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Perchlorate in Pleistocene and Holocene Groundwater in North-Central New Mexico

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Groundwater from remote parts of the Middle Rio Grande Basin in north-central New Mexico has perchlorate (ClO_4^-) concentrations of 0.12–1.8 μg/L. Because the water samples are mostly preanthropogenic in age (0–28 000 years) and there are no industrial sources in the study area, a natural source of the ClO_4^- is likely. Most of the samples have Br^-, Cl^-, and SO_4^{2-} concentrations that are similar to those of modern bulk atmospheric deposition with evapotranspiration (ET) factors of about 7–40. Most of the ET values for Pleistocene recharge were nearly twice that for Holocene recharge. The NO_3^-/Cl^- and ClO_4^-/Cl^- ratios are more variable than those of Br^-/Cl^- or SO_4^{2-}/Cl^-. Samples thought to have recharged under the most arid conditions in the Holocene have relatively high NO_3^-/Cl^- ratios and low $\delta^{15}N$ values (+1 per mil (‰)) similar to those of modern bulk atmospheric N deposition. The $\delta^{18}O$ values of the NO_3^- (−4 to 0 ‰) indicate that atmospheric NO_3^- was not transmitted directly to the groundwater but may have been cycled in the soils before infiltrating. Samples with nearly atmospheric NO_3^-/Cl^- ratios have relatively high ClO_4^- concentrations (1.0–1.8 μg/L) with a nearly constant ClO_4^-/Cl^- mole ratio of $(1.4 \pm 0.1) \times 10^{-4}$, which would be consistent with an average ClO_4^- concentration of 0.093 ± 0.005 μg/L in bulk atmospheric deposition during the late Holocene in north-central NM. Samples thought to have recharged under wetter conditions have higher $\delta^{15}N$ values (+3 to +8 ‰), lower NO_3^-/Cl^- ratios, and lower ClO_4^-/Cl^- ratios than the ones most likely to preserve an atmospheric signal. Processes in the soils that may have depleted atmospherically derived NO_3^- also may have depleted ClO_4^- to varying degrees prior to recharge. If these interpretations are correct, then ClO_4^- concentrations of atmospheric origin as high as 4 μg/L are possible in preanthropogenic groundwater in parts of the Southwest where ET approaches a factor of 40. Higher ClO_4^- concentrations in uncontaminated groundwater could occur in recharge beneath arid areas where ET is greater than 40, where long-term accumulations of atmospheric salts are leached suddenly from dry soils, or where other (nonatmospheric) natural sources of ClO_4^- exist.

Introduction

Ingestion of perchlorate (ClO_4^-) can interfere with the uptake of iodide by the thyroid gland and can affect regulation of metabolism and brain development, particularly in fetuses and children (*1*, *2*). Recent advances in analytical methods have significantly lowered the ClO_4^- minimum detection limit, and now widespread occurrences of ClO_4^- in groundwater are recognized in parts of the Southwest, even in areas where no industrial sources are known (*3*–*5*). Because of a lack of information on groundwater ages and water sources, the extent to which natural sources of ClO_4^- can contribute to background concentrations in groundwater, or whether the low-level detections must necessarily imply anthropogenic sources, has not been determined.

This paper evaluates the concentrations of ClO_4^- and other anions potentially of atmospheric origin in old (preanthropogenic, in the range of 0–28 000 years) groundwater from north-central New Mexico, as a means of investigating processes affecting natural deposition of ClO_4^- in soils and estimating the concentration of ClO_4^- in preanthropogenic bulk atmospheric deposition. The study is unique in that it builds on a previously established hydrologic and hydrochemical framework of groundwater in the Middle Rio Grande Basin (MRGB), north-central New Mexico (*6*–*10*) that (1) permits identification of sources of recharge that may contain an atmospheric signal and (2) identifies groundwater samples that have ages of thousands to tens of thousands of years with no possible anthropogenic sources of ClO_4^-.

Materials and Methods

There are no known industrial sources of ClO_4^- in the source areas of these wells. The median radiocarbon age of the dissolved inorganic carbon in the samples is 12.4 kiloannum (ka), with a range of approximately 0–28 ka (*6*, *7*). Most of the samples were free of tritium or chlorofluorocarbons, indicating little or no contamination with young water (<50 years). The waters sampled are mostly from aerobic parts of the aquifer, minimizing the potential for microbial degradation of NO_3^- and ClO_4^-, and occur beneath deep unsaturated zones, further isolating them from surficial sources. Water samples were selected from parts of the aquifer where previous hydrochemical investigations (*6*–*10*) demonstrated recharge from precipitation along the northern and eastern mountain margins of the basin. The hydrochemical framework permitted recognition of other sources of waters to the basin, such as infiltration of water from the Rio Grande, and other rivers and arroyos; inflow from adjacent basins; and leakage along faults that were excluded because they have complex origins that obscure the atmospheric signal (see Supporting Information). Methods of chemical analysis of Cl^-, SO_4^{2-}, NO_3^-, Br^-, ^{14}C, ^{3}H, and chlorofluorocarbons (CFCs) and of the stable isotopic composition of water are given in ref *7*. Perchlorate analysis was performed using an IC/MS/MS procedure with a detection limit of 0.01 μg/L, and the N- and O-isotopic composition of NO_3^- was 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 (further details are in the Supporting Information).

