Isotopic Tracing of Hydrological Processes in the Upper Rio Grande Basin

2004 Report to the IAEA Coordinated Research Project – Isotopic Tracing of Hydrological Processes in Large River Basins

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INTRODUCTION

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 known as Fort Quitman that is 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^2.

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 highly generalized 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^{-1} 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^{-1} and the driest areas only 160 mm yr^{-1}.

Summer temperatures are high and over most of the basin potential evapotranspiration varies from 1,000 to 2,000 mm yr^{-1}.

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^3 s^{-1}, although the natural flow would be about 40 m^3 s^{-1} without agricultural diversions (discharge and water use data are from Ellis et al., 1993). The river reaches its maximum discharge of 49 m^3 s^{-1} at Otowi, New Mexico, 430 km down the river. This would probably be closer to 70 m^3 s^{-1} under natural conditions. At Albuquerque, New Mexico, 550 km down river, the discharge is 44 m^3 s^{-1}. Above Elephant Butte Reservoir (800 km downstream and by far the largest reservoir on the river) the discharge amounts to 40 m^3 s^{-1}; below the reservoir it is about 33 m^3 s^{-1}. 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^3 s^{-1}, mostly due to agricultural diversions. Most of this flow is diverted for municipal use in El Paso and for additional irrigation downstream of El Paso. Below Fort Quitman the river is dry at most times.

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 1 to 2 m^3 s^{-1}.

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^3 s^{-1}, 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^3 s^{-1}.

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 mg L^{-1}. By the time the river reaches El Paso the average value is about 750 mg L^{-1}, and at Fort Quitman, south of El Paso, it commonly attains values in excess of 2,000 mg L^{-1}. Not only the solute concentration, but also the solute burden increase downstream, from about 100,000 tons yr^{-1} at Lobatos to about 600,000 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 except irrigation of salt-tolerant crops. 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. A famous agricultural engineer of the early 20th century, J.B. Lippincott (1939), laid most of the blame on irrigated agriculture: "The increase in the salinity of the waters of the Rio Grande [is] due to their use and re-use [for irrigation] in its long drainage basin…". 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 Resources Committee in 1938 and Trock et al. (1978) attributed it principally to displacement of natural, shallow, brackish ground water by infiltrating irrigation water. However, they did not explain the source of the brackish water. Hayward (1956) and Wilcox (1957) laid more emphasis on increases in the proportion of the more soluble salts during evaporation in irrigated soils.

SAMPLING PLAN

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 (SAHRA), funded by the U.S. National Science Foundation. High spatial-resolution sampling campaigns (~10 km sampling intervals) were conducted twice per year between the winter of 1999/2000 and the winter of 2001/2002. Sampling was conducted 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. Subsequent to the 2001/2002 winter similar sampling has also been performed, but at a lower spatial resolution. The main tracers employed to date have been $\delta^{2}H$ and $\delta^{18}O$ in the water molecule, Cl^{-}, Br^{-}, $^{36}Cl/Cl$, $^{87}Sr/^{86}Sr$, Sr^{2+}/Ca^{2+}, and $\delta^{238}U$. Most of the results given below have been presented and discussed by Mills (2004).

ENVIRONMENTAL TRACER RESULTS

Deuterium and Oxygen-18 in the Water Molecule

The variation of $\delta^{18}O$ composition of the river water with flow distance is illustrated in Figures 5 and 6. When $\delta^{18}O$ and $\delta^{2}H$ are plotted against each other (Figure 7), the two isotopes form a linear array with a slope of 5, which is considered diagnostic of evaporation. As expected, the initial $\delta^{18}O$ and $\delta^{2}H$ are relatively light (-14 and -100 ‰, respectively) and are consistent with winter precipitation for the mountainous headwaters (Adams et al., 1995). The plots of $\delta^{18}O$ against flow distance in Figures 6 and 7 show obvious trends that correspond to features of the river system. The data for summer 2001 are probably fairly representative of the stable isotope composition of the

river during normal summers. The peak in $\delta^{18}O$ at about 250 km is largely 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 $\delta^{18}O$ 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 applied to the $\delta^{2}H$ data to estimate the degree of evaporation necessary to produce the observed enrichment. Based on the summer 2001 data, and assuming an effective isotopic enrichment factor for $\delta^{2}H$ 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}H or ^{18}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 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 Cl/Br ratio is a conservative indicator for the origin of natural waters (Davis et al., 1998). Meteoric water is usually characterized by a Cl/Br mass ratio of 150 to 50. In contrast, most subsurface sources have substantially larger Cl/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.

Figures 8 and 9 shows the change in the Cl^- concentration with flow distance for the summer and winter sampling sequences. Chloride concentration in the headwaters is about 0.5 mg L^{-1}. It increases to about 9 mg L^{-1} at Albuquerque, 50 mg L^{-1} at Elephant Butte, and 100 mg L^{-1} at El Paso. Summer and winter Cl/Br ratios with flow distance are given in Figures 10 and 11. 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^- 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.

Close examination of Figures 8 and 9 shows that the Cl concentration tends to increase in a step-wise fashion, rather than gradually with distance. Major steps are observed at the outlet of the San Luis Basin, just south of Albuquerque, at San Acacia, at Elephant Butte Reservoir, and at the El Paso Narrows (these locations are marked on the figures). Consideration of the full range of tracers shows that these increases have differing origins. That at the outlet of the San Luis Basin is characterized by very significant summer increases in $\delta^{18}O$ and Cl, but little change in the Cl/Br ratio. During the winter, these perturbations disappear. The northern and eastern part of the San Luis Basin is a hydrologically closed basin with mildly saline groundwater. This groundwater is pumped during the summer to provide agricultural drainage and is exported to the Rio Grande. The addition of this evaporated meteoric water produces the fluctuations described above.

In contrast, the Albuquerque anomaly shows little stable-isotope variation, but increases in Cl and Cl/Br during both summer and winter. These changes can probably be ascribed to discharge of treated wastewater from the Albuquerque facilities. This wastewater is ultimately derived from groundwater pumping, and the groundwater has higher Cl than the river. Dietary salt, characterized by high Cl/Br, is also added.

