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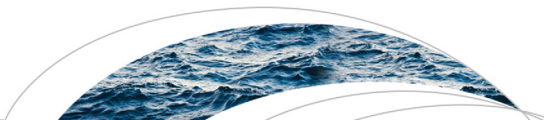
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### RESEARCH ARTICLE

10.1002/2016WR018970

## Variation of organic matter quantity and quality in streams at Critical Zone Observatory watersheds

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#### Key Points:

- Atmospheric, terrestrial, and aquatic ecosystem forcings interact to control DOM quantity and quality
- Collection of samples for DOM as part of monitoring programs provides an understanding of processes that influence stream water quality
- Analysis of DOM across gradients can only be conducted where errors linked to interinstrument comparisons do not play a large role

#### Supporting Information:

- Supporting Information S1

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**Abstract** The quantity and chemical composition of dissolved organic matter (DOM) in surface waters influence ecosystem processes and anthropogenic use of freshwater. However, despite the importance of understanding spatial and temporal patterns in DOM, measures of DOM quality are not routinely included as part of large-scale ecosystem monitoring programs and variations in analytical procedures can introduce artifacts. In this study, we used consistent sampling and analytical methods to meet the objective of defining variability in DOM quantity and quality and other measures of water quality in streamflow issuing from small forested watersheds located within five Critical Zone Observatory sites representing contrasting environmental conditions. Results show distinct separations among sites as a function of water quality constituents. Relationships among rates of atmospheric deposition, water quality conditions, and stream DOM quantity and quality are consistent with the notion that areas with relatively high rates of atmospheric nitrogen and sulfur deposition and high concentrations of divalent cations result in selective transport of DOM derived from microbial sources, including in-stream microbial phototrophs. We suggest that the critical zone as a whole strongly influences the origin, composition, and fate of DOM in streams. This study highlights the value of consistent DOM characterization methods included as part of long-term monitoring programs for improving our understanding of interactions among ecosystem processes as controls on DOM biogeochemistry.

### 1. Introduction

Water quality and aquatic ecosystems are strongly influenced by the quantity and chemical composition of dissolved organic matter (DOM). As a fundamental water quality characteristic of surface waters, DOM provides sources of carbon and energy for heterotrophic microorganisms [Fisher and Likens, 1973; Volk et al., 1997], fuels the food web in aquatic ecosystems [Meyer and Edwards, 1990; Roberts et al., 2007], affects light attenuation and photochemical processes in surface waters [Schindler et al., 1997; Scott et al., 2003; Cory et al., 2007], binds and transports aquatic trace elements [McKnight et al., 1992; Aiken et al., 2011; Yamashita and Jaffe, 2008; McIntyre and Gueguen, 2013], increases the solubility of organic pollutants [Chiou et al., 1986], and forms precursors for disinfection by-products that affect water treatment [Bergamaschi et al., 1999; Chow et al., 2003; Beggs et al., 2009; Kraus et al., 2011]. Further, inland waters play important roles as processors of organic matter derived from the landscape, as sinks and sources of atmospheric C, and in the delivery of organic matter to the oceans [Cole et al., 2007; Battin et al., 2008, 2009; Shih et al., 2010; Cory et al., 2014]. For example, it has been estimated that up to 1.4 of the 2.9 PgC/yr of terrestrially derived carbon that enters inland waters is processed and released to the atmosphere [Tranvik et al., 2009].

Research at Critical Zone Observatory (CZO) watersheds aims to understand coupled physical, chemical, and biological processes that shape the environment [White et al., 2015; Brantley et al., 2016], and site-

