Geologic origins of salinization in a semi-arid river: The role of sedimentary basin brines

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ABSTRACT

Semi-arid and arid rivers typically exhibit increasing salinity levels downstream, a trend often attributed to irrigated agriculture, primarily due to evapotranspiration. In contrast, the results of our investigations in one salinized river suggest that geological sources of salt added by groundwater discharge are more important than agricultural effects. We performed detailed synoptic sampling of the Upper Rio Grande–Rio Bravo, an arid-climate river with significant irrigated agriculture, and identified a series of salinity increases localized at the distal ends of sedimentary basins. Using Cl/Br, Ca/Sr, $^{87}Sr/^{86}Sr$, and $^{36}Cl/Cl$ ratios and $\delta^{234}U$ values as environmental tracers, we show that these increases result from localized discharge of high-salinity groundwater of a sedimentary brine source. These groundwater fluxes, while very small (<1 m^3s^{-1}), are the dominant solute input and, combined with downstream evapotranspirative concentration, result in salinization. Furthermore, $^{36}Cl/Cl$ ratios and $\delta^{234}U$ values for these brines are close to secular equilibrium, indicating brine ages on the order of millions of years. The recognition of a substantial geologic salinity source for the Rio Grande implies that alternative salinity management solutions, such as interception of saline groundwater, might be more effective in reducing salinity than changes in agricultural practices.

Keywords: salinity, brines, sedimentary basins, Rio Grande, isotope geochemistry.

INTRODUCTION

Salinization of rivers presents a major challenge to the sustainability of the world's water resources and agriculture (Postel, 1999). Currently 2.3 billion people live in water-stressed river basins (e.g., the Indus, Nile, Rio Grande, Tigris-Euphrates, and Orange), mostly in semi-arid and arid regions (Johnson et al., 2001), where in addition to water scarcity, the buildup of salinity limits both domestic and agricultural use of water (Ghassemi et al., 1995). River salinization results in great economic damage through direct reduction of crop productivity, long-term damage to agricultural soils, the necessity of treatment for municipal and industrial uses, and damage to pipes and fixtures (Ghassemi et al., 1995; Postel, 1999).

River salinization has been intensively studied for more than 50 yr (Ghassemi et al., 1995). Salinization results primarily from two factors, (1) solute addition (atmospheric deposition, mineral weathering, inflow of subsurface saline waters of connate, diagenetic, or geothermal origin, and anthropogenic sources), and (2) the concentrating processes of open-water evaporation and riparian and agricultural transpiration. Most frequently, the effects of irrigated agriculture are held responsible, either through evapotranspirative concentration, mobilization of salt stored in the vadose zone due to clearing of native vegetation and/or drainage of irrigation waters, or displacement of shallow saline groundwater (e.g., Allison et al., 1990; Herczeg et al., 1993; Ghassemi et al., 1995; Postel, 1999). Typically, salinization is treated locally (e.g., at the scale of an irrigation district) at the downstream end of the river; however, the actual sources of salinity may be upstream. In these upstream regions, natural solute inputs of geologic origin that may appear insignificant may be concentrated downstream through evaporation and transpiration. Thus in order to develop effective policy and management, salinity issues must be evaluated at the river-basin scale and must consider geologic as well as anthropogenic solute sources and the processes that may concentrate these sources.

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RIO GRANDE SALINIZATION

In this study we focus on the upper 1200 km of the Rio Grande–Rio Bravo (United States and Mexico), a highly stressed arid-region river in which chronic water shortages threaten food production and limit economic development (Johnson et al., 2001). The pattern of water use and salinization in the Rio Grande is typical of irrigated rivers in arid climates. Currently, 89% of the available water supply is used to support 370,000 ha of irrigated agriculture (Ellis et al., 1993). Total dissolved solids increase from ~40 mg L^{-1} at the headwaters in central Colorado to 500–1500 mg L^{-1} at El Paso–Ciudad Juárez on the U.S.-Mexico border (Moore and Anderholm, 2002), leaving down-river users with water of marginal utility (Ellis et al., 1993; Moore and Anderholm, 2002).

Although the cause of Rio Grande salinization has been investigated for 75 yr, no conclusive answer has been reached. Salinization has been attributed to (1) simple evapotranspirative concentration as the water is reused for irrigation (Lippincott, 1939; Haney and Bendixen, 1953); (2) displacement of shallow salty groundwater by irrigation (Wilcox, 1957); (3) regional saline groundwater discharge (Moore and Anderholm, 2002; Phillips et al., 2003); (4) riparian evapotranspiration (Moore and Anderholm, 2002); and (5) unspecified irrigation effects (Moore and Anderholm, 2002). As ~75% of river flow is lost to open-water evaporation, agricultural transpiration, and riparian transpiration, these processes clearly play a role in salinization. However, the results of a simple Cl mass-balance model indicate that they are insufficient to explain the greater than tenfold increase in salinity (Phillips et al., 2003). To test these competing salinization hypotheses we employ an approach that consists of (1) collecting water samples at a high spatial resolution along the full river length, and (2) using a suite of geochemical tracers to fingerprint and quantify salinity sources.

