Data Repository Item

Hogan J. F., Phillips F.M., Mills S.K., Hendrickx J., Ruiz J., Chesley J.T., Asmerom Y. Geologic origins of salinization in a semiarid river: the role of sedimentary brines, *Geology*. Article ID: G23976

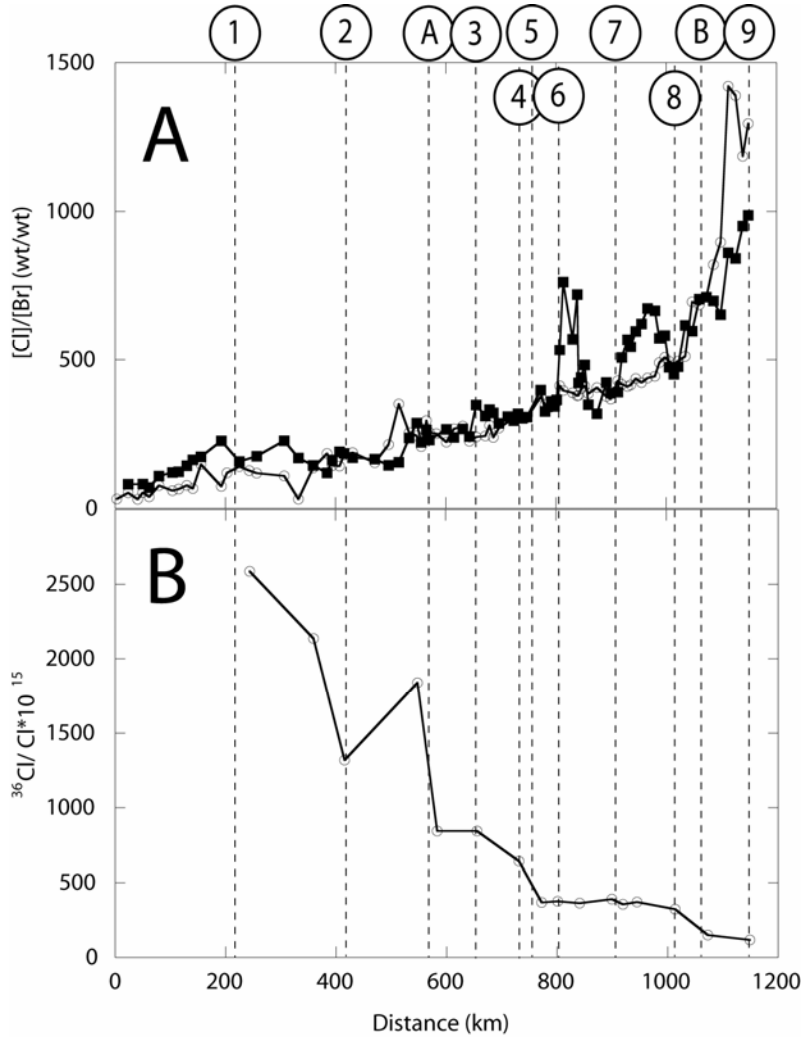

Figure DR1. Chlorine isotope system: (**A**) Cl/Br ratios and (**B**) ^{36}Cl versus distance down river. Open circles (○) are samples collected in August 2001, whereas solid squares (■) were collected in January 2002. Numbers correspond to locations where the Rio Grande exits the southern end of the alluvial basins shown in Figure 1. Locations marked with letters refer to additional salinity increases not associated with alluvial basin termini. (A) is the Albuquerque Wastewater Treatment Plant and (B) is a location within the Tularosa- Hueco Basin, see text for discussion. In the winter, marked variability is observed in the Cl/Br ratio of the lower Rio Grande as a result of very low flows due to highly restricted reservoir releases. The first increase occurs south of Elephant Butte Reservoir; ratios then decrease at Caballo Reservoir. South of Caballo, Cl/Br ratios increase until a second sharp decrease is observed at the point where El Paso wastewater enters the river.