Results and Discussion

Data on the water temperature, dissolved oxygen concentration, pH, specific conductance, radiocarbon age, ^{3}H, CFC-12, Cl^-, Br^-, SO_4^{2-}, NO_3^-, and ClO_4^- concentrations, and stable isotopic composition of 43 groundwater samples from 42 wells (Figure 1) in the MRGB that have <425 μmol/L Cl^- (<15 mg/L) were evaluated (see Table 1, Supporting Information). The median Cl^- concentration of the selected samples is 174 μmol/L (4.9 mg/L).

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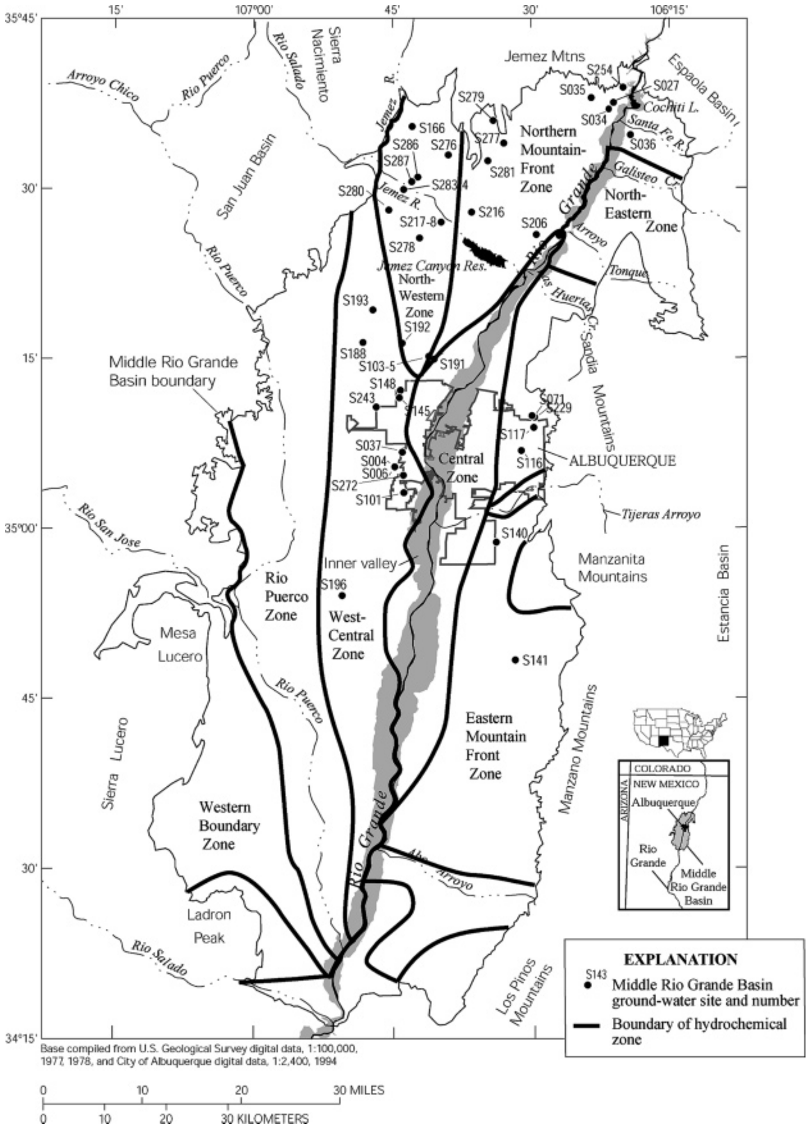

FIGURE 1. Location of wells sampled for perchlorate in the Middle Rio Grande Basin, NM, and location of hydrochemical zones. All samples are from the Northern Mountain Front, Northwestern, West-Central, or Eastern Mountain Front zones. Other hydrochemical zones are defined in refs *6* and *7*.

Anion Relationships. The relations among the various anions in the groundwater samples can be explained by three processes that may have affected some (or all) of the samples: (1) infiltration of meteoric waters that likely retain their atmospheric deposition anion ratios but have been concentrated by evapotranspiration processes; (2) addition of small amounts of chloride-enriched water, presumably associated with upward leakage of small amounts of saline water in the aquifer system; and (3) biological cycling of atmospheric constituents in soils prior to infiltration and recharge [for example, substantial amounts of NO_3^- and ClO_4^- may be taken up by plants and both are subject to microbial reduction under anaerobic conditions (see Supporting Information)].

