Anthropogenic sulfate loads in the Rio Grande, New Mexico (USA)

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ABSTRACT

The sources of SO_4 along a ~550 km stretch of the Rio Grande in New Mexico and western Texas were investigated using stable S isotopes. During 2007 and 2008, the $\delta^{34}S$ of dissolved SO_4 in the Rio Grande surface water varied over a narrow range from -1.6 to $+0.9‰$, which was consistent with the $\delta^{34}S$ of local fertilizers (-2.1 to $+1.6‰$) and was not consistent with Paleozoic evaporite sources of SO_4 in regional bedrock ($+7.6$ to $+12.9‰$). This is likely due the fact that SO_4 is the major component of N–P–K fertilizers used in the Rio Grande Valley, constituting about half of the total fertilizers by mass. The SO_4/Cl ratios of the groundwater system are relatively low (0.06 to 3) compared to the fertilizer source, suggesting that more Cl is added to the Rio Grande from geological sources as compared to SO_4. In the Mesilla Basin in southern New Mexico, we identified zones of mixing between recharging irrigation water with groundwater within the depth range of ~50–200 m below the ground surface. For this aquifer, Principal Component Analysis (PCA) indicated that Na–K–Cl concentrations were largely attributable to geological sources and SO_4–Mg–Ca concentrations to anthropogenic sources. Here, an additional anthropogenic source of SO_4 (with a $\delta^{34}S$ of $-2.7‰$) was linked to anaerobic decomposition of manure on a horse farm. In this case SO_4 concentrations (800 mg/L) increased by about three times compared to background SO_4 concentrations in groundwater (<300 mg/L). Because of the common application of H_2SO_4 in fertilizer manufacturing, anthropogenic SO_4 fluxes to rivers and shallow aquifers from irrigation waters can be significant worldwide.

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1. Introduction

Salinization of surface water and shallow groundwater in semi-arid and arid zones represents a significant global-scale environmental problem. The problem has intensified as population growth in desert areas has increased and more water has been used to support agriculture (e.g., Phillips et al., 2003; Oren et al., 2004; Farber et al., 2004; Hogan et al., 2007; Szynkiewicz et al., 2008a,b). High evaporation rates and groundwater recharge associated with salt-rich sedimentary rocks can increase the solute content of rivers and shallow aquifers; however, agricultural activity, including evapotranspiration and the application of fertilizers, can also degrade water quality and increase salinity (e.g., Oren et al., 2004; Farber et al., 2004). In addition to nitrogen (N), phosphorous (P) and potassium (K), fertilizers contain a variety of other ions, including the waste elements produced during their manufacturing. Therefore, the chemical composition of fertilizers varies locally and worldwide (e.g., Böhlke and Horan, 2000; Chae et al., 2009; Jiang et al., 2009) making it difficult to distinguish fertilizer inputs from natural solute

fluxes of sedimentary origin using major chemistry alone. Partly for this reason, accurate mass balance calculations that consider both natural and anthropogenic sources of salinization are problematic.

Sulfate (SO_4) is a common constituent among agricultural fertilizers (Mizota and Sasaki, 1996; Moncaster et al., 2000; Victòria et al., 2004; Brenot et al., 2007). High concentrations of SO_4 in fertilizers mainly result from the application of H_2SO_4 during the manufacturing process. In contrast to nitrate (NO_3), phosphate (PO_4) and K, which are largely consumed by plants, SO_4 and other major ions such as chloride (Cl), bromine (Br), magnesium (Mg), sodium (Na) and calcium (Ca) behave more conservatively in irrigation water (Oren et al., 2004). Therefore, the amount of SO_4 in a given hydrological system mainly depends on mixing between different end member sources that include, but are not limited to, the local bedrock, fertilizers and processes such as evapotranspiration.

The S isotope composition ($\delta^{34}S$) of dissolved SO_4 has been shown to be a good environmental tracer for investigations of hydrological systems because of the large variation of $\delta^{34}S$ in nature coupled with the small S isotope fractionation that occurs during dissolution of sulfate minerals and oxidation of sulfides in sedimentary and crystalline rocks (Krouse and Grinenko, 1991; Clark and Fritz, 1997), precipitation of sulfate minerals (Raab and Spiro, 1991) and uptake of SO_4 by plants (Krouse and Grinenko, 1991). Therefore, when

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the $\delta^{34}S$ values of natural geologic, anthropogenic and biogenic sources are different, S isotopes can provide estimates of the anthropogenic and biogenic impact on water resources (e.g., Krouse and Grinenko, 1991; Brenot et al., 2007; Szynkiewicz et al., 2008b).

In the northern hemisphere, the $\delta^{34}S$ of fertilizers ranges from -6.5 to $+11.7\permil$ (Table 1, mean $+3.7\permil$, n = 66; Mizota and Sasaki, 1996; Moncaster et al., 2000; Mallén, 2000; Victòria et al., 2004; Brenot et al., 2007) as they are mainly produced from crude oils, sulfide ores, and native S which have $\delta^{34}S$ values lower than most evaporites like gypsum and anhydrite (Mizota and Sasaki, 1996; Victòria et al., 2004). Conversely, fertilizers with significantly higher $\delta^{34}S$ of $+22\permil$ appear to be less common and applied locally (Knöller et al., 2005). Given that a large number of watersheds are dominated by sedimentary rocks of marine origin showing higher $\delta^{34}S$ values ($>+8$ to $+25\permil$) compared to lower $\delta^{34}S$ of SO_4 in fertilizers, S isotopes can be a useful tool for distinguishing among fertilizers and other geologic and biogenic sources. For example, the S isotope fingerprint of fertilizers has been successfully used to trace water contamination in countries such as Japan, Spain, France and Mexico (Mizota and Sasaki, 1996; Otero and Soler, 2002; Brenot et al., 2007; Szynkiewicz et al., 2008a,b). In contrast, considerably higher $\delta^{34}S$ values of fertilizers have been observed for the southern hemisphere (e.g., Australia, Brazil, and New Zealand), from $+6.6$ to $+20.7\permil$ (mean $+11.4\permil$, n = 13; Table 1); this is mainly due to the manufacturing of fertilizers from the imported S components (e.g., superphosphates and ammonia sulfates) which have considerably high $\delta^{34}S$ values (Mizota and Sasaki, 1996). In these countries, fertilizers generally cannot be successfully distinguished from geological SO_4 inputs because the S isotope compositions of natural and anthropogenic sources overlap.

The aim of this study was to use S isotopes, bulk chemical analyses and statistical modeling to evaluate the impact of fertilizers in increasing SO_4 concentrations (and overall salinity) in the Rio Grande, USA and its alluvial aquifers (Fig. 1A). The Rio Grande is the fourth longest river system in the U.S. and is the primary source of irrigation water for the Rio Grande Valley (Ellis et al., 1993). The fact that salt concentrations in the Rio Grande increase greatly from its headwaters in Colorado to West Texas has been known for decades (e.g., Lippincott, 1939; Haney and Bendixen, 1953; Wilcox, 1957). It has also been acknowledged that irrigation may contribute some salts to the Rio Grande (e.g., Wilcox, 1957; Moore and Anderholm, 2002); however, our study is motivated by the fact that no information has been collected to directly evaluate the impact of fertilizers on salt loads in the river. Instead, most investigations have focused on natural processes of salt addition such as high evaporation and evapotransporation rates attributable to the arid climate, groundwater recharge associated with Paleozoic sedimentary rocks of marine origin, and the upwelling of deep basinal waters and geothermal outflows (e.g., Phillips et al., 2003; Witcher, et al., 2004; Hibbs and Merino, 2006; Hogan et al., 2007; Moore et al., 2008). Here we report new data for S, H, and O isotopes and the concentrations of SO_4, Cl, Sr, Br, Ca, Mg, Na, K along a ~550 km stretch of the Rio Grande. We additionally measured the $\delta^{34}S$ and chemistry of several commonly used fertilizers in the lower Rio Grande Valley to establish the end member compositions for agricultural salt sources, which allowed for accurate estimations of SO_4 loads from fertilizers. Our investigation also included intensive sampling of surface and groundwater in the shallow aquifer of the Mesilla Basin of southern New Mexico to determine the current extent of mixing between recharging irrigation water and groundwater.

2. Study area

In New Mexico (Fig. 1A), the Rio Grande flows N–S along the Rio Grande Valley in the Rio Grande rift that began evolution ~30 Ma ago during widespread extension of the western United States (Keller and Baldridge, 1999). The Rio Grande flows through a series of alluvial-fill

Table 1
Variation of $\delta^{34}S$ value of common fertilizers applied in different countries.

| Country	Range of $\delta^{34}S$ [‰]	Reference
Japan	-4.9 to $+5.6\permil$ (mean $+1.3\permil$, n = 14)	Mizota and Sasaki (1996)
	-4.2 to $9.6\permil$ (mean $+2.7\permil$, n = 9)	
France	$+1.9$ to $4.1\permil$ (mean $+3.0\permil$, n = 3)	Brenot et al. (2007)
Spain	-6.5 to $+11.7\permil$ (mean $+4.4\permil$, n = 21)	Victòria et al. (2004)
England	$+1.0$ to $+10.3\permil$ (mean $+5.6\permil$, n = 4)	Moncaster et al. (2000)
Germany	-0.8 to $+11.3\permil$ (mean $+7.4\permil$, n = 10)	Mallén (2000)
USA (New Mexico)	-2.1 to $+4.8\permil$ (mean $+1.4\permil$, n = 5)	This study
Australia	$+6.6$ to $+8.5\permil$ (mean $+7.1\permil$, n = 4)	Mizota and Sasaki (1996)
New Zealand	$+15.7$ to $+20.7\permil$ (mean $+19.7\permil$, n = 6)	Mizota and Sasaki (1996)
Brazil	$+6.9$ to $+9.1\permil$ (mean $+7.5\permil$, n = 3)	Mizota and Sasaki (1996)

basins formed by a number of large extensional half grabens. These basins are filled with alluvial, fluvial, playa, and lacustrine sediments derived from erosion of adjacent Precambrian crystalline and Paleozoic sedimentary bedrock highlands and range in depth from less than 30 m to 4000 m (Keller and Cather, 1994). Recharge to the alluvial-fill basins mainly occurs from mountain recharge, inflow from adjacent aquifers, and infiltration of water from both the Rio Grande and its adjacent irrigation network (Ellis et al., 1993; Witcher et al., 2004; Sanford et al., 2004; Anning et al., 2007; Estaoe et al., 2008). However, some discharge to the surface-water system from the alluvial basins is thought to occur in the central and southern parts of the Rio Grande Valley; directly to the Rio Grande or indirectly through interception by agricultural drains (Ellis et al., 1993). Average annual precipitation delivered to the Rio Grande is less than 254 mm (Ellis et al., 1993) and decreases southward reaching less than 203 mm in El Paso, Texas. The highest water use in the Rio Grande Valley is for irrigation to support agriculture, which accounts for up to ~90% of all water use in the Rio Grande Valley (Ellis et al., 1993).

The concentrations of dissolved salts in the Rio Grande increase downstream. Salt concentrations are higher from October through February during the non-irrigation period (i.e., base-flow) as compared to concentrations during the irrigation period (March through September; e.g., Hogan et al., 2007). Irrigation water in southern New Mexico and south of El Paso is largely derived from storage in the Elephant Butte and Caballo Reservoirs located in central New Mexico (Fig. 1A). In addition to the possible impact from agricultural sources, salt loads in the Rio Grande are known to increase in part because of (i) the increasing annual temperatures southward which leads to higher evaporation and evapotranspiration rates in the irrigated fields, (ii) geothermal processes of the Rio Grande rift, which may enhance upwelling of highly mineralized groundwater from deeper parts of basins, and (iii) the dissolution of salt-rich sedimentary rocks in the central and southern parts of the Rio Grande Valley (e.g., Phillips et al., 2003; Hibbs and Merino, 2006; Witcher et al., 2004; Hogan et al., 2007; Moore et al., 2008).