The San Acacia "step" has characteristics similar to that at Albuquerque, but there is no sewage or other human discharge at this site. There is, however, a saline pond, apparently formed by discharge of deep-origin brines (Mills, 2004). Mixing relationships indicate that a significant portion of the salinity increase of the Rio Grande appears to originate by deep sedimentary or geothermal brine seepage between San Acacia and San Marcial.

The most dramatic step in the Cl concentration north of the Mesilla Valley is at Elephant Butte Reservoir. (Note that this step is apparent only in the summer 2000 and 2001 data; in subsequent years the drought-induced increases in Cl concentration actually cause the river discharge to be diluted in the reservoir.) It is accompanied by an equally dramatic $\delta^{18}O$ step, but virtually no change in Cl/Br. The lack of change in Cl/Br, as well as other evidence (Mills, 2004), indicates that the increases in the other tracers at Elephant Butte are simply due to evaporative concentration of the water under desert climate. Chloride has a multi-year residence time in the lake and can be evaporatively increased substantially above average inflow concentrations, especially when the storage in the reservoir is decreasing due to reduction of inflow.

Finally, the largest Cl increases of all are found at the southern end of the Mesilla Valley. These are accompanied by increases in Cl/Br, but virtually no change in the stable isotopes. These have been traced to inflow of saline water from agricultural drains, particularly the Mesquite and Montoya drains. In spite of the origin from drains, the water has a tracer signature characteristic of deep basin brines rather than evaporated agricultural water.

<u>Chlorine-36 ratio</u>

The $^{36}Cl/Cl$ ratio can provide a test of the hypothesis that leakage of deep subsurface brines is a major source of solute burden to the Rio Grande. Precipitation on the land surface contains a high ratio of ^{36}Cl to stable Cl because of deposition of ^{36}Cl produced by cosmic rays in the atmosphere. Chloride with a long residence time in the

subsurface where ^{36}Cl production is low will have a low $^{36}Cl/Cl$ ratio (see Phillips, 2000, for systematics of ^{36}Cl). Thus a sequence of measurements of $^{36}Cl/Cl$ down the Rio Grande should show a progressive decrease in the ^{36}Cl ratio as Cl increases, if the Cl is in fact derived from subsurface brines.

The results of the ^{36}Cl sampling are shown in Figure 12. The $^{36}Cl/Cl$ ratios range from 1,000 to 2,500 x 10^{-15} in the headwaters area, substantially higher than the natural local precipitation ratio of ~700 x 10^{-15} (Phillips, 2000). This can presumably be attributed to continuing flushing of ^{36}Cl resulting from atmospheric nuclear-weapons fallout. Downstream of approximately San Acacia (~650 km) these ratios decline to about 400 x 10^{-15}, and by El Paso reach ~100 x 10^{-15}. This progressive reduction strongly supports the hypothesis of subsurface salt addition.

<u>Strontium isotopes and Sr/Ca ratios</u>

We have measured $^{87}Sr/^{86}Sr$ and Sr^{2+}/Ca^{2+} to provide an independent check on the mixing hypotheses described above. Results are shown in Figures 13 and 14. In contrast to [Cl]/[Br] ratios, [Ca]/[Sr] ratios only exhibited a significant change in the middle portion of the study area, hence $^{87}Sr/^{86}Sr$ ratios were measured only for this stretch of the river. Sr in the headwater regions is likely derived from two sources – atmospheric deposition and bedrock weathering. In this region weathering of basalts associated with the Rio Grande rift are anticipated to be the dominant Sr source, resulting in low $^{87}Sr/^{86}Sr$ ratios (0.7045). In contrast, Sr derived from saline groundwaters is typified by $^{87}Sr/^{86}Sr$ ratios around ~0.710 and very low [Ca]/[Sr] ratios (10 to 50). As the Rio Grande enters to middle portion $^{87}Sr/^{86}Sr$ ratios are around ~0.709 and [Ca]/[Sr] ratios ~75, these values are consistent with a mixture of atmospheric deposition and basalt weathering with small contribution of saline groundwater. While passing through the middle section of the river $^{87}Sr/^{86}Sr$ ratios increase while [Ca]/[Sr] ratio decrease, a pattern consistent with discharge of saline groundwater. Again, as with the chlorine isotope system, river samples follow a clear two-end-member mixing relationship between river water entering the middle portion of the basin and saline groundwater. Mixing calculation indicate that a 5-10% contribution of saline groundwater can explain the salinity increases observed in the middle portion of the basin.

RESPONSE TO DROUGHT

The Rio Grande Basin has been gripped by drought since the mid-1990's, with the situation worsening substantially in the past three years (Figure 15). This affords the opportunity to examine the dynamic response of the system to changes in the water balance. The $\delta^{18}O$ of the river shows a dramatic increase at the southern end of the San Luis Basin over the last two years. This is probably because an increasing proportion of the river is being diverted for irrigation, while the amount of evaporated basin water being returned to the river has remained relatively constant. There is also an increase in $\delta^{18}O$ between northern New Mexico and Elephant Butte Reservoir. This can probably be attributed to inflow of tributaries (particularly the Rio Chama) that are discharging isotopically heavier water as the drought progresses. Finally, there is an increase in

Elephant Butte and the water discharged from it, due to the increasingly unfavorable water balance of the reservoir, which has declined to historically low levels.

Changes in Cl and Cl/Br have been even more significant. The most prominent feature is a region of increase extending from north of Albuquerque to San Marcial. At San Marcial the summer Cl concentrations have gone from 30 to 150 ppm. This is accompanied by an increase of the Cl/Br ratio from 300 to 730. This change partly reflects drastically decreased discharge of the river, which results in less dilution of the deep groundwater discharge by river runoff. Additionally, during drought, water is pumped from the drains to maintain flow in the river. However, the drain concentrations and ratios have also increased. This can probably be attributed to a decline in the proportion of drain flow derived from irrigation water. As hydraulic heads beneath the fields in the area decline, a larger proportion of deep saline discharge is probably allowed to flow out. The drought has revealed that there is a delicate balance between saline discharge and irrigation water that under normal conditions is masked by the large infiltration of irrigation water.

