

## **Environmental Tracers Applied to Quantifying Causes of Salinity in Arid-Region Rivers: Preliminary Results from the Rio Grande, Southwestern USA**

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### **Abstract**

The upper Rio Grande extends ~1,200 km between its headwaters in southern Colorado (USA) and the USA/Mexico border region. Over this distance the total dissolved solids content of the water increases from ~40 mg L<sup>-1</sup> to over 2,000 mg L<sup>-1</sup>. This increase has previously been attributed to evapotranspirative concentration and to flushing by irrigation water of salts accumulated by pre-irrigation evapotranspiration. We employed environmental tracers, including  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ,  $\text{Cl}^-$ , and the  $\text{Cl}/\text{Br}$  ratio to help identify the causes of salinization. Both  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  are enriched with flow distance due to evaporation, but not sufficiently to explain most of the salinization as caused by evapotranspiration. The  $\text{Cl}/\text{Br}$  ratio increases from about 50 in the headwaters to over 1,000 at the distal end of the river basin, indicating influx of subsurface saline waters, which are commonly characterized by high  $\text{Cl}/\text{Br}$  ratios. The  $\text{Cl}^-$  concentration and the  $\text{Cl}/\text{Br}$  ratio increase in a step-wise fashion and are typically localized at the southern ends of the sedimentary basins comprising the Rio Grande Rift, suggesting that the salts are from discharge of deep ground water where it is forced to the surface by bedrock highs, rather than due to flushing by irrigation water.

### **Introduction**

Water scarcity is commonly considered the major water-resources problem in arid regions, but in fact, poor water quality is in many cases as important a problem in these regions, or an even greater one. Although toxic contaminants have received a very large share of both the public and the scientific interest in water quality issues, the buildup of ordinary salinity in arid-region surface and ground water is generally of much greater practical significance. Understanding of the causes of salinization is a prerequisite to its management and possible mitigation. Although many studies have been conducted on specific salinization problems, most of these are focused on limited geographical areas that are usually only small fractions of entire river basins. Although such approaches may be locally effective, they ignore the large-scale linkages that cause progressive salinization at the basin scale. This paper will deal with salinization problems at the basin scale, using the Rio Grande basin in the southwestern United States as an example.

The solute burden of rivers can be divided into three major categories. The first is cyclical and surficial salts. These originate from atmospheric deposition (both in



precipitation and as dry fallout) and from weathering reactions of precipitation with surficial rocks and soil in the watershed. The spatial origin of such salts is very diffuse and they are virtually impossible to limit or control. The second category is the inflow of subsurface-origin saline waters. Such waters may be derived from solution of evaporite deposits, or may be of connate, diagenetic, or geothermal origin. If the points of introduction of such saline waters are localized, it may be possible to intercept them or otherwise mitigate their effects. The third category is anthropogenic salt inputs. These may arise from industrial and domestic waste streams, road salt, dietary salt, fertilizers and soil amendments, petroleum extraction, and many other human sources. Such anthropogenic sources are in principle controllable, but their limitation may in fact be economically or socially difficult. In arid and semiarid river basins the effects of evaporation and transpiration subsequently concentrate salts from all three categories above. Evaporative increases in concentration may tend to increase the importance of the more conservative solutes (e.g.,  $\text{Cl}^-$ ,  $\text{Na}^+$ ) in the solute burden, while decreasing the proportion of the more reactive ones (e.g.,  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$ ). The extent to which increases in dissolved solids can be attributed to evapotranspirative concentration as compared to solute addition can be difficult to quantify.

Traditional approaches to investigating river salinization have relied on water quality measurements made at river gaging stations to calculate salt burdens. Relatively constant burdens with distance down river are taken to imply that concentration increases can be attributed to evapotranspiration, whereas increasing burdens imply some additional source of salt. However, such studies are limited to gaged sites, which are frequently sparse, and they do little to identify sources of salt influx. In this study, we employ environmental tracers in addition to traditional salt-burden calculations. The tracers can be measured at any desired spatial frequency in order to pinpoint locations of salt addition, and can be used to fingerprint sources of salinity.

### **Rio Grande Basin**

The headwaters of the Rio Grande are in the southern Rocky Mountains, in the state of Colorado, USA (Figure 1). Most of the runoff that supplies the river originates as snowfall at elevations of 3,000 to 4,000 m in the San Juan, Sangre de Cristo, and Jemez mountain ranges. The river flows south through the states of Colorado and New Mexico before turning southeast to form the boundary between the United States and Mexico and ultimately flowing into the Gulf of Mexico. This study was limited to the northern portion of the drainage basin, down to a point 130 km south of the cities of El Paso and Ciudad Juarez. This point is 1,150 km downstream from the river's headwaters. Further downstream the river is frequently dry, although eventually additional tributaries restore perennial flow. The elevation at this point is 1,100 m and the area of the drainage basin above it is 120,000 km<sup>2</sup>.

