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DISSOLVED INORGANIC AND ORGANIC CARBON IN AN EPHEMERAL FRESH WATER STREAM IN SOUTHERN ARIZONA

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ABSTRACT. We report on an initial long-term study of dissolved inorganic and organic carbon (DIC) from Sabino Creek, located in Sabino Canyon, Pima County, Arizona. The purpose of this study was to monitor changes in dissolved radiocarbon (¹⁴C) with time and to understand the processes contributing to these variations. Our results span the period 2009–2016 and show a mixing trend between dissolved inorganic and organic carbon modern end-members with an older component. This study provides preliminary information for more detailed research on recycling of organic components in this stream system.

KEYWORDS: dissolved inorganic carbon, dissolved organic carbon, radiocarbon, stable isotopes.

INTRODUCTION

The distribution of radiocarbon (¹⁴C) between different components in freshwater streams has been the subject of study since the early days of radiocarbon (Broecker and Walton 1959). The sources of different components of dissolved inorganic (DIC) and organic carbon in riverine systems has been discussed extensively by Raymond and Bauer (2001), and more recently Barnes et al. (2018) have given an extensive survey of the origins of dissolved organic carbon (DOC). Butman et al. (2015) also have documented changes in the ¹⁴C ages of carbon in river systems in part due to human disturbance.

The study of ¹⁴C in freshwater systems is complex due to the many pathways that can exist in a freshwater ecosystem (Meltzer and Steinberg 1983). In the context of this paper, we define DIC, meaning mainly carbonates and bicarbonates in solution in fresh waters. These species are generally in equilibrium, depending on pH, such that:



where the left-hand species are more abundant at lower pH and the bicarbonate species predominate at the highest pH. pK_1 and pK_2 are the log of the two important equilibrium constants (Stumm and Morgan 1995). We note also that at high pH, carbonates can also precipitate depending on the cation chemistry of the waters. This equilibrium can be specified in artificial solutions, however it is not entirely correct in natural waters. It appears that at $\text{pH} > 8$, calculated values of CO_2 greatly exceed measured values. The

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reasons why these differences exist is in part due to interferences by organic acids and other organic constituents which disturb the purely inorganic equilibrium (Reddy 1975) and also the dissociation of HCO_3^- to CO_3^{2-} or release of CO_2 (Wetzel 1975).

DOC defines a wide range of species, which are operationally defined here as passing a <0.45 μm filter. They include fulvic acids, which are water-soluble acids at any pH and humic acids, which are higher molecular weight than fulvic acids and are base-soluble but acid-insoluble (Thurman 1985). Other DOC components might include low-molecular-weight acids, carbohydrates, lipids, aromatics, plant particulates, and animal particulates (Ishiwatari 1985; Malcolm 1985). Several different theories have been proposed as to how humic substances form, but all assume they are polymerized in some way from fulvic acids (Malcolm 1985). There are many different ways to extract DOC from natural waters, including: vacuum drying and subsequent combustion of the organic residues, solid-phase extraction, UV oxidation, chemical oxidation, and ultrafiltration (as summarized by Murphy et al. 1985; Leonard et al. 2013).

Several algae and macrophytes can process dissolved CO_2 or bicarbonate in different proportions in photosynthesis. *Elodea* (waterweeds) and *Lemna* (duckweed) can take up both CO_2 and HCO_3^- in varying proportions but algae take up mainly carbon from bicarbonate and little from CO_2 (Cleland 1967; Meltzer and Steinberg 1983). Aquatic plants such as *Potamogeton* are also known to photosynthesize carbon from bicarbonate, and not just CO_2 (Meltzer and Steinberg 1983). These processes can result in DIC being converted into DOC. *Lemna* and *Potamogeton* are found in the Sabino Canyon watershed (Shreve and Wiggins 1964).

Sabino Creek, Arizona

Sabino Creek is an ephemeral stream in Pima County, Arizona (<http://web.sahra.arizona.edu/sabinocanyon/intro.html>). It is the only stream in the Tucson region that flows for much of the year. Our rationale for sampling this stream is that we noted that there are very few reported ^{14}C measurements on this stream water and this warranted further investigation. Bennett (1965) reported a value for DIC collected in 1965 of 164 ± 9 percent modern carbon at close to the peak of the bomb pulse, about 175 percent modern for NH zone 2 (Hua et al. 2013). Eastoe et al. (2004) reported two values for Sabino Creek water downstream from our sample location.