Finally, there has been a steady increase of Cl concentration in and below Elephant Butte Reservoir (from 50 to 80 ppm). This, however, is not accompanied by any significant change in the Cl/Br ratio. As described above, this is consistent with increased evaporative concentration of the river water as the reservoir declines under drought, but is not consistent with the change resulting from increased saline groundwater input.

BASIN CHLORIDE BALANCE

One of the long-term goals of the Rio Grande project, under funding from the NSF Science & Technology Center SAHRA, has been to construct a dynamic model of the solute balance of the Rio Grande. As an early step toward this goal, Mills (2004) has performed an instantaneous chloride balance of the river for summer and winter 2001. The inputs to the model were the high-resolution (~10 km) solute measurements shown above and river discharge measurements performed by various public agencies. These were utilized in a water, chloride, and bromide mass-balance model that accounted for diversions, inflows, groundwater seepage in and out, evapotranspiration, and brine seepage into the river. The model attempted to match to both the Cl and the Cl/Br data. The results of these calculations are shown in Figure 16. The figures clearly illustrate the large increase in solute burden south of Albuquerque. Mass continuity is not maintained across Elephant Butte Reservoir because the large salt storage in the reservoir is not accounted for in this instantaneous mass-balance model. The differences in the summer and winter flux diagrams are dramatic and illustrate the highly dynamic nature of salt transport in the Rio Grande.

The model was also used to estimate the relative contributions of the various Cl sources to the Rio Grande. The results include transient salt release from Elephant Butte Reservoir as it drains. If this contribution (which presumably averages to zero over long periods of time) is not considered, then approximately 30% of the chloride burden of the Rio Grande at El Paso is provided by inflows from the main stem and tributaries, about 20% comes from wastewater treatment plants, and about 50% arises from discharge of deep, saline groundwater.

SUMMARY

The Rio Grande is a typical desert river, fed by snowmelt in high mountains at the headwaters and virtually completely consumed by irrigation and other uses in the course of its 1,200 km length. Water quality in the headwaters is very dilute and pure, but in the lower part of the drainage basin the dissolved solids rise to the point of rendering the river virtually unusable. Not only the dissolved solids content, but also the salt burden, increases markedly along the flow path. The causes of this salinization have never been adequately explained.

We have employed a variety of environmental and isotopic tracers to examine the evolution of water quality in the Rio Grande. The study has been conducted during a period of increasing drought, so dynamics of the system under stress can be examined. Results have shown that salts are introduced into the river at fairly discrete points. Some of these are easily identified as point of wastewater discharge. Others, however, are not associated with any known discharges to the river. Their geochemical characteristics are similar to those of deep sedimentary brines. These brines appear to be leaking upward along faults and other geological structures at the southern portions of the Albuquerque, Socorro, and Mesilla basins.

Changes in agricultural practices have frequently been proposed as a means of improving the water quality in the Rio Grande. Our results indicate that, although irrigated agriculture does cause a significant increase in the concentration of solutes due to evapotranspiration, increases in the salt burden are not related to agriculture. Changing agricultural practices would probably have little effect on salinity, and improvement in irrigation efficiency might even further degrade water quality. The best chance for water quality improvement is likely to be identification and interception of brine leakage at the points of discharge.

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FIGURES

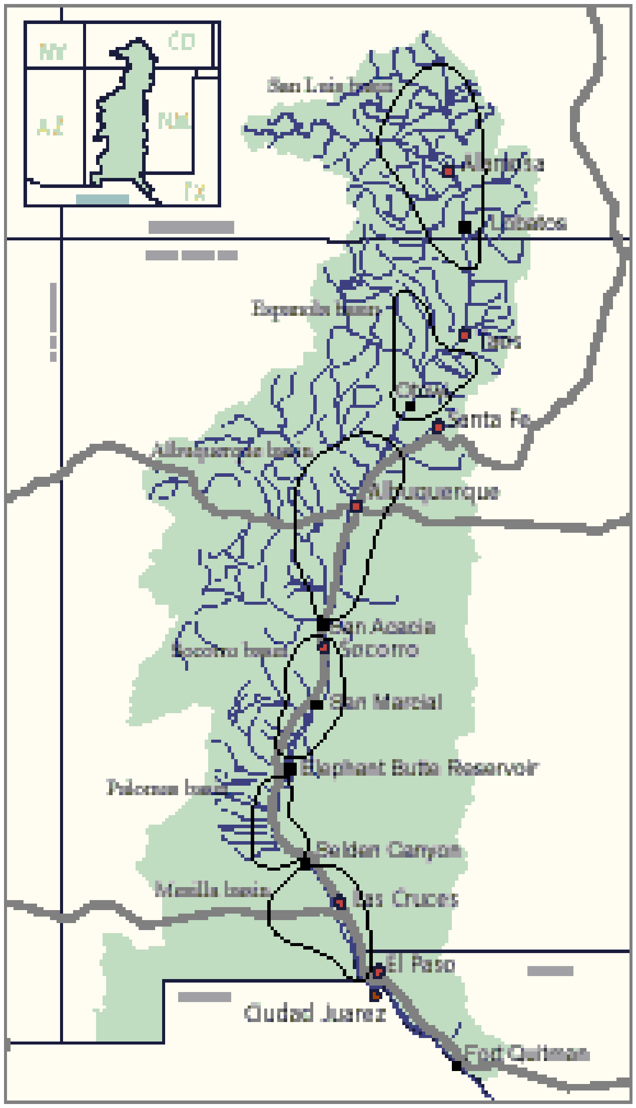

Figure 1. Map of the upper Rio Grande, showing population centers, gaging stations mentioned in text, and sedimentary basins that form the Rio Grande rift.