### **Hydrogeologic Framework**

The relatively linear course of the Rio Grande as it flows south is largely due to structural control by the Rio Grande rift. This is an intracontinental extensional feature similar in origin to the better-known East African rifts. Rifting was initiated at ~30 Ma and was

initially rapid, but has slowed with time (Keller and Cather, 1994). The rift consists of a series of elongate basins that are usually bounded on either side by Precambrian crystalline or Paleozoic sedimentary basement rocks (see Figure 1). The basins are formed by full or half grabens that are filled with up to 4,000 m of alluvial and lacustrine sediment (Keller and Cather, 1994; Wilkins, 1998). The grabens are terminated at either end by transform structures that bring basement rocks close to the surface. Figure 2 shows a cross-section of the basin structure parallel to the course of the river.

### Precipitation and Runoff

Although precipitation is as high as 1,300 mm yr<sup>-1</sup> over small areas in the mountainous headwaters, the majority of the drainage basin ranges from semiarid to arid. Most of the basin receives less than 300 mm yr<sup>-1</sup> and the driest areas only 160 mm yr<sup>-1</sup>. Summer temperatures are high and over most of the basin potential evapotranspiration varies from 1,000 to 2,000 mm yr<sup>-1</sup>.

Within the study area the river discharge first increases as tributaries flow in, then decreases, partly because no further significant tributaries join the river, and partly because of evapotranspirative losses from riparian vegetation and reservoirs, as well as irrigation and municipal diversions. At the Colorado-New Mexico border, about 270 km from the headwaters, the mean annual discharge is 17 m<sup>3</sup> s<sup>-1</sup>, although the natural flow would be about 40 m<sup>3</sup> s<sup>-1</sup> without agricultural diversions (discharge and water use data are from Ellis et al., 1993). The river reaches its maximum discharge of 49 m<sup>3</sup> s<sup>-1</sup> at Otowi, New Mexico, 430 km down the river. This would probably be closer to 70 m<sup>3</sup> s<sup>-1</sup> under natural conditions. At Albuquerque, New Mexico, 550 km down river, the discharge is 44 m<sup>3</sup> s<sup>-1</sup>. Above Elephant Butte Reservoir (800 km downstream and by far the largest reservoir on the river) the discharge amounts to 40 m<sup>3</sup> s<sup>-1</sup>; below the reservoir it is about 33 m<sup>3</sup> s<sup>-1</sup>. The difference is largely attributable to evaporation from the reservoir. At El Paso (1,025 km) this discharge has been further reduced to 20 m<sup>3</sup> s<sup>-1</sup>, mostly due to agricultural diversions.

### Water Use

There are five major population centers within the drainage basin: Santa Fe, New Mexico (450 km from the headwaters, population 70,000), Albuquerque, New Mexico (550 km, population 420,000), Las Cruces, New Mexico (950 km, population 75,000), and the twin cities of El Paso, Texas (1,025 km, population 600,000) and Ciudad Juarez, Chihuahua, Mexico (1,025 km, population 1,300,000). Most municipal water supply is from wells, but Santa Fe and El Paso do use significant amounts of surface water as well. Use of surface water by municipalities totals about 1 m<sup>3</sup> s<sup>-1</sup>.

Total irrigated area in the basin is approximately 370,000 ha, of which 260,000 ha are in Colorado, near the headwaters of the river. Withdrawals for irrigated agriculture amount to about 70 m<sup>3</sup> s<sup>-1</sup>, of which about half returns to the river. Losses due to open-water evaporation (especially from Elephant Butte Reservoir) and riparian evapotranspiration are difficult to quantify, but, based on balancing the various river discharges and consumptive uses given above, are probably about 18 m<sup>3</sup> s<sup>-1</sup>.

## Water Quality

The dissolved solids content of the Rio Grande increases markedly as it flows from its headwaters in Colorado to the southern limit of the study area (Figure 3). The total dissolved solids content in the headwaters region averages about  $40 \text{ mg L}^{-1}$ . By the time the river reaches El Paso the average value is about  $750 \text{ mg L}^{-1}$ , and at Fort Quitman, south of El Paso, it commonly attains values in excess of  $2,000 \text{ mg L}^{-1}$ . Not only the solute concentration, but also the solute burden increase downstream, from about  $100,000 \text{ tons yr}^{-1}$  at Lobatos to about  $600,000 \text{ tons yr}^{-1}$  south of San Marcial. The concentrations of dissolved solids vary seasonally, and during the winter, when base flow is not diluted by releases of irrigation water from dams, can greatly exceed the average values given above (Figure 4). Water quality in the vicinity of El Paso approaches the limits advised for both irrigation and drinking-water use. South of El Paso it is not usable for most purposes. Analysis of historical records shows that during periods of extended drought, such as the mid-to-late 1950's, salinity consistently exceeded the present-day averages. Population, and thus demand on the water resources, has greatly increased since the 1950's, and a repetition of such a long-term drought could have disastrous consequences with regard to water quality.

