 1.79

groundwater flows from southeastern Colorado (Whittemore and Fabryka-Martin, 1992).

Evidence of Mixing in Group 2 Samples

Clark *et al.* (1999) concluded that most of the Group 2 samples are mixtures of either modern and late Pleistocene–early Holocene age water or late Pleistocene–early Holocene age and older water that is geochemically similar to the Group 3 samples, or both. Most likely this is because the samples come from wells that withdraw water from multiple aquifer zones and, quite possibly, from flow systems with different flow-path lengths and residence times. The measurable ^3H and NO_3–N in Sample 52 and the relatively high NO_3–N concentration in Sample 60 indicates that both samples contain a significant fraction of modern recharge. Samples 52 and 55 have the highest Cl concentration and the highest ^4He content of the Group 2 samples and contain measurable NH_4–N (Fig. 2). This is taken to be evidence of mixing with older groundwater that is geochemically similar to the Group 3 samples.

Samples 56 and 63 have younger ^{14}C ages (ca. 6000 yr B.P.)
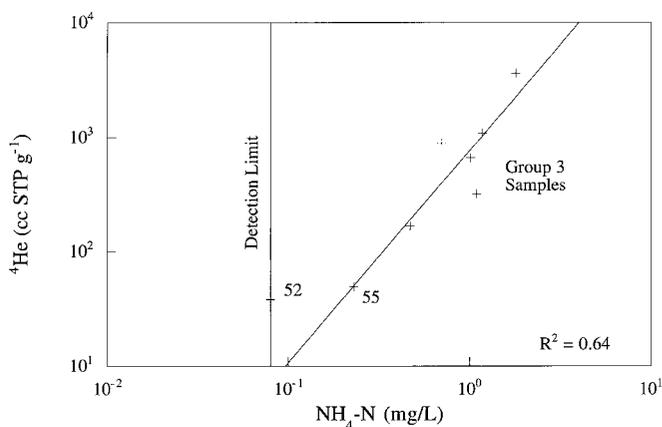
but with noble gas temperatures at least 4°C less than the present mean annual temperature (Tables 1 and 3). These cooler noble gas temperatures are inconsistent with a warm mid-Holocene climate (Bartlein *et al.,* 1984; Kutzbach, 1987; COHMAP, 1988) and suggest that these samples are most likely Pleistocene in age but with a small component (<30% of the total sample) of young recharge from warmer climates. Sample 62 is probably the only glacial end member in the Group 2 data set; the ^{14}C model age is approximately 11,000 yr B.P. and the noble gas temperature is about 5°C less than present mean annual temperature (Tables 1 and 3).

CALCULATION OF RECHARGE RATE

Sources of Cl in Shallow Aquifers

Within the study area, the low to moderate relief and sandy to silty surface soils favor infiltration. Infiltration is further enhanced by the numerous undrained depressions of varying sizes on the upland surface (McLaughlin, 1954). Also, most of the drainage consists of a network of dry stream beds with sandy bottoms or bedrock outcrops (Fig. 1). Therefore, runoff is assumed to be negligible. The low Cl groundwater (Group 1 and 2 Cl ranges from 7.7 to 49.1 mg/L and 2.6 to 23.6 mg/L, respectively) reflects long-term flushing by recharge from precipitation acting over millions of years (Whittemore and Fabryka-Martin, 1992). Hence, the only significant source of Cl is from infiltrated precipitation. In this analysis, accumulated Cl in the unsaturated zone is assumed to remain approximately at steady state over long periods of time.

Modern Annual Cl Deposition

Data on modern annual Cl deposition were obtained from four monitoring sites in the National Atmospheric Deposition Program (NADP (NRSP-3)/National Trends Network, 1999) that surround the study area (Fig. 1, Table 4). Because of the short (14-yr) monitoring period, the annual data were averaged to develop a regional relationship between Cl and precipitation. The average annual precipitation for the NADP sites (445 mm)

FIG. 2. Crossplot of ammonium–nitrogen (NH_4–N) and ^4He content from the Group 3 samples and Group 2 samples 52 and 55. Using only data from the Group 3 samples, the equation of the best-fit line is $[^4He] = 769.13[NH_4–N]^{1.855}$ with $R^2 = 0.64$ ($p = 0.05$).