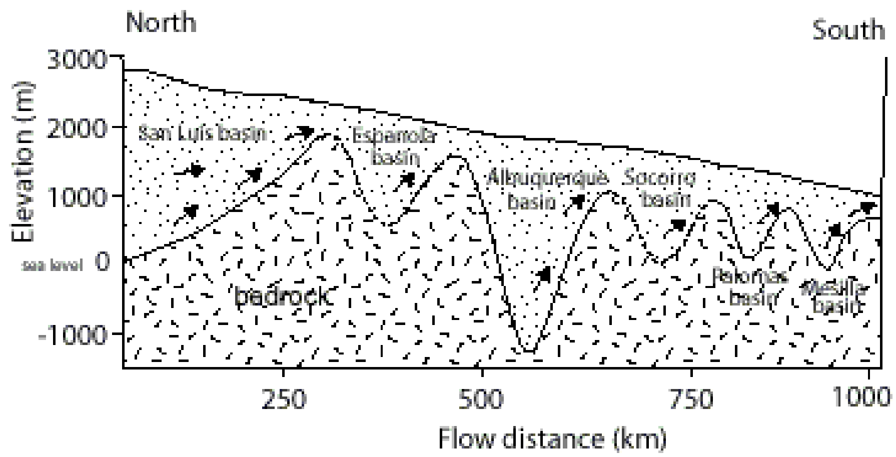

Figure 2. Schematic hydrogeologic cross-section of the Rio Grande rift, parallel to the path of the river. Basin fill depth dotted where not well-constrained. Basin structure is based on data from Hawley (1984), Anderholm (1987), Keller and Cather (1994), and Wilkins, (1998).

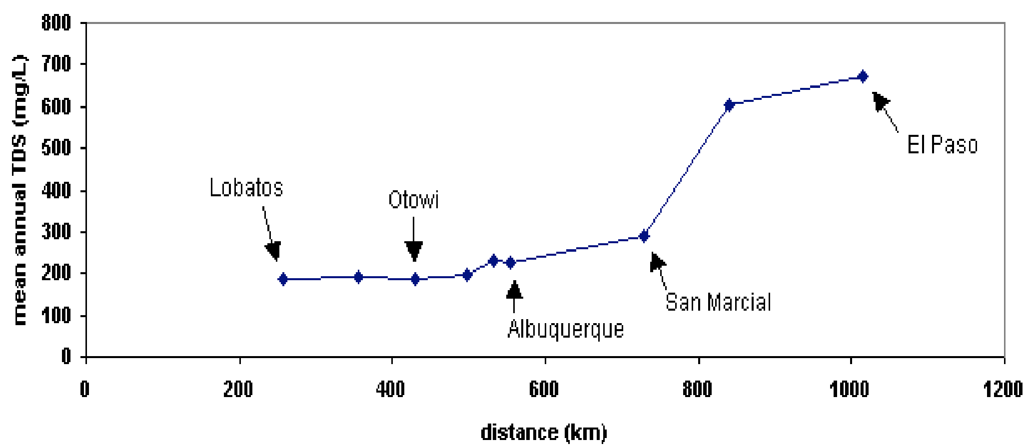

Figure 3. Variation of mean annual total dissolved solids (TDS) content of the Rio Grande with flow distance (data from U.S. Geological Survey gaging station records).

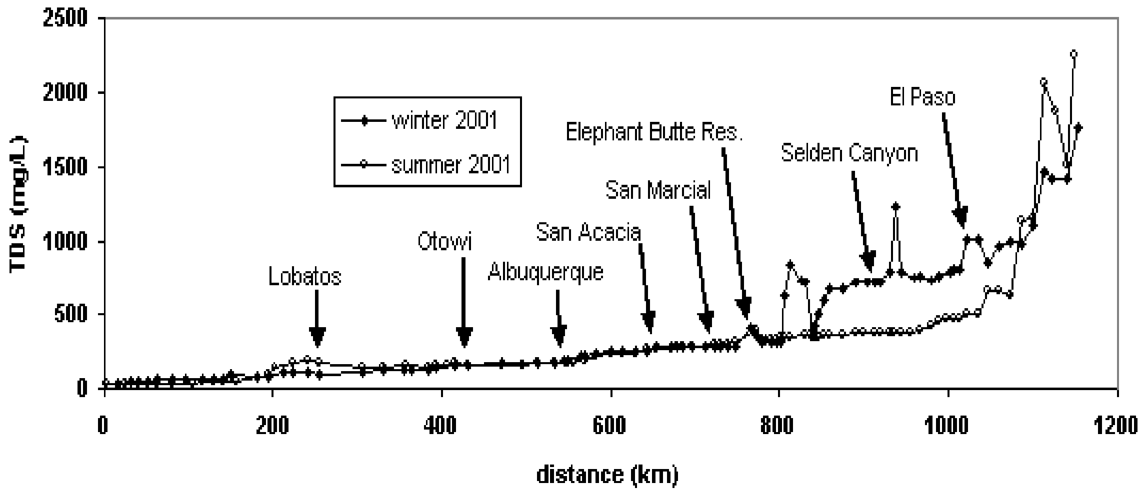

Figure 4. Variation of TDS in the Rio Grande with flow distance during the winter of 2000/2001 and the summer of 2001.

