Using isotope chemistry to find an alternate source of water for the Cienega de Santa Clara wetland: Implications for Arizona water users and the Yuma Desalting Plant.

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INTRODUCTION

The Colorado River (CR) is one of the most managed rivers in the world. Along its course, water regulatory practices have been implemented to provide the vital resource to more than 27 million people and 1.2 million ha of farmland in the Mexicali and Imperial Valley (Barnett and Pierce, 2009). The river exploitation has led to a massive biodiversity decrease in the Colorado River Delta (CRD, Figure 1). Today, the river no longer reaches the lower part of the CRD and the area formerly occupied by wetlands has been reduced to less than 5% of its original extent (Zamora-Arroyo and Flessa, 2009).

The Cienega de Santa Clara (Cienega) is the largest wetland remaining in the CRD (Figure 1). It provides habitat for more than 260 bird species, including marsh birds, shorebirds, waterfowl, and migratory birds (Flessa et al. 2012). The Cienega lies along a shallow depression on the eastern edge of the delta on a former active arm of the CR and covers an area of 6,000 ha (Glenn, 1996). The most important source of water for the Cienega is brackish groundwater derived from the Wellton-Mohawk Irrigation Drainage District of Arizona (WMIDD). This water is transported to the Cienega by an 80 km long, concrete-lined canal that carries $1.3 \times 10^8$ m$^3$ of water every year (Flessa et al. 2012). Artesian springs also discharge in the Cienega and support other smaller wetlands along the eastern coast of the northern Gulf of California and Bahia Adair.

Natural seepage, via artesian springs, is pronounced along the eastern escarpment of the CRD where it supports a continuous thread of brackish wetlands (Glenn et al. 1995) and along the salt flats of the Gran Desierto, near Bahia Adair. Despite their small size, these pozos as they are locally known, are important and interesting features of the CRD as they support a greater diversity of plant species than the Cienega due to the lower salinity (<1 ppt to 3 ppt; Ezcurra et al. 1998; Glen et al. 1996). We will pay special attention to this particular water source, where stable isotope data has not been used to derive its origin.

Steady increases in water demand and the effects of prolonged drought in the southwest U.S. have prompted interest in the use of non-conventional water sources such as WMID brackish water. The Yuma Desalting Plant (YDP) was built in 1992 with such a purpose in mind. Operation of the YDP would jeopardize the survival of the Cienega. In such over allocated system, distinguishing the different sources of water becomes increasingly important to manage not only agricultural resources, but also the natural spaces remaining in the area.

In this study, we use new environmental isotope data ($\delta^{18}$O, $\delta^2$H, $^3$H, and $^{14}$C), and earlier findings from the CRD, to provide a direct indication of artesian spring water source and its resident time. Groundwater residence time is an important component of water resource management and provides valuable understanding of hydrological and biogeochemical processes (McDonnell et al. 2010). This information is then used to evaluate the groundwater dynamics of the system and establish its potential to sustain the local wetlands and agricultural wells.
DATA AND ANALYTICAL METHODS

Water samples were collected from artesian springs discharging on the southeastern side of the Cienega in May 2013, October 2013, and July 2014. Three water samples were collected from the town of El Golfo the Santa Clara in March 2015. Surface water samples were also collected from the Cienega, lined canals, and Colorado River at Yuma, Arizona (Figure 1). Additional surface water samples from the Gila River, previously analyzed by the USGS as part of the National Stream Quality Accounting Network (NASQAN), and published data from wells in San Luis, Mexico (Payne, 1979) were also included in the dataset for this study. This data was used to derive an endmember of Gila River water in the CRD and for comparison with our samples. Due to the limited rainfall data in the study area, we modeled an average value for the $\delta^{18}O$ and $\delta^2H$ values in precipitation using The University of Utah waterisotopes.org isotope mapping application. The results of these analysis are shown in Table 1 and Figures 2 and 3.

Samples were collected directly into sample bottles. Temperature, pH, dissolved O$_2$, and electrical conductivity levels were measured until stabilized. Samples for stable oxygen, hydrogen, and carbon (DIC), were filtered with a 0.45-μm nylon filter and kept in capped glass vials with no headspace. Unfiltered water samples were collected for $^3$H and $^{14}$C analysis in rinsed 1-L HDPE and amber borosilicate glass bottles, respectively. Samples for cations, anions, and alkalinity were filtered with a 0.45-μm nylon filter and kept in HDPE bottles. All samples were kept on ice while in the field and then refrigerated at 4°C.

