ground water

Geochemical Tracers to Evaluate Hydrogeologic Controls on River Salinization

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Abstract

The salinization of rivers, as indicated by salinity increases in the downstream direction, is characteristic of arid and semiarid regions throughout the world. Historically, salinity increases have been attributed to various mechanisms, including (1) evaporation and concentration during reservoir storage, irrigation, and subsequent reuse; (2) displacement of shallow saline ground water during irrigation; (3) erosion and dissolution of natural deposits; and/or (4) inflow of deep saline and/or geothermal ground water (ground water with elevated water temperature). In this study, investigation of salinity issues focused on identification of relative salinity contributions from anthropogenic and natural sources in the Lower Rio Grande in the New Mexico-Texas border region. Based on the conceptual model of the system, the various sources of water and, therefore, salinity to the Lower Rio Grande were identified, and a sampling plan was designed to characterize these sources. Analysis results for boron ($\delta^{11}B$), sulfur ($\delta^{34}S$), oxygen ($\delta^{18}O$), hydrogen ($\delta^{2}H$), and strontium ($^{87}Sr/^{86}Sr$) isotopes, as well as basic chemical data, confirmed the hypothesis that the dominant salinity contributions are from deep ground water inflow to the Rio Grande. The stable isotopic ratios identified the deep ground water inflow as distinctive, with characteristic isotopic signatures. These analyses indicate that it is not possible to reproduce the observed salinization by evapotranspiration and agricultural processes alone. This investigation further confirms that proper application of multiple isotopic and geochemical tracers can be used to identify and constrain multiple sources of solutes in complex river systems.

Introduction

The salinization of rivers, as indicated by salinity increases in the downstream direction, is characteristic of arid and semiarid regions throughout the world (Postel 1993; Pillsbury 1981). Historically, salinity increases have been attributed to various mechanisms, including (1) evaporation and concentration during reservoir storage, irrigation, and subsequent reuse; (2) displacement of shallow saline ground water during irrigation; (3) erosion and dissolution of natural deposits; and/or (4) inflow of deep saline and/or geothermal ground water (ground water with elevated water temperature) (Pillsbury 1981; Allison et al. 1990; Hem 1992; Postel 1993; Moore and Anderholm 2002; Phillips et al. 2003; Farber et al. 2004).

Historically, many previous investigations of river salinization have focused on surface water alone and did not consider more complex hydrogeologic controls such as the effects of interconnection with adjacent basins (e.g., ground water flow from one basin to another) or ground water-surface water interaction that may significantly affect the system as a whole. In fact, even for areas where natural sources (specifically, erosion of natural deposits and inflow of deep saline and/or geothermal ground water) have been identified as contributors to river salinization, these sources are often not quantified or are even ignored, and efforts are focused instead on the perceived problem of agriculture as the root cause of salinization. In doing so, the contribution to salinization from natural causes (which may in fact be a larger contribution) is neglected and the problem of salinization remains unresolved.

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In order to find effective solutions to problems of river salinization, all causes of salinization must first be identified and the relative contributions of each determined, so that potential mitigation strategies can be developed. Several relatively recent developments have led to more holistic and comprehensive investigations of problems such as river salinization. Perhaps the most important factor is the concept of treating ground water and surface water as a single interconnected resource (e.g., Winter et al. 1999). As a result of this integrated view of ground water and surface water, investigators have begun to employ more holistic approaches, whereby ground water and surface water geochemistry are evaluated concurrently (e.g., Vengosh et al. 1991; Plummer et al. 2004; Kass et al. 2005; Ryu et al. 2007). In addition, isotopic analytical techniques are more widely available and understood, such that use of multiple chemical and isotopic tracers to characterize individual sources in a hydrogeologic system (e.g., Vengosh et al. 1999, 2002, 2005; Plummer et al. 2004; Farber et al. 2004) has become more common.

In this study, we emphasized the value of such a holistic and multiple-tracer approach in which the entire hydrogeologic system is considered to identify the actual causes of Rio Grande salinization in the New Mexico-Texas border region, where salinization has been the subject of ongoing interstate and international controversy for many years. The purpose of the study was to identify and characterize the principal sources of salinity to the Rio Grande. To accomplish that task, we reviewed and evaluated historical data and previous investigations, including the most recent hydrogeologic interpretations of the study area. Based on the working conceptual model of the study area, we identified the various sources of water (and therefore salinity) to the system. We then designed a sampling plan to characterize those possible sources, which include water released to the river from the reservoirs (referred to herein as "release water"), geothermal ground water, deep saline ground water (including sedimentary brines), waste water, and agricultural water. Isotopic candidates were selected based on their applicability to this hydrologic system and the cost-effectiveness of the analysis.

One particularly important aspect of the sampling plan was to obtain representative samples of each end-member in the study area. Although many previous investigators have concluded that natural sources of salinity, including geothermal and deep saline ground water, are important sources of salinity in the study area (Frenzel et al. 1992; Anderholm 2002; Moore and Anderholm 2002; Mills 2003; Phillips et al. 2003), only limited water quality data exist to characterize natural sources. In order to supplement existing data, several new monitoring wells (ISC4, ISC4a, and ISC5) had been installed during 2004 and screened over discrete horizons (Tetra Tech EM Inc. 2005); these wells were sampled as part of this investigation to characterize the local composition of deep sedimentary brine.

The potential anthropogenic sources (release water, waste water, and agricultural water) were also considered. Waste water is a possible source because it generally contains higher salinity and makes up a significant portion of streamflow during the winter season. Salinization has also often been attributed to agricultural causes because agricultural return flows (1) contain higher salinity than irrigation water and (2) are a significant source of streamflow during the winter season. Accordingly, we considered agricultural return flow to determine whether it is a unique and significant source of salinity.

Description of the Study Area

The study area lies within the Rio Grande Rift Basin and extends 254 km from San Marcial, New Mexico, to El Paso, Texas (Figure 1). It is located within the Basin and Range physiographic province. The climate is arid to semiarid, with large fluctuations in daily temperature, low relative humidity, and potential evaporation that far exceeds precipitation.

Anthropogenic Structures

A complex system of anthropogenic structures controls streamflow and affects ground water-surface water interactions throughout the study area. Streamflow in the study area is almost entirely regulated by releases from Elephant Butte and Caballo reservoirs (Figure 1), both of which are operated to meet the needs of irrigated agriculture in New Mexico and Texas and to meet international treaty obligations with Mexico. Inflow to Elephant Butte Reservoir at San Marcial is regulated and is controlled by release rates from upstream dams and diversion structures. Three diversion dams in the study area (Percha, Leasburg, and Mesilla dams) control diversions from the Rio Grande for agricultural use. Water from the diversion dams is delivered to agricultural fields by a system of canals; water is diverted from the canals to the fields by gravity.

A network of agricultural drains, which were constructed during the 1920s, prevents water levels from rising above land surface. The drains define the water table elevation and intercept shallow alluvial ground water, any unused irrigation water, and in some cases, waste water effluent. Water intercepted by the agricultural drains is returned to the main stem of the Rio Grande and is referred to as agricultural return flow. During periods of drought, there is increased reliance on ground water pumping, primarily for irrigation water supply, which can result in increased drawdown that disconnects the drains from the water table and significantly reduces agricultural return flow to the river (Frenzel et al. 1992; Bexfield and Anderholm 1997).