PATTERNS OF SALINIZATION

We performed synoptic sampling of the Rio Grande from the headwaters to ~150 km south of El Paso (Fig. 1) during a period of irrigation (August 2001) and non-irrigation (January 2002). In general, Cl concentrations along the river increased by about two orders of magnitude (Fig. 2). Concentrations were higher during the winter (particularly below Elephant Butte Reservoir at 800 km), a fact likely attributed to lower flows through-

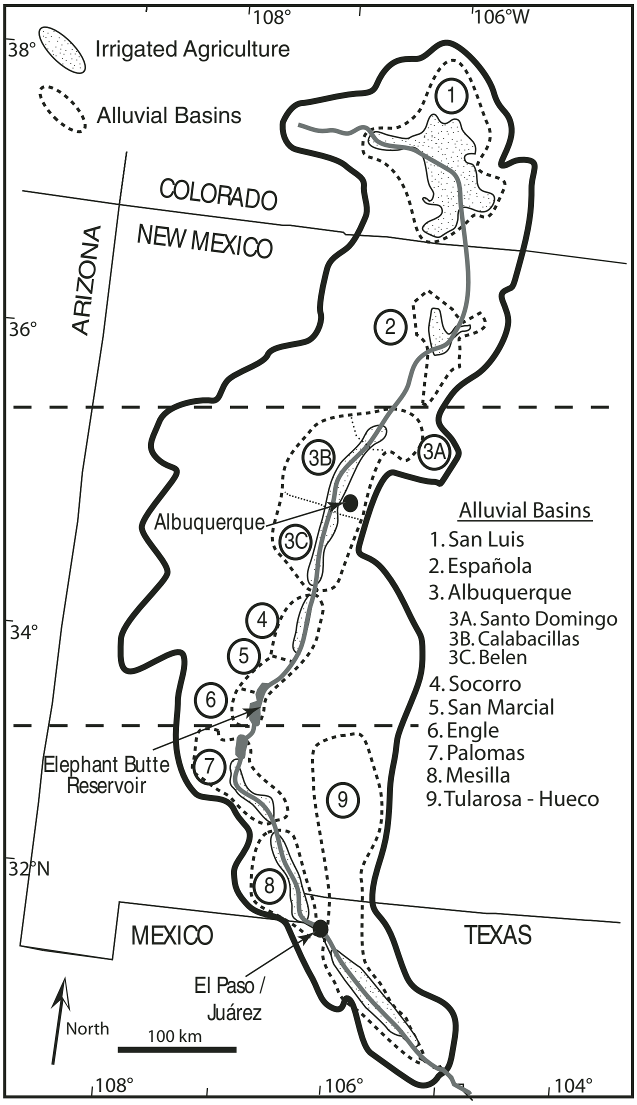

Figure 1. Map of the Rio Grande study area outlining drainage area, river course, irrigated agriculture, and alluvial basins (Wilkins 1998) with Albuquerque subbasins (Grauch et al., 2001).

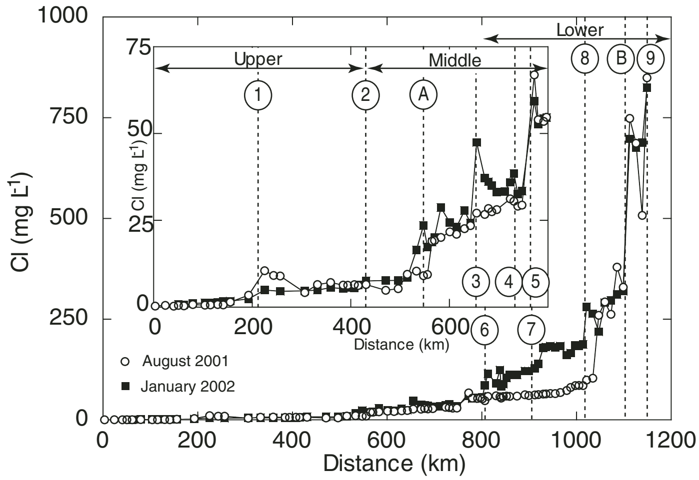

Figure 2. Chloride concentration versus river distance from the headwaters. Numbers correspond to locations where Rio Grande exits southern end of the alluvial basins shown in Figure 1. Locations marked with letters refer to additional salinity increases not associated with alluvial basin termini.