3. Methods

3.1. Field sampling

In 2001, the Mesilla Basin groundwater and surface-water samples (Witcher et al., 2004; Fig. 1B) selected for major cation analysis were filtered with a 0.45 μm filter and placed in cleaned and rinsed 250 mL HPDE plastic bottles along with 3 mL of high purity concentrated HNO_3. Samples collected for anion analysis were unfiltered and placed in 250 mL HPDE plastic bottles. Alkalinity was measured in the field by
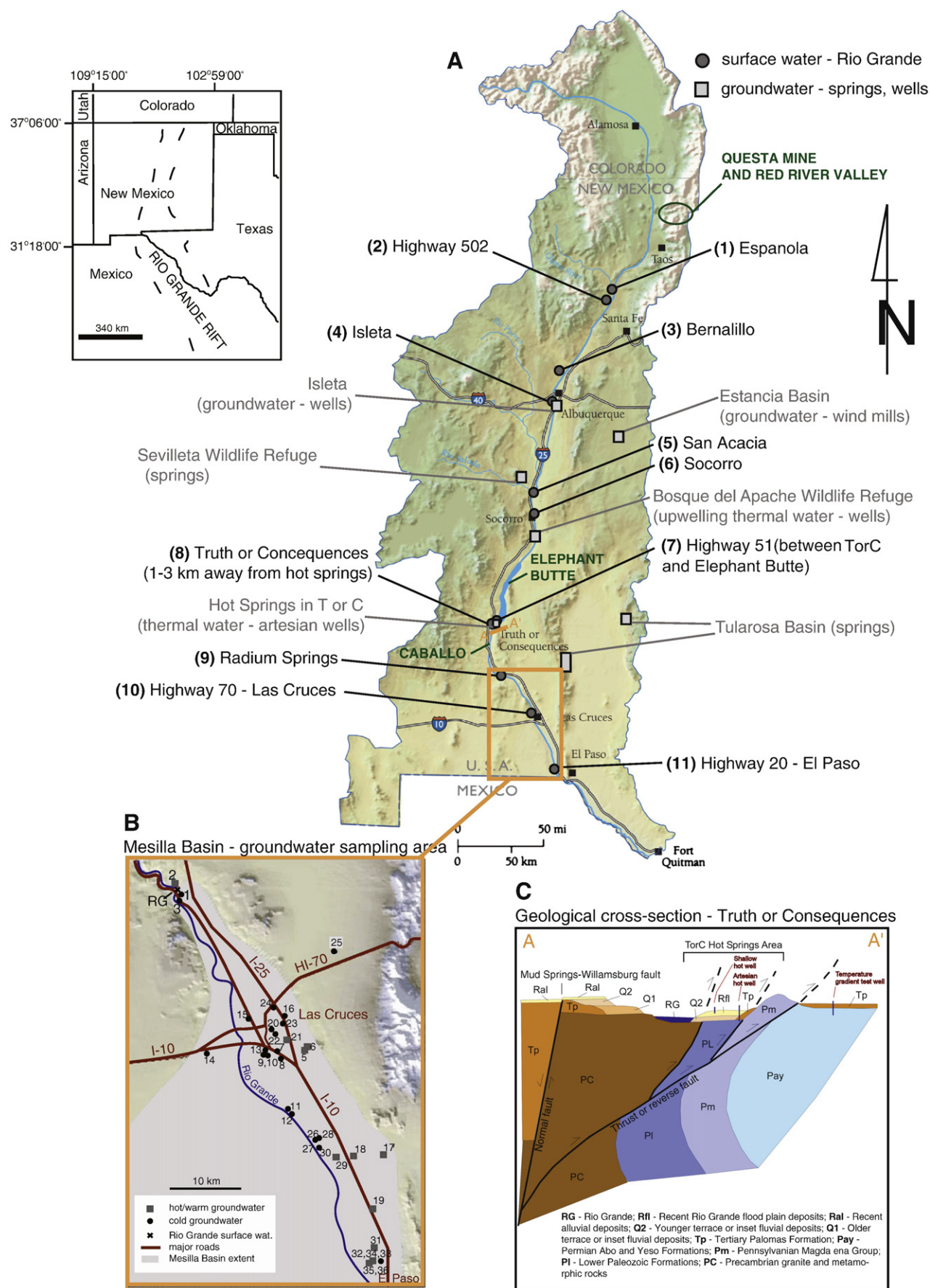
Fig. 1. (A) Location of surface and groundwater sampling points for the Rio Grande area in 2007–2008 and for (B) the Mesilla Basin in 2001. (C) The geological cross-section is presented for the Truth or Consequences area (A–A′). For figures in color the reader is referred to the online version of this manuscript.

adding a pre-measured packet of colorimetric reagent to a 50 mL water sample pipetted into a beaker over a battery-driven portable magnetic stirrer. The solution was titrated with 0.16 N H_2SO_4 until the required color change occurred. Temperature, pH, and conductivity were measured with Oakton series temperature compensated meters.

In October of 2007 and in April and November of 2008 surface-water samples were collected from the Rio Grande over a ~550 km distance from Española, New Mexico to northern El Paso, Texas (Fig. 1A). In most cases, samples were collected near major cities or next to the bridges crossing the Rio Grande at Española, Highway 502 to Los Alamos, Bernalillo, below Albuquerque at Isleta, San Acacia, Socorro, Highway 52 below the Elephant Butte Reservoir, Truth or Consequences, Radium Springs, Highway 70 at Las Cruces and Highway 20 in Northern El Paso (Fig. 1A). Surface water was collected in plastic bottles that were rinsed three times with the river water prior to sampling.

In addition to surface water samples, we expanded sampling (in 2007) to springs and groundwater from recharge areas in central and southern New Mexico (Fig. 1A) in order to determine major ion chemistry and $\delta^{34}S$ of SO_4 attributable to local bedrock sources. Specifically, samples were collected from recharge areas in the Estancia Basin and south of Albuquerque at Isleta, Sevilleta Wildlife Refuge, thermal waters near Socorro (Sedillo Spring), at Truth or Consequences (the Riverbend Hot Spring, the Artesian Hot Spring), and from the Tularosa basin (Fig. 1A). Additionally, groundwater samples were taken from two wells (including one thermal well) in the Bosque del Apache Wildlife Refuge; here, the upwelling of deeper circulating groundwater was previously reported by Barroll and Reiter (1995). Thermal waters are defined for this study as wells and springs with discharge temperatures of 10 °C above the local mean annual air temperature. Finally, five samples of commonly used, SO_4-rich fertilizers (two solid and three liquid) were obtained from the Mesilla irrigation district and analyzed for their chemical and S isotope compositions.

3.2. Chemical analyses

Laboratory analyses of elemental concentrations for the samples collected in the Mesilla Basin in 2001 (Witcher et al., 2004) were performed by Actlabs-Skyline in Tucson, Arizona, using an Elan 6100 ICP mass spectrometer for cations and an ion chromatograph for Cl, and SO_4. The spring and groundwater samples from the recharge areas were analyzed for SO_4 and Cl concentrations using a Dionex ICS-2000 ion chromatograph with a 30 mM KOH eluent. Anions were run on an IonPac®AS11-HC ion exchange column. Concentrations of Ca, Mg, Na and K were measured using a Perkin Elmer Analyst 800 atomic absorption spectrometer with hollow cathode lamps and a flame analyzer.

Surface water samples from the Rio Grande were analyzed for SO_4, Cl, Ca, Mg, Na, K, Sr and Br using an Alliance 2695 HPLC coupled with the PDA and conductivity detectors, an IC-Pak Anion HR column (glauconate/borate eluent) and IC-Pak Cation M/D column (EDTA/HNO_3 eluent) in the University of Wroclaw, Poland. The overall analytical precision was better than $\pm 5\%$ for all surface water and groundwater samples reported herein.

The chemical composition of solid and liquid fertilizers was measured using a Perkin Elmer 5300 DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) at the University of Texas at El Paso and an Alliance 2695 HPLC. Samples were analyzed using matrix-matched, multi-element atomic adsorption standards (diluted from 1000 ppm stock solutions) and U.S. Geological Survey standard reference water samples were used as an external check of precision and accuracy. Because of required dilution, particularly for the highly concentrated samples of liquid fertilizers, the analytical error was considerably bigger (10 to 20%) as compared to the natural water samples (<5%). Charge balance calculations indicated a 20–40% deficiency of cations among all the analyzed liquid fertilizers. Because we were able to duplicate S and P concentrations using the ICP-OES (S was recalculated as SO_4 and P as PO_4) and the HPLC techniques, we believe this is a result of underreporting of cations and not over-reporting of anions. The missing cations in this case are almost certainly protons. The pHs of the liquid fertilizers are around 0.5, demonstrating that the activity of H^+ is extremely high. However, because activity coefficients in these brine-like solutions are highly uncertain, it is difficult to quantify the exact molar concentration of protons. In addition to protons, volatilization of small amounts of ammonium (NH_4^+) might also account for some charge imbalance.

3.3. Sulfur, oxygen and hydrogen isotope analyses

Ground water and surface water samples in the Mesilla Basin, collected for $\delta^{34}S$ analysis in 2001(Witcher et al., 2004), were filtered in the field with a 0.45 μm filter into a 1 L HPDE bottle and, after lowering the pH to less than 3, about 5 to 10 g of granular (solid) $BaCl_2$ was added. The $BaSO_4$ precipitate was filtered on to a 0.45 μm filter and the precipitate and filter was placed wet in a small glass bottle and sent to Geochron Laboratories in Cambridge, Massachusetts for analysis, using a VG Micromass gas source stable isotope mass spectrometer. Laboratory results were reported with reference to the V-CDT standard. Analytical reproducibility was better than 0.2‰ for $\delta^{34}S$ analysis. Water samples collected for $\delta^{13}C(DIC)$ analysis were treated with sodium azide in the field, to inhibit any microbial activity, and stored in 250 mL HPDE bottles. Carbon isotope analysis was performed at Geochron Laboratories in Massachusetts using a VG Micromass gas source isotope ratio mass spectrometer. Isotopic data are reported with respect to the V-PDB standard. Analytical precision was about 0.2‰. Hydrogen and oxygen stable isotope analyses in 2001 (Witcher et al., 2004) were performed at the New Mexico Institute of Mining and Technology (NM Tech) in Socorro, New Mexico with a Thermo Finnigan Delta Plus XP mass spectrometer. Results are reported with respect to the V-SMOW standard and have analytical reproducibility better that 2‰ for δ^2H and 0.5‰ for $\delta^{18}O$ for duplicate samples.

Surface water and groundwater samples collected in 2007–2008 were analyzed for $\delta^{34}S$ using the methods previously described by Szynkiewicz et al. (2008a,b). In the laboratory, dissolved SO_4 was precipitated as $BaSO_4$ by reaction with 10–20 mL of 10% $BaCl_2$. The $\delta^{34}S$ of $BaSO_4$ was determined using an EA1110 elemental analyzer coupled to a Finnigan Mat 252 isotope ratio mass spectrometer via a ConFlo II split interface in the Stable Isotope Research Facility at Indiana University. Isotopic data are reported with respect to V-CDT (Vienna Cañon Diablo Troilite). Analytical reproducibility was better than 0.2‰ based on duplicates. Hydrogen and oxygen isotope compositions of waters were analyzed using a Hydrogen Device and Gas Bench, respectively. Isotopic data are reported with respect to V-SMOW and SLAP standards. Analytical reproducibility was better than 1‰ for δ^2H and 0.2‰ for $\delta^{18}O$ values based on duplicates.