Streamflow

Most of the water in the Rio Grande originates as precipitation in the San Juan or Sangre de Cristo mountains in the headwaters of the Rio Grande watershed (Ellis et al. 1993; Moore and Anderholm 2002). This water is stored in Elephant Butte and Caballo reservoirs and is released primarily for irrigation purposes, typically from March through October. During the irrigation season, discharges greater than 28.4 cubic meters per second

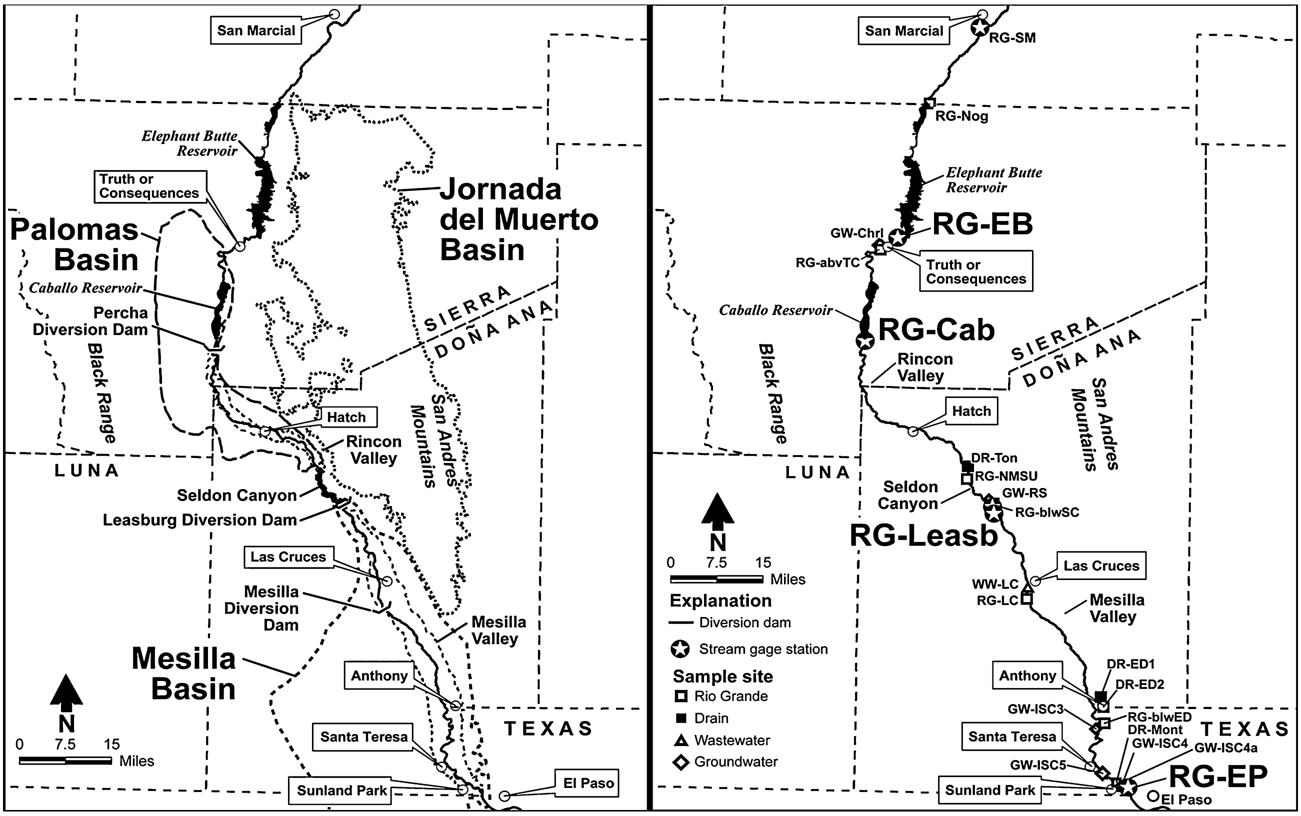

Figure 1. Study area and sampling locations.

(m[3]/s) are released from Caballo Reservoir, and irrigation diversions and return flows make up the majority of the flow in the river (Anderholm 2002).

Generally, little to no water is released from Caballo Reservoir during the winter season (November through February). Accordingly, any surface flow during those months is derived primarily from (1) seepage from Caballo Reservoir; (2) drainage of the irrigated soils and the attendant agricultural return flows to the river from the ground water drains; and (3) waste water discharges from treatment plants and industry.

No perennial tributaries to the Rio Grande are present within the study area, except for the agricultural drains and waste water treatment plants (WWTPs), and even the agricultural drains may become intermittent during periods of drought. Several ephemeral tributaries flow primarily in response to late summer and early fall thunderstorms and provide only a small amount of inflow to the Rio Grande.

Hydrogeologic Setting

The major physiographic components of the study area are the Rincon and Mesilla valleys (Figure 1), which are located in the Palomas and Mesilla basins, respectively, and include the active channel and floodplain of the modern Rio Grande. The hydrogeologic setting of the study area is distinguished "by high heat flow, recently active volcanoes, exceptionally deep [alluvial] basins and late Quaternary faulting" (Seager and Morgan 1979). The Las Cruces East Mesa Geothermal System is associated with a buried horst that separates the Jornada del Muerto from the Mesilla Basin (Witcher and Cunniff 2002; Witcher et al. 2004).

Four major aquifer systems are present within the study area:

- Rio Grande floodplain alluvium (shallow, unconfined, alluvial aquifer) of the Rincon and Mesilla valleys
- Basin-fill aquifer of the Palomas Basin
- Basin-fill aquifer of the Mesilla Basin
- Basin-fill aquifer of the Jornada del Muerto Basin.

The Rio Grande is hydraulically connected to the shallow alluvial aquifers of the Rincon and Mesilla valleys, which in turn are hydraulically connected to the basin-fill aquifers of the Palomas and Mesilla basins. Also, previous studies have confirmed the presence of minor ground water flow from the Jornada del Muerto Basin into the Mesilla Basin (Frenzel et al. 1992; Witcher et al. 2004).

Depending on the hydrologic conditions of the Rio Grande and the shallow alluvial aquifer, sections of the river may be classified as either gaining or losing reaches. The Rio Grande is generally a gaining stream (due to ground water inflow) throughout the Rincon and Mesilla valleys. Under certain hydrogeologic conditions, however, some areas may become losing reaches (Anderholm 2002; Nickerson 1995, 2005; Wilson et al. 1981), especially during times of drought, when increased ground water pumping causes drawdown and reversed gradients (Conover 1954; Frenzel et al. 1992). Additionally, there are many anthropogenic factors that influence streamflow in the Rio Grande. Downstream increases in streamflow result from inflow from an ephemeral stream, waste water effluent, or an agricultural drain. Decreases in streamflow in a downstream direction result from direct diversions (e.g., at Percha, Leasburg, or Mesilla diversion dams), open water evaporation, or riparian transpiration.

The Rio Grande is the ultimate point of discharge for the regional flow system (Bexfield and Anderholm 1997; Wilson et al. 1981; Hibbs et al. 1998), which includes both the shallow alluvial aquifer of Rincon and Mesilla valleys and the deeper regional system (Palomas, Mesilla, and Jornada del Muerto basins and the Las Cruces East Mesa Geothermal System). This fundamental concept of topographic lowlands acting as the major discharge point for the regional flow system is supported by many previous investigators (Meinzer 1917; Mifflin 1968; Eakin et al. 1976; Feth 1964).