Most of the samples have Br^-/Cl^- and SO_4^{2-}/Cl^- ratios similar to those in modern bulk atmospheric deposition (Figure 2a,b). The volume-weighted mean concentrations of Cl^-, SO_4^{2-}, NO_3^- (as N), and NH_4^+ (as N) in bulk atmospheric deposition at Sevilleta National Wildlife Refuge in the southeastern part of the MRGB (1989–2001) were 6.69, 16.15, 24.41, and 34.10 μmol/L (0.24, 1.55, 0.34, and 0.48 mg/L), respectively (*11*). The bulk deposition values include both wet and dry deposition and probably are more representative of solute concentrations that are recharged to aquifers than the wet-only deposition values. In comparison, the volume-weighted mean concentrations of Cl^-, SO_4^{2-}, NO_3^-, and NH_4^+ in wet deposition (only) at Sevilleta (1989–2001) were 3.80, 13.63, 20.74, and 21.75 μmol/L (0.13, 1.31, 0.29, and 0.30 mg/L), respectively (*11*). The Cl^-/Br^- weight ratio in potable meteoric groundwater containing less than 300 μmol/L (<10 mg/L) chloride in north-central New Mexico is approximately 75 (*12*), which corresponds to a Br^- concentration of 0.040 μmol/L (0.0032 mg/L) in bulk atmospheric deposition for the study area.

Concentrations of all major anions were substantially higher in groundwater than in atmospheric deposition, largely because of evapotranspiration. The concentration factor due to evapotranspiration (ET), relative to modern atmospheric deposition, was assumed to be given by the relative enrichment of Cl^-:

$$ET_{(\text{sample})} = Cl^-_{(\text{sample})}/Cl^-_{(\text{atm. dep.})} \qquad (1)$$

For comparison with atmospheric inputs, the concentrations, C_i, of Br^-, SO_4^{2-}, NO_3^-, and ClO_4^- in MRGB groundwater were adjusted for ET effects using

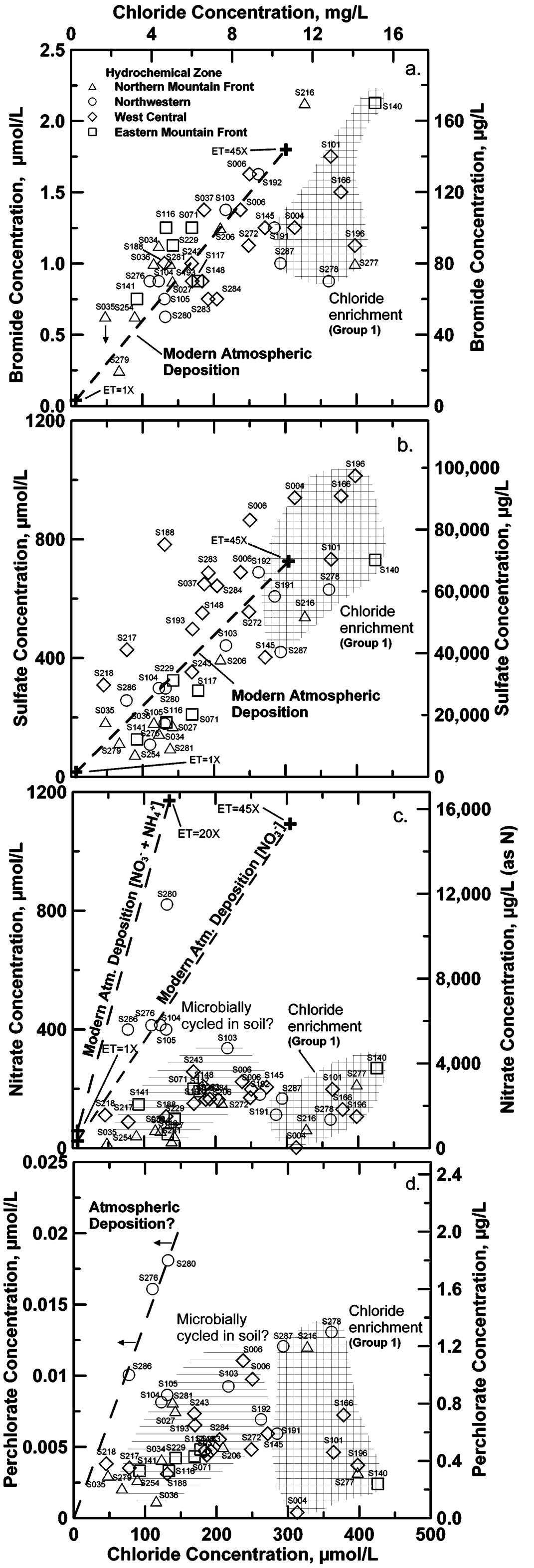

FIGURE 2. Relations of (a) Br^-, (b) SO_4^{2-}, (c) NO_3^-, and (d) ClO_4^- concentrations to Cl^- concentrations in the MRGB groundwaters. The dashed lines represent solute ratios in modern bulk atmospheric deposition in New Mexico for Br^- (*12*) and for Cl^-, SO_4^{2-}, NO_3^- and NH_4^+ (*11*). The inferred ClO_4^-/Cl^- mole ratio in bulk atmospheric deposition is $\geq 1.4 \times 10^{-4}$ (d), or $\geq 3.8 \times 10^{-4}$ as weight ratio. The group 1 samples (orthogonal lines) have excess Cl^-, presumably from deep saline sources. Samples in the horizontal-line pattern have NO_3^- and ClO_4^- concentrations that may have been lowered by biological processes in soils.