3.4. Principal Component Analysis (PCA)

Principal Component Analysis was done for the Mesilla Valley sample locations only because sampling density along the Rio Grande would not support the statistical approach. Chemical and isotope compositions of the shallow aquifer of the Mesilla Basin are expected to be controlled by a number of natural and anthropogenic factors and PCA can help to resolve these differences. Generally, this method involves limiting the number of useful variables and describing the relationships among them (Manly, 1998). Factor analysis requires normal distribution of all variables (Drever, 1997; Manly, 1998), and this condition was confirmed by the Shapiro–Wilk test of normality for temperature, pH, Ca, Mg, SO_4, $\delta^{34}S(SO_4)$, δ^2H and $\delta^{18}O$ values of water, and $\delta^{13}C$ of dissolved inorganic carbon (DIC) used in

transformation. Normal distribution for Na, K, HCO_3, and Cl was attained by log transformation (Shapiro et al., 1968).

During standardized processing, all values of selected variables were replaced by standardized values (0 is a mean value, −1 and +1 are standard deviations). Transformation factors were estimated based on PCA to create the matrix of loadings. The values calculated from factor loadings vary from −1 to +1. Child (1970) has determined that values from −1.0 to −0.6 and from +0.6 to +1.0 are "significant" and thus these are the values we considered in our interpretation. If loadings for a particular factor have positive numbers, the variables are positively correlated and if they have negative numbers, the variables are negatively correlated (Drever, 1997). In order to achieve a more accurate interpretation of the results, the "varimax" rotation was used, and the percentage quota of each factor was calculated (Johnson, 1978). In this matrix, the number of factors was determined based on a statistical screen test (Cattell, 1966).

3.5. Mass balance calculations

Because water flow volumes were not quantified in all sampling sites (8 gauging stations available compared to 11 locations of sampling points selected along the studied portion of the Rio Grande), the bulk of our data treatment considers concentration and isotope data as opposed to elemental mass loads. However, we were able to reconstruct the volumetric flow rates for a number of the sampling sites using a combination of online gauging station data collected from the U.S. Geological Survey, the Elephant Butte Irrigation District, and the International Boundary and Water Commission. In most cases, we were able to pinpoint the flow rates for the exact days and sampling locations, but for a few samples it was necessary to use information collected from nearby locations (not more than a few kilometers from the sample site) and from flow data collected within a week of the sampling event. Using these volumetric flow rates we were able to calculate elemental mass loads for most river water samples (Table SI-1) by multiplying the stream water concentrations (in mg/L) by the flow rates (in L/s) and then converting the units of mg/s to kg/day.

4. Results and discussion

4.1. Concentration and mass load changes in the Rio Grande

Studying sources of salinization in the Rio Grande is a challenging problem because various environmental conditions such as climate and geology fundamentally change with downstream flow of the river and it is nearly impossible to quantify all the individual inputs to the salt load. Generally, concentrations of dissolved solids in the Rio Grande increase downstream and reach the highest concentrations in the southern alluvial-fill basins of the Rio Grande Valley near El Paso, Texas (Mills, 2003; Hibbs and Merino, 2006; Hogan et al., 2007; Moore et al., 2008). Similar to previous studies, we found that the conductivity and concentrations of major cations and anions showed a progressive, increasing trend with the downstream flow of Rio Grande during all sampling events (Figs. 2, 3). The concentrations of elements were slightly higher for the non-irrigation (base-flow) period in November when the streamflow of the Rio Grande was low compared to October and April (Figs. 2, 3; Table SI-2). This is due in part to the lack of snowmelt runoff from the Rio Grande headwaters in November and to the managed sections of the river where streamflow is controlled by release of water from the Elephant Butte and Caballo dams according to agricultural needs. During the November 2008 base-flow sampling period a distinctive increase in conductivity and

concentrations of Cl, K, Na, Ca, Sr, and Br was observed for the area of Truth or Consequences (Fig. 2) where thermal waters are used in spas and mineral baths. These thermal waters show high concentrations of Cl (1552 to 2053 mg/L), Na (710 to 922 mg/L), Ca (151 to 185 mg/L), and high values of conductivity (4.5 to 4.8 mS/cm) (Table SI-3). After water use in spas and mineral baths, the thermal waters flow directly to the Rio Grande. It is likely that some thermal waters also discharge naturally in the same location, which explains the locally important increase in salt concentrations (Fig. 2). The thermal waters of Truth or Consequences contribute dissolved solids from geological sources; even though the increase of salinity is attributed at least in part to anthropogenic activities because some of the thermal water is delivered through artesian wells managed by private owners of local spas.

The calculated mass fluxes (Fig. 4) for April 2008 and November 2008, show that water management practices, related primarily to storing of water in the Elephant Butte Reservoir (central New Mexico) for the irrigation season, essentially control the seasonal fluxes of dissolved solids in the Rio Grande. The highest fluxes of SO_4, Cl, Na, Mg and Ca were noted below the Elephant Butte Reservoir for April 2008 when larger amounts of water had been released to support agriculture (Fig. 4). A large loss of surface water (via irrigation and presumably some to the near-surface aquifer) and a decrease of chemical flux appear to take place below the Elephant Butte Reservoir because the fluxes of most elements decreased downstream to El Paso, Texas in April 2008 (Fig. 4). The Rio Grande is a losing stream over much of the southern Rio Grande Valley due in large part to the increasing municipal and agriculture water demands of the regions around Las Cruces, New Mexico and El Paso, Texas (Nickerson, 1986).

In contrast to April 2008, the opposite trend was observed for the base-flow condition of November 2008 when the mass fluxes of SO_4, Cl, Mg, Ca, Na, K, Sr increased downstream from the Elephant Butte Reservoir to El Paso (Fig. 4). These increases might have resulted from both i) the discharge of upwelling saline and thermal groundwater (e.g., Witcher et al., 2004; Hogan et al., 2007), which is expected to have the largest impact during base-flow conditions, and/or ii) the return flows of irrigated water into drains and canals that are part of the Rio Grande diversions within the irrigation districts.

Most of the Rio Grande surface water samples had relatively low NO_3 concentrations, <0.5 mg/L, with three exceptions for Socorro (3 mg/L), Truth or Consequences (91 mg/L) and northern El Paso (11 mg/L) in November 2008 (Table SI-2). Consistent with previous work, our results indicate that agriculture is an important sink of N in the Rio Grande Valley and the wastewater effluents from nearby cities are likely the largest sources of N to the river (Oelsner et al., 2007). Low N loads and concentrations in the Rio Grande are proposed to result from cultivation of crops that do not require much nitrogen fertilization (e.g., alfalfa), from significant loss of water due to infiltration and from the relatively low NO_3 content in agriculture return flows (Oelsner et al., 2007). Although fertilizers do not contribute large amounts of NO_3 to the river, the chemistry of the tested N–P–K fertilizers from the Mesilla Basin (southern Rio Grande Valley; Fig. 1B) indicates that other constituents (e.g., SO_4, Na, Cl, and Br) are loaded in greater quantities and SO_4 constitutes about half of the total fertilizer by mass (Fig. 5, Table SI-4). Sulfate (SO_4) is a major anion constituent in the Rio Grande and exceeds Cl concentrations for many locations (e.g., Healy, 1996; Moore and Anderholm, 2002). While chemical data alone cannot distinguish between geological and anthropogenic SO_4 loads, S isotopes can help to distinguish between these end members.

Fig. 2. Variations of conductivity and Cl, K, Mg, Na, Ca, Sr, and Br concentrations along the Rio Grande for irrigation periods (Oct 2007 and Apr 2008) and base-flow condition (Nov 2008). Numbers above the dotted lines indicate locations of sampling points in Fig. 1A.
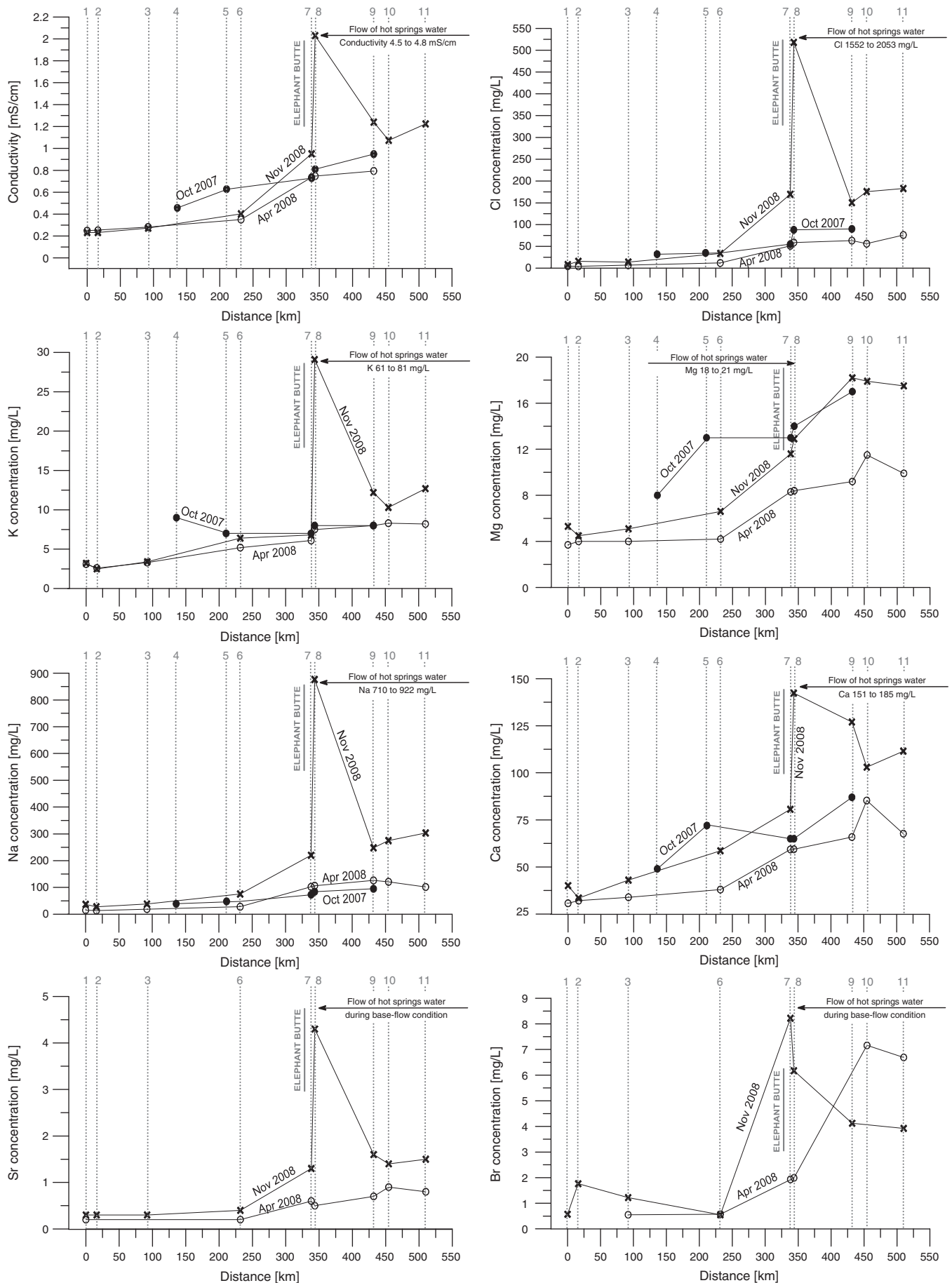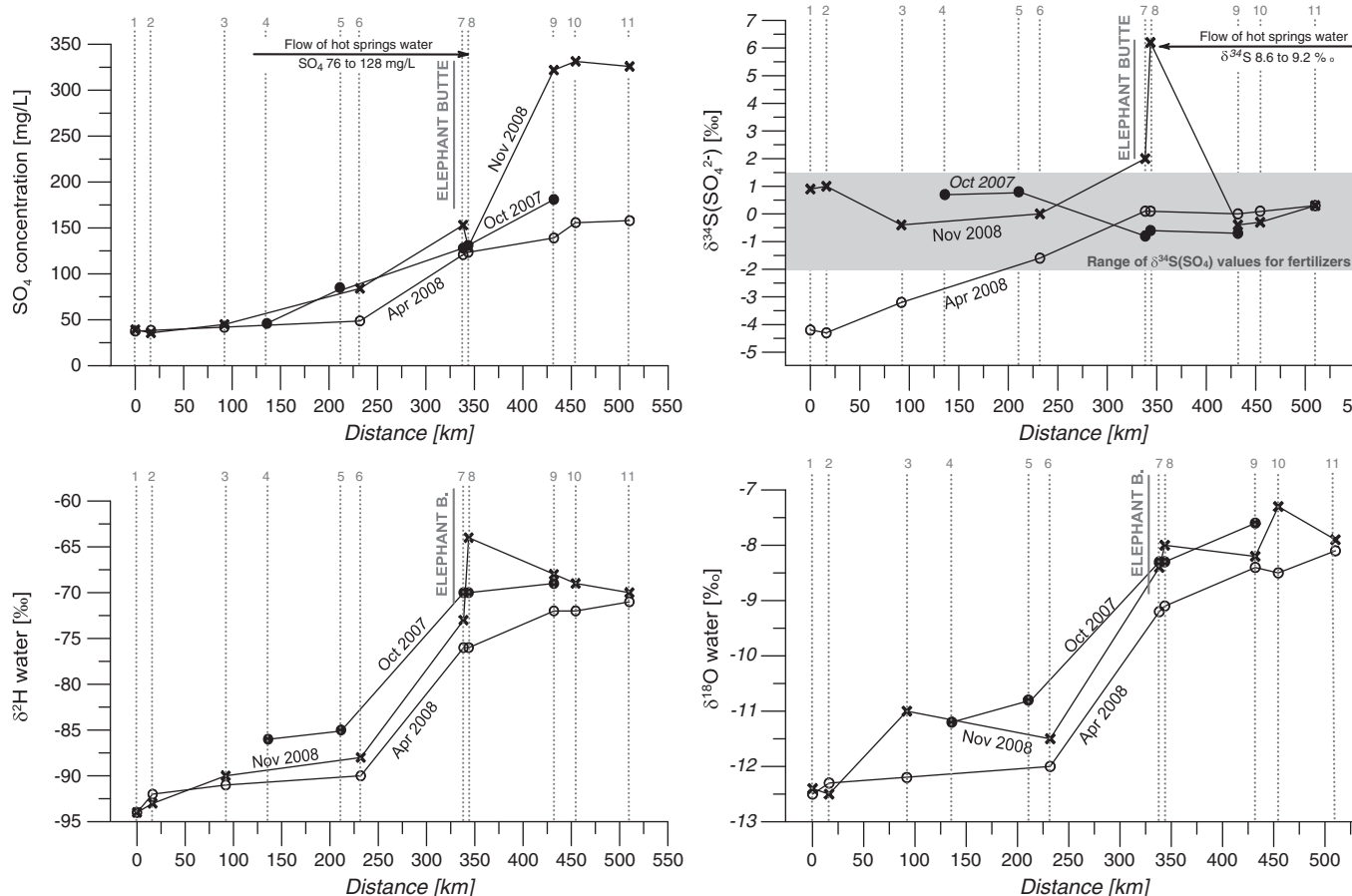
Fig. 3. Variations of SO$_4$ concentrations, δ^{34}S(SO$_4$), δ^2H and δ^{18}O values of surface water along the Rio Grande for irrigation periods (Oct 2007 and Apr 2008) and base-flow condition (Nov 2008). Numbers above the dotted lines indicate locations of sampling points in Fig. 1A.