Methods

The study consisted of two steps. First, we conducted two synoptic sampling events to test for a suite of geochemical and environmental tracers and, based on analytical results, identified the unique geochemical signature for each source. Second, we compared recent data collected during the synoptic sampling events as part of this investigation to historical data.

Historical Data

We compiled historical streamflow and water quality data and evaluated those data using statistical methods and a mass balance approach. These data were compiled from numerous sources, including the USGS, U.S. EPA STORET, Stabler (1911), Boyle Parsons (2000), and Williams (2001). Chloride concentration was chosen as the main water quality parameter for comparison with the recent data because (1) chloride is a conservative tracer and its movement within the hydrologic cycle is largely controlled by physical processes; (2) measurement of chloride concentration is one of the "simplest and most dependable procedures in water analysis" (Hem 1992); (3) a large amount of historical chloride concentration data is available for a variety of water types; and (4) chloride concentration is one of the primary water quality concerns in the study area.

Historical chloride loads in individual reaches were evaluated to determine salt addition from sources other than the Rio Grande (e.g., Moore and Anderholm 2002). Annual loads were calculated as the sum of monthly loads, which were calculated as the product of mean monthly chloride concentration and mean monthly streamflow (variations in streamflow affect variations in water quality and are needed to calculate loads). Mean monthly chloride concentrations used to calculate loads were measured in composite samples collected between 1929 and 1963; samples were collected on a daily basis and compiled into a single composite sample to be analyzed for chloride. Mean monthly streamflow was determined from daily mean streamflow data. Chloride loads were calculated only for the period 1929 to 1963 because after 1963, monthly composite samples were no longer collected in the study area and the available data are not sufficient to calculate average monthly concentrations.

Synoptic Sampling Events

Two synoptic sampling events were conducted: (1) first, from August 3 to 5, 2004, to coincide with the irrigation season and (2) second, from January 24 to 27, 2005, to coincide with the winter season. During each event, sample collection began at the upstream locations and proceeded downstream toward El Paso. Water quality samples were collected from a variety of locations and sources, including the main stem of the Rio Grande, ground water wells, the Las Cruces WWTP, and agricultural drains. To characterize and evaluate the effects of seasonal variations in streamflow, which are typical of the irrigation and winter seasons (Stabler 1911; Frenzel et al. 1992; Moore and Anderholm 2002), components of the surface water system (e.g., the river, agricultural drains, and waste water discharges) were sampled during both synoptic sampling events. Sampling locations representing ground water and geothermal endmembers were sampled in just one of the two sampling events, under the assumption that the chemical composition of these water does not vary seasonally. Samples were analyzed for a suite of constituents, including major ions, total dissolved solids (TDS), specific conductance, alkalinity, trace elements (arsenic, boron, and strontium), nutrients (total nitrogen and phosphorus), stable isotopes (δ^2H, δ^{18}O, δ^{11}B, and δ^{34}S), and radioactive isotopes (^{87}Sr/^{86}Sr).

Though not collected as part of this investigation, streamflow data were available for four of the sampling locations that coincided with streamflow gauges (Figure 1). Because variations in streamflow affect variations in water quality, a general understanding of streamflow in the study area is therefore necessary to provide the context in which to understand variations in water quality.

Daily chloride loads were calculated for both the August 2004 and the January 2005 sampling events in order to evaluate contributions to the study area from various sources. Loads were calculated at sampling locations that coincided with streamflow gauging stations. At each of those stations, the chloride concentration measured during a given sampling event was assumed to represent the mean chloride concentration for the 3- to 4-d sampling event. The mean streamflow for a given sampling event was calculated as the mean of the daily mean streamflow for each day in that sampling event. The daily chloride load was calculated as the product of the mean chloride concentration and mean streamflow and is reported in kilograms per day.

Source Water Characterization

To identify and characterize salinity sources that may impact the Rio Grande, we sampled five potential sources of water to the system, as identified by previous investigators and in the working conceptual model of the system: release water, basin saline ground water, geothermal ground water, waste water, and agricultural water.

Release water represents streamflow that it is released from Elephant Butte and Caballo reservoirs and enters the study area; this is the "baseline" Rio Grande water that enters the study area, before it is mixed with any other sources. Two sampling locations were used to characterize release water as it enters the study area: RG-EB and RG-Cab. RG-EB is located immediately below Elephant Butte Dam, and RG-Cab is located immediately below Caballo Dam. Only those samples collected during the irrigation season (August 2004) were used to characterize release water.

The goal of ground water quality sampling for this study was to sample saline ground water that is representative of natural salinity sources. Two types of saline ground water were identified by previous investigators and sampled as part of this investigation: deep saline ground water and geothermal ground water. Two ground water wells (GW-ISC4 and GW-ISC4a) completed at or near the base of the Santa Fe Group were sampled to characterize the chemistry of deep saline ground water. Two geothermal wells located in areas of known geothermal activity (GW-Chrl and GW-RS) and one well with an elevated water temperature (GW-ISC5) were sampled to characterize the chemistry of geothermal water.

Waste water effluent is a significant source of water to the Rio Grande during the winter season, when no water is released from Caballo Dam. Data from the Las Cruces WWTP, the largest WWTP in the study area, were used to characterize waste water.

Previous investigators have suggested that agricultural practices are a source of salinization in the study area. In an attempt to test this hypothesis and characterize agricultural sources, several agricultural drains were sampled. Tonuco Drain (DR-Ton) represents the cumulative agricultural effects of the Rincon Valley. The East Drain, which is located in the southern Mesilla Valley, was sampled at two locations, one above and one below the Anthony WWTP at the state line (DR-ED1 and DR-ED2). The Montoya Drain (DR-Mont) is at the terminus of the Mesilla Basin and was sampled just upstream from where it discharges to the Rio Grande.

Results

Historical Data

Historical data indicate that chloride concentrations increase in the downstream direction throughout the study area, between the gauges at San Marcial and El Paso (RG-SM and RG-EP) (Figure 2). This spatial pattern of increasing chloride concentrations in the downstream direction is consistent during both the pre-reservoir period (1905 through 1907 data) and the post-reservoir period (data collected after 1929).

Statistical analysis of historical data collected between 1929 and 1963 indicates seasonal variation in chloride concentrations for most sites in the study area (Figure 3). In general, chloride concentrations are lower during the irrigation season, when streamflow is high, and higher during the winter season, when streamflow is low.