out much of the river system, as water is stored in reservoirs until the irrigation season, and thus a greater proportion of groundwater discharge. The series of discrete Cl^- concentration increases observed during both irrigation and non-irrigation periods is particularly interesting. Comparison with geologic structure of the Rio Grande rift (Fig. 2) shows that these increases are typically located at the southern, low-elevation end of alluvial sedimentary basins, raising the possibility that salinity increases result from the discharge of sedimentary brines. Note, however, that regions of irrigated agriculture are typically located within sedimentary basins (Fig. 1) and thus high-Cl agricultural return flows may also enter there.

The salinity pattern of the upper Rio Grande can be roughly divided into three equal portions (Fig. 1). The upper portion (0–400 km) is typified by very low Cl concentration that increases in a roughly linear fashion with flow distance (Fig. 2). There is only one noticeable stepwise increase at ~215 km at the southern end of the San Luis Basin. In the middle portion (400–800 km), Cl concentration exhibits three stepwise increases that correspond with three alluvial basins (Albuquerque, Socorro, and San Marcial–Engle). A fourth increase (point A in Fig. 2) is located within the Albuquerque Basin and is likely associated with the Albuquerque wastewater treatment plant, a hypothesis supported by an associated nitrate increase (Moore and Anderholm, 2002). However, this location (as well as a point at ~515 km, where there is a small increase in Cl) also corresponds to a structural high marking a subbasin boundary (Fig. 1). In the lower part of the river (800–1200 km) there are two small Cl increases above El Paso–Ciudad Juárez (most clearly seen during winter low flow) and a very large increase ~50 km south of El Paso. The first increase at the northern end of the Mesilla Basin is in an area of known geothermal activity (Reiter, 1999), the second is at the southern end of the Mesilla Basin, and the third is located within the Tularosa-Hueco Basin (B in Fig. 2), in a zone where high-salinity groundwater is believed to discharge to the Rio Grande (Hibbs and Boghici, 1999).

ENVIRONMENTAL TRACERS OF SALINIZATION

To distinguish between saline groundwater discharge and effects associated with irrigated agriculture, we have employed $^{87}Sr/^{86}Sr$ and $^{36}Cl/Cl\cdot 10^{15}$ ratios and $\delta^{234}U$ isotopic values, along with the associated solute ratios Cl/Br and Ca/Sr, as environmental tracers. We selected these tracers for three reasons. First, these isotopic and solute ratios are minimally affected by evapotranspiration, and thus are tracers of solute inputs only. Second, in all three systems sedimentary brines are expected to have distinct compositions (GSA Data Repository Table DR1[1]). Third, the high concentration of sedimentary brines results in mixing relationships with large changes in isotopic values or solute ratios with addition of small saline groundwater fluxes.

The generally conservative nature of Cl and Br, combined with the distinct Cl/Br ratios (mass/mass) for atmospheric deposition (~100) and sedimentary brine (≥1000) (Whittemore, 1995; Davis et al., 1998), make it an extremely useful tracer. In general, Cl/Br ratios increase from ~100 to >1000 in a stepwise fashion (Fig. DR1; see footnote 1) mirroring the increasing Cl concentration. Comparing Cl/Br and Cl concentration changes (Fig. 3) provides a clear illustration of the combined effect of evapotranspirative concentration and solute addition in explaining down-

[1]GSA Data Repository item 2007265, Figure DR1 (downriver variation in Cl), Figure DR2 (downriver variation in Sr), Figure DR3 (downriver variation in U), Figure DR4 (U isotope mixing plot), and Table DR1 (geochemical end members), is available online at www.geosociety.org/pubs/ft2007.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

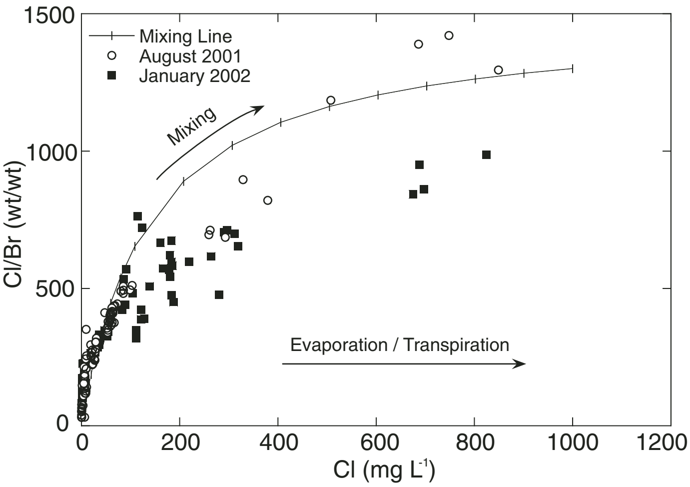

Figure 3. Cl/Br ratios versus Cl concentration mixing plot using illustrating combined effect of evapotranspirative concentration and solute addition in explaining Rio Grande salinization.