4.2. Sulfur isotopes in the Rio Grande basins and in fertilizers

Results for δ^{34}S measurements of dissolved SO$_4$ in natural samples and fertilizers of the Rio Grande Valley are presented in Tables SI-2 to SI-5 and in Fig. 6. These results show a significant difference in δ^{34}S between geological and fertilizer SO$_4$ sources for the studied area. Generally, the springs and groundwater from the recharge areas of the Rio Grande Valley (Fig. 1A) have δ^{34}S values ranging from $+5.6$‰ to $+13.1$‰ (median $+10.0$‰, n = 16; Fig. 6, Table SI-3). These values are consistent with the δ^{34}S of sulfate minerals in Paleozoic sedimentary formations and weathered sulfide magmatic accessory minerals of the Precambrian and Tertiary plutonic and volcanic rocks that dominate this part of the Rio Grande rift.

The highest values of δ^{34}S were noted for the Estancia ($+12.9$ and $+13.1$‰) and Tularosa ($+10.0$ to $+11.6$‰) basins, which are comprised of thick, sulfate-rich sequences of Lower and Middle Permian evaporites. The δ^{34}S values for the Lower and Middle Permian gypsum/anhydrite-rich formations in central and southern New Mexico show consistent ranges from $+12.5$ to $+15.1$‰ (median 13.0‰, n = 13) and from $+10.9$ to $+12.8$‰ (median 12.0‰, n = 10), respectively (Szynkiewicz et al., 2010a), and they appear to be in a good agreement with δ^{34}S values observed for springs and groundwater of the Estancia and Tularosa basins (Fig. 6).

Slightly larger variability and lower δ^{34}S values were noted for springs and groundwater in the Sevilleta Wildlife Refuge ($+8.1$ and $+10.4$‰) and south of Albuquerque at Isleta ($+7.6$ and $+12.9$‰) located in Central New Mexico (Fig. 6). This variation is most likely due to higher contributions of SO$_4$ coming from the dissolution of the

Lower Paleozoic and/or Mesozoic formations. The δ^{34}S of these formations have not been studied in detail. However, the Paleozoic units are the most likely source for some locations, as groundwater from the thermal waters in Truth or Consequences, which is thought to originate from deep circulation in the Lower Paleozoic rocks (Fig. 1C), contains sulfate with a δ^{34}S ($+8.9$ and $+9.1$‰) comparable to the Sevilleta and Isleta samples (Fig. 6).

Another geological SO$_4$ source with lower δ^{34}S may come from oxidation of sulfides in the Paleozoic shales and limestone with wide negative δ^{34}S, -30 to 0‰ (e.g., Clark and Fritz, 1997). Additionally, hydrothermal sulfide-rich ores of Tertiary age along the Rio Grande rift have negative δ^{34}S values of -26 to -3‰. These sulfides likely precipitated from hydrothermal fluids influenced by S from the thermal decomposition of evaporites and organic matter in Paleozoic strata (Lueth et al., 2005). Although sulfide oxidation may be important in the upper Rio Grande, it is less likely that sulfide weathering is a dominant mechanism for SO$_4$ generation under the semi-arid conditions of the middle and lower Rio Grande Valley; particularly, in downstream locations where surface runoff is limited because of low precipitation and leaching of oxidative products from surface/subsurface environments is minimized. This suggestion is supported by the fact that sulfide oxidation signatures are largely absent from SO$_4$ in the alluvial-fill basins within the Rio Grande rift because of the prevailing sedimentary source of SO$_4$ (Szynkiewicz et al., 2009). In our study, the lowest δ^{34}S values for ground water sources were observed for the Sedillo Spring at Socorro ($+6.1$‰) and the Upper Ash Spring at the San Andres Mountains of Tularosa Basin ($+5.9$‰); these values could be consistent with the local mixing of sedimentary SO$_4$ and SO$_4$ from sulfide weathering. Weathering of
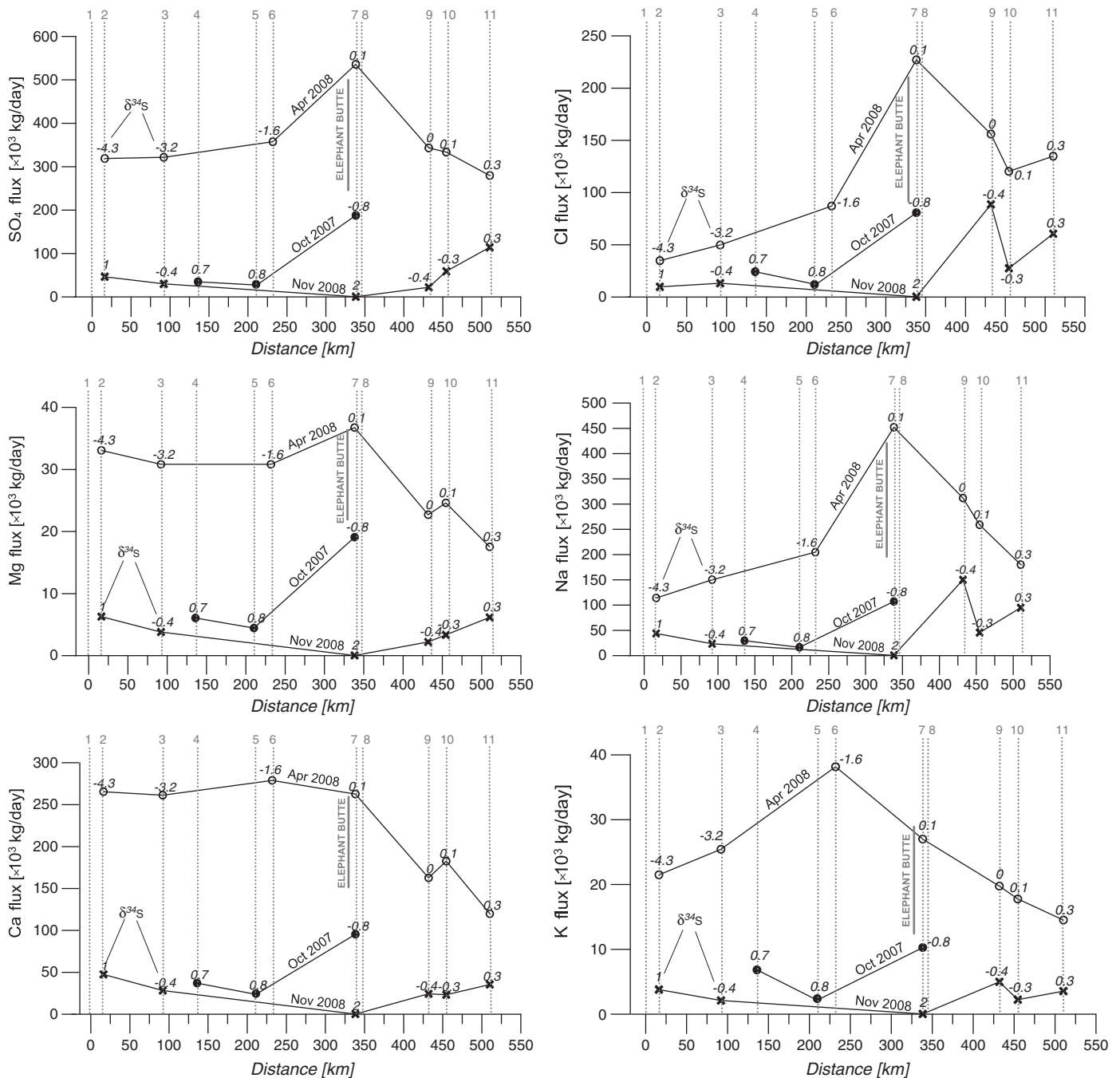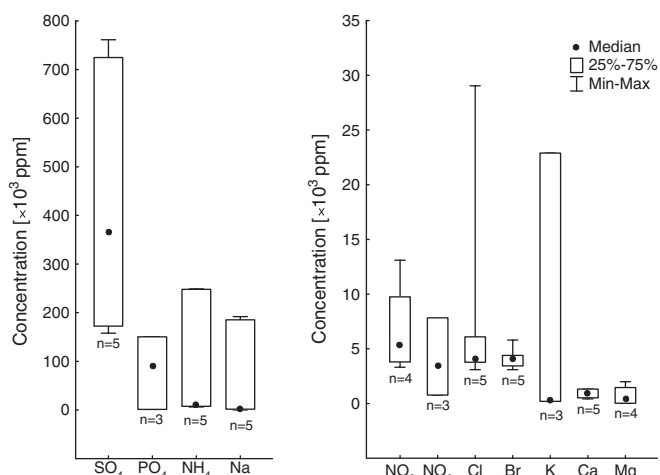
Fig. 4. Estimated fluxes of SO₄, Cl, Mg, Ca, Na, and K to the Rio Grande for irrigation periods (Oct 2007 and Apr 2008) and base-flow condition (Nov 2008). The $\delta^{34}S$ of SO₄ is presented for each data point for comparison. Numbers above the dotted lines indicate locations of sampling points in Fig. 1A.

sulfides is likely more important at these locations because of the abundance of Tertiary magmatic/volcanic deposits.