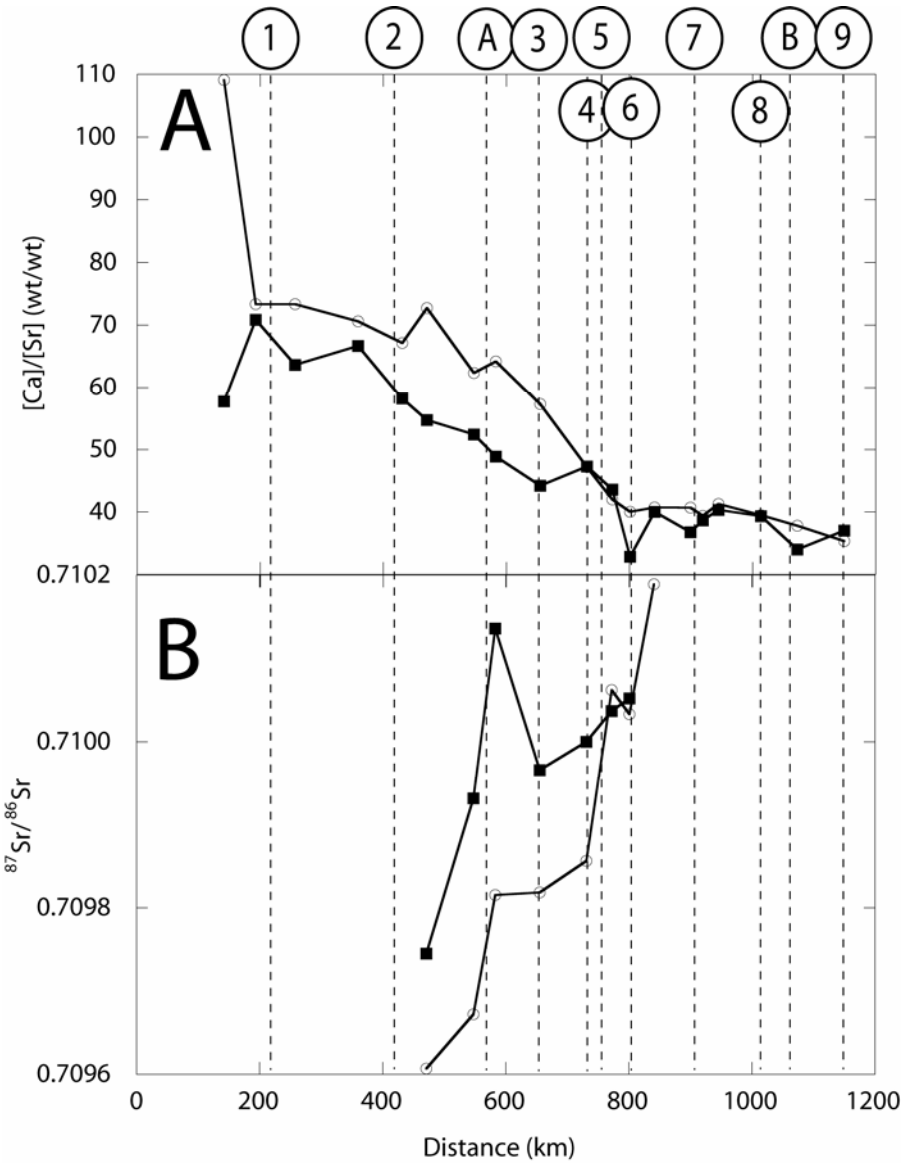

Figure DR2. Strontium isotope system: (**A**) Ca/Sr ratios and (**B**) $^{87}Sr/^{86}Sr$ ratios versus distance down river. Open circles (○) are samples collected in August 2001 whereas solid squares (■) were collected in January 2002. Numbers correspond to locations where the Rio Grande exits the southern end of the alluvial basins shown in Figure 1. Locations marked with letters refer to additional salinity increases not associated with alluvial basin termini. (A) is the Albuquerque Wastewater Treatment Plant and (B) is a location within the Tularosa- Hueco Basin, see text for discussion.