TABLE 3

Recharge Temperatures from Noble Gases and Recharge Rates Derived from the Cl Concentration in Groundwater Samples from Southeastern Colorado and Western Kansas

Sample no.	Aquifer units[a]	Recharge T (°C) (Clark *et al.,* 1999)	Recharge (mm/yr) ($D_{Cl} = 0.48 \pm 0.06$ kg/ha)	Recharge (mm/yr) ($D_{Cl} = 0.32 \pm 0.06$ kg/ha)
Group 1				
53	H, D	14.5 ± 0.6	1.92 ± 1.29	
54	D	13.3 ± 0.6	2.35 ± 1.28	
57	D	—[b]	6.23 ± 1.28	
58	D	13.1 ± 0.6	0.98 ± 1.29	
59	D	13.1 ± 0.6	2.11 ± 1.29	
69	H	13.1 ± 0.6	1.56 ± 1.28	
Average			2.52 ± 1.75	
Group 2				
52	M	10.6 ± 0.6	—[c]	—[c]
55	D	—[b]	—[c]	—[c]
56	D	8.5 ± 0.6	18.46 ± 1.31	12.31 ± 1.91
60	D	11.7 ± 0.6	—[c]	—[c]
61	D	—[b]	5.22 ± 1.29	3.47 ± 1.90
62	D, M	7.8 ± 0.6	8.89 ± 1.30	5.93 ± 1.91
63	D	4.8 ± 0.6	4.03 ± 1.29	2.69 ± 1.90
Average			9.15 ± 1.79	6.10 ± 2.64

Note. Group 2 sample recharge rates were calculated in two ways to provide a range of possible values. The upper and lower ends of the range are based on the modern rate of Cl deposition ($D_{Cl} = 0.48 \pm 0.06$ kg/ha) and a lower rate of deposition ($D_{Cl} = 0.32 \pm 0.06$ kg/ha) assuming a 25% decrease in average annual precipitation, respectively.

[a] Aquifer units: H, High Plains, D, Dakota; M, Morrison-Dockum.

[b] No data.

[c] Recharge rate not calculated due to evidence of significant mixing with younger late Holocene groundwater.

is within 10% of the average annual precipitation recorded at other weather stations in southeastern and western Kansas with longer-term records. The calculated annual Cl deposition for each monitoring site is derived from measurements of annual precipitation and mean annual Cl concentration and not field measurements of total annual deposition. The average annual regional Cl deposition is therefore positively correlated with average annual precipitation (Fig. 3); their relationship is described by the linear regression equation

$$D_{Cl} = 1.406 \times 10^{-3} P - 0.14481$$
$$R^2 = 0.49 \ (p = 0.005), \tag{1}$$

where D_{Cl} is the annual Cl deposition (kg/ha) and P is the annual precipitation (mm). Equation (1) accounts for about half of the variation in D_{Cl} as a result of variations in P, which provides an estimate of the variability in Cl concentration. However, this is misleading because although the equation variables are not fully independent, the differences between the actual and calculated total annual values should not be significant in terms of the groundwater data with which the model estimates are compared.

Estimation of Average Annual Paleoprecipitation and Cl Paleodeposition Rates

Annual paleorecharge can be estimated from the annual Cl paleodeposition, which depends on the annual paleoprecipitation–Cl paleodeposition relationship and the paleoprecipitation. In this paper we assume that the relationship between

TABLE 4

Summary Statistics on Annual Precipitation and Cl Deposition at Monitoring Sites Maintained by the National Atmospheric Deposition Program