The causes of this prominent increase in salinity with flow distance have never been fully explained. Evapotranspiration during irrigation and by riparian vegetation clearly plays a role, but cannot explain the observed increase in solute burden. The work of the National Resource Committee (1938) attributed it principally to displacement of natural saline ground water by infiltrating irrigation water. Hayward (1956) and Wilcox (1957) laid more emphasis on increases in the proportion of the more soluble salts during evaporation in irrigated soils.

### **Application of Environmental Tracers**

Studies employing environmental tracers to investigate the sources of salinity have been pursued as part of the Rio Grande Basin project carried out through the Center for Sustainability of semiArid Hydrology and Riparian Areas, funded by the U.S. National Science Foundation. High spatial-resolution sampling campaigns ( $\sim 10 \text{ km}$  sampling intervals) have been conducted by the authors twice per year since the winter of 1999/2000: during late summer when irrigation water is being released from the reservoirs, and during mid-winter when there are no irrigation releases and flows are minimal. The main tracers employed to date have been the stable isotopes of oxygen and hydrogen in the water molecule, chloride, and bromide.

#### Stable isotopes of oxygen and hydrogen

The stable isotopes of oxygen ( $^{18}\text{O}/^{16}\text{O}$ ) and hydrogen ( $^2\text{H}/^1\text{H}$ ) in the water molecule are a commonly-employed tool for understanding the origins and circulation of natural waters (Coplen et al., 1999; Gat, 1996). The stable isotope content of precipitation at middle and northern latitudes is most strongly controlled by the temperature at the time of the precipitation event, with isotopically lighter precipitation being associated with colder temperatures (Dansgaard, 1964). Inasmuch as most of the

runoff for the Rio Grande originates as snow at high elevation, it can be expected to be isotopically light.

One of the most important controls on the stable isotope composition of surface water is evaporation. The heavier isotopic species ( $\text{H}_2^{18}\text{O}$  and  $^2\text{HHO}$ ) are less volatile than their lighter (and more common) counterparts and thus tend to be retained during evaporation. This causes progressive isotopic enrichment during the process of evaporation. In contrast, transpiration does not affect the isotopic composition of the residual water because plants transmit water from the soil to the atmosphere without isotopic separation. Measurement of the stable isotope composition of salinized water is a useful method for discriminating the cause of the salinity because water that is saline due to evaporation will be isotopically more enriched than the source water, whereas water that is saline due to salt addition or transpiration will not change isotopic composition.

The variation of stable isotope composition of the river water is illustrated in Figure 5. When plotted against each other (Figure 5a), the two isotopes form a linear array with a slope of 5, which is considered diagnostic of evaporation. As expected, the initial  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  are relatively light (-14 and -100 ‰, respectively) and are consistent with winter precipitation for the region (Adams et al., 1995). The plot of  $\delta^2\text{H}$  against flow distance in Figure 5b shows obvious trends that correspond to features of the river system. The peak in  $\delta^2\text{H}$  at about 250 km is explained by inflow of evaporated drainage water from the Closed Basin Project in the San Luis Valley. This isotopically heavy inflow is diluted downstream by isotopically light tributaries. The major step in  $\delta^2\text{H}$  at 800 km is at Elephant Butte Reservoir, which is known to be the single largest evaporative sink in the entire river system. Downstream of Elephant Butte Reservoir the isotopic composition is surprisingly stable, given the large amount of diversion for irrigation and inflow of return waters in the Mesilla Valley. This may indicate that most water loss in this stretch is by transpiration.

A simple Rayleigh distillation model (Campbell and Larson, 1998) can be used to estimate the degree of evaporation necessary to produce the observed enrichment. Assuming an effective isotopic enrichment factor for  $^2\text{H}$  of -89 ‰ during evaporation, the Rayleigh model indicates that about 35% of the river flow has been evaporated by the time the river reaches El Paso. This differs from the water balance based on gaging that was described above, which indicates that about 75 % of the water is lost to evapotranspiration above El Paso. However, transpiration does not fractionate  $^2\text{H}$  or  $^{18}\text{O}$ . The stable isotopes thus indicate that about half of the river losses are due to evaporation and the other half due to transpiration from irrigated fields and riparian areas.

### Chloride/Bromide Ratio

Chloride has many uses as a tracer in natural water (Feth, 1981). It is normally present only in the form of  $\text{Cl}^-$  and does not participate in precipitation or adsorption reactions. Chloride is thus highly conservative under natural conditions. Bromide generally exhibits similar geochemical characteristics, and thus the  $\text{Cl}/\text{Br}$  ratio is a conservative indicator for the origin of natural waters (Davis et al., 1998). Meteoric water is usually characterized by a  $\text{Cl}/\text{Br}$  mass ratio of 150 to 50. In contrast, most subsurface sources have substantially larger  $\text{Cl}/\text{Br}$  ratios, ranging from ~200 for many

oilfield brines up to over 10,000 for solutions from the dissolution of marine evaporites (Davis et al., 1998; Whittemore, 1995). Many anthropogenic sources of chloride, such as sewage, also have high Cl/Br ratios (Vengosh and Pankratov, 1998). If the progressive increase in salt burden of the Rio Grande with flow distance can be attributed to influx of subsurface or anthropogenic salts, it should be accompanied by a similar progressive increase in the Cl/Br ratio.

