

# Influence of Land Use on the Stable Carbon Isotopic Composition and Concentration of Dissolved Organic Carbon and Dissolved Inorganic Carbon in Georgia Piedmont Headwater Streams

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## Introduction

Headwater streams are the dominant land-water interface across much of the landscape and provide many important ecological services. Cycling and transport of various carbon fractions, which serve as important food sources for downstream aquatic ecosystems, are among the important functions of headwater streams. Dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) are two ecologically important carbon fractions.

The watershed of the South Fork Broad River (SFBR) on the Georgia piedmont has been heavily impacted by extensive agricultural development and rapid human population growth. Land application of organic wastes produced as a result of poultry and beef production to pastures has the potential to adversely impact stream water quality. Pasture grasses are typically a mixture of species using  $C_4$  (average stable carbon isotopic composition ( $\delta^{13}C$ ) = -27 ‰) and  $C_3$  (average  $\delta^{13}C$  = -12 ‰) photosynthetic pathways.

## Objective

Evaluate, and develop simple models to describe, the impact of land use on the concentrations and  $\delta^{13}C$  of DOC and DIC in headwater streams.

## Approach

Fifteen headwater watersheds with a wide range of land cover, and ranging in size from 0.9 to 3.2 km<sup>2</sup>, were selected for study (Figure 1). A set of twelve landscape indicators was developed from readily obtainable data bases. Land use in the watersheds and in stream buffers, which extend 90 m on both sides of each stream, were characterized with the National Land Cover Data (NLCD) database (USGS, 2007) (Figure 2). The USDA Web Soil Survey tool (USDA, 2007) and the Soil Survey Geographic (SSURGO) data set (Soil Survey Staff, 2006) were used to calculate soil organic carbon and clay stocks in the small watersheds.

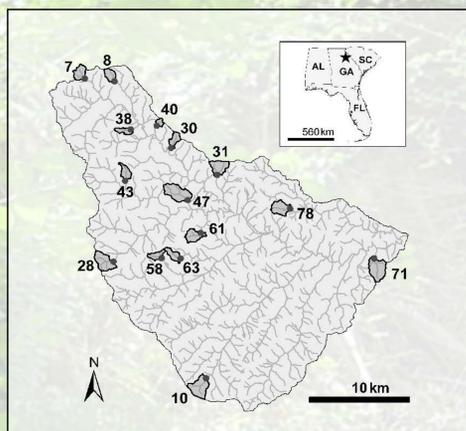


Figure 1. Location of sampling sites in the SFBR watershed

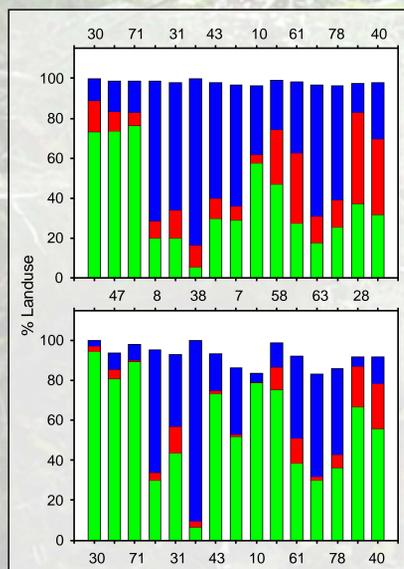


Figure 2. Land use in the SFBR watersheds and stream buffers in 2001 as determined with the NLCD database. Bar colors: Green – Forested, Red – Developed, and Blue – Pasture land cover

For this on-going study, water samples are collected on a monthly basis from well-mixed areas of the streams and filtered with GF/F syringe filters into VOA vials with either Teflon septa (DOC) or butyl septa (DIC).

Concentration and  $\delta^{13}C$  are determined with an OI Analytical 1030W total organic carbon (TOC) analyzer coupled to a Thermo Electron Delta V isotope ratio mass spectrometer (IRMS) using the high-ohmic resistor configuration of Osburn and St-Jean (2007).

Discharge (Q) is estimated by the current meter method.

Robust linear regression was used with the landscape indicators to develop empirical models that describe the measurements of concentration and stable isotopic composition of DOC and DIC made to date.