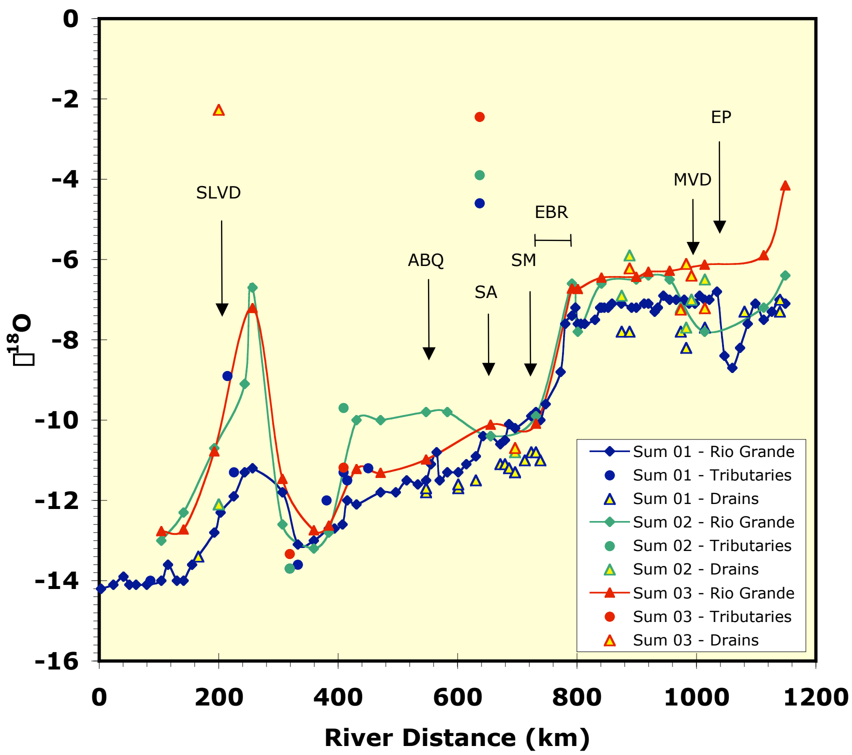

Figure 5. Variation of $\delta^{18}O$ with distance down the Rio Grande during the summers (August) of 2001, 2002, and 2003. Distances are measured relative to the outlet of Rio Grande Reservoir in Colorado. SLVD = San Luis Valley Drains, ABQ = Albuquerque, SA = San Acacia, SM = San Marcial, EBR = Elephant Butte Reservoir, MVD = Mesilla Valley Drains, EP = El Paso.

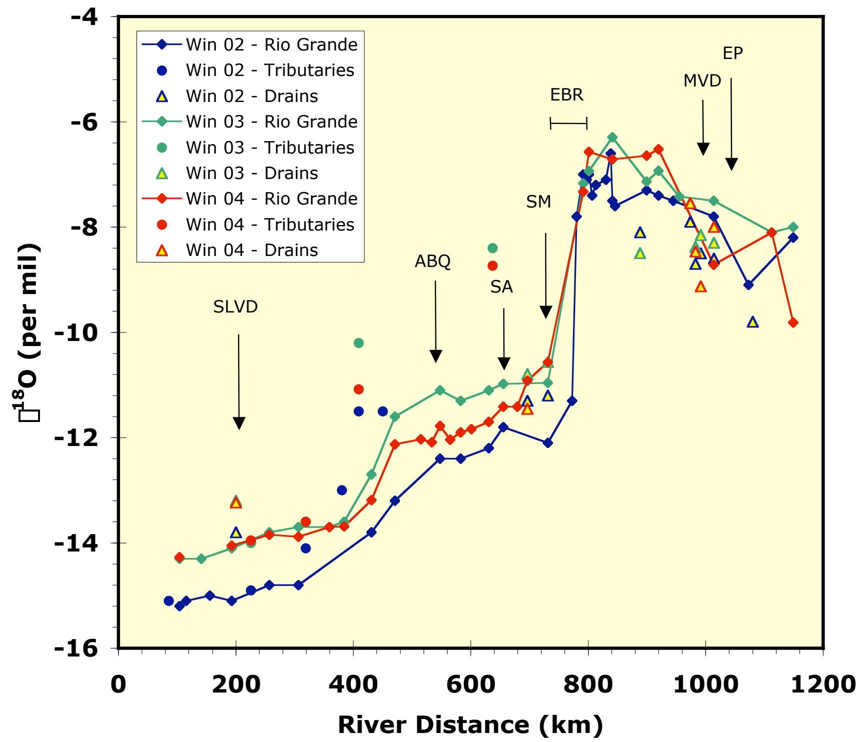

Figure 6. Variation of $\delta^{18}O$ with distance down the Rio Grande during the winters (January) of 2002, 2003, and 2004. Abbreviations are in caption to Figure 5.

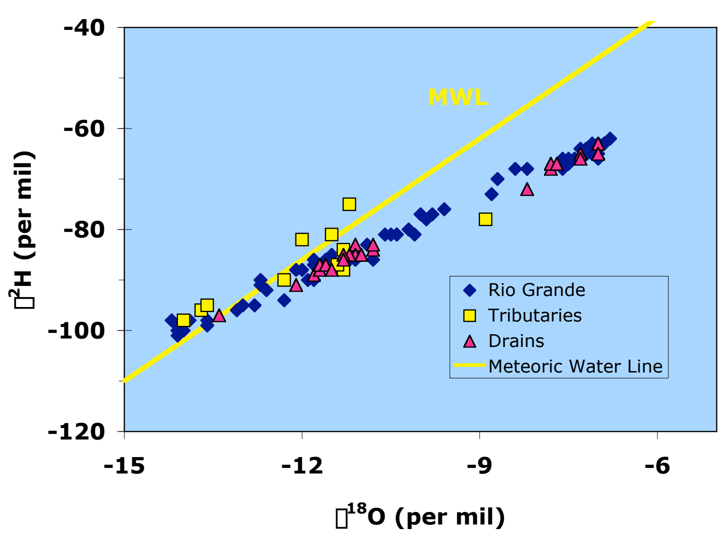

Figure 7. $\delta^{18}O$ versus $\delta^{2}H$ for the summer 2001 sampling.

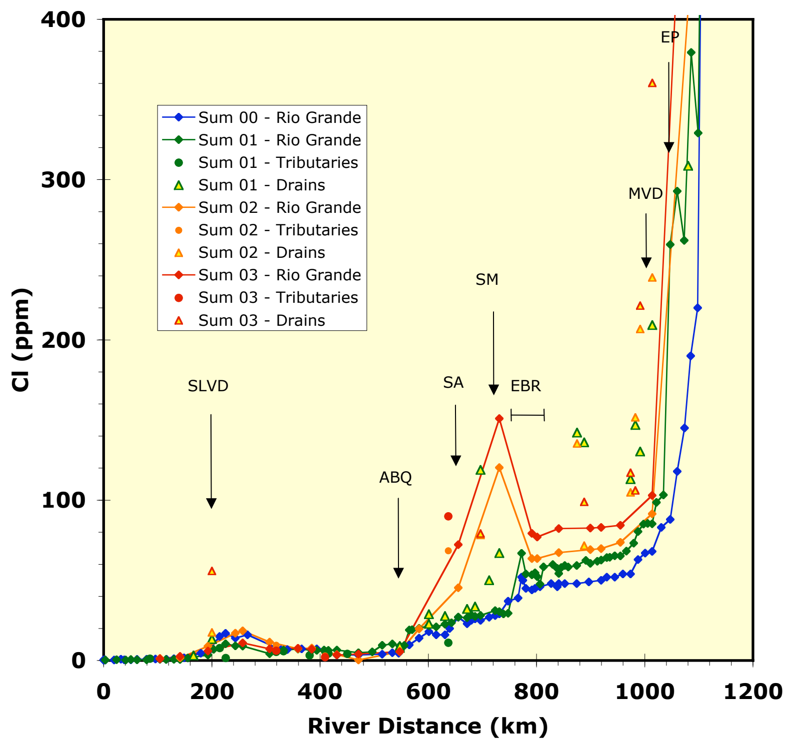

Figure 8. Chloride concentration as a function of flow distance for summer sampling campaigns. Abbreviations are given in caption to Figure 5.