Sabino Creek is characterized by flow during most of the year, with flow peaks in the mid-winter (Jan.–Feb.) and the summer rainy season (Jul.–Sept.). The average annual precipitation data for this region is shown in Figure 1. The flow station is located 9 m upstream from the Lower Sabino Dam ($32^\circ 19' 00''\text{N}$, $110^\circ 48' 35''\text{W}$), which is shown in Figure 2. The mean flow rate is $0.15 \text{ m}^3/\text{s}$ with intermittent extreme flows of over $30 \text{ m}^3/\text{s}$. The highest flow rate ever recorded was on July 31, 2006, with a transient flow of $437 \text{ m}^3/\text{s}$, during a flash flooding event, as documented in detail by Webb et al. (2008). The flow rate over the period 2009–2016 is shown in Figure 3.

Sampling Plan

We collected freshwater samples from Sabino Creek at various times over the last 7 years, to try to understand the relationship between DIC and atmospheric ^{14}C and also the relation between DIC and DOC. Apart from the samples collected on June 30, 2009, all samples were collected

Table 1 Dissolved inorganic and organic carbon in Sabino Creek, Arizona.

Date (M/D/Y)	Flow rate (m ³ /s)	Sample	$\delta^{13}\text{C}$ DIC ($\pm 0.1\%$)	F (DI ¹⁴ C)	$\delta^{13}\text{C}$ DOC ($\pm 0.1\%$)	F (DO ¹⁴ C)
2/24/2009	0.86	AA84738	-4.8	1.049 \pm 0.005	-25.9	1.109 \pm 0.007
3/1/2009	0.34					
6/30/2009 bridge 4	0	AA86264	-3.1	1.069 \pm 0.012		
6/30/2009 bridge 5	0	AA86265	-9.4	1.071 \pm 0.004		
3/21/2010	1.95	AA89378	-4.2		...	1.039 \pm 0.007
9/4/2011	0	AA95751	-13.1	1.060 \pm 0.004	-24.7	1.065 \pm 0.005
9/25/2011	0.026	AA95752	-12.6	1.034 \pm 0.005	-19.4	0.880 \pm 0.011
9/29/2011	0.026	AA95753	-11.9	1.025 \pm 0.005	-18.1	0.859 \pm 0.014
4/12/2012	0.042	AA98441	-12.1	0.989 \pm 0.005	-23.2	1.052 \pm 0.005
5/3/2012	0.0008	AA98784	-17.2	1.034 \pm 0.005	-23.0	1.059 \pm 0.005
8/17/2013	0.046	AA102553	-11.8	0.934 \pm 0.004	-24.7	1.074 \pm 0.005
9/15/2013	0.10	AA102743	-12.2	0.885 \pm 0.004	-23.9	1.077 \pm 0.005
1/20/2016	0.72	AA107268	-4.7	1.023 \pm 0.003	-25.3	1.109 \pm 0.003
9/15/2016	0.22	AA108829	-11.3	1.036 \pm 0.005	-25.6	1.070 \pm 0.003
9/15/2016	0.22	AA108830	-11.6	0.978 \pm 0.003	-25.3	1.073 \pm 0.003

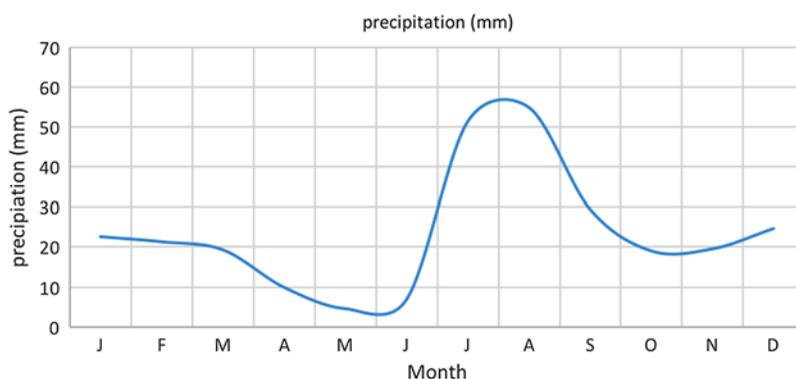


Figure 1 Annual average precipitation data for Tucson, for the period 2009–2017 derived from National Weather Service data.

from water in the pool exiting the Lower Sabino Dam. We sampled at times with different flow rates over this period. Results are shown in Table 1 and compared to historical flow rates (USGS 2018), noting that zero flow means that there is no surface flow at the USGS sensor, not that there is no water.