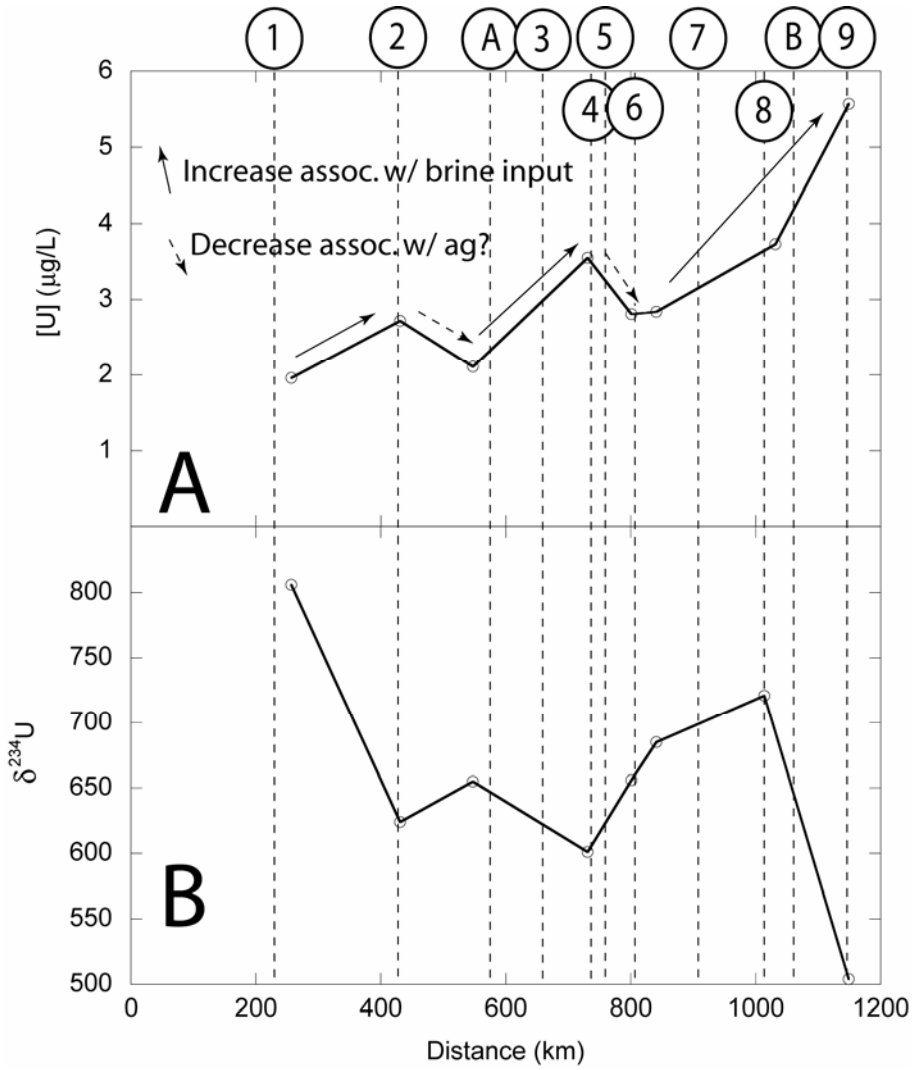

Figure DR3. Uranium isotope system: (**A**) U and (**B**) δ^{234}U values versus distance down river. Only samples collected during August 2001 (○) were analyzed. Numbers correspond to locations where the Rio Grande exits the southern end of the alluvial basins shown in Figure 1. Locations marked with letters refer to additional salinity increases not associated with alluvial basin termini: (A) is the Albuquerque Wastewater Treatment Plant and (B) is a location within the Tularosa-Hueco Basin, see text for discussion.

In general the headwaters have high δ^{234}U values and low U concentrations indicative of recent water-rock interaction. In contrast, waters downstream have low δ^{234}U and high U concentration values. Note that there are two marked decreases in concentration that reflect the non-conservative behavior of this solute, likely as a result of removal during application onto irrigated lands (first decrease) or by processes within Elephant Butte Reservoir (second decrease).