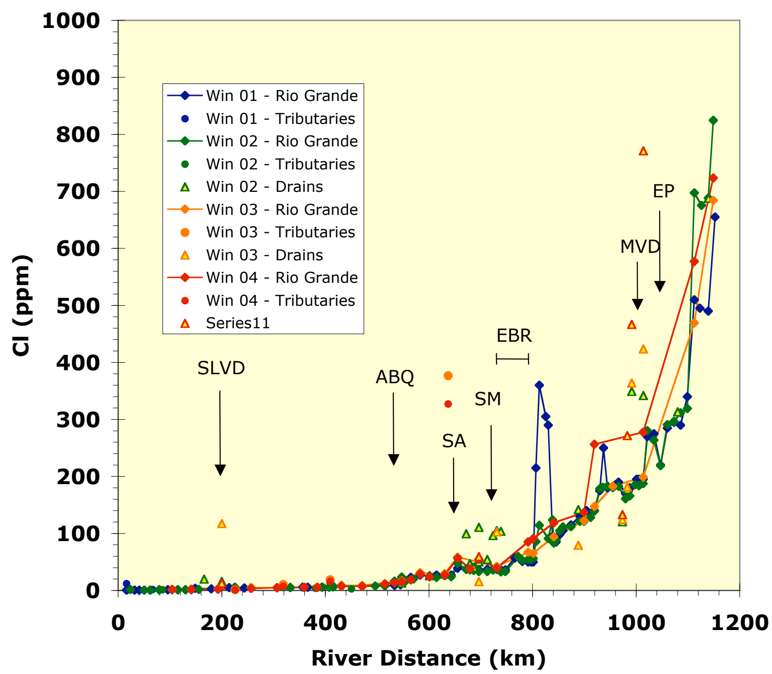

Figure 9. Chloride concentration as a function of flow distance for winter sampling campaigns. Abbreviations are given in caption to Figure 5.

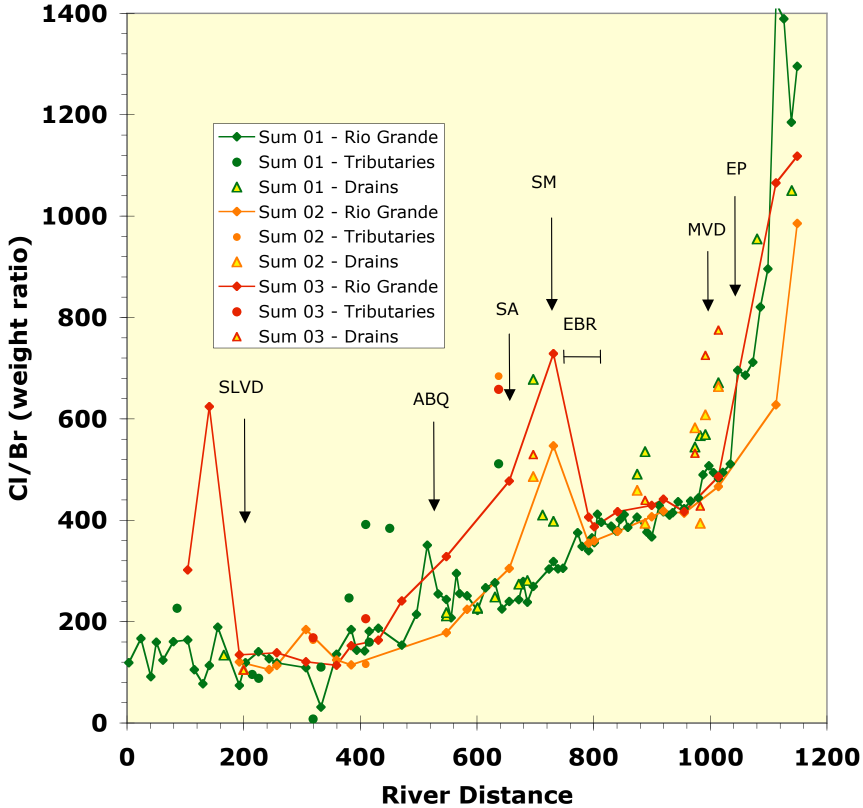

Figure 10. Cl/Br ratio as a function of flow distance for summer sampling campaigns. Abbreviations are given in caption to Figure 5.

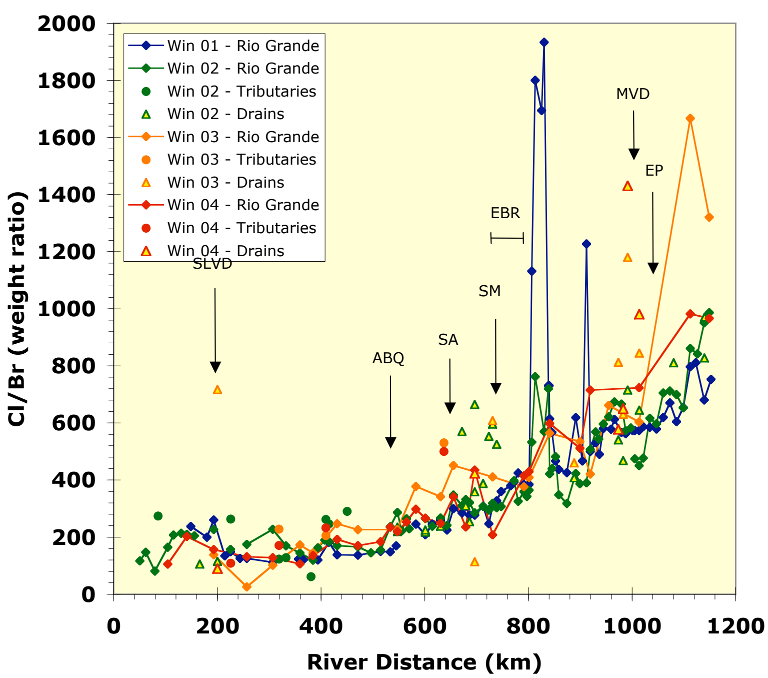

Figure 11. Cl/Br ratio as a function of flow distance for winter sampling campaigns. Abbreviations are given in the caption to Figure 5.