METHODS

Samples of fresh water from Sabino Creek were collected in 2-L plastic containers and sealed. The containers were flushed several times with the water before the final sample.



Figure 2 A relatively high flow event ($1.37 \text{ m}^3/\text{s}$) at Lower Sabino Dam on February 5, 2017.

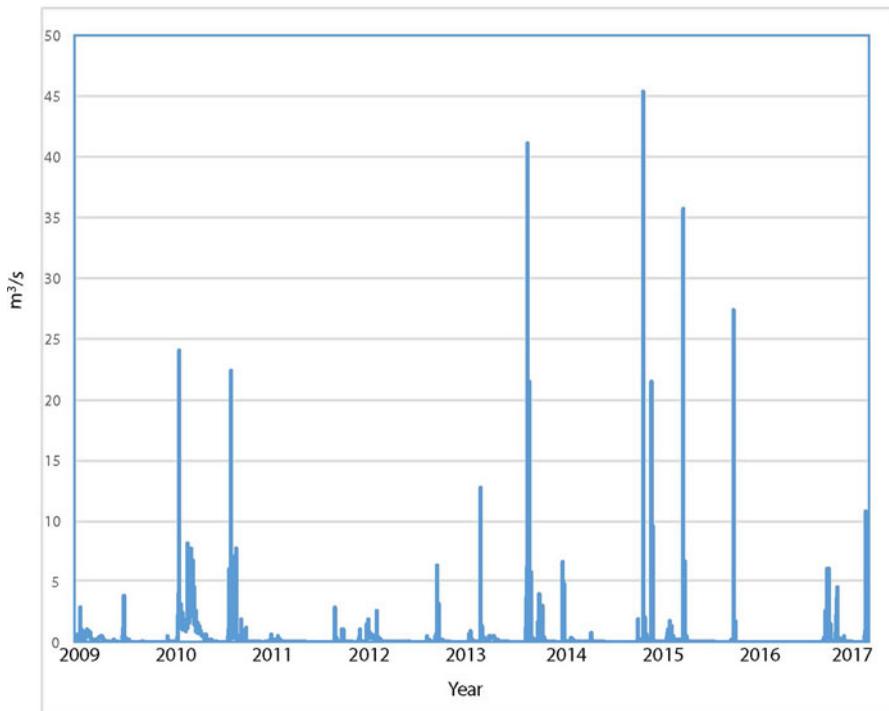


Figure 3 Discharge flow pattern for Sabino Creek, Arizona, derived from USGS (2018) data. Note that the peak events reflect major precipitation events.

Samples were then transferred to the AMS Laboratory at the University of Arizona and processed as rapidly as possible. Samples were refrigerated before processing. We handled dissolved inorganic carbon (DIC) samples by transferring about 250 mL of water to a sample vessel, evacuated of the head space and acidified the water with

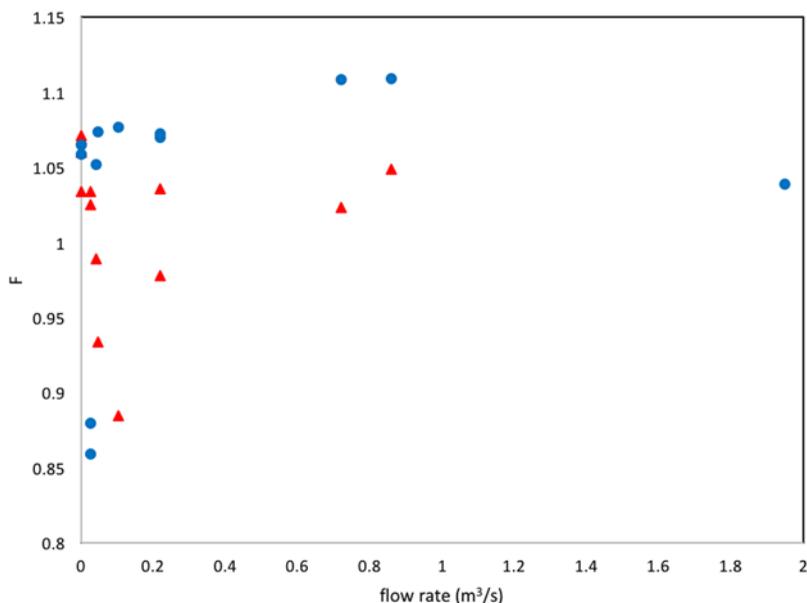


Figure 4 Dependence of F(DOC) and F(DIC) versus flow rate (m^3/s). DOC is given as blue circles and DIC as the red triangles.

