

CARBON CYCLING IN TWO SMALL STREAMS IN CENTRAL ARIZONA – AN ISOTOPE PERSPECTIVE

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Fossil Creek, Arizona



Oak Creek, Arizona

Abstract

The effects of recreational use and seasonal changes on carbon cycling were evaluated from monthly water samples collected along Oak Creek and Fossil Creek in north-central Arizona during 2003-04. Samples were analyzed for stable carbon isotope ratios ($\delta^{13}\text{C}$) and concentrations of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) using a TOC analyzer interfaced with an isotope ratio mass spectrometer. Spatial and temporal patterns in both streams indicate an indeterminate recreational effect and a moderate seasonal effect. Travertine formation in Fossil Ck, and effluent from a local trout farm on Oak Ck showed site-specific effects on DIC and DOC values, respectively.

Introduction

Carbon cycling in streams can be affected by a variety of factors including recreational use (e.g., disturbance, resuspension, and introduction of organic matter), seasonal changes (e.g., summer rain, winter snowmelt, terrestrial inputs) and physical barriers (e.g., dams and water diversions). To better understand how some of these factors affect carbon flow in small streams, we monitored dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) concentrations and stable isotope ratios ($\delta^{13}\text{C}$) in two spring-fed streams in north-central Arizona. Oak Creek experiences high recreational use and storm activity in summer months. This activity has been shown to agitate sediments resulting in high fecal coliform counts in the water column (Crabill et al. 1999). Fossil Creek is a travertine-depositing stream with high dissolved CO_2 concentrations. It has been diverted from its natural channel since the early 1900s to supply two hydroelectric power plants resulting in disruption of the natural travertine formation (Malusa et al. 2003).

Some of our initial hypotheses about carbon cycling were: (1) that recreational activity and monsoonal rains would increase DOC concentrations in Oak Creek during summer months, (2) that $\delta^{13}\text{C}$ values of DOC would identify relative contributions from aquatic and terrestrial inputs throughout the season, and (3) that $\delta^{13}\text{C}$ values of DIC would shift downstream as a result of outgassing and travertine formation in Fossil Creek.

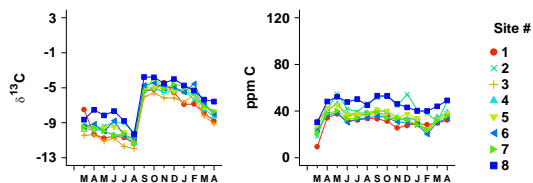
Methods

In the field, water samples were collected in duplicate from several locations along Fossil Creek and Oak Creek, Arizona, from March 2003 – April 2004 (Fig. 1). Samples were field-filtered using pre-combusted Whatman GFF series 0.7- μm glass-fiber filters, spiked with 250 μl of a saturated HgCl_2 solution, and stored (without headspace) in 40-ml glass ICHM vials with open-top 0.125" septum-lined caps.

In the laboratory, stock solutions of KHP and NaHCO_3 (O.I. Analytical) were serially diluted to generate concentration curves for ppm C correction. Prepared solutions (20-ppm) of sucrose (-11.2‰), citric acid (-16.7‰), and humic acid (-25.6‰) were used for $\delta^{13}\text{C}$ correction. Samples were analyzed using the new TOC-IRMS system (St-Jean 2003) where an O.I. Analytical Model 1010 TOC analyzer is interfaced to a Thermo-Finnigan Delta^{plus} XL isotope-ratio mass spectrometer (Fig. 2). In waters with high DIC concentrations, residual DIC can interfere with DOC analysis. For this reason, we analyzed the first sample for DIC without pre-treatment. The second sample was pre-treated with 20 μl of 85% H_3PO_4 and sparged with helium for 10 min to remove DIC prior to DOC analysis. Concentration data are reported in parts-per-million carbon (ppm C). Isotope data are reported in per mil (‰) using conventional delta (δ) notation. Precision is ± 0.2 ppm C on the TOC, and ± 0.2 ‰ on the IRMS. Optimal sample sizes of 5-120 μg C were obtained using 1-5 ml of water.

OAK CREEK

Dissolved Inorganic Carbon



Dissolved Organic Carbon

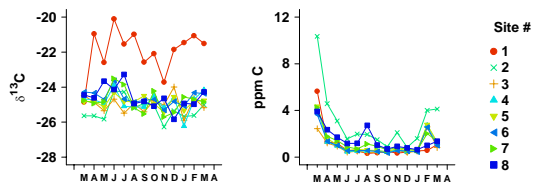
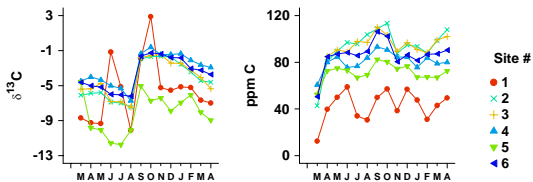


Figure 3. ppm C and $\delta^{13}\text{C}$ data for DIC and DOC in Oak Creek, Arizona

FOSIL CREEK

Dissolved Inorganic Carbon



Dissolved Organic Carbon

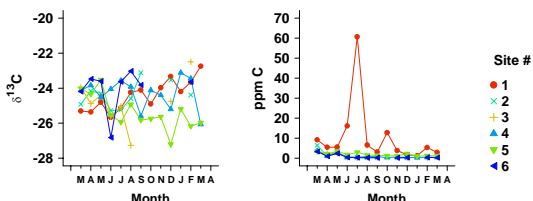


Figure 4. ppm C and $\delta^{13}\text{C}$ data for DIC and DOC in Fossil Creek, Arizona.