Microbial dissimilatory sulfate reduction has been recognized in many aqueous environments as a distinctive process causing withdrawal of SO₄ and significantly increasing its $\delta^{34}S$ (Krouse and Grinenko, 1991; Canfield, 2001). Particularly, wetland areas and riparian zones where reducing conditions are constant in the near-surface throughout the year can be greatly affected by this process. In the semi-arid region of the Rio Grande rift, however, the effect of sulfate reduction on aqueous SO₄ only occurs locally in areas with larger amounts of organic matter in sediments. Szynkiewicz et al.

(2009) reported increases in $\delta^{34}S$ of SO₄ attributable to microbial processes of about 7‰ (from +14 to +21‰) in playa-lake settings of Pleistocene and Holocene age with larger accumulations of organic matter. In the far southern region of the study area, the prevailing dry conditions and lower rates of organic matter accumulation related to sparse vegetation cover are likely major factors accounting for smaller rates of sulfate reduction in the rift basins (Szynkiewicz et al., 2009, 2010b). Since all the studied waters from recharge zones had a $\delta^{34}S$ of SO₄ within the expected range of $\delta^{34}S$ for Paleozoic bedrock (Fig. 6), we infer that sulfate reduction has negligible effect on SO₄ in groundwater that both infiltrates through poorly developed soil

Fig. 5. Variations of anion and cation concentrations in five samples of the tested N–P–K fertilizers from the Mesilla irrigation district.

Table 2
Variation of $\delta^{34}S$ in various SO_4 sources present in the Rio Grande rift.

SO_4 source	$\delta^{34}S$ [‰]
Paleozoic bedrock (evaporites)	$+8$ to $+15$
Sedimentary and hydrothermal sulfides	-30 to 0
Sulfate reduction — playa lakes	$+14$ to $+21$
Fertilizers	-2.1 to $+4.8$

and highly populated regions of the Eastern United States and Central Europe, there are lower rates of atmospheric S deposition in the Rio Grande rift because of limited precipitation and lesser human settlement (EPA report, 1999). Table 2 summarizes the $\delta^{34}S$ variation of the various SO_4 sources expected to be important in the hydrological system of the Rio Grande Valley.

4.3. Impact of fertilizers on salt loads in the Rio Grande

Except for three sampling sites in upstream locations in Española, Highway 502 near Los Alamos and Bernallilo in April of 2008 (Fig. 3), the $\delta^{34}S$ of dissolved SO_4 in the Rio Grande varied over a narrow range from -1.6 to $+0.9$‰ during the investigated seasons of 2007 and 2008 (Fig. 3, 6; Table SI-2) and overlapped with similar low $\delta^{34}S$ reported by previous investigators for the Middle and Southern Rio Grande (e.g., Plummer et al., 2004; Witcher et al., 2004; Moore et al., 2008). The range of $\delta^{34}S$ in the Rio Grande considerably differed from the range of $\delta^{34}S$ measured for the recharge areas of the Rio Grande Valley in central and southern New Mexico, $+7.6$ to $+12.9$‰ (Fig. 6, Tables SI-2 and SI-3) and from the upwelling groundwater in the Socorro and Mesilla basins, the alluvial basins of the Rio Grande (about $+8$ to $+10$‰; see Sections 4.4 and 4.5 below for details). Conversely, the low $\delta^{34}S$ of the Rio Grande SO_4 overlapped with the $\delta^{34}S$ for the measured fertilizers, suggesting a significant contribution of SO_4 in the Rio Grande is from anthropogenic sources (Figs. 3, 6). Despite this clear overlap in $\delta^{34}S$ of fertilizers and river SO_4, the $\delta^{34}S$ measured in a few upstream locations probably reflects inputs from geologic SO_4 sources. For example, the $\delta^{34}S$ measured in April 2008

profiles and/or interacts with ancient playa deposits and alluvial formations formed in earlier stages of rift evolution.

In contrast to geological SO_4 sources, the various N–P–K fertilizers from the Mesilla irrigation district show significantly lower $\delta^{34}S$ values, ranging from $+1.4$ to $+1.6$‰ for liquid fertilizers and -2.1 to $+4.8$‰ for solid fertilizers (Table SI-4, Fig. 6). These values overlap with the $\delta^{34}S$ reported for fertilizers elsewhere (Table 1; Mizota and Sasaki, 1996; Moncaster et al., 2000; Mallén, 2000; Victòria et al., 2004; Brenot et al., 2007). Because they significantly differ in $\delta^{34}S$ from the geological SO_4 inputs of sedimentary origin (Fig. 6) and agriculture is the major use (~90%) of Rio Grande surface water, the $\delta^{34}S$ of fertilizers can be used for tracing the anthropogenic flux of SO_4 to the hydrological system (i.e., surface and shallow ground water) within the Rio Grande Valley. We assume that other anthropogenic sources of SO_4 such as atmospheric deposition are considerably smaller compared to the fertilizer source. In contrast to industrialized
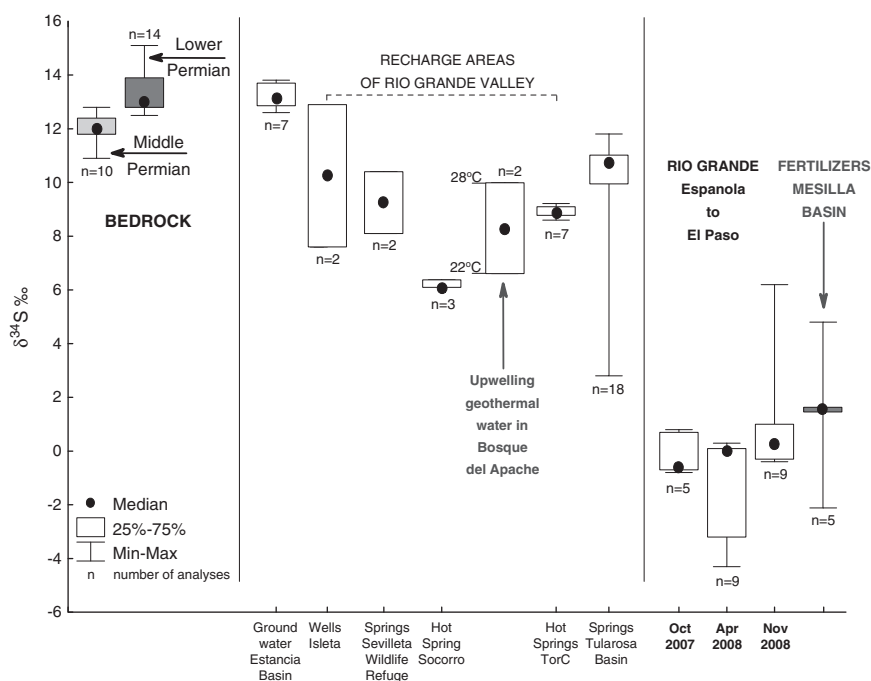

Fig. 6. Variations of $\delta^{34}S(SO_4)$ values for springs and wells from Estancia Basin, Isleta below Albuquerque, Sevillieta Wildlife Refuge, Socorro, Bosque del Apache, Truth of Consequences and Tularosa basin compared to $\delta^{34}S(SO_4)$ values for the Rio Grande surface water and fertilizers from the Mesilla Basin irrigation district. Data of $\delta^{34}S$ presented in Table SI-3 for Estancia and Tularosa basins were combined with additional seasonal observations presented by Szynkiewicz et al. (2009).

between Española and Bernalillo (-4.3 to $-3.2‰$; Fig. 3) is likely related to SO_4 influx from sulfide oxidation.

In the northern part of the rift, the Rio Grande flows through the extensive Neogene Taos volcanic plateau which receives snow cover during the winter. In addition, the Taos recharge area is abundant in hydrothermal sulfide-rich mineralization (e.g., Schilling, 1956; Ross et al., 2002) which has been mined at the Questa mining district located in the Red River Valley (Fig. 1A). This valley is drained by the Red River which flows to the Rio Grande over a distance of ~20 km from the abandoned Questa mine. SO_4 concentrations in the mine acid drainage of this area are high, up to ~2500 mg/L (Nordstrom et al., 2005). Therefore, it is inferred that particularly after the snowmelt in April of 2007 a large volume of melt water interacted with the surface/ subsurface environments of the Red River Valley and leached out higher quantities of SO_4 from sulfide sources with low $\delta^{34}S$ values. The $\delta^{34}S$ of SO_4 in surface water of the Red River Valley shows negative values of -8.5 to $-3.1‰$ (Nordstrom et al., 2005), which is derived mainly from oxidation of pyrite with $\delta^{34}S$ of -13.6 to $0.0‰$ (Campbell and Lueth, 2008). In April 2008, the $\delta^{34}S$ of the Rio Grande surface water was $-4.3‰$ which was similar to the average $\delta^{34}S$ of $-5.4‰$ reported for the surface water of Red River Valley after Nordstrom et al. (2005).

Several studies have emphasized the importance of the discharge of saline groundwater of thermal origin to increasing salt loads in the Rio Grande (e.g., Swanberg, 1975; Frenzel and Kaehler, 1992; Reiter, 1999; Witcher et al., 2004). This suggestion was largely inferred from increasing Cl concentrations and increasing Cl/Br ratios (typical of thermal water) at many downstream locations near the distal ends of alluvial sub-basins (e.g., Reiter, 1999; Hibbs and Boghici, 1999; Hogan et al., 2007; Moore et al., 2008; Hibbs and Merino, 2006). However, this suggestion is not compatible with our results for SO_4 loading in the studied section of the ~550 km Rio Grande stretch.

If geothermal groundwater contributed important amounts of SO_4 to the Rio Grande, the $\delta^{34}S$ of the river water would have reflected the $\delta^{34}S$ of the sedimentary bedrock of the Rio Grande Valley, which is characterized by relatively high $\delta^{34}S$ values ($+7.6$ to $12.9‰$; Fig. 6). Evidence of geothermal groundwater SO_4 was observed only in the Truth or Consequences area in November 2008 ($+2.0$ and $+6.2‰$) and related to the inflow of thermal water ($+8.6$ to $+9.2‰$; Table SI-3) from spas and mineral baths common in this area (Figs. 2, 3). During this period of the year there is very little flow of the Rio Grande below the Elephant Butte Reservoir, located ~10 km upstream of Truth or Consequences. Therefore, the impact of the geothermal water is magnified locally, but decreases in the irrigation season when the water is diluted by water released from the dam (Fig. 2). During our sampling periods, the concentrations of SO_4 in the Rio Grande were higher (up to 330 mg/L) than those for Cl (up to 180 mg/L) and they increased downstream while the $\delta^{34}S$ of the river water remained distinctively low (-1.6 to $+0.9‰$) and varied over a range typical for regional fertilizers (-2.1 to $+1.6‰$; Fig. 7). Similar to surface water, a $\delta^{34}S$ of $-0.5‰$ (Table SI-2) was observed for the Isleta drain located below the city of Albuquerque.