$$C_{\mathrm{i(adjusted)}} = C_{\mathrm{i(sample)}}/\mathrm{ET}_{\mathrm{(sample)}} \qquad (2)$$

The Cl^-, Br^-, and SO_4^{2-} concentrations in most samples are consistent with ET factors in the range of about 7–40 (Figure 2a,b). A subset of the samples, referred to as group 1 (samples S004, S166, S191, S196, S278, S287, S140, S101, and S277), appears to have relatively high Cl^- concentrations and Cl^-/Br^- ratios compared to other samples (Figure 2a) and may contain small fractions of saline water from upward leakage along faults in the basin (*7*).

Unlike Br^- and SO_4^{2-}, most of the NO_3^- concentrations are only about 30–50% of the values expected for atmospheric deposition (NO_3^- or $[NO_3^- + NH_4^+]$) concentrated by ET (Figure 2c). All but two of the groundwater samples are aerobic. Two samples (S004, S279) with low dissolved oxygen (see Table 1, Supporting Information) probably have been denitrified within the aquifer. Five samples from the Northwestern hydrochemical zone have NO_3^- concentrations relative to Cl^- that are similar to those of modern atmospheric deposition of NO_3^- or $[NO_3^- + NH_4^+]$ (Figure 2c). These five samples (S104, S105, S276, S286, and S280) may be the most representative of the bulk atmospheric deposition flux of N in the paleowaters of the MRGB.

There is remarkable similarity in the relations of NO_3^- and ClO_4^- relative to Cl^- in the MRGB waters (Figure 2c,d). Three of the samples that had NO_3^-/Cl^- concentrations consistent with modern bulk atmospheric deposition are among those with the highest ClO_4^- concentrations in the MRGB waters (S280, S276, and S286) and have a common ClO_4^-/Cl^- mole ratio of $(1.4 \pm 0.1) \times 10^{-4}$ (Figure 2d). The rest of the samples (excluding the group 1 samples) have ClO_4^-/Cl^- ratios lower than 1.4×10^{-4} and suggest a deficiency of ClO_4^- relative to Cl^-, following a pattern similar to that observed in the NO_3^- and Cl^- data (Figure 2c,d).

Spatial and Temporal Variations. Perchlorate has persisted in aerobic groundwater from the MRGB for tens of thousands of years, indicating long-term stability in aerobic aquifers and potential for extraction of environmental records of ClO_4^- concentrations in recharge. Two patterns are evident in ClO_4^- concentrations as a function of radiocarbon age (Figure 3). The highest ClO_4^- concentrations are in waters from the Northwestern zone, in the range of 0.6–1.8 μg/L, with radiocarbon ages of about 2–15 ka. The rest of the samples have relatively low ClO_4^- concentration in waters recharged within the past 10 ka and higher ClO_4^- concentrations in most waters recharged between 10 and 25 ka.

The apparent temporal trend in ClO_4^- concentrations is at least in part related to temporal variations in the estimated ET factors. The Cl^- data suggest an ET factor during the late Pleistocene (10–25 ka) nearly twice that within the Holocene (past 10 ka), which may be a response to greater plant abundance during the wetter climate (see Supporting Information) of the late Pleistocene (Figure 4). The ET factor also varied spatially (Figure 4), yielding low values from some waters apparently recharged at high altitude (depleted in ^2H from primarily the West-Central zone). The nine group 1 samples with elevated Cl^- concentration have apparent ET factors of 40–60 (Figure 4), presumably due to addition of small fractions of Cl^--rich saline water. The highest ET factor among samples with an atmospheric Cl^-/Br^- ratio is 48 (sample S216, Figure 4). Location of the recharge area and climate change over the past 28 ka may account for much of the observed temporal and spatial variation in ET.