Figure 6 shows the change in the Cl<sup>-</sup> concentration and the Cl/Br ratio with flow distance, sampled in August 2001. Chloride concentration in the headwaters is about 0.5 mg L<sup>-1</sup>. It increases to about 9 mg L<sup>-1</sup> at Albuquerque, 50 mg L<sup>-1</sup> at Elephant Butte, and 100 mg L<sup>-1</sup> at El Paso. The Cl/Br ratio at the headwaters is about 50, at the lower end of the meteoric range. Were all of the increase in Cl<sup>-</sup> concentration attributable to evapotranspirative consumption of the water, this ratio would remain relatively constant downstream. (Minor geographical variations in the Cl/Br ratio of atmospheric deposition and possible effects of preferential uptake of Br by plants could cause small downstream variations in the river Cl/Br ratio). In fact, it increases to about 200 at Albuquerque and 500 at El Paso. Thus it is clear that the salinization is caused, at least in part, by addition of saline water having high Cl/Br ratios, most likely of subsurface origin.

In order to help quantify the mechanisms of salinization, the Cl<sup>-</sup> and Br<sup>-</sup> concentrations were modeled using a simple two-component mixing and evaporation model:

$$m_i = e[m_{s,i}f + m_{a,i}(1 - f)]$$

where m is salt concentration, i indicates Cl<sup>-</sup> or Br<sup>-</sup>, a is the atmospherically-derived end member, s is the subsurface end member, f is the fraction of water originating from subsurface inflow, and e is inverse evaporative loss (i.e., e is equivalent to V<sub>o</sub>/V<sub>x</sub> where V<sub>o</sub> is the original volume of runoff water and V<sub>x</sub> is the volume remaining after evapotranspirative loss at some distance x down the river). These two equations (for Cl<sup>-</sup> and Br<sup>-</sup>) were solved simultaneously for e and f using the Cl<sup>-</sup> and Br<sup>-</sup> measured at each point down the river. The meteoric end-members were taken as the Cl and Br data for the next station upstream from each measurement point. The end-member concentrations for the subsurface (i.e., saline groundwater) were chloride, 280 mg L<sup>-1</sup> and bromide, 0.5 mg L<sup>-1</sup>. These values were taken from the most concentrated ground waters identified by Bexfield (2001) in the “discharge zone” of the Albuquerque Basin, which is located at its southern end.

The results of the mixing/evaporation model calculations are shown in Figure 7. The model employed is very simplistic and the results should be considered as only semi-quantitative (for example, anthropogenic sources of Cl<sup>-</sup>, effects of varying composition of the subsurface end member, or mixing of tributaries of differing compositions are not considered). However, it does illustrate the major trends of salinization. The evaporative fraction (i.e., the fraction of the original runoff remaining after evapotranspiration) shown in Figure 7a decreases from 1 in the headwaters to about 0.4 at El Paso. The basin water balance based on stream gaging, given above, indicates that about 75% of the flow at Otowi is evaporated by the time the river reaches El Paso, thus the two estimates are in general agreement. The fluctuations around the regional trend are strongly influenced by

variations in the  $\text{Cl}^-$  and  $\text{Br}^-$  concentrations of the various inflows and probably do not accurately reflect variations in evaporation at the local scale.

The calculated relative salt additions are shown in Figure 7b. This graph shows that  $\text{Cl}^-$  is added to the river in a series of distinct steps, rather than the relatively uniform distribution of  $\text{Cl}^-$  concentration increase caused by evapotranspiration. Six localities of apparent salt addition can be identified. The first step is south of Alamosa, the second at the south end of Albuquerque, the third just north of San Acacia, the fourth at Elephant Butte Reservoir, the fifth at the head of Seldon Canyon, and the sixth north of El Paso. Most of these have a similar geological setting. The first step is at the south end of the San Luis Basin. The third is at the south end of the Albuquerque Basin. The fourth is at the southern termination of the Socorro Basin and the fifth at the southern end of the Palomas Basin. Finally, the last is at the southern end of the Mesilla Basin. The only step that does not correspond to this pattern is the second one, and this increase in  $\text{Cl}^-$  may be related to discharge from the Albuquerque sewage treatment facility. In general, these salinity inputs do not appear to be closely related to agricultural drainage. Most of the major drain outflows were sampled and those north of Elephant Butte Reservoir showed only slight enhancement of  $\text{Cl}^-$  concentrations over the diverted river water. One notable exception is a drain near Socorro having both high  $\text{Cl}^-$  and a high  $\text{Cl}/\text{Br}$  ratio. The source of this saline water is not known. South of Elephant Butte most of the drains have moderately elevated  $\text{Cl}^-$  and slightly elevated  $\text{Cl}/\text{Br}$ . One drain at the far south end of the Mesilla Basin is strongly elevated in both parameters. This drain is not in a heavily irrigated area and appears to be intercepting mostly natural ground-water discharge.