phosphoric acid. The evolved CO_2 was collected cryogenically, the volume is measured and the gas converted to graphite using our standard protocols (Jull et al. 2008). We processed DOC samples using the procedure on similar-sized samples as described in the wet chemistry approach of Leonard et al. (2013) using KMnO_4 as the oxidizing agent, after the DIC component has been removed. The evolved CO_2 is then measured volumetrically and converted to graphite for AMS measurement. ^{14}C is measured using the NEC Pelletron AMS machine at the University of Arizona, running at 2.5 MV. Measurements for $\delta^{13}\text{C}$ were done off-line using a split of the sample gas, and run on a VG Optima stable-isotope mass spectrometer.

RESULTS AND DISCUSSION

We found a distinct relationship between our ^{14}C data and flow rates. We have plotted F(DIC) and F(DOC) against flow rate in Figure 4, where F is the fraction of modern carbon (Donahue et al. 1990). Higher-flow events are characterized by F (DIC) values closer to atmospheric and less negative $\delta^{13}\text{C}$. The trends for $\delta^{13}\text{C}$ in both DIC and DOC are shown in Figure 5. Periods of lower flow, particularly after the summer rainy season (in July–September) show more negative $\delta^{13}\text{C}$ values for DIC, while the DOC $\delta^{13}\text{C}$ values are generally unchanged. DIC tends to have depressed ^{14}C at these times, yet DOC remains close to contemporary. Similar trends are observed for the April–May values, which is the driest season of the year (see Figure 1). These trends are conspicuous in the data for the years 2012–2013 (Table 1). This suggests that the summer rainy season dislodges older organic carbon, perhaps tied up in soils, which are then released during large flow events. These results can be understood in terms of different sources of DOC originating from terrestrial sources (Raymond and Bauer 2001; Barnes et al. 2018).

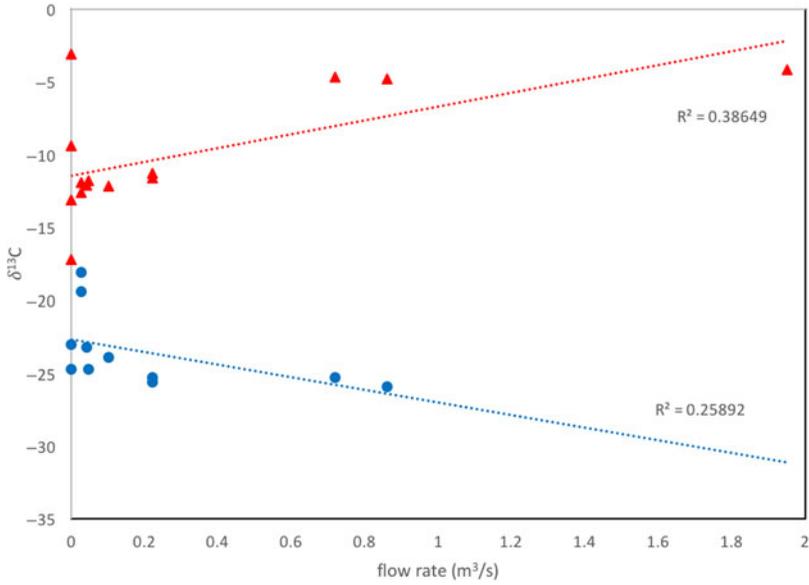


Figure 5 Dependence of $\delta^{13}\text{C}$ on flow rate (m^3/s). DOC is given as blue circles and DIC as the red triangles. Note the opposite trends for DOC and DIC.