The magnitude of seasonal variation increases in the downstream direction (Figure 3). At RG-EB, the median chloride concentrations are similar for both the irrigation and the winter seasons. At RG-Cab, RG-Leasb, and RG-EP, median chloride concentrations are larger and chloride concentrations exhibit greater variation (i.e.,

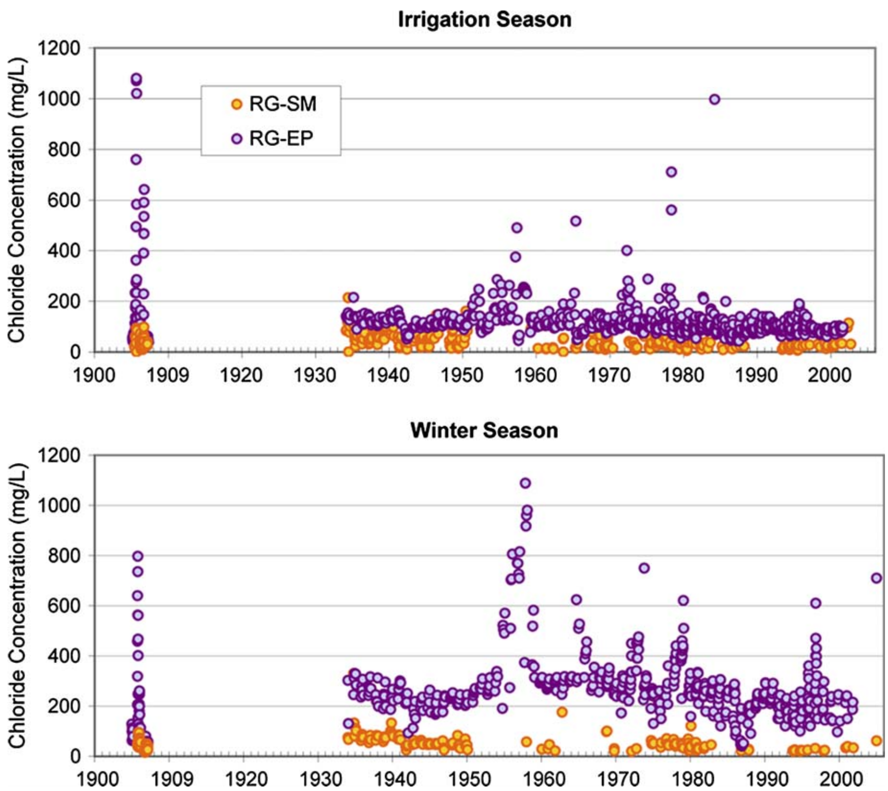

Figure 2. Historical chloride concentrations.

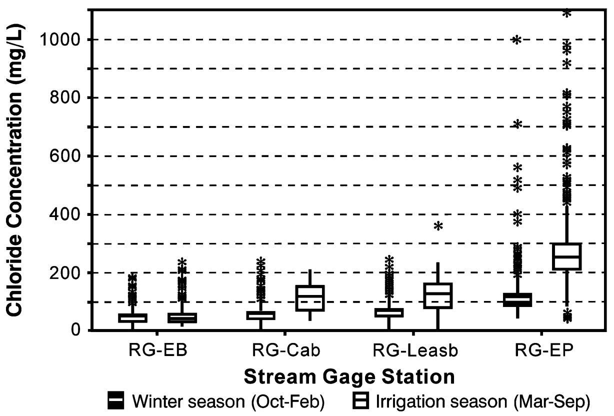

Figure 3. Seasonal and spatial variation in chloride concentrations for selected stations.

larger interquartile range) during the winter season. During the irrigation season, median chloride concentrations are smaller and chloride concentrations exhibit less variation (smaller interquartile range) at these three sampling locations.

Statistical analysis of historical data confirms the spatial trend of increasing chloride concentrations in the downstream direction (Figure 3). Median chloride concentrations increase in the downstream direction during both irrigation and winter seasons. However, the largest increases in chloride concentration occur during the winter season. In addition, the largest variation in chloride concentrations and the largest increase in median chloride concentrations occur at RG-EP, at the distal end of the Mesilla Basin.

Median chloride concentrations at the distal end of the basin (RG-EP) have generally decreased since the 1950s (Figure 4). The largest median chloride concentration (232 mg/L) occurred in the 1950s, during which time the entire Rio Grande Basin experienced an extended period of below-normal precipitation (Frenzel et al. 1992; Hendrickx 1998).

Annual chloride loads generally increase throughout the study area in the downstream direction (Figure 5) despite decreases in streamflow. However, annual chloride

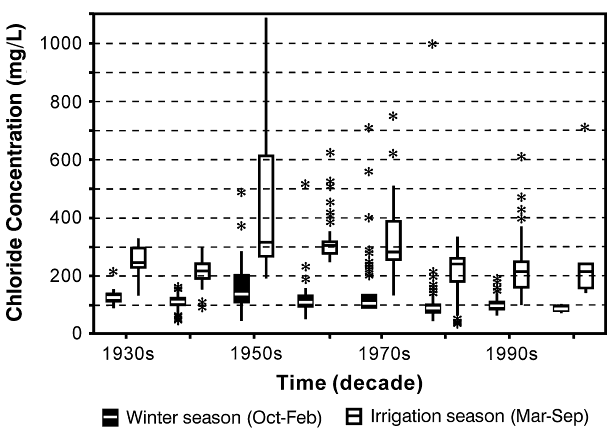

Figure 4. Seasonal and decadal variations in chloride concentrations at RG-EP.

loads decreased throughout the study area from 1954 to 1957.

August 2004 Synoptic Event

Streamflow data and analytical results of key chemical and isotopic parameters for the August 2004 synoptic sampling event are shown in Table 1 and Figure 6. Daily mean streamflow was 15.3 m^3/s at RG-EB and increased to 31.1 m^3/s at RG-Cab because of releases for the irrigation season. Between Caballo Reservoir and RG-EP, daily mean streamflow decreased from 31.1 to 21.9 m^3/s because outflows were greater than inflows.

During the August 2004 sampling event, release water was generally low in chloride and TDS and exhibited little variation in major ion concentrations between Rio Grande at Nogal Canyon (RG-Nog) and RG-EP (Table 1; Figure 7). The largest variation in major ion concentrations along the Rio Grande was between RG-Nog and RG-EB, where sulfate concentration decreased from 190 to 140 mg/L. The drains (DR-Ton and DR-ED2), waste water (WW-LC), and geothermal water (GW-RS) were more saline than release water. The highest major ion concentrations were measured in the geothermal water (GW-RS).

In August 2004, the daily chloride load increased in the downstream direction (Figure 6). Between RG-EB and RG-Cab, the daily chloride load increased (from 83,100 to 179,000 kg/d) because of increasing streamflow (15.3 to 31.1 m^3/s). Between RG-Cab and RG-EP, there was a slight increase in daily chloride load (from 179,000 to 181,000 kg/d), despite a substantial decrease in streamflow (from 31.1 to 21.9 m^3/s).

January 2005 Synoptic Event

Streamflow data and analytical results of key chemical and isotopic parameters for the January 2005 synoptic sampling event are shown in Table 1. In contrast to the August 2004 sampling event, daily mean streamflow was 0.3 m^3/s below Caballo Reservoir (RG-Cab) (Figure 6). Below Caballo Reservoir, the Rio Grande gained streamflow because of ground water inflow, agricultural return flows, and waste water effluent. However, despite inflows from various sources, streamflow was not continuous between RG-Cab and RG-EP. During the January 2005 sampling event, the river was dry in several locations and therefore could not be sampled. Water quality of the river is essentially "reset" at each location where the river goes dry and streamflow is not continuous. The discontinuous nature of streamflow during January 2005 (and throughout much of the winter season) has important consequences for water quality interpretation and mixing calculations.