Several patterns are evident in the ET-adjusted Br^-, SO_4^{2-}, NO_3^-, and ClO_4^- data as a function of radiocarbon age (Figure 5). The ET-adjusted Br^- concentrations and Br^-/Cl^- ratio were similar to the ratio in modern bulk atmospheric deposition during the Pleistocene but appear to have increased into the mid-Holocene and then decreased back to modern values more recently (Figure 5a). These trends

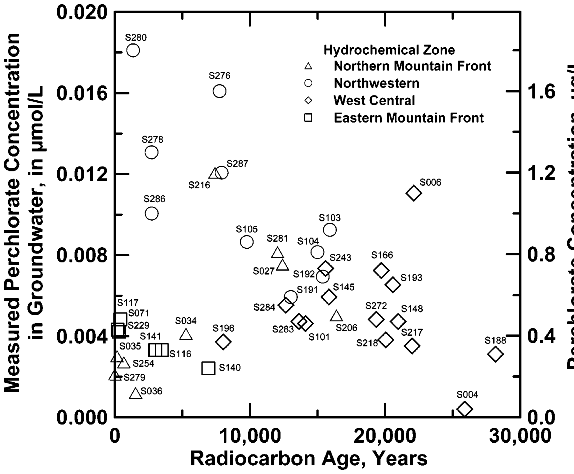

FIGURE 3. Measured perchlorate concentration in the MRGB groundwaters as a function of radiocarbon age and hydrochemical zone.

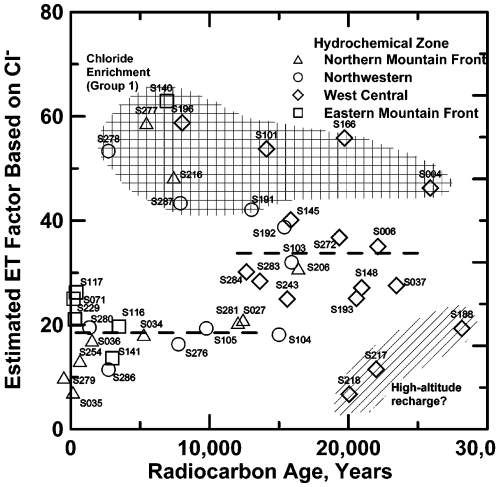

FIGURE 4. Evapotranspiration factor, ET, calculated from eq 1 as a function of radiocarbon age and hydrochemical zone. The orthogonal pattern represents waters that are enriched in chloride relative to atmospheric deposition (group 1), except for sample S216 which has an atmospheric Cl^-/Br^- ratio (Figure 2a). The slanted pattern represents waters thought to be recharged at high altitude (West-Central zone), during the last glacial period. The data suggest elevated ET during the last glacial maximum and pluvial period following and somewhat lower ET during the Holocene.

could reflect variations in the Br^-/Cl^- ratio of atmospheric deposition, or other processes, such as regional gains or losses of salts from deflation of desiccated lakes.

The ET-adjusted SO_4^{2-} concentrations were a minimum at the beginning of the Holocene, increasing in the younger waters toward that of modern bulk atmospheric deposition and increasing back through the Pleistocene to values higher than that of modern bulk atmospheric deposition in the oldest waters (28 ka). Values of $\delta^{34}S$ [SO_4^{2-}] were available for selected samples (see Table 1, Supporting Information) (Figure 5b). Samples from the mid- to late-Holocene have $\delta^{34}S$ [SO_4^{2-}] values of 3.5–3.9 ‰, nearly identical to those of modern atmospheric deposition from northern New Mexico (*13*). With increasing groundwater age, values of $\delta^{34}S$ [SO_4^{2-}] decrease to −3.1 ‰ as the ET-adjusted SO_4^{2-} concentrations increase (Figure 5b). This pattern in SO_4^{2-} concentration and $\delta^{34}S$ [SO_4^{2-}] is consistent with oxidation of small amounts of sulfide minerals, such as pyrite; traces of this are associated with the crystalline and volcanic rock detritus of the MRGB. The increase in ET-adjusted SO_4^{2-} concentration in the Pleistocene samples (Figure 5b) represents a maximum oxidation of about 15 μmol/L of pyrite of average $\delta^{34}S$ composition of about −5 ‰. This pyrite oxidation would utilize a maximum of about 56 μmol/L of O_2 in the aquifer, well within the range of variations in dissolved oxygen content of waters in the MRGB. The SO_4^{2-}/Cl^- ratio of the Holocene groundwater appears to be somewhat lower than the modern bulk atmospheric deposition value, perhaps because of anthropogenic enrichment of modern atmospheric SO_4^{2-} or minor loss of SO_4^{2-} during recharge. Overall, though, most of the ET-adjusted SO_4^{2-} concentrations are within a factor of 2 of modern bulk atmospheric deposition (Figure 5b).

Most of the ET-adjusted NO_3^- concentrations are only about 30−50% of the values in modern bulk atmospheric deposition. Low NO_3^-/Cl^- ratios may reflect N loss during biologic cycling processes in soils prior to recharge. Holocene groundwaters from the Northern Mountain Front zone appear to have somewhat lower ET-adjusted NO_3^- concentrations than Pleistocene groundwaters from the West-Central zone (Figure 5c). This difference may be related in part to the location or elevation of the recharge, as the West-Central zone recharge occurred at higher elevation. The highest values of the ET-adjusted NO_3^- concentration are from the Northwestern zone (Figure 2c) and are similar to NO_3^- concentrations observed in modern bulk atmospheric deposition of NO_3^- or are intermediate between NO_3^- and $NO_3^- + NH_4^+$ concentrations in modern bulk atmospheric deposition (Figure 5c).