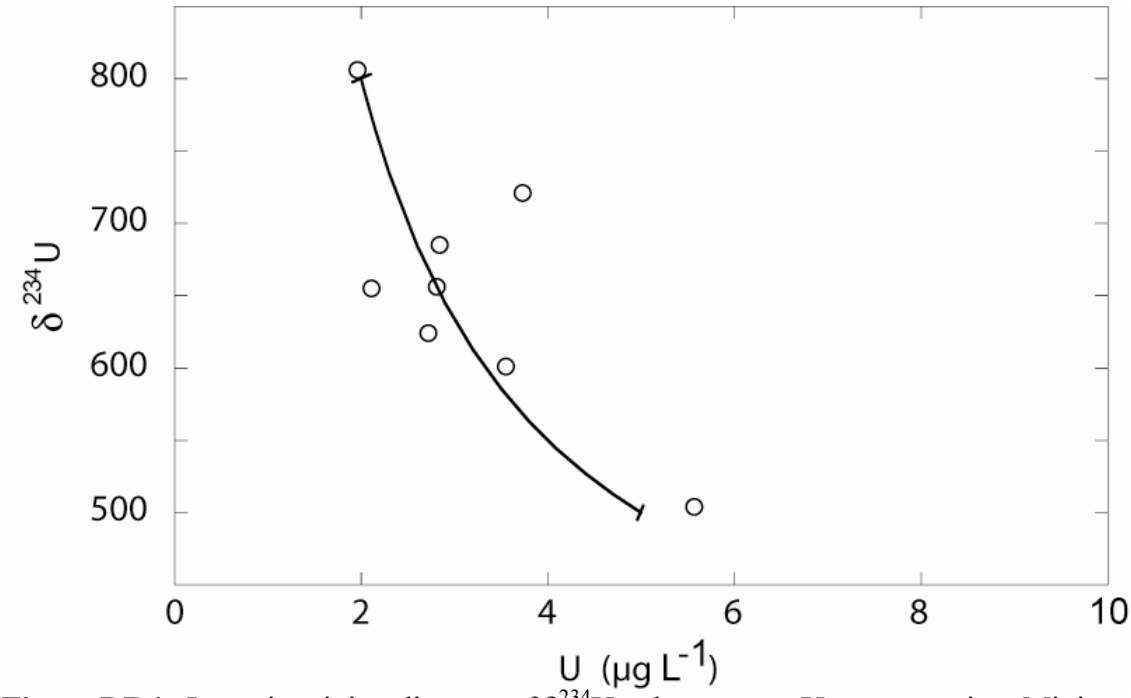

Figure DR4. Isotopic mixing diagram of $\delta^{234}U$ values versus U concentration. Mixing lines were calculated using the end-members in Table DR1. Percentages are not included on the U-isotope mixing plot because of its non-conservative behavior.

The $^{234}U/^{238}U$ ratio of waters, expressed as $\delta^{234}U$ per mil deviation from the secular equilibrium ratio, reflects both the extent of water-rock interaction and the residence time. ^{234}U is preferentially leached from rocks because its crystal site is damaged when ^{238}U decays to ^{234}U, thus, groundwater with short residence times and/or strong water-rock interaction typically has high $\delta^{234}U$ values (Dickson and Davidson, 1985). If the residence time is significant with respect to the half-life of ^{234}U, the $\delta^{234}U$ value is lowered by radioactive decay of ^{234}U (Dickson and Davidson, 1985).

TABLE DR1. ISOTOPIC AND SOLUTE RATIOS FOR POTENTIAL SOLUTE SOURCES AND SELECTED END-MEMBER COMPOSITIONS.

End-member	Cl (mg/l)	Cl/Br (wt/wt)	$^{36}Cl/Cl*10^{15}$	Ca (mg/l)	Ca/Sr (wt/wt)	$^{87}Sr/^{86}Sr$	U (µg/l)	$\delta^{234}U$
Atmospheric deposition	0.2 to 2*	40 to 200*	700†		430 to 603§	0.709 to 0.713§		
Basalt weathering					100 to 240#	0.704 to 0.705#		
Rio Grande headwaters**	10	100	2500	15	75	0.7096	2	800
Magmatic geothermal sources		250 to 350††	1 to 6††					
Sedimentary brines		1000 to 10,000*	5 to 35§§		10 to 50##	0.708 to 0.716***		
Rio Grande saline groundwaters		400 to 1300†††	35§§§		20 to 44†††	0.7093 to 0.7118###		500§§§
Saline groundwater end-member****	1000	1300	35	350	33	0.71015	5	500

Note: Concentrations are reported only for end-members used in the mixing calculations. Basalt weathering is not considered to be a major source of chloride, thus associated values are not included. Likewise we report no values for Sr in geothermal waters as values reflect the local rock type (Goff and Gardener, 1994) not a magmatic source. For the emerging U-isotope system, limited data on potential solute sources explains the lack of reported values.

*Precipitation values from Davis et al. (1998) for Nevada and Arizona; †Values from Phillips (2000); §Values from Graustein and Armstrong (1983); #Values from Dugan et al. (1986); **End-member values based on measured samples from the headwater of the Rio Grande; ††Values from Fehn et al. (1992); §§Value based on secular equilibrium (Phillips, 2000); ## Values from Banner (1995) and Musgrove and Banner (1993); *** Values from Musgrove and Banner (1993) and McNutt (2000); note individual basins have significantly narrower ranges; †††Data compiled from Brandvold (2001) and Plummer et al. (2004) using only samples over 500 ppm Cl; §§§This study, n=1; ### Saline groundwater samples collected by Plummer et al. (2004), measured for this study, n=5; ****For saline groundwater end-member we used the upper end of concentration values compiled from Brandvold (2001) and Plummer et al. (2004) which represent shallow saline groundwaters; saline waters at depth are likely more concentrated. The isotope and solute ratios were selected to be within the observed values for saline groundwaters in the Rio Grande as well as to best fit the observed mixing trend.

Additional References

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