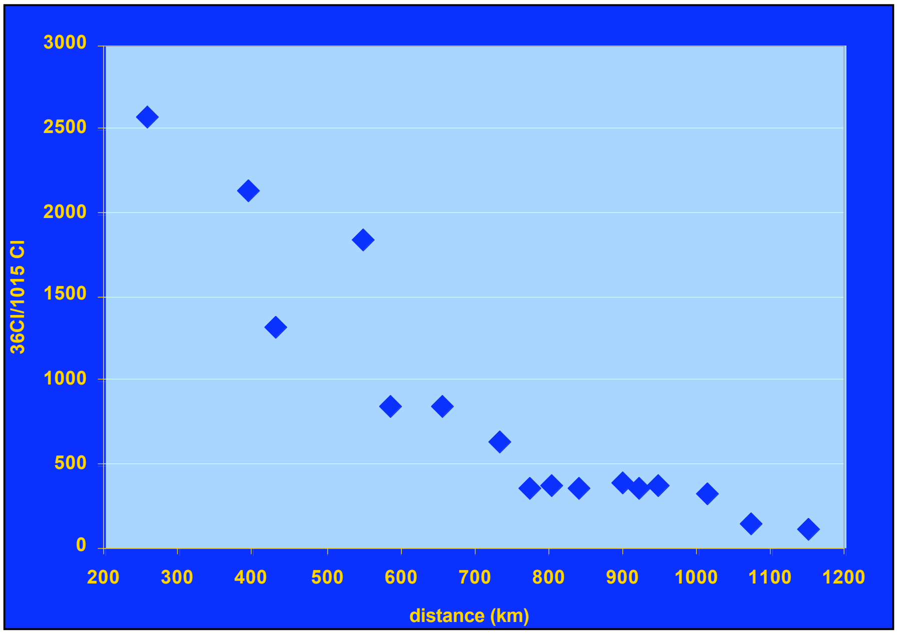

Figure 12. Chlorine-36 ratio as a function of flow distance (summer 2001).

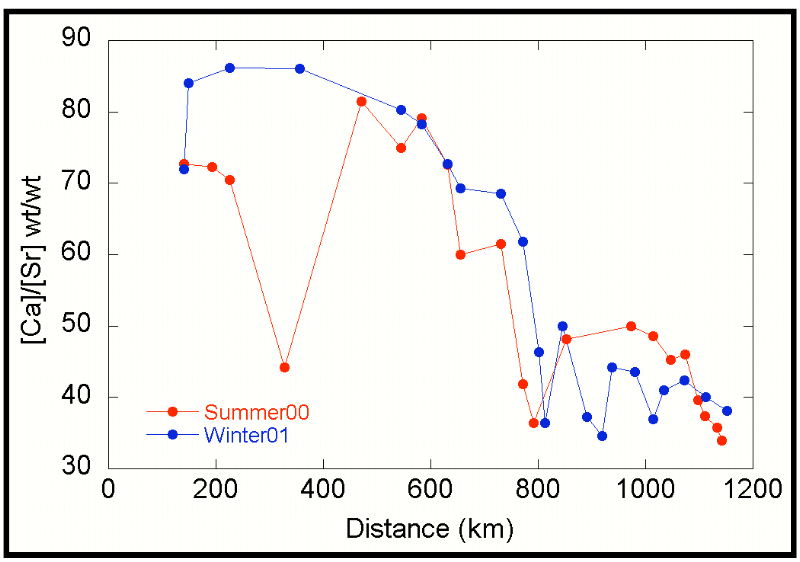

Figure 13. Calcium/strontium ratio as a function of flow distance for summer 2000 and winter 2001 samples.

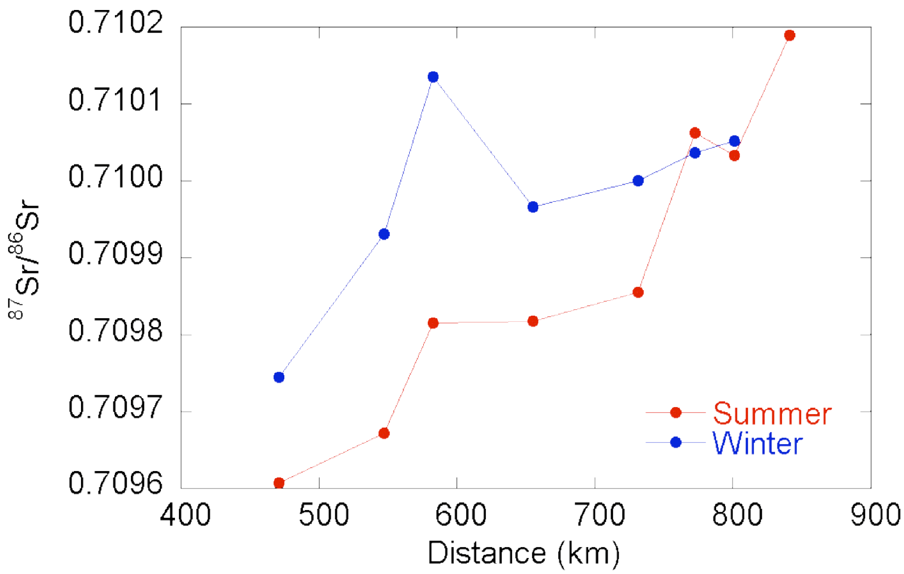

Figure 14. Strontium isotope ratios as a function of flow distance for summer 2000 and winter 2001 sampling.