During the January 2005 sampling event, the highest major ion concentrations were measured at wells ISC4 and ISC4a, which had chloride concentrations of 18,000 and 7900 mg/L, respectively (Table 1). Major ion concentrations increased in the downstream direction. Chloride concentrations increased from 86 to 380 mg/L between RG-EB and RG-abvTC and increased by a factor of 4 over a distance of roughly 23 km between RG-blwED and RG-EP (180 to 710 mg/L). TDS and sodium

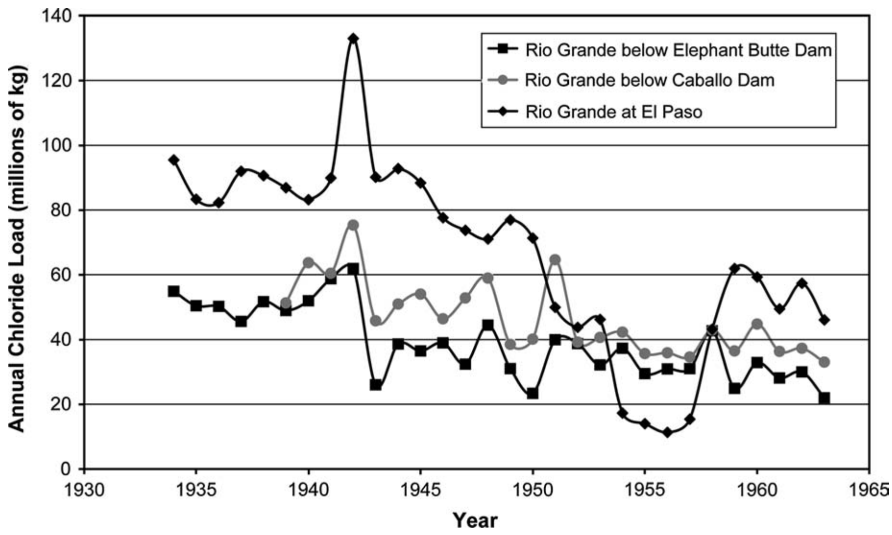

Figure 5. Historical chloride loads.

concentrations exhibited similar variations to chloride concentrations (Table 1). Sulfate concentration increased between RG-Cab and RG-blwSC (150 to 320 mg/L) and increased dramatically below RG-LC (140 to 960 mg/L) (Table 1).

In January 2005, the daily chloride load increased overall in the downstream direction (Figure 6). Between RG-EB and RG-Cab, the daily chloride load decreased with decreasing streamflow because of reservoir operations. Between RG-Cab and RG-blwSC, there was

Table 1
Selected Geochemical and Isotopic Data during August 2004 and January 2005

Site ID	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	SO_4 (mg/L)	TDS (mg/L)	Cl (mg/L)	Br (mg/L)	HCO_3 (mg/L)	Total N (mg/L)	B (mg/L)	Sr (mg/L)	$\delta^{11}B$ (‰)	$\delta^{34}S$ (‰)	$^{87}Sr/^{86}Sr$
August 2004														
RG-Nog	71	15	100	190	640	80	0.14	200	0.25	0.15	10.69	3.3	0.2	0.7101
RG-EB	52	13	81	140	510	63	0.15	160	0.14	0.13	0.635	4.7	1.3	0.7102
RG-Cab	54	13	85	140	520	67	0.14	160	0.11	0.14	0.681	4.7	1.0	0.7103
RG-EP	55	13	99	180	610	96	0.17	140	0.18	0.17	0.789	7.1	2.2	0.7104
DR-Ton	110	24	150	360	1000	160	0.28	180	0.22	0.24	1.521	7.0	2.6	0.7111
DR-ED2	57	19	390	340	1400	280	0.31	300	0.46	0.44	1.753	7.0	3.0	0.7127
WW-LC	79	21	130	130	740	190	0.24	220	7.2	0.25	1.089	3.9	6.1	0.7099
GW-RS	160	22	860	490	3200	1300	1.20	340	0.31	0.63	2.417	5.9	4.7	0.7154
GW-ISC3	14	ND	420	310	1200	400	0.28	60	0.14	0.82	0.316	−7.0	4.2	0.7103
January 2005														
RG-Nog	56	11	72	120	540	61	0.2	190	0.38	0.12	0.646	8.6	1.7	0.7101
RG-EB	50	14	94	170	560	86	0.2	130	0.20	0.14	0.698	NA	0.4	0.7102
RG-abvTC	88	16	220	180	1000	380	0.3	170	0.25	0.18	1.66	10.8	4.5	0.7137
RG-Cab	59	17	120	150	680	120	0.2	280	0.16	0.15	0.772	11.2	2.8	0.7111
RG-NMSU	91	20	140	330	880	150	0.4	210	0.11	0.21	1.23	16.7	0.9	0.7111
RG-SC	84	20	140	320	870	150	0.3	180	0.08	0.20	1.19	14.5	1.6	0.7110
RG-LC	69	15	120	140	760	200	0.2	350	7.0	0.21	0.899	0.3	6.2	0.7099
RG-blwED	72	22	190	300	990	180	0.3	220	0.27	0.23	1.4	9.7	−2.2	0.7111
RG-EP	120	36	580	960	2500	710	1.2	280	0.31	0.75	2.22	13.5	2.2	0.7097
DR-Ton	120	26	190	440	1200	210	0.5	270	0.32	0.23	1.62	NA	6.1	0.7113
DR-Mont	120	37	560	800	2400	640	0.72	340	0.16	0.70	1.88	16.0	6.1	0.7098
DR-ED1	69	26	330	370	1400	260	0.4	410	0.16	0.41	1.91	13.6	1.7	0.7127
DR-ED2	48	16	260	280	1100	220	0.3	230	0.23	0.35	1.19	9.9	2.5	0.7123
WW-LC	69	15	120	140	770	190	0.2	140	8.42	0.23	0.923	3.4	5.5	0.7099
GW-ISC5	300	19	1300	1200	4500	1800	0.69	30	0.16	0.84	2.19	5.3	7.9	0.7089
GW-ISC4a	670	340	4700	5100	19,000	7900	10	270	0.96	2.50	16.5	30.8	12.2	0.7101
GW-ISC4	840	670	7700	6200	30,000	18,000	25	200	0.49	2.20	19.6	31.8	12.4	0.7097
GW-Chrl	140	15	700	75	2600	1400	1	180	0.43	0.27	3.45	5.6	9.7	0.7204

NA = not available; ND = nondetect.