## Conclusions

The Rio Grande presents a classic case study of arid-region river salinization. At the headwaters of the river both the TDS and the  $\text{Cl}^-$  concentrations are low (40 and  $0.5 \text{ mg L}^{-1}$ , respectively). These both increase progressively during flow through approximately 1,000 km of desert environment, to values of about 750 and  $100 \text{ mg L}^{-1}$ , respectively, at El Paso/Ciudad Juarez, the last major population center on this section of the river. Both conventional river gaging and stable isotopes of oxygen and hydrogen indicate that only approximately 30% of the inflow across the Colorado/New Mexico border escapes evapotranspiration to reach El Paso. However, evapotranspirative concentration of the cyclic salts from the headwaters area can account for less than 20% of the increase in total dissolved solids.

The most common explanations of the additional salt input have been that infiltration of excess irrigation water raised the water table and flushed soils and shallow ground water made saline by natural, pre-irrigation evapotranspiration in the desert environment, or that water logging of irrigated fields prior to the installation of drains accumulated salts that were flushed after drainage was installed. Were either of these the case, the salinity inputs should be localized at agricultural drains and the  $\text{Cl}/\text{Br}$  ratio should remain approximately constant (since the salt was derived from pre-irrigation evapotranspiration of river water or direct precipitation). However, the increase of the  $\text{Cl}/\text{Br}$  ratio with flow distance indicates that most of this additional salinity accrues from influx of saline subsurface waters. The salinity increase is not gradual, but rather stepwise, with most of the steps at the southern ends of the major sedimentary basins that

form the Rio Grande Rift. These observations indicate that most of the salinization of the Rio Grande is probably due to regional discharge of ancient ground water that has followed deep flow paths through the basins and acquired high salinity due to diagenetic or geothermal reactions. Additional studies are planned to more definitively identify the sources and locations of these discharges. This may ultimately enable some amelioration of the salinization of the Rio Grande.

### Acknowledgements

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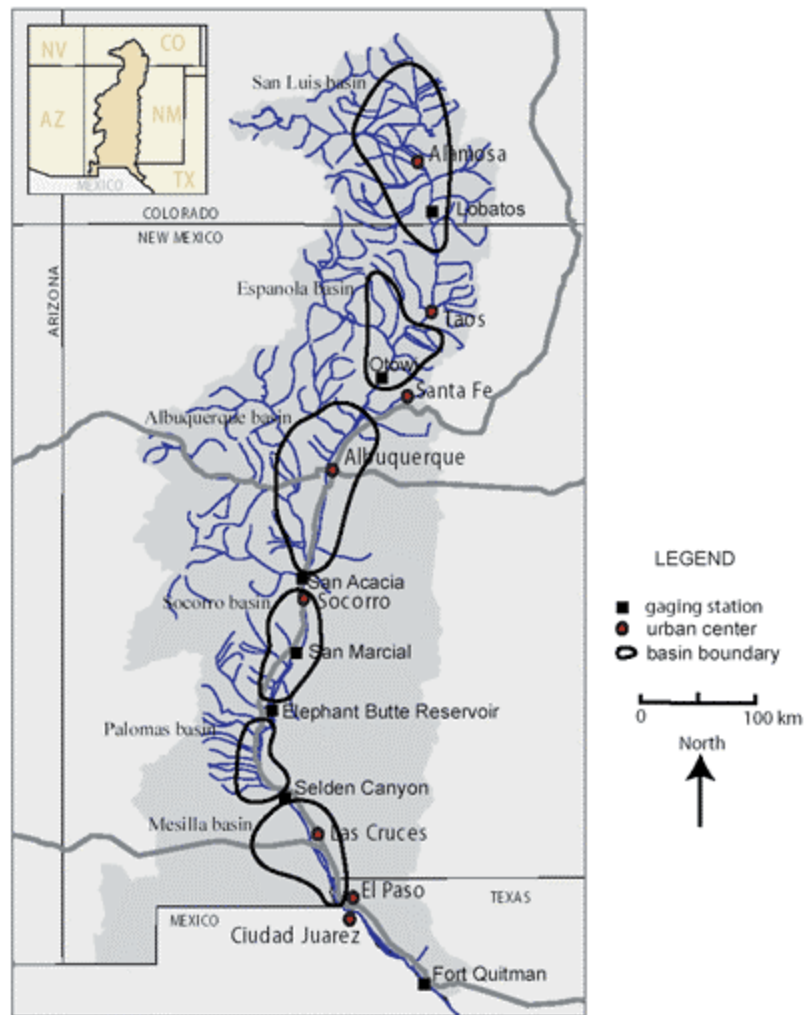


Figure 1. Map of the upper Rio Grande, showing population centers, gaging stations mentioned in text, and sedimentary basins that form the Rio Grande rift.