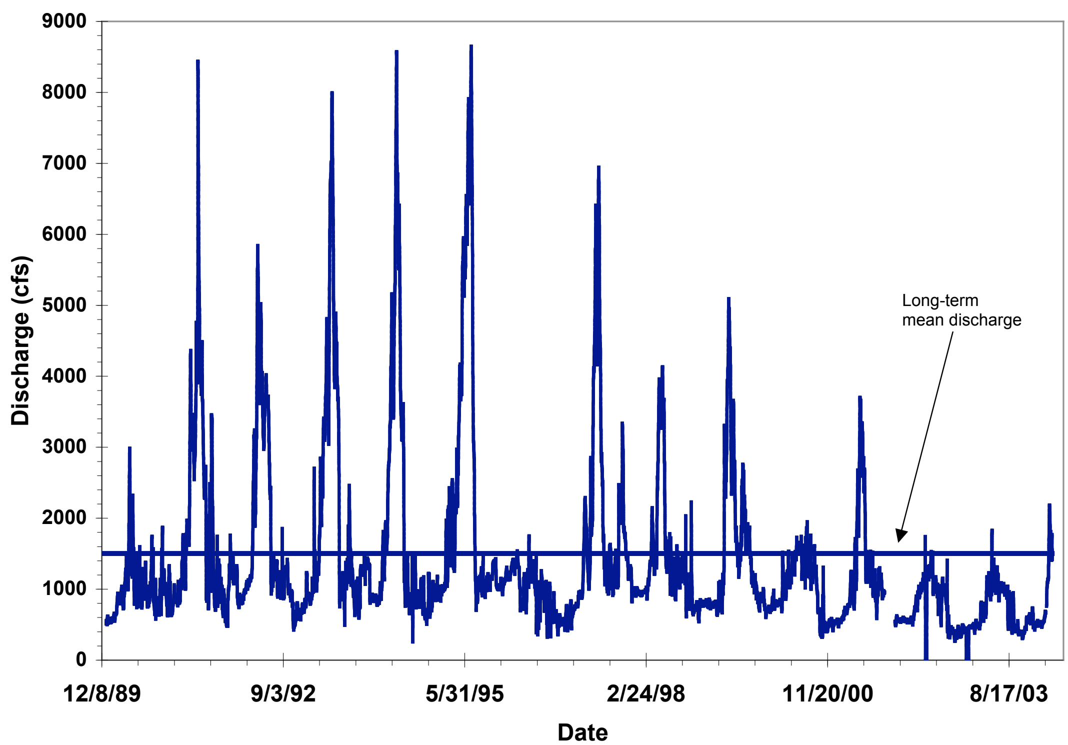

Figure 15. Discharge of the Rio Grande at Otowi Bridge, 1990-2004, showing worsening drought since 1995.

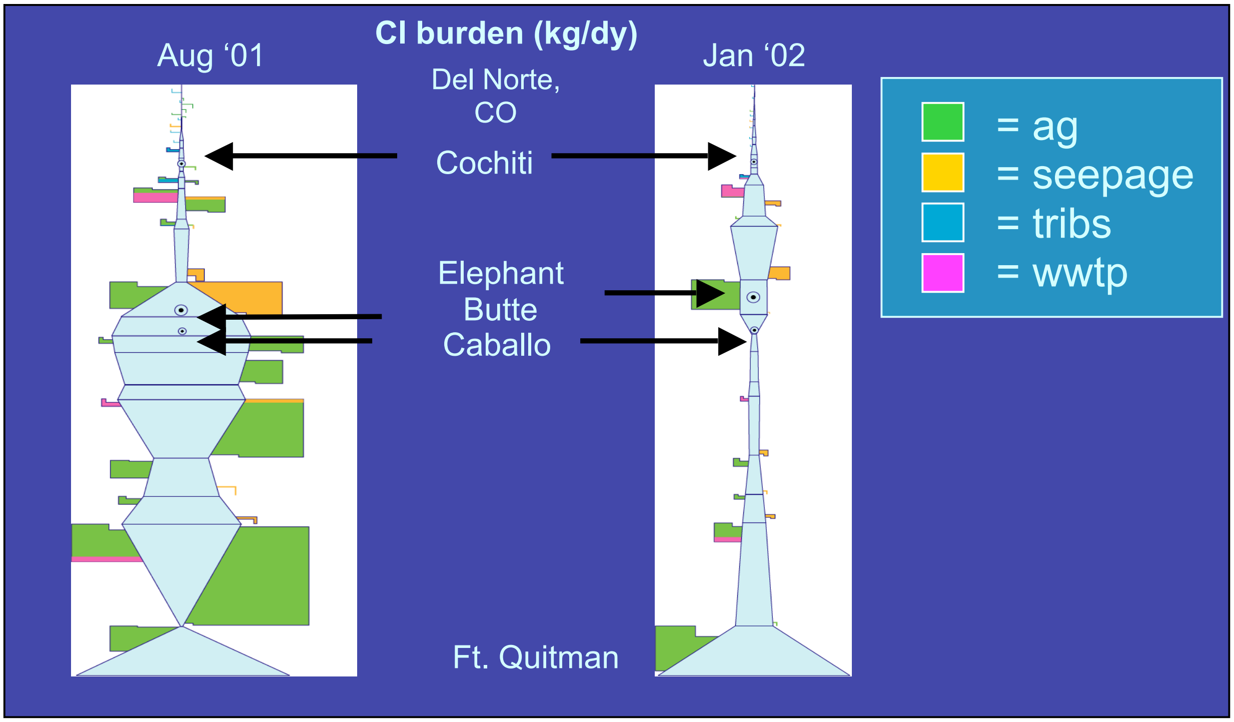

Figure 16. Chloride budget of the Rio Grande for summer 2001 and winter 2001/2002. Chloride burden (kg day^{-1}) is proportional to the width of the pipes. Chloride inputs are shown on the left of the pipes and outputs on the right. Inputs and outputs are color coded: "ag" is inputs from agricultural drains and deep groundwater seepage and outputs from agricultural diversions, "seepage" is loss from channel seepage to the groundwater, "tribs" is input from natural tributaries, and "wwtp" is inputs from municipal wastewater treatment plants.