$\delta^{15}N$ and $\delta^{18}O$ of Nitrate. The N- and O-isotope ratios of NO_3^- in the MRGB groundwater (expressed as $\delta^{15}N$ and $\delta^{18}O$ values; see Supporting Information), potentially provide information about N sources and recharge mass balances. The $\delta^{15}N$ values of NO_3^- range from about +1 to +7 ‰ (Figure 6), equal to or slightly higher than expected for atmospheric N deposition or N_2 fixation, which typically have average values of around 0 ± 4 ‰ (*14*, *15*). The $\delta^{18}O$ values of the NO_3^- range from about −4 to 0 ‰, much lower than those commonly reported for atmospheric NO_3^- deposition (+40 to +90 ‰), but similar to values commonly reported for NO_3^- formed by nitrification in soils (*15*−*17*). These data are consistent with an atmospheric source of the N, provided the NO_3^- formed largely after incorporation of the N in soils or plants and provided the N was isotopically fractionated to varying degrees prior to recharge as NO_3^-.

Variation in the $\delta^{15}N$ values of the NO_3^- may be related to soil processes that varied in relation to climate, topography, and moisture conditions in the recharge areas (Figure 6). Samples from the West-Central zone have relatively high $\delta^{15}N$ values between about +4 and +7 ‰, whereas samples from the Northwestern zone have lower $\delta^{15}N$ values (+1 to +5 ‰). Furthermore, there is an overall inverse relation between $\delta^{15}N$ values and N/Cl ratios (Figure 6), consistent with isotopic fractionation that might occur as a result of biologic cycling and return of varying amounts of N with low $\delta^{15}N$ from soils to the atmosphere prior to recharge.

Among the samples from the Northwestern zone, there appears to be a general increase in $\delta^{15}N$ with increasing age, from values near that of modern atmospheric N in the youngest waters to about 5 ‰ in the earliest Holocene waters (see Figure B, Supporting Information). Pleistocene waters from the West-Central zone have the highest average $\delta^{15}N$ values (up to about 7 ‰). This overall apparent trend toward decreasing $\delta^{15}N$ from Pleistocene to Holocene would seem to be in contrast to global analyses of $\delta^{15}N$ in plants and soils in forest ecosystems, which tend to be higher in warmer and drier conditions (*18*, *19*). Nevertheless, the MRGB data may be related similarly to variations in climate or vegetation. The young groundwaters with the highest NO_3^-/Cl^- ratios and lowest $\delta^{15}N$ values are thought to have been recharged in low-altitude arid regions where low water availability