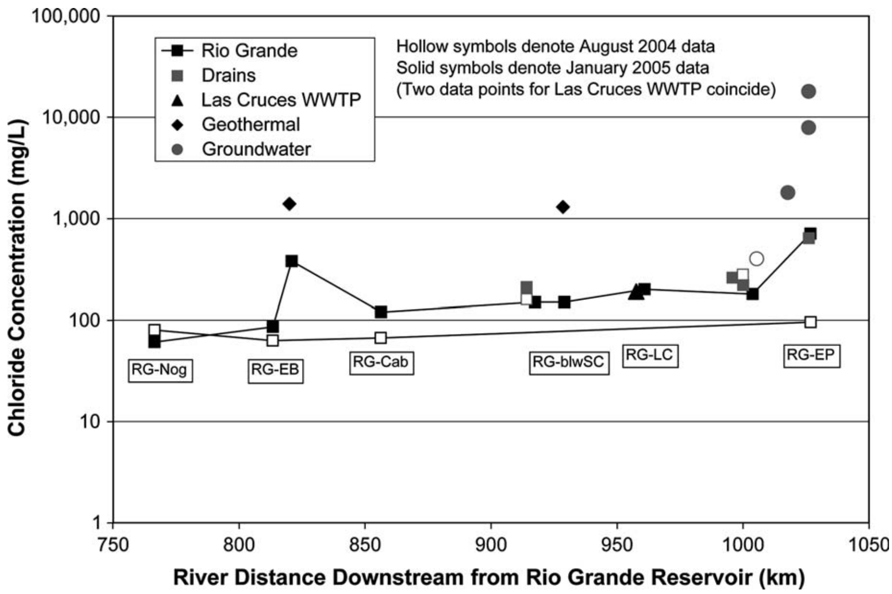

Figure 6. Chloride concentrations during August 2004 and January 2005.

a small increase in daily chloride load and streamflow. The largest increase in daily chloride loads was between RG-blwSC and RG-EP; between these two sites, the daily chloride load increased by a factor of 11 (from 2600 to 28,000 kg/d), and streamflow increased by a factor of 2.5 (from 0.2 to 0.5 m^3/s).

Discussion

Implications of Pre- and Postreservoir Historical Data

One method of evaluating the effects of natural sources on salinization in the study area is to compare historical data with recent data. By comparing data collected prior to widespread agricultural use or the presence of WWTPs with more recent data, the effects of natural salinity sources (specifically, nonagricultural sources) can be evaluated.

The earliest available data for the study area were published by Stabler (1911) for the period January 1905 through May 1907. Data for that study were collected at the Rio Grande at San Marcial and Rio Grande at El Paso gauging stations prior to the construction of Elephant Butte and Caballo reservoirs and the network of agricultural drains in the study area. Mills (2003) used the data of Stabler (1911) to calculate monthly mean chloride loads to be 110,000 kg/d at RG-SM and 145,000 kg/d at RG-EP, for an increase of approximately 35,000 kg/d between RG-SM and RG-EP. The similar spatial pattern of chloride concentrations shown by these pre- and postreservoir data collected from 1929 to 2002 (Figure 2) indicates that salinization in the study area occurred before the reservoirs, agricultural drains, or large-scale waste water discharges were present and must therefore be attributable primarily to natural salinity sources discharging to the Rio Grande.

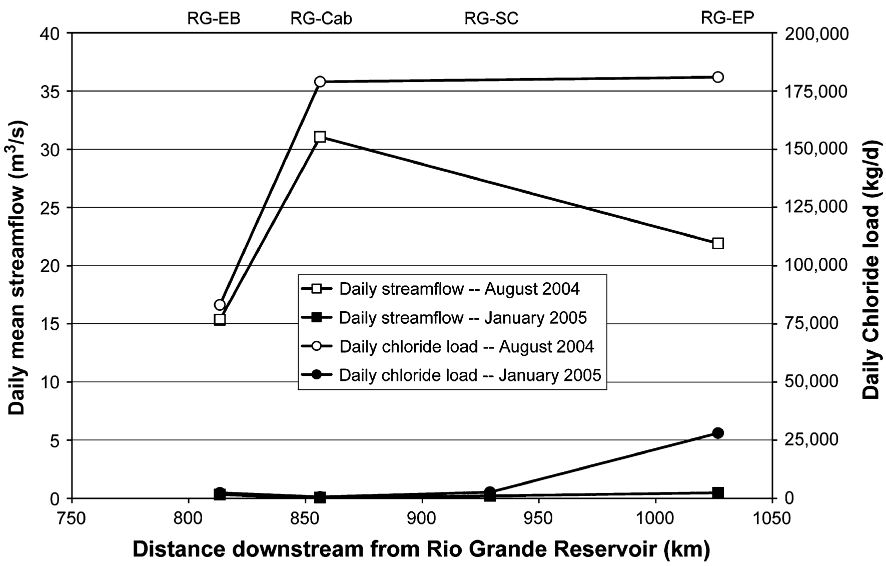

Figure 7. Daily chloride loads and streamflow during August 2004 and January 2005.

Spatial and Temporal Variations in Chloride Concentrations and Loads

Comparison of historical data and data collected as part of this investigation (August 2004 and January 2005 synoptic sampling events) indicates similar spatial and temporal patterns of salinization. Regardless of the season, chloride concentrations in the main stem of the Rio Grande generally increase in the downstream direction. However, the largest increases in chloride concentration occur during the winter season, when no water is being released from Caballo Reservoir.

As shown by historical data and indicated by previous investigations (Moore and Anderholm 2002), streamflow is inversely related to chloride concentration in the study area; that is, chloride concentrations are high when streamflow is low and low when streamflow is high. The seasonal variations in chloride concentrations (or salinity) can be explained by the dynamics of the system, in which streamflow is highly regulated by the reservoir releases.

During the winter season, water is not usually released from the reservoirs, and water in the Rio Grande is composed almost entirely of ground water inflow, return flows from agricultural drains, and waste water effluent. Because those sources usually contain higher chloride and TDS than the releases from the reservoirs, the salinity of the stream is controlled by the relative contributions of those sources. It has been observed that large increases in salinity along the Rio Grande usually occur in the areas where upward movement of geothermal ground water or basin saline ground water exists (Bexfield and Anderholm 1997; Mills 2003; Phillips et al. 2003; Witcher et al. 2004). For example, chloride concentrations measured during the January 2005 sampling event increased from 86 to 380 mg/L in a distance of about 7 km between RG-EB and RG-abvTC (Figure 7); this increase coincides with the existence of significant geothermal ground water discharges from the hot springs in this area.

Historical data indicate that the largest increases in chloride concentrations occur between RG-Leasb and RG-EP (Figure 3), and recent data, collected at a higher spatial resolution, show that the largest increases in chloride concentrations occur between RG-blwED and RG-EP (Figure 7; Table 1). In January 2005, chloride concentration increased by a factor of 4 (180 to 710 mg/L) between RG-blwED and RG-EP, a distance of roughly 23 km. This reach is located near the distal end of the Mesilla Basin, which is the regional discharge point of the entire study area; as has been confirmed by previous investigators, this is an area where deep saline ground water of the sedimentary basin is forced upward along the bedrock so that it can pass through the basin constriction. The extremely saline water found in wells ISC4 and ISC4a (Table 1) supports our hypothesis that the primary contributor of salinity to the Rio Grande is upwelling basin saline ground water rather than anthropogenic sources.

During the irrigation season, on the other hand, the streamflow is dominated by releases from the reservoirs. Most streamflow released from Caballo Reservoir is derived from snowmelt runoff, which originates in the headwater of the Rio Grande watershed. Because snowmelt has a low chloride concentration (and generally low TDS) relative to other sources (basin saline ground water, geothermal water, agricultural return flows, or waste water effluent), releases from Caballo Reservoir dilute the input from those sources and result in lower and relatively constant chloride concentrations throughout the study area (Table 1; Figure 7).

The relationship between chloride loads, streamflow, and chloride concentrations is more complicated because loads are controlled by both streamflow and chloride concentrations. Historical data indicate that throughout the study area, annual chloride loads increase in the downstream direction, with the exception of the severe drought of the 1950s. Historical data show that annual chloride loads generally increase between Elephant Butte and Caballo dams (Figure 5), most likely due to inflow of saline ground water rather than changes in reservoir storage since there is little change in streamflow between these two stations. Annual chloride loads generally increase between Caballo Dam and El Paso (Figure 5), despite decreases in streamflow.