One would expect that discharge from upwelling thermal and non-thermal groundwater with higher $\delta^{34}S$ to have the largest impact during base-flow conditions. In November 2008, the fluxes of SO_4, Cl, Mg, Ca, K, and Na increased downstream from the Elephant Butte Reservoir to El Paso (Fig. 4), these increases were still accompanied by low $\delta^{34}S$ values (-0.4 to $+0.3‰$) excepting the one sample collected at Truth or Consequence ($+6.2‰$) where the inflow of geothermal water is related to the mineral baths and spas (Fig. 2). Therefore, the $\delta^{34}S$ values demonstrate that the bulk of the SO_4 in the Rio Grande is coming from shallow sources, not evaporate-derived brine. Whereas some SO_4 loading from the geological sources does occur over the study area (e.g., Española area in April 2008, Truth or Consequences in November 2008), our data suggest that these sources represent only a minor, localized flux for SO_4 over the studied ~550 km distance
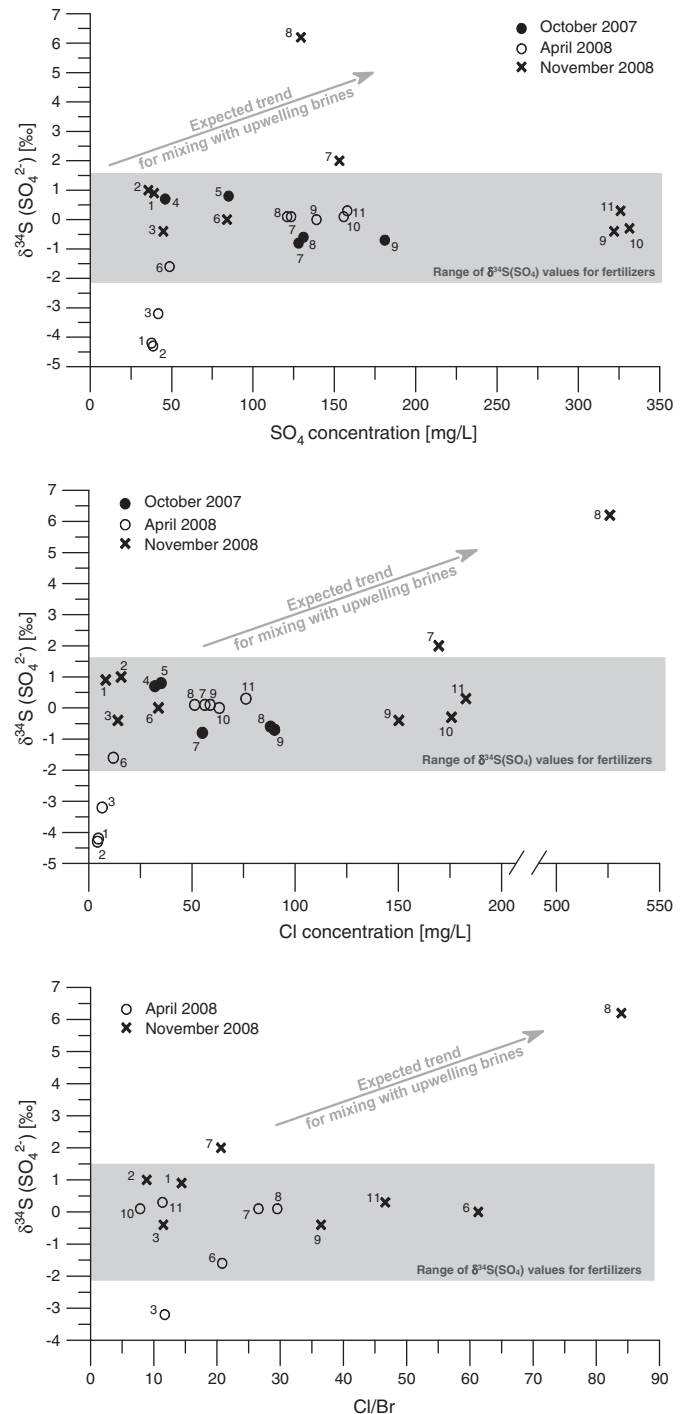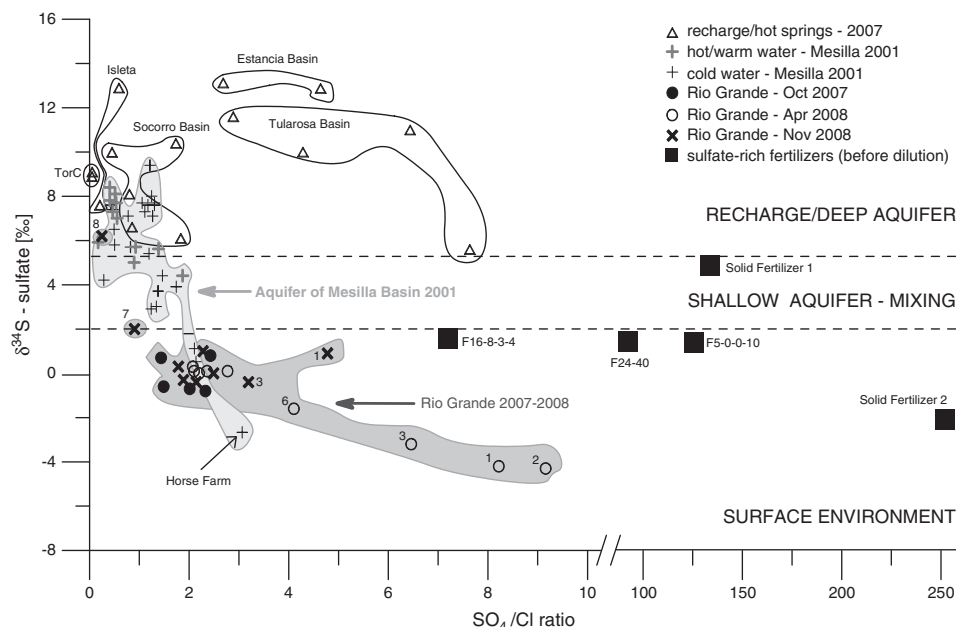

Fig. 7. Variation of $\delta^{34}S(SO_4)$ compared to SO_4 and Cl concentrations, and Cl/Br ratio for the Rio Grande in October of 2007, April and November of 2008. Numbers for each data point indicate locations of sampling points in Fig. 1A.

between Española, New Mexico and El Paso, Texas. Given that the tested fertilizers are significantly enriched in SO_4 ions, half of the total fertilizer by mass (Fig. 5, Table SI-4), and that use of water for irrigation increases downstream in the Rio Grande Valley, it is likely that the Rio Grande received significant SO_4 fluxes from fertilizers returned to the river from irrigation canals and drains.

Because elements like Cl, Br, Ca, Mg, and Na (in addition to SO_4) are also present in significant amounts in the tested fertilizers (Fig. 5, Table SI-4), it is likely that fertilizers add more than just SO_4 to the Rio Grande. For example, Cl and Br concentrations in the tested fertilizers were as great as 29,055 and 5,811 mg/L, respectively, accounting for

Fig. 8. Variations of $\delta^{34}S(SO_4)$ compared to SO_4/Cl ratio for i) the pristine groundwater in Estancia, Albuquerque, Socorro and Tularosa basins, ii) the groundwater from shallow aquifer of Mesilla Basin, iii) the surface water of Rio Grande, and iiii) tested N–P–K fertilizers. Numbers for Rio Grande data points indicate locations of sampling points in Fig. 1A.

up to 7% and 1% of the fertilizers by mass. Despite these complexities in interpretation, it does appear that water in the Rio Grande has considerably lower SO_4/Cl ratios (~1 to 5) than the tested fertilizers (~7 to 250) which may suggest an important influx of Cl from geologic sources along the river (Fig. 8). The SO_4/Cl ratios for groundwater from Albuquerque, Socorro, Mesilla basins and Truth or Consequences appear to be considerably low (~0.1 to 3; Fig. 8); thus, the geologic source would be predicted to add much greater amounts of Cl relative to SO_4 to the studied area. This, in turn, is compatible with the interpretation of previous investigators that Cl concentrations in the Rio Grande are largely attributable to geologic sources (e.g., Hogan et al., 2007). Additionally, in the Rio Grande Valley a significantly smaller SO_4/Cl ratio compared to the higher SO_4/Cl ratio in fertilizers might result from SO_4 uptake by plants in the agriculture fields and precipitation of SO_4 minerals as observed in many areas near the Rio Grande in the form of salt crusts. Because of prevailing semi-arid conditions and limited precipitation, the secondary salts may be stored on the surface for considerable periods of time. Both the plant uptake and precipitation of SO_4 minerals involve relatively small S isotope fractionation (e.g., Krouse and Grinenko, 1991; Raab and Spiro, 1991); thus, these processes may involve to some extent the withdrawal of SO_4 from the hydrological system but they would not change significantly the primary $\delta^{34}S$ value of SO_4.

In return irrigation flows, an additional SO_4 flux may come from mineralization of organic S in the agricultural soil. Soil mineralization linked to hydrolysis of ester sulfates and oxidation of carbon-bound organic S has been indicated as a local source of organic-derived SO_4 in groundwater recharging forested areas with developed soil horizons (e.g., Mayer et al., 1995; Knöller et al., 2005). Inorganic and organic SO_4 sources, however, cannot be easy distinguished because their $\delta^{34}S$ usually overlap (Knöller et al., 2005). Since the $\delta^{34}S$ of Rio Grande irrigation water varied over a narrow range (−1.6 to +0.9‰) that was closely aligned to the fertilizer source and the major fraction of cultivated crops is removed from the fields after irrigation season, we suspect that the SO_4 flux due to organic mineralization is probably minor in the semi-arid regions of the Rio Grande. The prevailing dry conditions, particularly during non-irrigation seasons, may be a significant factor in slowing down microbial activity within the soil as compared to forested areas where the high soil moisture content prevails throughout the year. Future measurements of the oxygen

isotope composition ($\delta^{18}O$) of SO_4 may provide better constraints on the organic-derived SO_4 flux because redox processes in soil horizons generate SO_4 with lower $\delta^{18}O$ as compared to fertilizers and geological sources (e.g., Mayer et al., 1995; Knöller et al., 2005; Mayer et al., 2010).

4.4. Mixing of geologic and anthropogenic sulfate sources

Although the Rio Grande did not show significant contribution of SO_4 from sedimentary sources over the studied period of time (Figs. 3, 6, 8), the evident mixing between recharging irrigation water and thermal/nonthermal groundwater was noted for the Mesilla Basin in southern New Mexico (Fig. 1B). In this basin, the inflow of thermal groundwater occurs along the eastern portions and at the distal (southern) end of the Mesilla Valley (Frenzel and Kaehler, 1992; Witcher et al., 2004; Moore et al., 2008). In 2001, the $\delta^{34}S$ of dissolved SO_4 in groundwater from the Mesilla Basin varied by a wide range, −2.7 to +9.4‰ (median 7.1‰, n = 36; Table SI-5) indicative of multiple SO_4 sources (Fig. 9). The Mesilla aquifer contains alluvial, fluvial, playa, and lacustrine sediments with provenance from Precambrian, Paleozoic, Mesozoic, and Cenozoic rocks. These are the likely sources of SO_4 with high $\delta^{34}S$ values (+8 to +9‰) for most of the studied thermal and nonthermal groundwater (Fig. 9); these high values are in good agreement with $\delta^{34}S$ values observed for the recharge areas of the Rio Grande Valley to the north and geothermal water from the alluvial aquifer of the Socorro basin (Fig. 6). Nevertheless, a large number of wells from the Mesilla Basin showed negative excursion of $\delta^{34}S$ (down to −2.7‰) accompanied by an increase in SO_4 concentration up to 800 mg/L. These changes are consistent with mixing of Paleozoic SO_4 with SO_4 from other sources that we propose to contain biogenic and anthropogenic sourcing (Fig. 9).