## Results

A substantial amount of the observed variability in the concentrations and  $\delta^{13}C$  of DOC and DIC in these streams is explained by empirical models using landscape indicators as independent variables (Table 1). Watershed pasture land cover (Wpas) is the single best descriptor of mean DOC concentration and  $\delta^{13}C$ -DOC (Figure 3). Watershed open water (Wwat) and watershed developed (Wdev) land cover are the best single descriptors of mean DIC concentration and  $\delta^{13}C$ -DIC, respectively (Figure 4). Descriptive capability was considerably improved (adj R<sup>2</sup> of 0.48 to 0.81) by inclusion of additional landscape indicators for all parameters except DOC concentration (Table 1).

Large variations in Q and the carbon parameters have been observed (Figures 5a and 5b).

**Table 1.** Robust linear regression analysis results (Huber function, t=2) for mean values of carbon parameters and landscape indicators at watershed and buffer scales (\* / p < 0.05; \*\* / p < 0.01; \*\*\* / p < 0.001). I – intercept; RC – regression coefficient; Xi – independent variable; AdjR<sup>2</sup> – adjusted R<sup>2</sup>; R<sup>2</sup><sub>pred</sub> – prediction R<sup>2</sup>. Wpas – watershed pasture land cover (%); Wwat – watershed open water (%); Bwat – stream buffer open water (%); Wfor – watershed forest land cover (%); Wdev – watershed developed land cover (%); Wclay – watershed soil clay content (Gg clay km<sup>-2</sup>)

	I	RC1	X1	RC2	X2	RC3	X3	R <sup>2</sup> <sub>pred</sub>	AdjR <sup>2</sup>
DOC (mg C L <sup>-1</sup> )	1.415	0.032	Wpas					0	0.55***
DIC (mg C L <sup>-1</sup> )	4.406	0.844	Wwat	-0.855	Bwat			0	0.26*
	4.186	4.456	Wwat					0	0.48***
$\delta^{13}C$ -DOC (‰)	-28.83	0.017	Wpas					0.52	0.61***
	-28.78	0.019	Wpas	-0.185	Wwat			0.64	0.71***
	-26.27	-0.020	Wfor	-0.263	Wwat	-0.0015	Wclay	0.74	0.81***
$\delta^{13}C$ -DIC (‰)	-15.26	-0.0591	Wdev					0.15	0.41**
	-21.53	0.077	Wfor	0.055	Wpas			0.30	0.56**

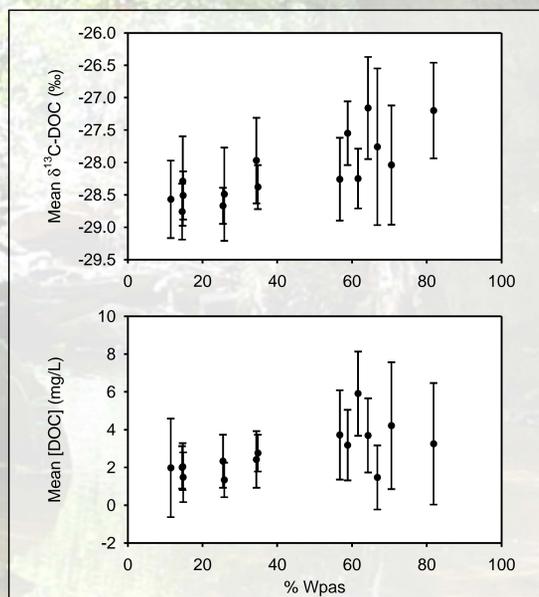


Figure 3. Mean  $\delta^{13}C$ -DOC and DOC concentration versus watershed pasture land cover (Wpas) in SFBR streams

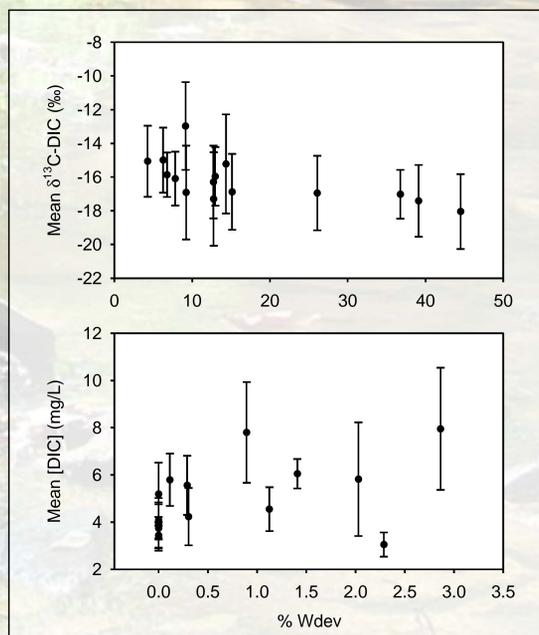


Figure 4. Mean  $\delta^{13}C$ -DIC versus watershed developed land cover (Wdev) and mean DIC concentration versus watershed open water land cover (Wwat) in SFBR streams