The spatial pattern of increasing chloride loads in the downstream direction was also observed during the August 2004 and January 2005 synoptic sampling events (Figure 6). Between Caballo Reservoir and the distal end of the basin (RG-EP), chloride loads increased by 2000 kg/d during the August 2004 sampling event and by 27,470 kg/d during the January 2005 sampling event (Figure 6). The chloride loads determined from historical postreservoir data (Figure 5) and our synoptic sampling data (Figure 6) are again consistent with those determined from the prereservoir data and with the findings of the extremely saline water in wells GW-ISC4 and GW-ISC4a.

Historical data and data from our synoptic sampling events reveal two unique patterns that occurred during the severe drought of the mid-1950s, when the entire Rio Grande Basin experienced an extended period of below-normal precipitation (Frenzel et al. 1992; Hendrickx 1998). The first unique pattern is elevated chloride concentrations throughout the study area and especially at RG-EP (Figure 2); the effect of these elevated chloride concentrations can be seen in the median chloride concentrations at RG-EP during both the winter and the irrigation seasons of the 1950s (Figure 4). The second unique pattern is decreasing chloride loads between RG-EB and RG-EP. Under normal conditions, the chloride load increases between RG-EB and RG-EP; however, from 1954 to 1957, the chloride load decreased between RG-EB and RG-EP (Figure 5), suggesting that the chloride source, which normally contributes to the increase in chloride load between these two sites, was cut off from the river during that period.

To determine a possible cause for these unique patterns (elevated chloride concentrations and decreased chloride loads), we examined the agricultural drains. U.S. Bureau of Reclamation records indicate that drain flow in the Mesilla Valley portion of the lower Rio Grande was close to zero from 1954 to 1956 because of regional drought conditions (Frenzel et al. 1992). When drains are flowing, under "normal" conditions, the chloride load decreases in the study area (between RG-EB and RG-EP); however, when drains are not flowing, such as under drought conditions, chloride concentrations are elevated and chloride loads increase throughout the study area (between RG-EB and RG-EP). Based on these observations, it appears that the agricultural drains could be a significant source of chloride that results in the normal increase in chloride loads between RG-EB and RG-EP. However, because we know that evapotranspiration cannot cause an increase in chloride loads in a closed system (e.g., Moore and Anderholm 2002), then the drains must be a conduit of another source of inflow, such as sedimentary brine. This concept is supported by previous investigators (Mills 2003; Phillips et al. 2003), who proposed that the primary means by which agricultural drains contribute to the salinization of the Rio Grande is by intercepting sedimentary brines.

Source Water Characterization

Water quality data collected during the August 2004 and January 2005 synoptic sampling events allowed for a detailed characterization of the various streamflow and salinity sources in the study area. Based on the results of this and previous studies (Frenzel et al. 1992; Anderholm 2002; Moore and Anderholm 2002; Mills 2003; Phillips et al. 2003), the salinity of the Rio Grande is impacted by various sources entering the system downstream from the reservoirs. Streamflow downstream from the reservoirs represents mixes of the release water and inputs from other sources.

We used geochemical and isotopic fingerprints to characterize potential sources of salinity entering the system. Although the geochemical and isotopic composition of one particular element alone may not suffice to uniquely distinguish multiple sources in a complex system, a suite of geochemical and isotopic signatures can provide better constraint. We employed major ions and trace elements (chloride, total nitrogen, boron, sulfate, and strontium, and chloride-to-bromide [Cl/Br] ratio) and multiple isotopes (boron [δ^{11}B], sulfur [δ^{34}S], and strontium [^{87}Sr/^{86}Sr]) to characterize the various salinity sources based on the synoptic sampling events conducted as part of this investigation (Table 2). Using a comprehensive suite of tracers, each source can be characterized and unique sources can be distinguished from other nonunique types of water (Figures 8 through 10).

Based on our evaluation of these tracers, release water entering the study area is relatively dilute compared to the more downstream locations in the Rio Grande (Table 2; Figures 8 through 10) as well as to the other water types:

- Release water is characterized by low chemical concentrations, low Cl/Br ratio, low δ^{34}S, and medium δ^{11}B and ^{87}Sr/^{86}Sr.
- Geothermal water is characterized by medium chemical concentrations, high Cl/Br ratio, medium δ^{34}S, and medium to high ^{87}Sr/^{86}Sr.
- Deep saline ground water (or sedimentary brine) is characterized by high chemical concentrations, medium Cl/Br ratio, high δ^{34}S and δ^{11}B, and medium ^{87}Sr/^{86}Sr.
- Waste water is characterized by high total nitrogen concentration, low ^{87}Sr/^{86}Sr, and low to medium chemical concentrations.

The endmember signatures of geothermal ground water and deep saline ground water determined from data collected as part of this study are supported by previous investigators. Witcher et al. (2004) reported Cl/Br ratios greater than 600 to 800 and ^{87}Sr/^{86}Sr greater than 0.710 for saline water. Phillips et al. (2003) and Mills (2003) reported similar Cl/Br ratios for sedimentary brines.

Examination of the geochemical fingerprints of potential sources indicates that agricultural water, as represented by the agricultural drains, is not a unique source of water because (1) Cl/Br ratios of drains cannot be caused by evapotranspiration alone (Figure 8) and (2) the boron and strontium geochemical and isotopic signatures indicate that drains are a mix of river and other sources (Figures 9 and 10). Evapotranspiration can increase chloride concentration and salinity of water, but the Cl/Br ratio will remain constant because both are conservative chemical elements. As indicated by the higher Cl/Br ratios for the drains (Figure 8), concentration of the water releases through the evapotranspiration process in the

Table 2
Geochemical Signatures of Salinity Sources in Study Area

		Saline Ground Water		
Constituent	**Rio Grande Water**	**Geothermal Ground Water**	**Deep Saline Ground Water**	**Waste Water**
B (mg/L)	<0.15	0.2 to 1.0	>2.0	~0.2
δ^{11}B (‰)	~5.0	5.0 to 6.0	>30.0	~4.0
Cl (mg/L)	<150	1000 to 2000	>7000 to 18,000	~200
Cl/Br ratio	<500	>1400	700 to 800	~1000
SO_4 (mg/L)	<150	<100 to ~1000	>5000	<150
δ^{34}S (‰)	~1.0	4.0 to 10.0	~12.0	~6.0
Total N (mg/L)	<0.15	0.1 to 0.5	<1.0	7.0 to 9.0
Sr (μg/L)	<700	2000 to 4000	>15,000	~1000
^{87}Sr/^{86}Sr	~0.7100	>0.7100	~0.7100	<0.7100