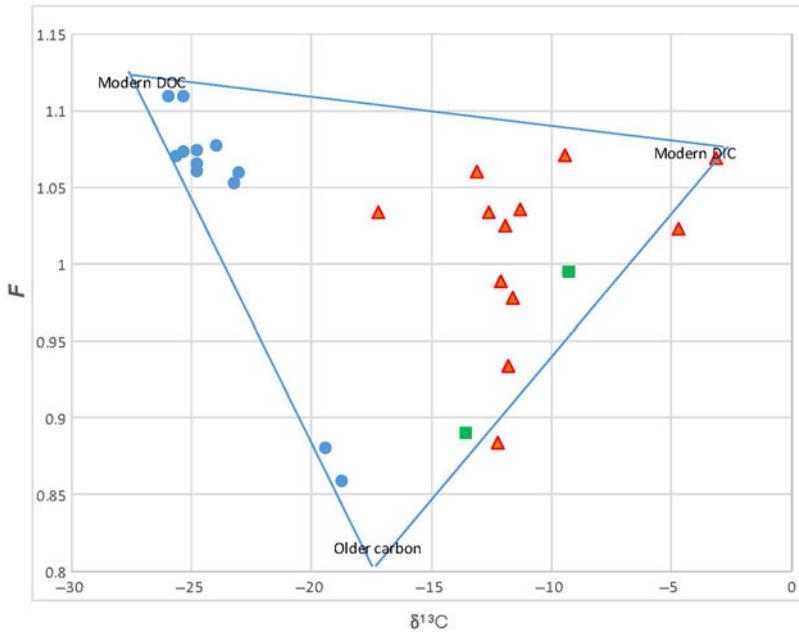


Figure 6 Isotope plot of fraction of modern ^{14}C (F) vs $\delta^{13}\text{C}$ for Sabino Creek water samples. Values for DOC are shown as blue circles, DIC as red triangles. Two additional DIC points (Eastoe et al. 2004) are included as green squares. The “old carbon” component is extrapolated from the data.

We have plotted these results in Figure 6 as a function of F vs. $\delta^{13}\text{C}$. Figure 6 can be understood as a mixing diagram, where there are modern DIC and DOC components with characteristic $\delta^{13}\text{C}$ and an older component extrapolated from the data. We expect that the “modern” DOC component has higher F due to residence time of the DOC which would have higher F due to higher level of bomb ^{14}C in subsurface water. We also include two previous $F(\text{DIC})$ data from Eastoe et al. (2004). Surprisingly, both $F(\text{DIC})$ and $F(\text{DOC})$ show opposite trends. Another observation is that DIC tends to decrease in F with more negative $\delta^{13}\text{C}$, with a weak correlation coefficient, $R = 0.30$, whereas DOC tends to move towards less negative $\delta^{13}\text{C}$ with decreasing F . Further, there is a high correlation between F and $\delta^{13}\text{C}$ for DOC, where there is a correlation of $R=0.96$. This suggests that there is a source of “old carbon,” that we can extrapolate from both trends, which is generating both the changes in DIC and DOC and has a $\delta^{13}\text{C}$ closer to -12 to -15‰ . An explanation for the trend in DIC is also explicable from studying the flow rates in Table 1. High flow rates generally have $\delta^{13}\text{C}$ closer to -4‰ and ^{14}C closer to the atmospheric value, whereas lower flow rates appear to track much lighter values of $\delta^{13}\text{C}$ and lower ^{14}C . This can be explained by reprocessing of older organic material in sediments into carbon which would have lighter $\delta^{13}\text{C}$ and also some residence time in the sediment. DIC seems to be incorporating modern DOC-related carbon, accounting for the spread of samples with F values > 1 . We could also consider photosynthesis of DIC to DOC, although this would not result in a lower ^{14}C value for DOC.

The trend from January 20 to September 15, 2016, illustrates this transformation. Where paired samples are available, it appears that the DOC has higher values of $F(^{14}\text{C})$ than the DIC. This can be understood by the DOC sampling organic material from sediments with a residence time of 5–10 years, since the level of bomb ^{14}C has been declining during that time (Hua et al. 2013). Barnes et al. (2018) suggest that “aged” DOC with a longer residence time is consistent with deeper flow paths, particularly in arid environments. Other interesting trends can be observed. For example, DOC shows a stronger correlation with flow rate than DIC, with a Pearson correlation coefficient $R=0.23$. However, if the one highest flow rate on March 21, 2010, is excluded, $R=0.44$. This can be explained as due to the fact that since DIC is effectively sampling the atmosphere, it is less dependent on flow rate. However, values of DIC where $F<1.0$ are occasionally observed. A longer-term monitoring of these values and a closer investigation of the organic geochemistry of the DOC at this site is planned for the future.

CONCLUSIONS

We observe three consistent end-member dissolved carbon components in groundwater from Sabino Canyon, collected from 2009 to 2016. These are (1) modern DOC component (2) modern DIC component, and (3) an older DOC-DIC component. Our results suggest variable degrees of mixing between all three components in the case of DIC, and two-component mixing only for DOC. Although consistent with wider studies (e.g. Barnes et al. 2018), we believe these interesting trends warrant a more detailed monitoring of ^{14}C and the geochemistry this stream.

We propose to continue these measurements using other DOC oxidation methods to compare using both chemical and UV approaches. It would also be advantageous to expand ^{14}C measurements to aquatic flora and sediment sampling in this region.

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