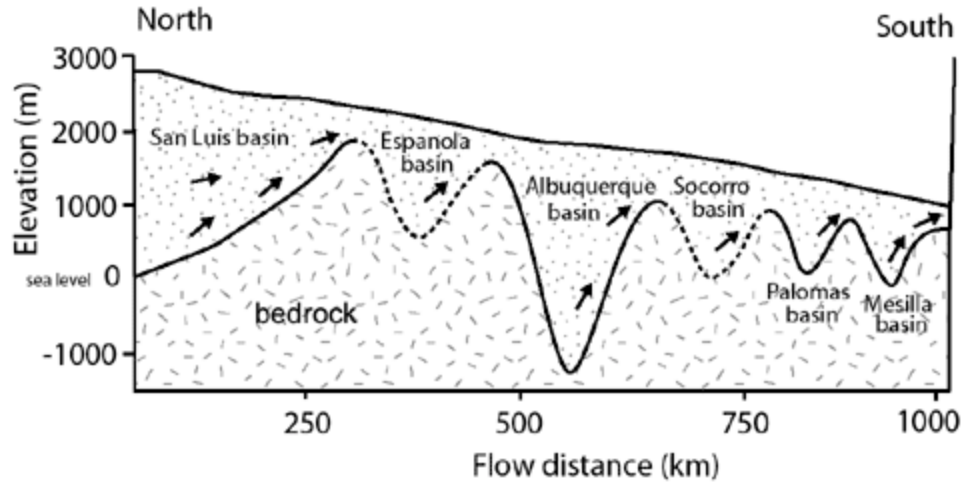


Figure 2. Schematic hydrogeologic cross-section of the Rio Grande rift, parallel to the path of the river. Arrows indicate direction of groundwater flow. Basin fill depth dotted where not well-constrained. Basin structure is based on data from Anderholm (1987), Hawley (1984), Keller and Cather (1994), and Wilkins (1998).

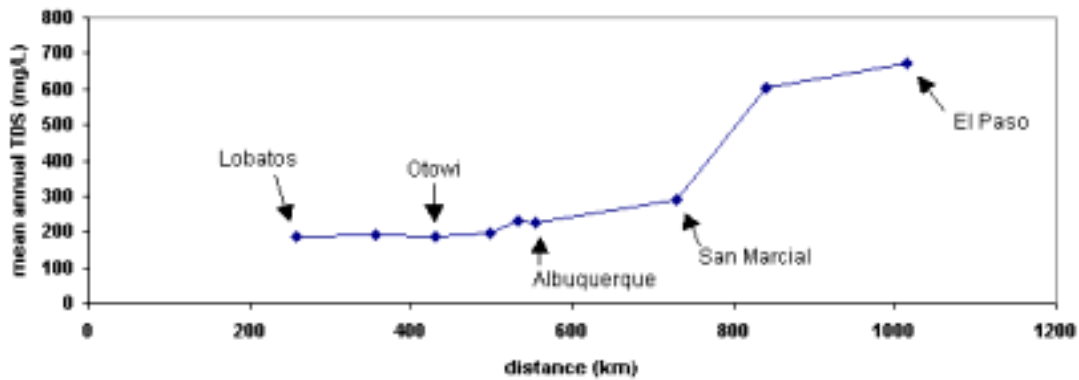


Figure 3. Variation of mean annual total dissolved solids (TDS) content of the Rio Grande with flow distance (data from U.S. Geological Survey gaging station records).

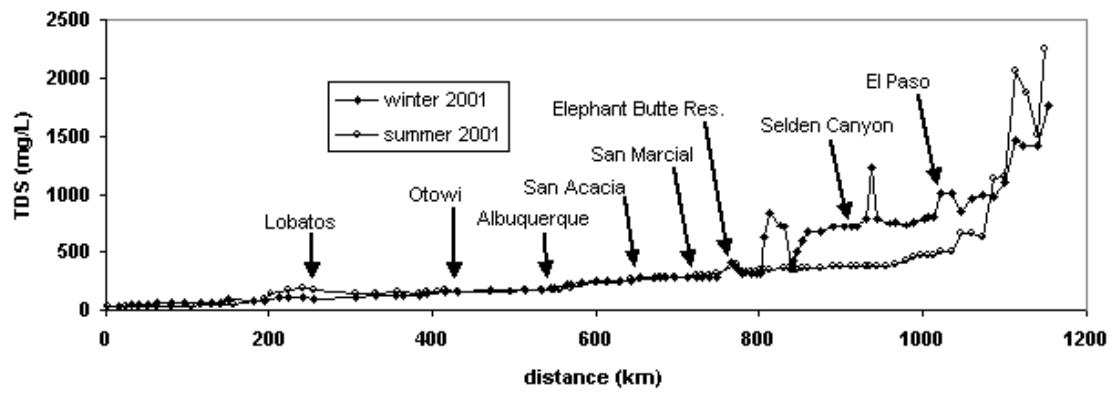


Figure 4. Variation of TDS in the Rio Grande with flow distance during the winter of 2000/2001 and the summer of 2001.