Alkalinity was determined by the Gran-Alk titration method (Gieskes and Rogers, 1973) within 12-h of collection. $\delta^{18}O$, $\delta^4H$, and $^3H$ values were measured at the University of Arizona’s Geoscience Laboratory of Isotope Geochemistry. $\delta^{18}O$ and $\delta^2H$ were determined on a Finnigan Delta-S mass spectrometer with automated CO$_2$ equilibration and Cr reduction attachments. Analytical precisions (1σ) for these techniques are 0.08% for $\delta^{18}O$ and 0.8% for $\delta^2H$. All stable isotope data are reported in delta notation where $\delta = \left( \frac{R}{R_{std}} - 1 \right) \times 1000$ (‰), and R is the ratio of the heavy over the lighter isotope in the sample and $R_{std}$ is the isotope ratio of VSMOW (Vienna Standard Mean Ocean Water).

$^3H$ values were measured by liquid scintillation counting on electrolytically enriched water in a Quantulus 1220 Spectrophotometer, with a detection limit of 0.7 tritium units (TU) for 8-fold enrichment and 1,500 min of counting. $^{14}$C was measured as liberated CO$_2$ reduced to graphite at the University of Arizona Accelerator Mass Spectrometer facility. These results are reported as percent of modern carbon (PMC) relative to a NBS oxalic acid standard. Cation and anion concentrations were determined in the Department of Hydrology and Water Resources at the University of Arizona using an inductively coupled plasma optical emission spectrometer (ICP-OES; precision <1%) and ion chromatograph (precision <2%), respectively.
Colorado River Evaporation Line

$\delta^{18}O$ and $\delta^2H$ values of surface CR water from previous studies and unpublished data were used to investigate the evolution of evaporating CR water as it flows south the CRD under modern environmental conditions (Figure 2). A regression of this data defines the Colorado River Evaporation Line (CREL). This evaporation trend has a slope of 5.2 in the $\delta^{18}O$ vs $\delta^2H$ plot. The slope of the CREL falls within the range (5-6) observed in evaporating CR water by other studies and is characteristic of CR water (Robertson, 1991; Guay et al. 2006). The CREL is used as a reference to compare and understand the dynamics from the different sites under study.

Gila River

Gila River water collected from three different USGS stations along the Gila River during the 1980’s high flows show the variability from headwaters to the delta (Figure 4). $\delta^{18}O$ and $\delta^2H$ values for Gila River at Redrock, New Mexico plot very close to the GMWL. At Red Rock, NM, the $\delta^{18}O$ and $\delta^2H$ values are range between -11.29 to -8.59‰ and -77.7 to -64.8‰, respectively. At Dome, Arizona, $\delta^{18}O$ and $\delta^2H$ values range between - 13.36 to - 7.61 and -104.5 to -64.9‰, respectively. These samples plot along an evaporation line parallel to the CREL with a slope of 5.16, but higher on the GMWL.

Calculated Evaporation

Evaporation within the Cienega was calculated as described by Clark and Fritz (1997). A displacement of data away from the GMWL reflects evaporative loss. To calculate the average evaporative loss, the local “evaporation slope” is assumed to be 5.2. The evaporation slope is largely dependent on relative humidity, and with a slope of 5.2 relative humidity will be close 0.75 (Gat, 1971). Equilibrium and kinetic fractionation factors are calculated using:

1) $10^3ln\alpha^{18}O_{l-v} = 1.137\left(\frac{10^6}{T^2}\right) - 0.4156\left(\frac{10^3}{T}\right) - 2.0667,$ \hspace{1cm} (Majoube,1971)

2) $\Delta\varepsilon^{18}O_{l-v} = 14.2 \left(1 - h\right),$ \hspace{1cm} (Gonfiantini,1986)