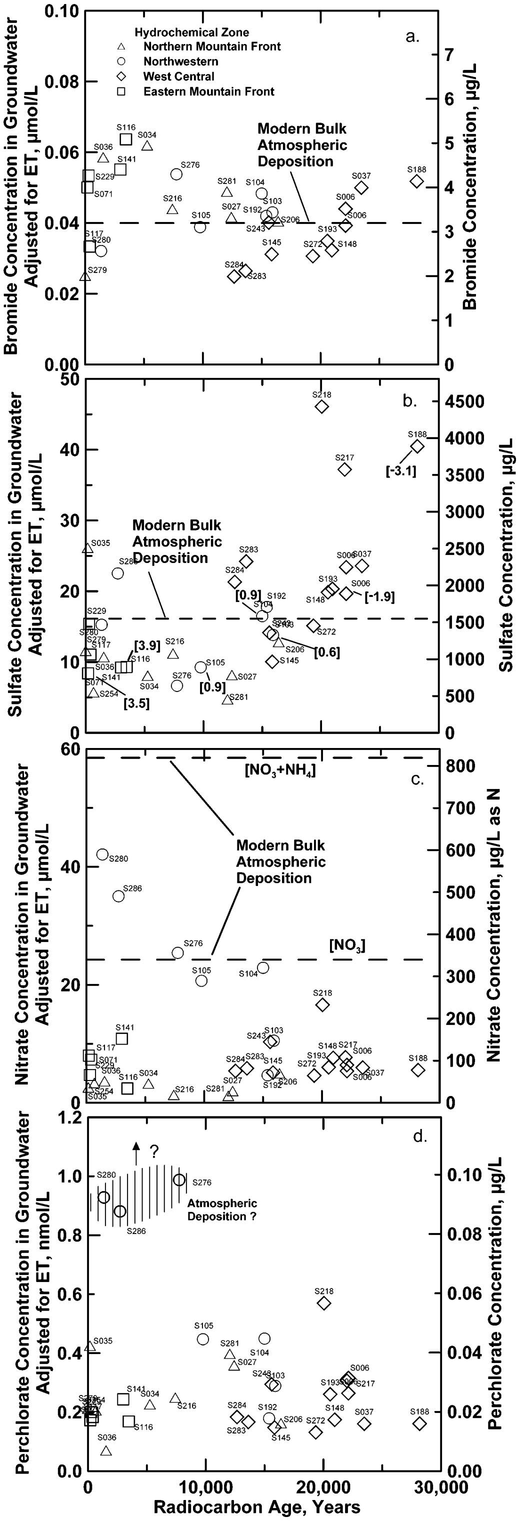

FIGURE 5. Concentrations of (a) Br$^-$, (b) SO$_4^{2-}$, (c) NO$_3^-$, and (d) ClO$_4^-$ in groundwater, after adjustment for evapotranspiration (ET) based on Cl$^-$, as a function of radiocarbon age. The group 1 samples (Figure 2a) were excluded throughout. Values in brackets in b are δ^{34}S[SO$_4^{2-}$]. The dashed lines in a–c indicate concentrations of Br$^-$, SO$_4^{2-}$, and NO$_3^-$ in modern bulk atmospheric deposition. Samples in the vertical-line pattern may represent bulk atmospheric deposition of ClO$_4^-$. The upward arrow and question mark in d indicate that the estimated ClO$_4^-$ concentration in atmospheric deposition could be higher than shown, if the remaining three samples in the patterned area also were affected by biological cycling prior to recharge.

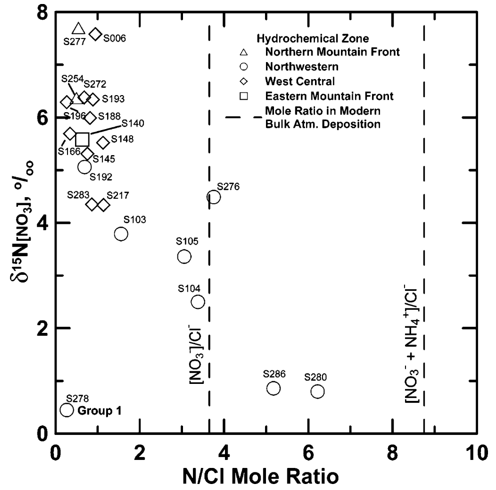

FIGURE 6. δ^{15}N of dissolved NO$_3^-$ as a function of the N/Cl mole ratio in groundwaters of the MRGB. The dashed lines represent NO$_3^-$/Cl$^-$ and [NO$_3^-$ + NH$_4^+$]/Cl$^-$ mole ratios in modern bulk atmospheric deposition at the Sevilleta National Wildlife Refuge (*11*), New Mexico.

limited biologic activity, whereas other groundwaters presumably were recharged in wetter, higher altitude areas with more biologic activity.

It is considered unlikely that the major variations in NO$_3^-$/Cl$^-$ and δ^{15}N were caused by denitrification within the aquifer after recharge. Even though dissolved oxygen content (DO) decreases over the age range of the samples, almost all waters remained aerobic (see Figure B and Table 1, Supporting Information). The apparent trend to lower DO in older waters is related in part to differences in DO of waters from different hydrochemical zones that happen to have different ages, different recharge temperatures, and different altitudes of recharge. Extensive denitrification is not supported by the NO$_3^-$ concentrations or dissolved N$_2$ data (*7*). Furthermore, increases in SO$_4^{2-}$ (Figure 5b) attributable to pyrite oxidation can be accounted for with O$_2$ as the terminal electron acceptor. Even if pyrite oxidation was coupled with denitrification, the maximum amount of pyrite oxidation (15 μmol/L for the West-Central zone waters, Figure 5b) would reduce only about 45 μmol/L of NO$_3^-$, which is only a small fraction of the amount present.

Atmospheric Deposition of ClO$_4^-$. Although the concentrations of ClO$_4^-$ in the MRGB groundwaters vary with age (Figure 3), when adjusted for temporal variations in the ET factor, the adjusted concentrations are mostly independent of age (Figure 5d). Two ranges in the ET-adjusted ClO$_4^-$ concentrations are shown in Figure 5d. The majority of the samples have concentrations of about 0.1–0.4 nmol/L. The ET-adjusted ClO$_4^-$ concentrations for this set (which excludes samples S280, S286, and S276 and all group 1 samples) are 0.26 ± 0.12, 0.34 ± 0.13, 0.24 ± 0.12, and 0.19 ± 0.03 nmol/L (0.026 ± 0.012, 0.034 ± 0.013, 0.024 ± 0.012, and 0.019 ± 0.003 μg/L) for waters from the Northern Mountain Front, Northwestern, West-Central, and Eastern Mountain Front hydrochemical zones, respectively. The average ET-adjusted value for ClO$_4^-$ from all 31 samples in the first set (excluding samples S280, S286, and S276 and all group 1 samples) is 0.25 ± 0.11 nmol/L (0.025 ± 0.011 μg/L), and the average ClO$_4^-$/Cl$^-$ mole ratio is $(0.4 \pm 0.1) \times 10^{-4}$. The second set consists of only three samples (S280, S286, and S276) from the Northwestern zone that have an average ClO$_4^-$ concentration of 0.93 ± 0.05 nmol/L (0.093 ± 0.005 μg/L) and an average ClO$_4^-$/Cl$^-$ mole ratio of $(1.4 \pm 0.1) \times 10^{-4}$.