Mean DOC concentration and  $\delta^{13}C$ -DOC have generally increased with increasing Q in several of our sites (Figures 5a and 5b), as previously observed (Dalzell et al., 2006). The observed relationships between Q and mean DIC concentration and  $\delta^{13}C$ -DIC are more variable (Figures 5a and 5b) and suggest different controls on DIC in different streams.

Considering all of the watersheds together, no significant relationships between Q and any of these carbon parameters were observed. Significant positive (DOC concentration and  $\delta^{13}C$ -DOC) or negative (DIC concentration and  $\delta^{13}C$ -DIC) relationships with Q are observed in several of these streams (not shown), however.

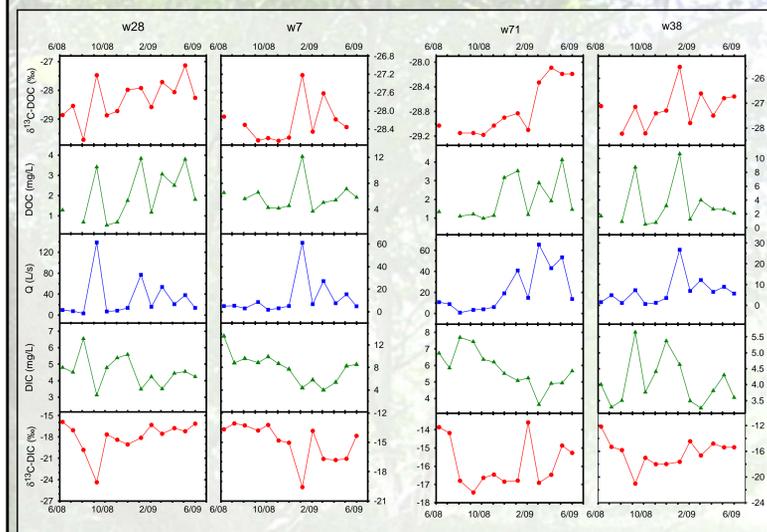


Figure 5.  $\delta^{13}C$ -DOC, DOC concentration, Q,  $\delta^{13}C$ -DIC, and DIC concentration versus sampling date in selected SFBR streams

## Discussion

Our results suggest that animal agriculture alters the source, concentration, and  $\delta^{13}C$  of DOC exported from impacted watersheds to receiving streams. The slight but significant  $\delta^{13}C$ -DOC increase with increasing watershed pasture land cover observed in this study likely reflects the increased importance of relatively <sup>13</sup>C-enriched organic wastes or  $C_4$  pasture grasses in watersheds impacted by poultry and cattle production. The positive correlation observed between Q and  $\delta^{13}C$ -DOC in many of these streams suggests the flushing of waste-derived or  $C_4$ -derived organic matter from shallow flow paths during storm events, and supports the hypothesis that DOC contributing areas vary depending on hydrograph stage (e.g., McGlynn and McDonnell (2003).

Important controls on  $\delta^{13}C$ -DIC in SFBR streams likely include the  $\delta^{13}C$  of watershed DIC sources, in-stream organic matter decomposition, and out-gassing of CO<sub>2</sub> to the atmosphere. Previous unpublished measurements found highly elevated dissolved CO<sub>2</sub> concentrations in these streams, which means it is likely that CO<sub>2</sub> out-gassing, which leaves the remaining DIC relatively <sup>13</sup>C-enriched (Doctor et al., 2008), is an important control of  $\delta^{13}C$ -DIC. The relatively negative  $\delta^{13}C$ -DIC and high DIC concentration observed during the 9/08 sampling in the w38 stream (Figure 5b) at relatively low flow likely result from in-stream organic matter decomposition. The relatively negative  $\delta^{13}C$ -DIC and low DIC concentrations observed during high flow conditions in the w28 stream during the 9/08 sampling and in the w7 stream during the 1/09 sampling likely reflect input of shallow soil water with low concentrations of relatively <sup>13</sup>C-depleted DIC (Doctor et al., 2008).

## References

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