Where T is the mean annual temperature (295 Kelvin) and h is the relative humidity (0.75). These equations yield $\varepsilon^{18}O_{l-v} = 9.64\%$ and $\Delta\varepsilon^{18}O_{v-bi} = -3.55\%$. The overall enrichments ($\varepsilon^{18}O_{total} = \varepsilon^{18}O_{v-l} + \Delta\varepsilon^{18}O_{v-bi}$) for evaporation under these conditions is then -13.19‰ for $^{18}O$. The fractional water loss can be modelled according to Rayleigh distillation (Clark and Fritz, 1997). For $^{18}O$, the evaporative enrichment is up to 10.07‰ (Site 4 to Site 8). Using $\varepsilon^{18}O_{total} * lnf = 9.67\%$ yields a residual water fraction of 0.47, so the average evaporative loss is 53%.
**KEY FINDINGS**

The chemical composition of water drastically changes from the entrance of the Cienega (Site 4) to the southernmost part it (Site 8, Table 1). This dramatic increase in Cl⁻ and SO₄²⁻ concentrations results from the high evaporation rates in this dry region and transpiration by hydrophyte vegetation. Conversely, NO₃⁻ concentration drops below detection levels in most of the samples. This decrease is likely caused by nitrogen reducing bacteria present in the Cienega. NO₃⁻ is likely to vary between seasons and depending on irrigation practices. A more detailed monitoring of NO₃⁻ and the use of δ¹⁸O_NO₃ and δ¹⁵N_NO₃ could be used to establish the fate and quantify the loss of NO₃⁻ in the system. Cienega surface water samples plot very close to the CREL (Figure 3). The conservative nature of ¹⁸O and ²H results in the observed increase in δ¹⁸O and δ²H values due high evaporation rates. From the entrance of the Cienega (Site 4) to the South Lagoon (Site 8) an average of 53% of the water is loss due to evaporation. This estimate is very similar to those previously obtained in the Cienega using different methods (Flessa et al. 2012). Water evaporating in the Cienega shows a distinct pattern towards higher values as observed in δ¹⁸O vs δ²H graph. Sites 9 and 10 are located in the southernmost, non-vegetated portion of the Cienega subject to extreme evaporation and tidal exchange which explains the subtle deviation of these two samples from the CREL.

The water chemistry of samples from the pozos and El Golfo are very similar and they seem to be derived from the same source. Samples from these two areas cluster very closely to each other near the CREL in our δ¹⁸O vs δ²H plot (Figure 3). Aliquots from Site 17 were collected from an evaporating pond and follow an evaporation trend away from this cluster of points. Interestingly, water from the pozos and El Golfo do not vary very much among them (Figure 3). They plot above modern C.R. water at Yuma and most of the Cienega samples. This would suggest that if water from the pozos and El Golfo is C.R. water, it would have seen fair degree of evaporation to acquire its modern δ¹⁸O and δ²H values. However, major ion chemistry (Cl⁻ and SO₄²⁻) shows that some of the spring samples are actually similar to CR/GR mixtures observed by Payne et al. (1979). Tritium activity from a spring sample resulted in 0.5 TU. This activity is far below from modern CR water (7 or 8 TU), and pre-dates the atmospheric detonation of thermo-nuclear devices, which is, before 1950. ¹⁴C analysis for three spring samples yielded ¹⁴C PMC of 24.9, 11.7, and 2.9 from north to south, respectively. These PMC values yield uncorrected ¹⁴C ages of 11,500, 17,700, and 29,000 ¹⁴C yrs B.P.

The stable isotope data obtained in this study suggest that water from the springs, CSC, and local wells all have a common origin, CR water. However, given the low ³H activity and low ¹⁴C PMC obtained from the spring samples, it is possible that this spring system is not being currently recharged with modern CR water. The origin of this water could be from old, pre-dam CR spring floods ponding on the surface and percolating into the local groundwater reservoir which would explain the plotting position in the δ¹⁸O vs δ²H plot and its higher values than CSC water. Given the high evaporation rates in the area and the low discharge volume of artesian springs cutting water delivery from the WMIDD to the Cienega will severely affect its survival.
REFERENCES


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Figure 1. Study Area and Sampling Sites
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Table 1. Summary of Results for Samples from the CRD.
Figure 2. Colorado River Evaporation Line. For data details see Guay et al. 2004.
Figure 3. Stable Isotope Results for CRD samples.
Figure 4. Stable Isotopes Results from USGS NASQAN Program for Gila River water.