stream salinization. If evapotranspirative concentration were the only factor, the Cl/Br ratio would not change as Cl concentration increased. Conversely, if only saline groundwater discharge was important, increases would follow the calculated mixing curve. Data for the Rio Grande are intermediate between these two cases, illustrating their combined effect.

The ^{36}Cl ratios, measured along the length of the study area, exhibit a decreasing trend from ~2500 in the headwaters to ~100 at the southern end (Fig. DR1). Headwater values are consistent with an atmospheric source; however, a ^{36}Cl ratio of ~2500 is significantly higher than present-day precipitation (Phillips, 2000), indicating a component from nuclear weapons testing fallout in these waters. In contrast, the very low ^{36}Cl and high Cl/Br ratios in the lower portion are indicative of a sedimentary brine source. When ^{36}Cl ratios are plotted against Cl/Br ratios (Fig. 4A), a clear two-end-member mixing relationship is observed, with all river samples plotting close to the mixing curve. This mixing curve is calculated using Rio Grande headwater values and an estimated higher salinity end member based on groundwaters that are likely a mix of dilute shallow groundwater with a deeper sedimentary brine source (Table DR1). The volumes of saline groundwater contributions are small, <1% of river flow, in the upper part of the study area. In the middle portion of the study area, the cumulative saline groundwater contribution increases from 1% to ~5% of river flow as it passes through three large and deep sedimentary basins. In the lower portion a small volume of discharge occurs at the southern end of the Mesilla Basin. South of this increase there is a dramatic rise in the percentage of saline groundwater, reflecting both saline groundwater discharge from the Hueco Bolson and the diversion of almost all remaining water for irrigated agriculture. Overall, saline groundwater fluxes appear to be greatest from large and deep alluvial basins (Albuquerque and Tularosa-Hueco; Wilkins, 1998) or smaller basins with significant geothermal activity (Socorro, Engle, Mesilla; Reiter, 1999). Note that ^{36}Cl and Cl/Br ratios indicate that this geothermal activity is not the source of the salinity (Table DR1), but rather it may mobilize the sedimentary brine. Closed—i.e., internally drained—basins (San Luis; Wilkins, 1998) and small and/or shallow basins (Española and Palomas; Wilkins, 1998) appear to make smaller contributions.

In contrast to Cl/Br ratios, Ca/Sr ratios exhibit a significant change only in the middle portion (Fig. DR2), hence ^{87}Sr/^{86}Sr ratios were measured only for this stretch of the river (400–800 km). In the headwater regions, Sr is likely derived from two sources: atmospheric deposition and mineral weathering (basalt is the dominant lithology through which the upstream Rio Grande flows), both of which have ratios distinct from sedimentary