Previous investigations suggested that salinization of shallow aquifers can be partly attributed to surface recharge of salt-rich irrigation waters (Böhlke and Horan, 2000; Otero and Soler, 2002; Jiang et al., 2009; Chae et al., 2009), which would lead to a decrease of $\delta^{34}S$ for dissolved SO_4 (Mizota and Sasaki, 1996; Oren et al., 2004; Victòria et al., 2004). Because agriculture is the primary land use for much of the Rio Grande Valley, fertilization of these fields could be a source of SO_4. Moreover, the Rio Grande is a losing stream over most
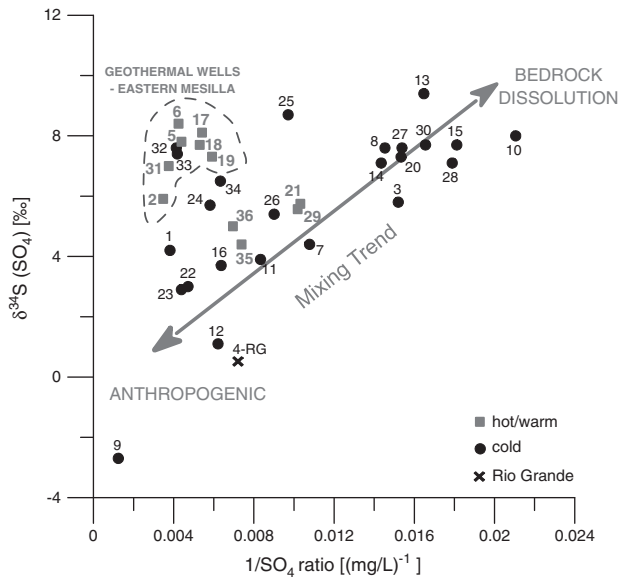
Fig. 9. Variation of $\delta^{34}S(SO_4)$ compared to SO_4 concentrations for groundwater from the Mesilla Basin (2001). Numbers for Mesilla data points indicate locations of sampling points in Fig. 1B.

of the Mesilla Valley (Nickerson, 1986), thus, mixing of irrigation water with fresh groundwater is likely to occur in the shallow aquifer system. Principal Component Analysis (PCA) was applied to the samples collected in the Mesilla Valley to better distinguish the hydrogeological processes controlling the water quality and its isotope compositions (e.g., Panagopoulos et al., 2004; Daniele et al., 2008; Venugopal et al., 2008; Jiang et al., 2009).

For the groundwater from the Mesilla Basin, PCA was able to correlate 73% of the observed variables (Table 3). The remaining 27% constituted random noise, and were therefore impossible to interpret using this technique (Drever, 1997; Manly, 1998). Generally, PCA suggests that chemical and isotope compositions in the studied groundwater are controlled by at least two different factors (Table 3). Factor 1 accounts for nearly 38% of the total variance and had high positive loadings for temperature (0.86), Na (0.74), K (0.81), Cl (0.67), $\delta^{13}C$ of dissolved inorganic carbon (DIC, 0.91), and negative loading values for pH (-0.70). Because the elevated temperatures of groundwater in the Mesilla Basin are directly controlled by geothermal flows (Frenzel and Kaehler, 1992) related to the higher thermal gradient of the Rio Grande Rift (Sass and Morgan, 1988), Factor 1 may be linked to natural dissolution of the sedimentary bedrock and

increasing water–rock interaction at higher temperatures. Apparently, the high geothermal gradient within the Mesilla Valley is a major reason of the increasing concentrations of Na, Cl, and K in the groundwater with increasing temperatures. The significantly positive loadings for Na, Cl, K and $\delta^{13}C$ of DIC (Table 3) suggest that evaporates such as halite and limestone are the major chemical contributors to the groundwater. Marine limestones of the Paleozoic and Mesozoic ages show high $\delta^{13}C$ values, ~-2 to $+2‰$ (e.g., Clark and Fritz, 1997). Given that the loadings for temperature and $\delta^{13}C(DIC)$ were always positively correlated (Table 3), this provides further support for the suggestion that limestone is a major source of ions for groundwater with elevated temperatures and the highest $\delta^{13}C$ values.

Factor 2 accounts for 35% of the total variance and had high positive loadings for Ca (0.90), Mg (0.75), SO_4 (0.92), δ^2H (0.67), $\delta^{18}O$ (0.73) and negative loading values for $\delta^{34}S$ (-0.62) (Table 3). Because irrigation comprises the major use of water in this area and agricultural activity is often marked by a shift to Ca–Mg–SO_4 groundwater (e.g., Kelly, 1997; Böhlke, 2002; Chae et al., 2009; Jiang et al., 2009), Factor 2 likely reflects the surface recharge of irrigation water. Ca, Mg, and SO_4 are common constituents of various fertilizers such as urea, gypsum, and N–P–K components (Mizota and Sasaki, 1996; Victòria et al., 2004; Table 1, SI-4). In addition, nitrification of reduced N from fertilizers and manure as well as application of Ca–Mg-rich fertilizers, to provide Ca and Mg for plant growth, may result in unnaturally high Ca and Mg concentrations in recharging irrigation water (e.g., Böhlke, 2002). Therefore, irrigation water is probably a major source of these ions in the shallow aquifer of Mesilla Basin. Alternatively, elevated contents of Ca and Mg may result from the enhanced weathering of sedimentary rocks in the shallow aquifer (e.g., dissolution of carbonates) since some of the liquid fertilizer applications are done at low pH. Similar positive loadings were noted for the δ^2H and $\delta^{18}O$ values (Table 3), which indicate the substantial evaporation of irrigation water prior to infiltration; this follows field observations from other areas showing a strong influence of evaporation and evapotranspiration on recharging irrigation water in arid environments (Criss and Davisson, 1996; Oren et al., 2004; Phillips et al., 2003; Szynkiewicz et al., 2008a). Most importantly, the SO_4 loadings were negatively correlated with $\delta^{34}S$ values (Table 3). Because the tested fertilizers have considerably lower $\delta^{34}S$ values (-2.1 to $+1.6‰$) compared to geologic SO_4 inputs in the Rio Grande Rift ($+7.6$ to $+12.9‰$; Fig. 6), the negative excursion of $\delta^{34}S$ values in groundwater from Mesilla Basin is most likely the result of both the anthropogenic inputs from fertilizer SO_4 and the SO_4 flux due to pyrite weathering in upstream locations of the Rio Grande.

Additional sources of anthropogenic SO_4 with low $\delta^{34}S$ values (relative to evaporites in the Rio Grande Valley) could come from organic decomposition of manure and animal feces from horse/dairy farms, which are common in the central Mesilla Basin. In fact, the lowest $\delta^{34}S$ values ($-2.7‰$), accompanied by the highest SO_4 concentration (800.6 mg/L), were noted for Well 9 located in the irrigation horse farm of the New Mexico State University at Las Cruces (Fig. 9). Microbial anaerobic decomposition of manure has been shown to produce high quantities of H_2S gas (e.g., Rappert and Müller, 2005; Blunden et al., 2008). In contrast, microbial anaerobic processes linked to sulfate reduction generate H_2S with negative $\delta^{34}S$ values (e.g., Canfield, 2001), this H_2S could become oxidized, contributing to the higher quantities of SO_4 with low $\delta^{34}S$ values in the shallow groundwater. This mechanism might have been important for shallow Well 9 (47 m deep), as a strong smell of H_2S was present during sampling in 2001. In this case S isotopes cannot be used to differentiate between the fertilizer SO_4 and the oxidation of biologically-derived H_2S gas from the manure decomposition as their isotope compositions could overlap with each other. However, as the concentration of SO_4 in the horse irrigation farm was substantially higher (800 mg/L) than that for any of the other wells (<300 mg/L), we speculate that local anthropogenic processes were important.

Table 3
Results of Principle Component Analysis (PCA) for the Mesilla Basin groundwater sampled in 2001. Bold text indicates statistically significant loading values for the analyzed parameters.

Parameter	Factor 1	Factor 2
Temperature	**0.86**	0.08
pH	**−0.70**	−0.53
log Na	**0.74**	0.54
log K	**0.81**	0.31
Ca	0.26	**0.90**
Mg	0.17	**0.75**
log HCO$_3$	0.6	0.53
SO$_4$	0.07	**0.92**
log Cl	**0.67**	0.58
SiO$_2$	**0.84**	0.03
$\delta^{13}C(DIC)$	**0.91**	−0.01
$\delta^2H(H_2O)$	0.43	**0.67**
$\delta^{18}O(H_2O)$	0.11	**0.73**
$\delta^{34}S(SO_4)$	0.54	**−0.62**
Factor quota [%]	**38**	**35**
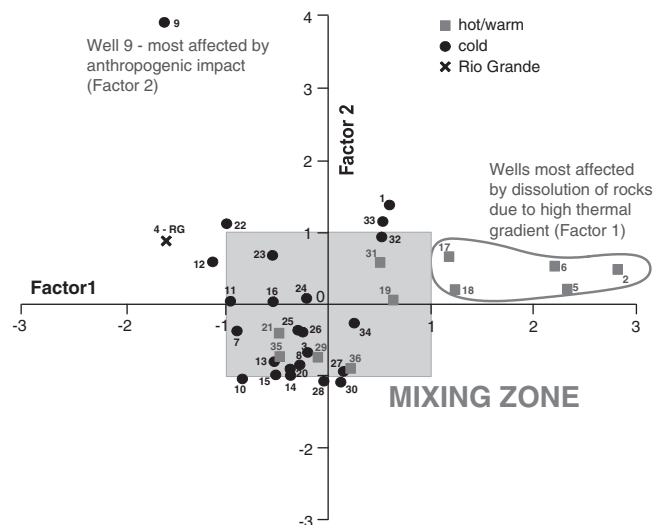
Fig. 10. Variations of Factor 1 versus Factor 2 for the Mesilla groundwater samples. The grey box indicates water samples most affected by mixing of upwelling groundwater with irrigation recharge. Numbers for Mesilla data points indicate locations of sampling points in Fig. 1B.