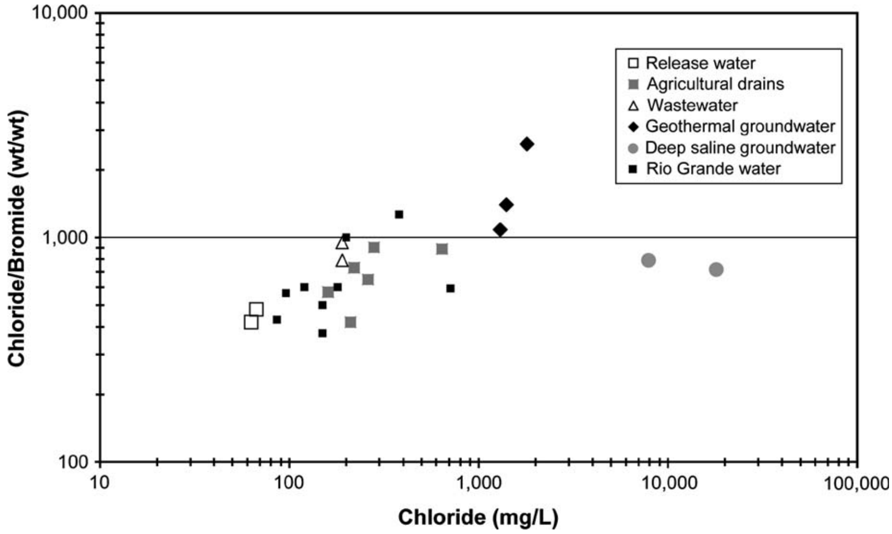

Figure 8. Chloride and bromide results during August 2004 and January 2005.

field alone cannot produce the chemistry of the drains observed in these data. Evidentially, water from other sources with a higher Cl/Br ratio must be added to the drains to achieve the observed Cl/Br ratios. Boron and strontium isotopic signatures (Figures 9 and 10) indicate that release water, geothermal water, and deep saline ground water are unique sources with distinctive characteristics; however, the isotopic signatures of the drains fall within the ranges of the other sources, indicating that the drains are most likely a mix of those sources rather than a unique source of salinity.

The geochemical and isotopic fingerprints identified in Table 2 are important reference values that are being used as part of ongoing work to quantify the salinity contribution from each individual source. This suite of geochemical and isotopic tracers could be used to identify other potential salinity sources within the study area.

Summary and Conclusions

Salinization of rivers is a common issue, particularly in arid regions. Although it may be convenient to attribute salinization to agricultural causes, it would be a mistake to do so without a thorough and comprehensive investigation of the hydrogeology of the specific region. The use of multiple isotopic and chemical tracers can elucidate the true causes of salinization and provide useful information on ground water-surface water interaction in complex hydrogeologic regimes. Historical water quality data often provide valuable information on the design of sampling schemes. It is essential to incorporate all available hydrogeologic information to the working conceptual model, which is then used as the foundation for establishing the study design. This investigation confirms that proper application of multiple isotopic and geochemical tracers can be used to identify and constrain multiple sources of solutes in complex river systems.

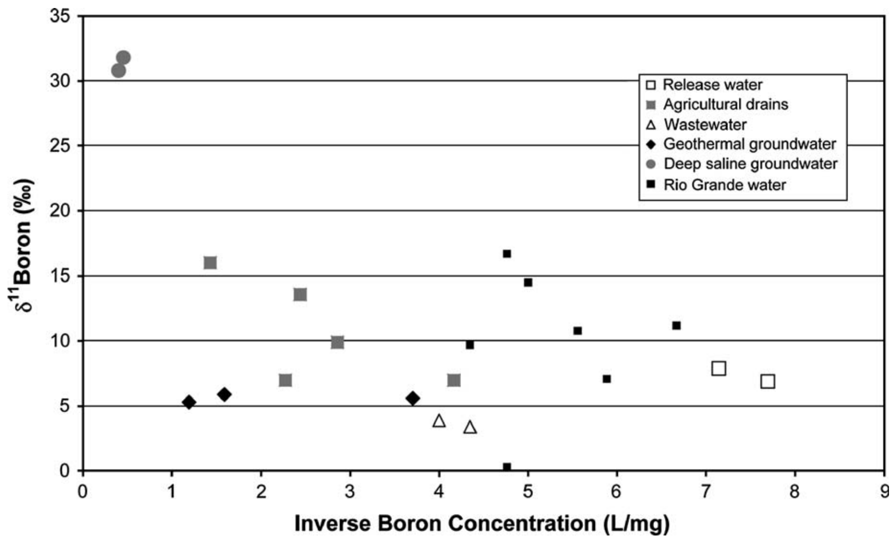

Figure 9. Boron results during August 2004 and January 2005.

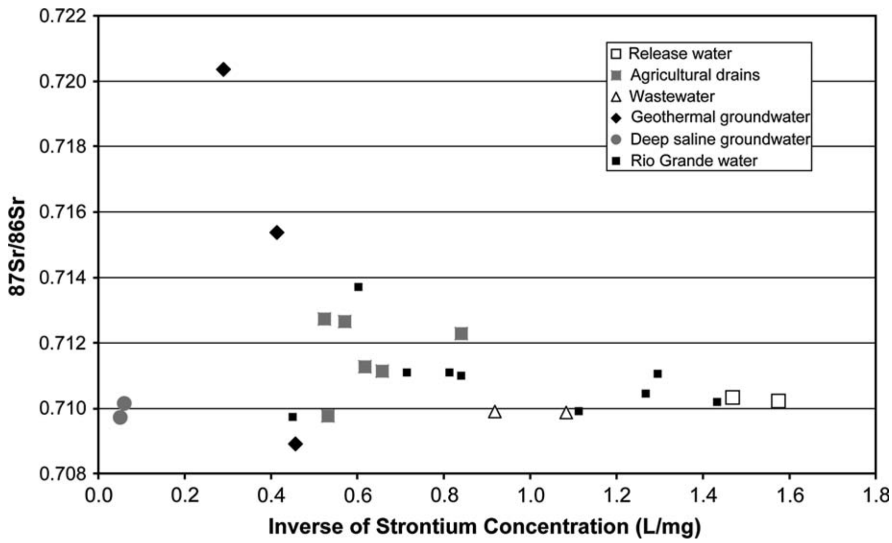

Figure 10. Strontium results during August 2004 and January 2005.

Conclusions specific to this particular investigation are summarized subsequently. The current downstream pattern of salinization in the Rio Grande is similar to that observed prior to the construction of the reservoirs, agricultural drains, and waste water facilities. This indicates that salinization in the study area occurred before the reservoirs, agricultural drains, or large-scale waste water discharges were present and must therefore be attributable primarily to natural salinity sources discharging to the Rio Grande.

Large increases in salinity along the Rio Grande generally occur in the areas where upward movement of geothermal ground water or basin saline ground water exists; the extremely saline water found in wells at the distal end of the Mesilla Basin and the study area supports our hypothesis that the primary contributor of salinity to the Rio Grande is upwelling basin saline ground water rather than anthropogenic sources.

Median chloride concentrations at the distal end of the study area (RG-EP) have generally decreased since the 1950s and tend to increase during periods of low precipitation (e.g., during the 1950s drought). Chloride loads decrease throughout the study area during periods of regional drought because the agricultural drains and the Rio Grande cease to act as discharge points for sedimentary brine associated with the regional ground water system.

Major sources of water and salinity to the study area include the incoming release water, sedimentary brine, geothermal ground water, and waste water. These sources can be uniquely identified by their geochemical and isotopic fingerprint. Agricultural drains represent a mixture of release water, sedimentary brine, and geothermal ground water rather than a unique source of water to the system. The observed salinization of the agricultural drains cannot be caused by evapotranspiration and agricultural processes alone, as indicated by similar Cl/Br ratios in Rio Grande source water and drain water.

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