NADP atmospheric monitoring site	Years of record	Average annual Cl^- deposition (kg/ha)	Average annual precipitation (cm)
Las Animas Fish Hatchery, CO	1985–1997	0.39	34.81
Lake Scott, KS	1985–1997	0.48	50.39
Capulin Mt., NM	1985–1997	0.50	47.98
Goodwell Research Station, OK	1985–1997	0.54	44.46
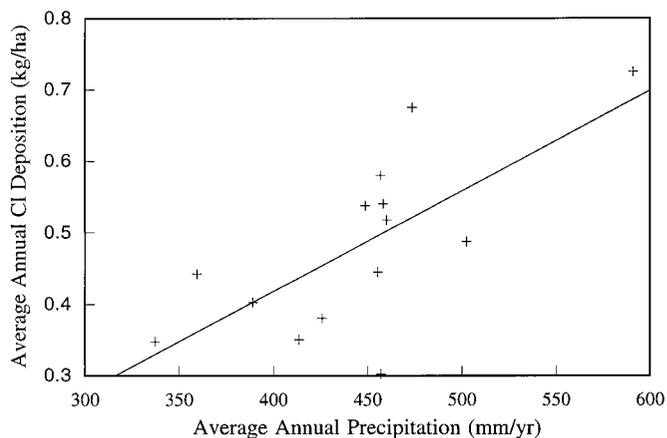
FIG. 3. Log-linear plot of average annual precipitation (*P*) vs average annual Cl deposition (D_{Cl}) for four stations in the National Atmospheric Deposition Program for the years 1985–1998.

modern annual Cl deposition and annual precipitation in Eq. (1) is valid during the late Pleistocene and Holocene.

Quantitative estimates of long-term annual precipitation for the late Pleistocene and Holocene are not available from studies of Quaternary deposits in this part of the Great Plains. Paleoclimate model results show that annual precipitation during the Altithermal climatic interval from 8000 to 5000 yr B.P. may have been as much as 25% less than present values in the region (Kutzbach, 1987). On the basis of preserved fossil pollen suites from Minnesota, Bartlein *et al.* (1984) suggested a 20% decrease in precipitation during this period for the larger midcontinent region. While useful, these estimated decreases in annual precipitation are for the region as a whole and do not take into account subregional effects, such as the rain shadow effect of the Rocky Mountains on the western Great Plains.

We calculate annual recharge rates from the Cl in the Group 1 samples using the modern average annual Cl deposition rate from the four monitoring sites (D_{Cl} = 0.48 kg/ha). For the Group 2 samples the paleorecharge rates are calculated in two ways to give a range of values. To calculate the upper end of the range, we assume that the modern, pooled mean annual precipitation is representative of annual paleoprecipitation for the study area during the late Pleistocene and Holocene. In this scenario, we calculate paleorecharge rates using the modern average annual Cl deposition rate from the four monitoring sites. To calculate the lower end of the range we assume that the average annual precipitation during the late Pleistocene and Holocene was 25% less than at present, with a D_{Cl} = 0.32 kg/ha. This approach is consistent with the estimated changes in annual paleoprecipitation deduced from the proxy data sets (Bartlein *et al.,* 1984) and the paleoclimate models (Kutzbach, 1987), and it reflects our uncertainty about the ^{14}C ages of the Group 1 and Group 2 samples. We also recognize the mixing of groundwaters produced by recharge events that occurred under different climatic conditions. Hence, these estimates present the likely minimum and maximum Cl-derived annual

paleorecharge rates for each Group 2 sample. Paleorecharge rates were not calculated for Group 2 samples 52, 55, and 60 because the data suggest that they contain a significant component (>30%) of either modern groundwater or older and more saline groundwater.

Annual Paleorecharge Rates During the Late Quaternary

Group 1 recharge rates based on Cl range from 0.98 ± 1.29 to 6.23 ± 1.28 mm/yr and the average recharge rate is 2.52 ± 3.15 mm/yr (Table 3). None of the annual recharge values is >2.5 mm with the exception of the value calculated from the Cl in sample 57. Unfortunately, the noble gas data are not available for this sample to allow assessment of the possibility that the sample contains a significant fraction of older low Cl groundwater. If this is an unmixed sample, this sample should be considered an outlier and may reflect recharge during a very wet period in the later Holocene (Madole, 1994; Fredlund, 1995). Discounting the results from sample 57 yields an average recharge rate of 1.78 ± 2.88 mm/yr.