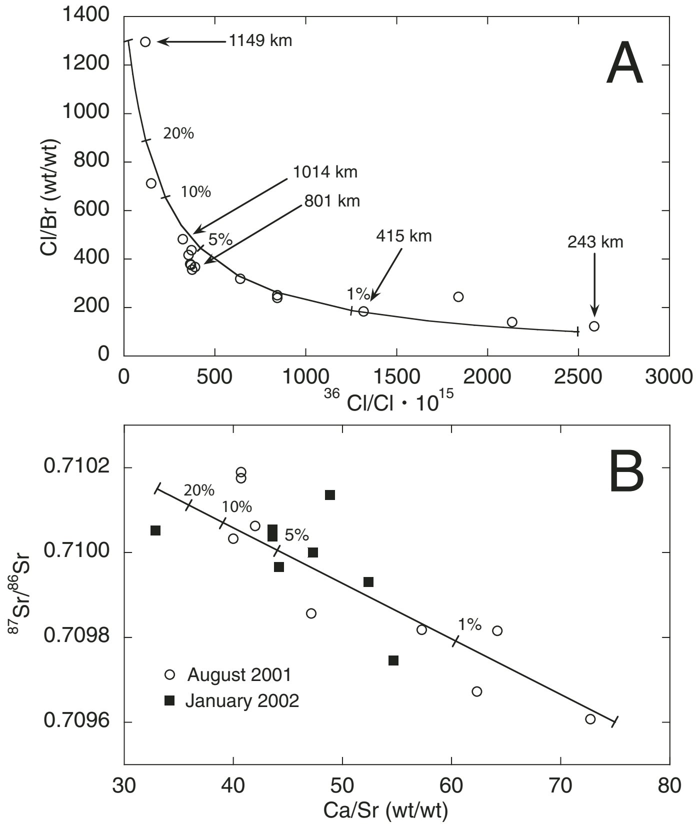

Figure 4. Isotopic mixing diagrams quantifying saline groundwater discharge, with distance from headwaters noted for some samples. A: ^{36}Cl vs. Cl/Br ratios. B: ^{87}Sr/^{86}Sr versus Ca/Sr ratios. Mixing lines were calculated using end members discussed in text.

brines (Table DR1). As the Rio Grande enters the middle portion, ^{87}Sr/^{86}Sr ratios are ~0.709 and Ca/Sr ratios are ~75, consistent with a mixture of headwater sources with a small contribution of saline groundwater. In the middle section of the river, ^{87}Sr/^{86}Sr ratios increase while Ca/Sr ratios decrease (Fig DR2). As for the Cl isotopic system, Ca/Sr and Sr isotopes for river samples indicate a clear two-end-member mixing relationship (Fig. 4B) between river water entering the middle portion of the study area and sedimentary brine. Mixing calculations indicate that a cumulative saline groundwater contribution between 5% and 10% of river flow can explain the observed salinity increases in the middle portion of the study area.

Uranium isotopes also help in salinity source interpretation. The reactive nature of uranium, as illustrated by both increasing and decreasing concentrations (Fig. DR3), limits use of this isotopic system to qualitative interpretation. Consistent with the ^{36}Cl and ^{87}Sr/^{86}Sr, δ^{234}U data are best explained by two-component mixing (Fig. DR4) where one end member is modern surface water and the other is sedimentary brine. The low δ^{234}U value (~500) and elevated U concentration of the saline end member is consistent with very old brine. Typically groundwaters have high ^{234}U excesses (Dickson and Davidson, 1985); however, with long residence times, on a scale of millions of years given the ^{234}U half-life of ~245 k.y. (Cheng et al., 2000), this is reduced.

CONCLUSIONS

Our data show an increase of about two orders of magnitude in the Cl content of the Rio Grande across the study area. In contrast, estimates of evapotranspiration can only explain a factor of four increase in Cl content. The results of all three isotopic systems exhibit mixing relationships between only two end members: Rio Grande headwaters composed of atmospheric deposition plus mineral weathering and higher salinity groundwater of sedimentary brine origin. Thus, our calculations and observations lead us to conclude that natural discharge of saline groundwaters is more important than evapotranspiration associated with irrigation in increasing the salinity of the Rio Grande.

The calculated percentages of saline groundwater needed to explain the observed salinity increases using different elemental and isotopic systems are relatively consistent. For example, in the middle portion of the river, which includes three distinct inputs, a 5%–10% saline groundwater contribution is capable of explaining the observed changes in both the Cl and Sr isotopic systems. During the summer of 2001, Rio Grande flow was 24 m^3s^{-1}, whereas in the winter of 2002 flow was 20 m^3s^{-1}. Using these flow rates and our calculated percentage implies a saline groundwater flux of 1–2 m^3s^{-1} over this stretch of the river. These values, although uncertain due to a likely range in saline groundwater composition, are broadly consistent with recent discharge estimates from a groundwater model of the Albuquerque Basin (Sanford et al., 2004). Given that the saline groundwater end member is based on relatively shallow samples that are probably a mixture of shallow groundwater and deep brine, which may be an order of magnitude more concentrated (Table DR1), the actual flux of deep brine could be as low as 0.1 m^3s^{-1}.

The above observations are significant for two reasons. First, they indicate that brines of geological origin may play a much larger role in the salinization of arid-zone rivers than previously suspected. Second, within the Rio Grande they limit the possible role of agricultural return flows as the major factor affecting river salinity. Recognition of saline groundwaters associated with alluvial sedimentary basin brines as a significant factor in river salinization has important management implications. The reduction of agricultural return flows by improving water use efficiency, lining of canals, and even reusing waters are commonly proposed to mitigate salinity increases (Chhabra, 1996). The sedimentary brine source identified for the Rio Grande in this study suggests that alternative approaches to salinity management, such as interception wells to capture sedimentary brines (e.g., McElwee, 1985; Gillespie and Hargadine, 1986), may offer more practical and effective long-term solutions for rivers with similar salinity sources.

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