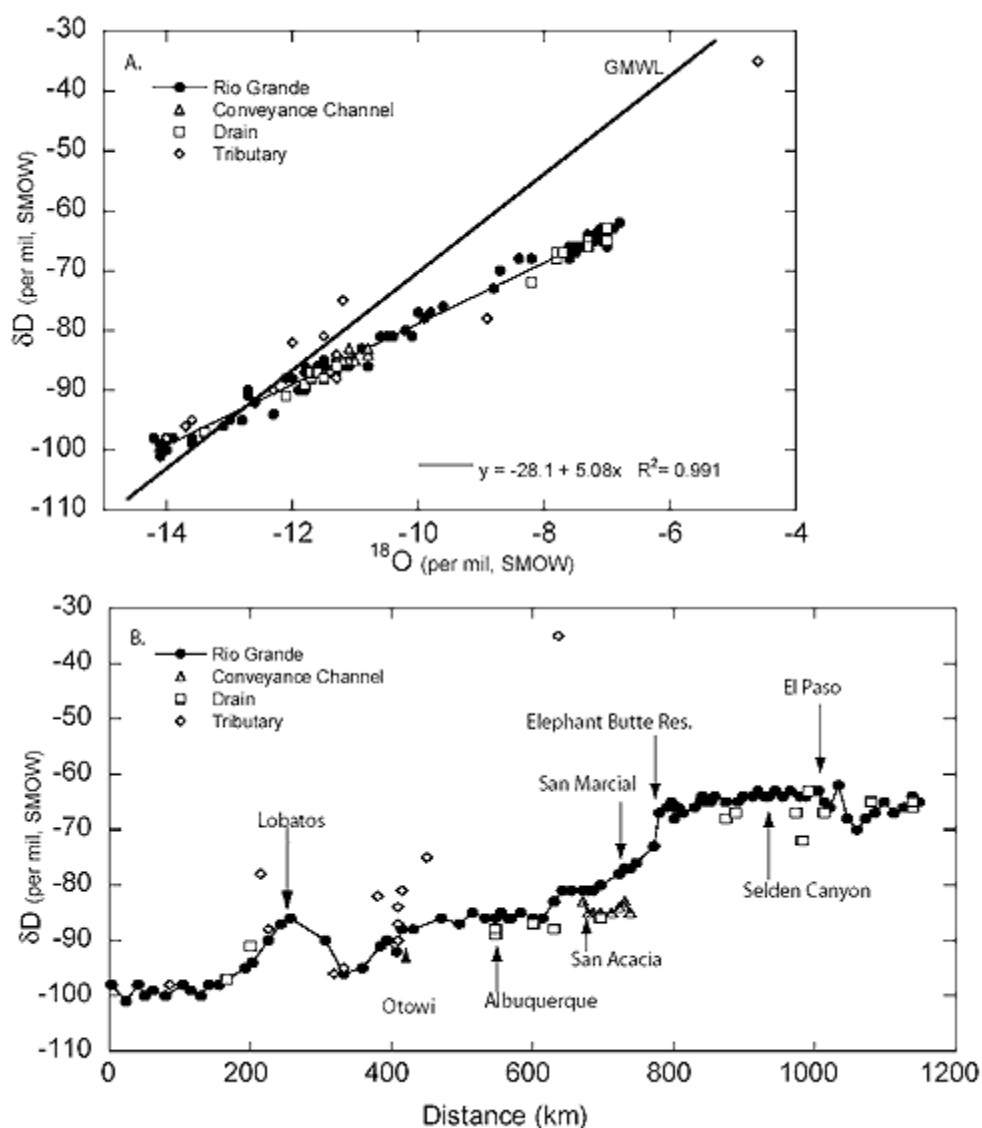


Figure 5. Stable oxygen and hydrogen isotopes in waters of the Rio Grande during August 2001. “GMWL” is the global meteoric water line. (a)  $\delta^{18}O$  versus  $\delta^2H$ . Values are in per mil relative to the SMOW standard. (b)  $\delta^2H$  in per mil as a function of flow distance.