Group 1 rates are in good agreement with other estimates of modern groundwater recharge in the region. For eastern New Mexico (381 mm average annual precipitation), Stone and McGurk (1985) estimated a regional recharge rate of 1.5 mm/yr using the Cl mass balance in the unsaturated zone above the High Plains aquifer. Wood and Sanford (1995) estimated a much higher average annual regional recharge rate of 11.1 mm/yr (485 mm/yr average annual precipitation), considering the Cl mass balance from the High Plains aquifer of both eastern New Mexico and the Texas Panhandle. The estimated average recharge is very close to the estimated modern maximum potential recharge (<2.5 mm/yr) of Dugan and Peckanpaugh (1985). From steady-state, groundwater flow-model results, Macfarlane (1995) reported an average recharge of 1.8 mm/yr in southeastern Colorado.

The average recharge rate from the Cl in the older Group 2 samples ranges from 9.15 ± 2.60 to 6.10 ± 3.80 mm/yr. The lower end of this range in values is at least 100% higher than the modern rate using the Cl mass balance method (Table 3). Stute *et al.* (1993) reported late Pleistocene–early Holocene recharge rates ranging from 9.6 to 13.1 mm/yr using the Cl mass balance method on sample data from the Carrizo aquifer near the Texas Gulf Coast. These estimates compare favorably with the range of recharge values calculated from the Cl concentration in sample 62 (8.89 mm/yr to 5.93 mm/yr), the only sample in our data set believed to be late Pleistocene in age. Samples 56 and 63 are mixtures of older and much younger groundwater and yield recharge values that range from 18.46 to 12.31 mm/yr and 4.03 to 2.69 mm/yr, respectively (Table 3).

The high variability in calculated recharge rates within each sample set may reflect local variability in recharge mechanisms. For example, Wood and Sanford (1995) found that the recharge rate beneath one playa was seven times higher than

the regional rate in the southern High Plains of Texas and eastern New Mexico because of infiltration of collected runoff and macroporosity in the unsaturated zone beneath the basin floor.

DISCUSSION

The difference between the average late Holocene Group 1 and the late Pleistocene–early Holocene Group 2 sample estimates of annual recharge (Table 3) is consistent with the shift from a mesic to a progressively more xeric environment that began during the early Holocene (Arbogast, 1996; Arbogast and Johnson, 1998; Fredlund, 1995). The paleoclimate models suggest that prior to this transition, climatic conditions south of the shrinking Laurentide Ice Sheet were similar to the present, but with cooler January temperatures, drier conditions just south of the ice sheet, and wetter conditions in the southwest (COHMAP, 1988; Bartlein et al., 1998). From 12,000 to 6000 yr B.P. a stronger-than-present monsoon developed due to the enhanced thermal contrast between the ocean and the continent from increased insolation. NCAR Community Climate Model Version 1 results indicate drier conditions than present for both January and July beginning 11,000 yr B.P. because of earlier summer heating, but with a more pronounced seasonality in the distribution of precipitation than at present. In an earlier version of this model, summer temperatures were estimated to have been as much as 2–4°C higher than present (COHMAP, 1988). The Version 1 model results suggest that after 6000 yr B.P., summer temperatures declined and the monsoon weakened because of decreased summer insolation. The almost 5°C increase in noble gas temperatures between the late Holocene Group 1 and the older Group 2 samples (Table 3) is consistent with these simulated changes in the paleoclimate (Clark et al., 1999).