Two scenarios seem possible for interpretation of the observed ClO$_4^-$ concentrations in the MRGB groundwater. In the first case, if atmospherically deposited ClO$_4^-$ passes through the soil environment without removal by soil processes, then a value of 0.025 ± 0.011 μg/L seems possible for the ClO_4^- concentration in Pleistocene–Holocene bulk atmospheric deposition in New Mexico. In such a case, the three samples with relatively high ClO_4^- concentrations (S280, S286, and S276) could indicate mobilization of concentrated ClO_4^- salts in the unsaturated zone. It is perhaps a coincidence that the estimate of the preanthropogenic concentration of ClO_4^- in bulk atmospheric deposition in this scenario is similar to the lowest values of ClO_4^- concentration reported in 17 samples of precipitation from Lubbock, TX (<0.01–0.02 μg/L) (*5*). The relatively wide range in reported ClO_4^- concentrations (*5*) in the majority of Texas precipitation samples (as high as 1.6 μg/L) might then include recycled (dust) components in addition to anthropogenic components, which would not be reflected in the net fluxes in MRGB recharge.

In the second scenario, ClO_4^- may have been partially lost in the soil environment before recharge of most of the MRGB groundwaters, as appears likely for NO_3^-. In this case, most of the ET-adjusted ClO_4^- concentrations of Figure 5d would be minimum estimates of bulk atmospheric deposition. Samples S280, S286, and S276 may best represent the preanthropogenic concentration of ClO_4^- in bulk atmospheric deposition in the MRGB, yielding an average of 0.93 ± 0.05 nmol/L (0.093 ± 0.005 μg/L), and a ClO_4^-/Cl^- mole ratio of $(1.4 \pm 0.1) \times 10^{-4}$. However, the possibility of some microbial cycling of ClO_4^- during recharge of samples S280, S286, and S276 cannot be eliminated. The estimates from samples S280, S286, and S276 are well within the reported range for the concentration of ClO_4^- and the ClO_4^-/Cl^- mole ratio in Lubbock, TX, precipitation [average ClO_4^- concentration = 3.3 ± 3.9 nmol/L (0.33 ± 0.39 μg/L), $n = 17$; ClO_4^-/Cl^- mole ratio of $(2.7 \pm 2.8) \times 10^{-4}$, $n = 8$] (*5*).

There is a strong similarity in the distribution of NO_3^- and ClO_4^- in the MRGB groundwaters (Figures 2c,d and 5c,d). The N-isotope data indicate varying amounts of biologic cycling of NO_3^- in soil zones prior to recharge (Figures 6 and 5c). Further, the ClO_4^-/Cl^- ratios are highest in samples S280, S286, and S276 from the Northwestern zone that also have the highest ET-adjusted NO_3^-/Cl^- ratios and low δ^{15}N values that are similar to those of modern bulk atmospheric deposition (Figures 2c,d and 5c,d). On the basis of the similarity of the variations of NO_3^- and ClO_4^- in these samples, the concentration of ClO_4^- in bulk atmospheric deposition in the MRGB implied by the second scenario (approximately ≥0.93 ± 0.05 nmol/L or ≥0.093 ± 0.005 μg/L, with a ClO_4^-/Cl^- mole ratio of $\geq(1.4 \pm 0.1) \times 10^{-4}$) is considered more likely than that derived from the first scenario.

Estimate of the Maximum ClO_4^- Concentration in Preanthropogenic Groundwater of the Southwest. If bulk atmospheric deposition had a ClO_4^- concentration of 0.093 μg/L, then it may be inferred that ClO_4^- concentrations as high as 4 μg/L are possible in preanthropogenic groundwater where ET approaches a factor of 40, assuming deposition and infiltration were in steady state. Higher ClO_4^- concentrations in groundwater could occur in recharge beneath arid areas where ET is greater than 40, where long-term accumulations of atmospheric salts are leached suddenly from dry soils, where other (nonatmospheric) natural sources of ClO_4^- exist, or where there are additional anthropogenic sources. Cl^- and Br^- data for groundwaters in parts of Arizona, Nevada, California, and New Mexico (*20*) with Cl^-/Br^- mass ratios of <200 have Cl^- concentrations of as much as 50 mg/L, implying ET factors as high as 200 and potential ClO_4^- concentrations of atmospheric origin reaching 19 μg/L.

Acknowledgments

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Supporting Information Available

Additional information on the occurrence of ClO_4^- in the environment, the hydrochemical properties of the MRGB, paleoclimatic information for the MRGB, and the analytical methods, Table 1 containing all the chemical and isotopic data from the MRGB used in this study, and two figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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