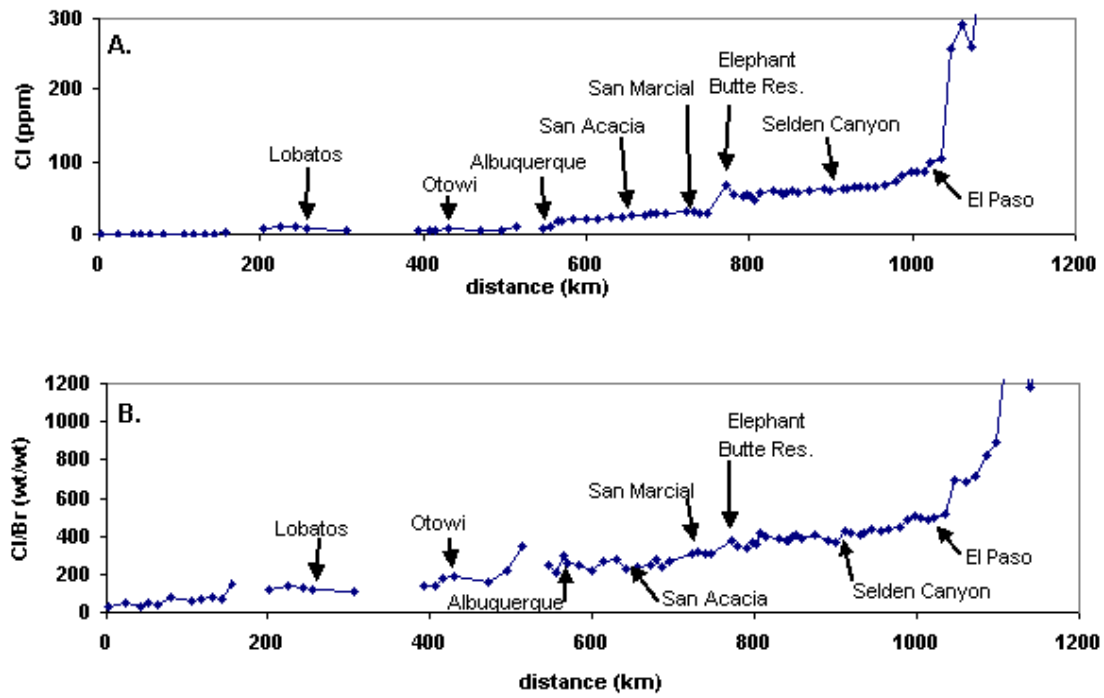


Figure 6. Chloride and bromide in waters of the Rio Grande. (a) Chloride as a function of flow distance during August 2001. (b) The Cl/Br ratio as a function of flow distance.

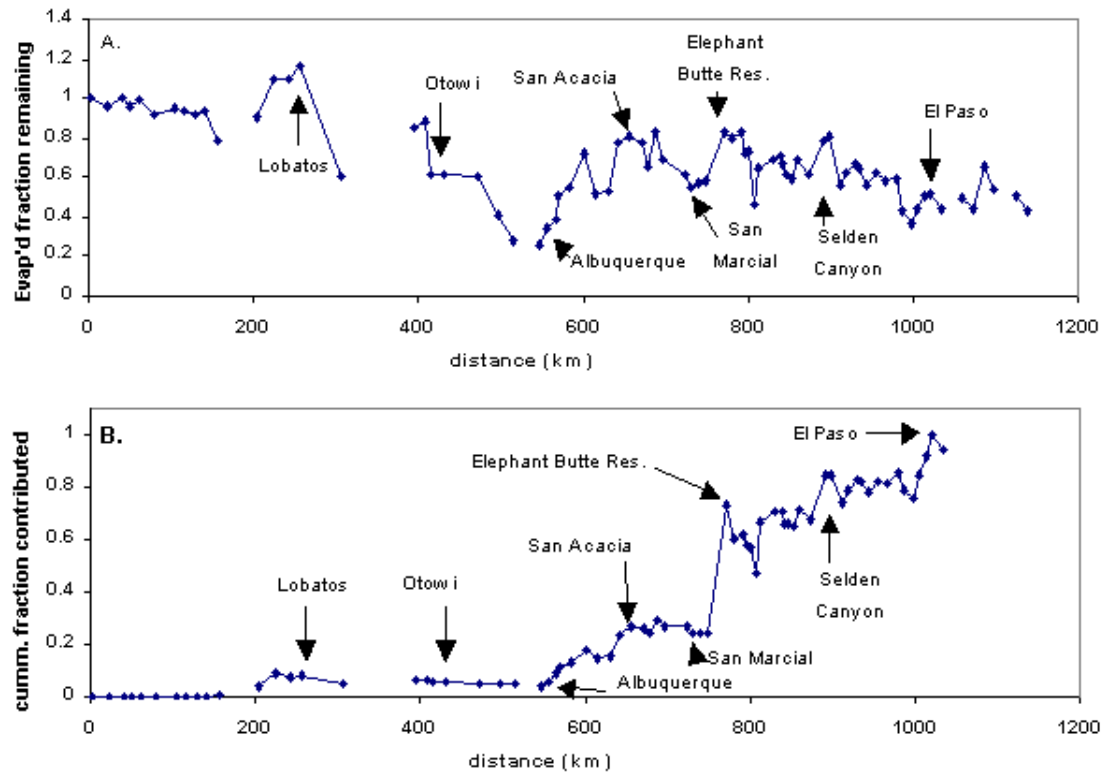


Figure 7. Preliminary interpretation of effects of evaporation and salt addition on chloride concentration of the Rio Grande, based on August 2001 data. (a) Evaporative fraction (volume remaining after evapotranspiration/original volume) as a function of flow distance. (b) Relative chloride addition (as fraction of final chloride added) as a function of flow distance.



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