The average Cl concentration of the Group 1 samples is much higher than the average for the Group 2 samples (Table 1). In the middle to late Holocene, the higher temperature and lower precipitation would have increased evaporation at the expense of recharge, producing water-level declines in shallow aquifers (Fredlund, 1995; Mandel, 1994; Holliday, 1989). Hence, infiltrating water would more likely evaporate completely before reaching the water table. Also, a thicker unsaturated zone would have been available for storage of accumulated salts. Consequently, the dissolved solids concentration, including Cl, would be higher for recharge during this period (Prill, 1977) than for recharge during the wetter and cooler period prior to the Pleistocene–Holocene transition (Sukhija et al., 1998).

The close affinity of $\delta^{18}O/\delta D$ data for all of the samples to the meteoric water line (Fig. 4) indicates that none has been significantly affected by evaporation (Fontes, 1980). The absence of significant evaporative effects on the Group 1 samples suggests that recharge pulses formed during infrequent periods
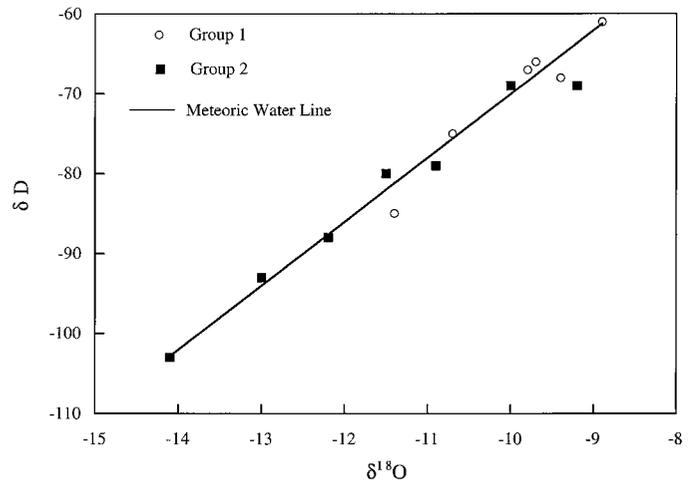
FIG. 4. Crossplot of the ^{18}O vs D content in the Group 1 and 2 water samples. Error bars are not shown because they are smaller than the size of the symbols used in the plot. All samples plot along the meteoric water line (Craig, 1961), which indicates that none has been affected significantly by evaporation.

of higher precipitation, possibly during an extreme hydrologic event, such as the 1993 flood (Sophocleous et al., 1996).

SUMMARY AND CONCLUSIONS

The groundwater system is a natural archive of long-term climate change because of the influence of climate on recharge and the natural flow of groundwater from recharge to discharge areas. In this pilot study we have used the Cl mass balance method and other geochemical data from groundwater to support the hypothesis that recharge rates declined by at least 50% during the Pleistocene–Holocene transition in response to increasingly xeric conditions in the central Great Plains.

The late Holocene Group 1 samples have average annual recharge rates consistent with modern recharge rates for the High Plains aquifer in Texas and New Mexico estimated using the Cl mass balance method and are in close agreement with recharge estimated for the region by other means. Higher noble gas temperatures, enrichment of ^{18}O and D, and the higher Cl concentrations of the Group 1 samples are consistent with the warmer climatic conditions of the late Holocene. The higher Cl concentrations and the close affinity of the $\delta^{18}O/\delta D$ data to the meteoric water suggests that late Holocene recharge occurred only during extended wet periods.

The late Pleistocene–early Holocene Group 2 samples yield paleorecharge rates that are consistent with rates estimated using the same method on Cl data on the Carrizo aquifer near the Texas Gulf Coast for the Pleistocene–Holocene transition. The results from our research should be evaluated with caution because of the small number of samples and the evidence of mixing in Group 2 samples.

Further sampling is needed in the study area to allow a more

detailed reconstruction of the paleorecharge rates in the late Pleistocene and Holocene. This study demonstrates that the groundwater geochemistry can be used quantitatively to define paleoclimatic conditions in areas where the proxy data from other studies are sparse or inconclusive. In particular, additional information is needed to understand better the carbon budget in the aquifer systems and the overlying vadose zone in the study area.

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