Results and Discussion

DIC levels in Oak Ck ranged from 9.4 to 54.6 ppm C over the 14 months that sampling occurred (Fig. 3). Snowmelt in March 2003 resulted in lower DIC values than in other months. DIC $\delta^{13}\text{C}$ values in Oak Ck ranged from -12.0‰ to -3.7‰. The strong ^{13}C -enrichment between August and September may be an artifact of long-term storage. To investigate this further samples will be collected in both ICHM vials and Qorpak bottles with polysyal caps. DOC levels in Oak Ck were generally very low ranging from 0.3 to 10.4 ppm C. There were no obvious seasonal trends with the exception of snowmelt events in March 2003 and February 2004. Site 2 (West fork of Oak Ck) showed higher concentrations of DOC than other sites. This site drains a different portion of the Mogollon Rim than the rest of Oak Ck. DOC $\delta^{13}\text{C}$ values ranged from -26.3‰ to -20.1‰. There were no apparent seasonal trends or effects of recreation on DOC $\delta^{13}\text{C}$. More enriched values at Site 1 in Oak Ck may have been due to the presence of a trout farm upstream, where waste products derived from fish raised on commercial feeds are likely ^{13}C -enriched.

DIC levels in Fossil Ck were much higher than Oak Ck ranging from 12.4 to 113.5 ppm C over the 14 months sampled (Fig. 4). Site 1 had lower DIC concentration than all other sites. This site is upstream of Fossil Springs and receives minimal to no flow during dry summer months. Snowmelt diluted stream water and resulted in lower DIC levels in March 2003. DIC concentrations decreased downstream of Fossil Springs (Site 2), as a result of travertine formation and CO_2 release from supersaturated water. DIC $\delta^{13}\text{C}$ values in Fossil Ck ranged from -11.8‰ to +2.9‰ and were generally more enriched than in Oak Ck, suggesting that limestone dissolution was more important in Fossil Ck than in Oak Ck. Due to its isolation during dry summer months, DIC $\delta^{13}\text{C}$ values at Site 1 were much more variable than at other sites. DIC $\delta^{13}\text{C}$ values at Site 5 were generally the most depleted values in Fossil Ck. Isotopic depletion in DIC probably occurred because ^{13}C - CaCO_3 is favored over ^{12}C - CaCO_3 during travertine formation (Friedman 1970). Typical of spring-fed streams, DOC levels in Fossil Ck were generally very low (with the exception of Site 1) and ranged from 0.2 to 60.7 ppm C. DOC concentrations at Site 1 were very high in July 2003 and may indicate some short-term disturbance by recreational activity. However, despite heavy recreational use during summer months, DOC concentrations remained low in Fossil Ck. DOC $\delta^{13}\text{C}$ values ranged from -27.3‰ to -22.5‰, typical of streams draining catchments dominated by C_3 plants. Variability in DOC $\delta^{13}\text{C}$ may relate to relative contributions of terrestrial and algal material. This will be investigated further upon collection and analysis of leaf litter and biofilm as part of ongoing food-web studies in Fossil Ck by Dr. Jane Marks (NAU Biology).

Summary

Analysis of monthly water samples for DIC and DOC concentrations and $\delta^{13}\text{C}$ values revealed no strong recreation effect in Fossil Ck or Oak Ck. Other than snowmelt in March 2003, no strong seasonal effect was apparent either. In Fossil Ck, the ephemeral pool at Site 1 experienced site-specific effects during dry summer months. Site 5 in Fossil Ck also displayed site-specific effects resulting from travertine deposition. Site 1 in Oak Ck showed ^{13}C -enriched DOC values relating to effluent from a trout farm upstream. Improper sample storage may have altered DIC $\delta^{13}\text{C}$ values in both streams. In future, trials will be set up to investigate potential storage issues. As well, attempts will be made to capture short-term disturbances from monsoonal summer rains using more discrete and better-timed sampling trips.

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Literature Cited:
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Malusa J. et al. 2003. *Applied Geochemistry* 18:1081-1093.
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Site 1. Ephemeral pool above springs, Fossil Creek, Arizona

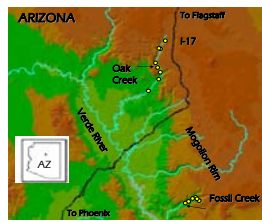


Figure 1. Map showing location of Oak Creek and Fossil Creek in central Arizona.

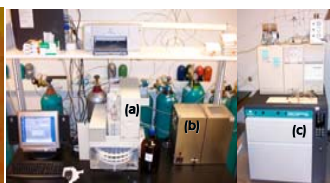


Figure 2. TOC-IRMS setup showing (a) TOC analyzer, (b) interface, and (c) IRMS.