The scores of Factors 1 and 2 were compared in Fig. 10. The values of factor scores are lower or higher than 0 depending upon their relationship to the intensity of chemical processes that each factor represents. Extreme negative values (<-1) reflect the water samples not affected by the specific process that each factor represents, in contrast to positive values ($>+1$) which indicate the water samples were strongly impacted by the process. Most wells from the Mesilla Basin showed a varied mixing ratio between groundwater and irrigation recharge because the scores for Factors 1 and 2 varied over a small range, from -1 to $+1$ (Fig. 10). Highest scores of Factor 1 (likely geologic), from $+1$ to $+3$, were mainly observed for thermal wells which indicate a significant contribution of dissolved solids from the dissolution of sedimentary rocks in the region. In contrast, the highest score of Factor 2 (likely anthropogenic), $+4$, was noted for Well 9 which was inferred to be extensively contaminated by biogenic and/or anthropogenic sources of SO_4.
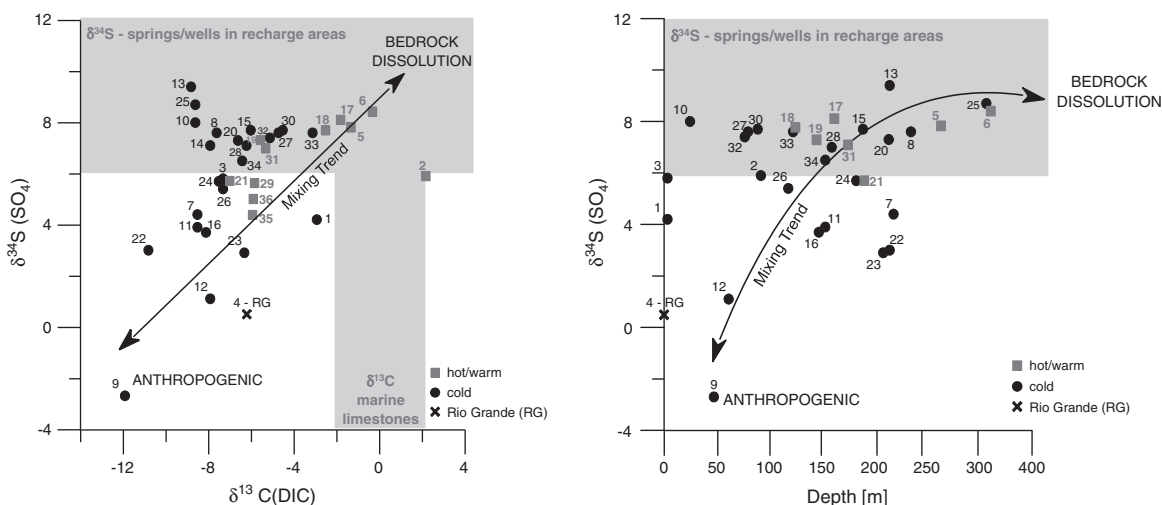
Mixing between anthropogenic recharge and groundwater in the Mesilla Basin is also reflected in plots of $\delta^{34}S$ versus $\delta^{13}C(DIC)$ and $\delta^{34}S$ versus well depth (Fig. 11). The main sources of DIC in natural systems come from bedrock dissolution (higher $\delta^{13}C$ values) and organic

activity in soil (negative $\delta^{13}C$ values) (e.g., Krouse and Grinenko, 1991; Clark and Fritz, 1997). In the studied area, lower $\delta^{34}S$ values were always accompanied by negative $\delta^{13}C$ (Fig. 11). Because irrigation water, containing both varied fertilizers and the Rio Grande surface water with lower $\delta^{34}S$, directly infiltrates through the cultivated fields, it is implied that the positive correlation between $\delta^{13}C(DIC)$ and $\delta^{34}S(SO_4)$ results from a continuous leaching of soil CO_2 by recharging irrigated water. In the case of regional microbial sulfate reduction, decreasing values of $\delta^{13}C$ would be accompanied by increasing values of $\delta^{34}S$. This is not the case in the studied aquifer (Fig. 11). Moreover, $\delta^{34}S$ appeared to increase with the increasing depth of wells (Fig. 11) which suggests mixing between recharging irrigation water and upwelling groundwater in the shallow river-connected aquifer of the Mesilla Basin. Here, lower $\delta^{34}S$ ($<+6‰$) was accompanied by negative $\delta^{13}C(DIC)$ ($<-4\%$) in shallow wells of 50 to 200 m in depth (Fig. 11); this depth range likely determines the current mixing zone between recharging irrigation water and upwelling groundwater for the shallow aquifer of the Mesilla Basin.

4.5. Discharge of basinal brines versus playa waters

Similar to the Mesilla Basin, mixing with groundwater was evident in the shallow aquifer of the Bosque del Apache thermal water area located in the Socorro basin, central New Mexico (Fig. 1A). A geothermal well (28.3 °C) from the Bosque del Apache had a $\delta^{34}S$ of $+10.0‰$, and SO_4 and Cl concentrations of 624 mg/L and 1382 mg/L, respectively. We suggest that this SO_4 and Cl were derived mainly from the Paleozoic sedimentary bedrock (Figs. 6 and 8); however, for some parts of the Rio Grande there is disagreement over the ultimate source of high salinity groundwater.

One study south of El Paso in the Hueco basin emphasized the role of saline groundwater originating from an ancient playa setting buried beneath the contemporary Rio Grande floodplain (e.g., Hibbs and Merino, 2006). Although the $\delta^{34}S$ values of SO_4 cannot clearly discriminate between direct dissolution of the Paleozoic bedrock or the sediments and waters of the ancient playa, the δ^2H and $\delta^{18}O$ values of the water can be used to better pinpoint the dissolution of SO_4 minerals versus the paleo-water discharge from playa sediments because high evaporation rates in playa settings of the Rio Grande rift cause a considerable increase of δ^2H and $\delta^{18}O$ (Szynkiewicz et al., 2009). The δ^2H and $\delta^{18}O$ of the geothermal well in the Bosque del Apache had negative values of $-82‰$ and $-10.6‰$, respectively, which were closely aligned to groundwater from other places of the Rio Grande Valley and modern precipitation (Fig. 12). This suggests

Fig. 11. Mixing between anthropogenic recharge and upwelling groundwater in the Mesilla Basin based on relationships of $\delta^{34}S$ versus $\delta^{13}C(DIC)$ and $\delta^{34}S$ versus well depth. Numbers for Mesilla data points indicate locations of sampling points in Fig. 1B. The range of $\delta^{13}C$ for marine limestones was adopted after Clark and Fritz (1997).
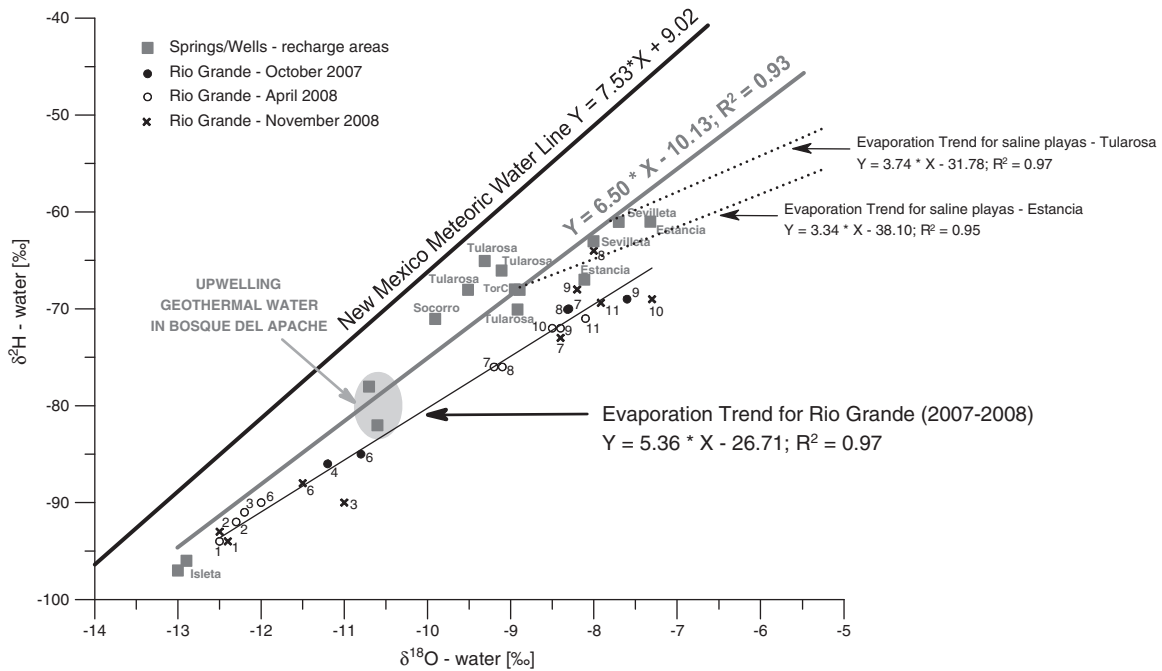
Fig. 12. Variations of δ^2H and $\delta^{18}O$ values of water for springs and wells from recharge areas, Rio Grande surface water compared to the geothermal warm water from Bosque del Apache. Numbers for Rio Grande data points indicate locations of sampling points in Fig. 1A. Evaporation trends for the saline playas of Estancia and Tularosa were adopted after Szynkiewicz et al. (2009).

that thermal water in the Socorro basin most likely originated from deep groundwater flows fed by infiltration of modern precipitation from the surrounding highlands and not by relicts of playa waters underlying the contemporary Rio Grande floodplain.

5. Conclusions

Our sampling of the Rio Grande in 2007 and 2008 found distinctively low $\delta^{34}S$ values (−1.6 to +0.9‰) for dissolved SO_4 over the >550 km distance between Española, New Mexico and El Paso, Texas. The $\delta^{34}S$ values were consistent with a fertilizer source of SO_4 (−2.1 to +1.6‰) in the Rio Grande and were not consistent with geologic evaporite sources of SO_4 (+7 to +15‰). Particularly, in downstream locations (below the Caballo Reservoir) a significant SO_4 flux appeared to come from irrigation canals, drains and/or return flows of irrigated water impacted by high concentrations of SO_4 in N–P–K fertilizers; in these locations, $\delta^{34}S$ significantly decreased by ~6‰ compared to the thermal water from the mineral baths and spas of Truth or Consequence (+8.6 to +9.2‰) which contribute geologic SO_4 to the Middle Rio Grande below the Elephant Butte Reservoir. However, we did recognize that SO_4 derived from sulfide weathering partly controlled the $\delta^{34}S$ in upstream locations (−4.3 to −3.2‰) where the Rio Grande flows through the Taos volcanic plateau and was largely fed by snow melt water during the spring of 2008. Apparently, in upstream locations higher SO_4 fluxes with negative $\delta^{34}S$ values are controlled by the acid rock drainage of the Rio Grande tributaries.

Because elements like Cl, Br, Ca, Mg, and Na (in addition to SO_4) were also present in significant amounts in the tested fertilizers, it is likely that fertilizers add more than just SO_4 to the Rio Grande; however, the contribution of these ions to the river salinization cannot be easily evaluated based on chemistry alone. Geological sources may contribute higher quantities of Cl to the Rio Grande since the SO_4/Cl ratios for recharge areas and thermal/nonthermal groundwater were considerably low (0.1 to 3) and were more closely aligned with the river SO_4/Cl ratios (1 to 5) than with the local fertilizers (7 to 250).

The Rio Grande is a losing stream over most of the southern alluvial basins of the Rio Grande Valley. Particularly, a large loss of surface water occurs during irrigation periods when water is released from the Elephant Butte Reservoir located in central New Mexico. Therefore, in the Mesilla alluvial basin mixing of recharging irrigation water with groundwater occurs in the shallow aquifer. For the Mesilla aquifer, an additional anthropogenic SO_4 load to shallow groundwater ($\delta^{34}S = -2.7$‰) appeared to come from anaerobic decomposition of organic matter associated with a horse farm. This local anthropogenic source increased SO_4 concentrations by three times compared to the less polluted groundwater. Therefore, it is inferred that in addition to fertilizer SO_4 microbial anaerobic sulfate reduction, followed by re-oxidation of produced H_2S, during decomposition of manure in the horse/dairy farms of Mesilla Basin may be an additional, localized source of SO_4 with low $\delta^{34}S$ into the return flows of irrigated water.

Given that application of H_2SO_4 is common worldwide in fertilizer manufacturing, we infer that anthropogenic SO_4 loads to rivers and freshwater aquifers may be significant globally because of high SO_4 concentrations in N–P–K fertilizers; in fact, SO_4 concentrations often greatly exceed the concentrations of basic N, P, and K nutrients required for crop growth. S loading from fertilizers is frequently overlooked because the problems associated with elevated N and P contents often command our attention. However, in this case we demonstrate that S loading alone from fertilizers can be important and may lead to substantial increases of salinity in rivers and shallow aquifers, particularly, in arid and semi-arid regions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi: 10.1016/j.chemgeo.2011.01.017.

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