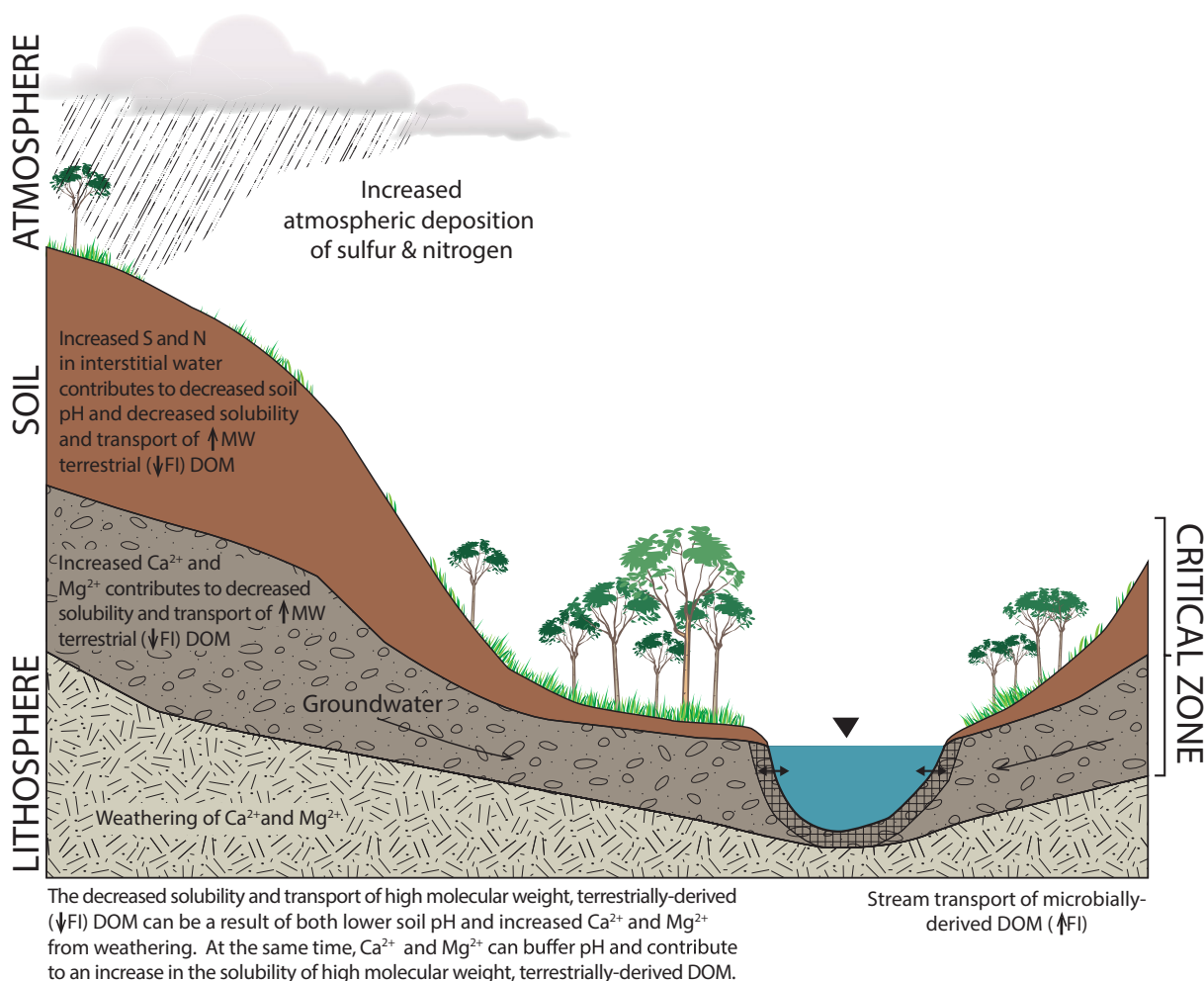
specific studies of DOM biogeochemistry are ongoing. Observed spatial and temporal variability in dissolved organic carbon (DOC) in the Shale Hills CZO watershed was reported to be indicative of flushing and biological controls on DOC export [Andrews *et al.*, 2011]. The source and redox state of water-soluble soil organic matter was shown to vary with soil horizon in the Boulder Creek CZO watershed, with more oxidized and microbially derived organic matter at greater depths [Gabor *et al.*, 2014]. In the same watershed, stream water DOM was observed to shift during the course of spring snowmelt from having higher contributions of amino acid-like fluorescence from groundwater to humic-like contributions from soil water [Burns *et al.*, 2016].

Notwithstanding the important insights gained from site-specific work, questions remain regarding understanding regional variation in DOM among watersheds. Measures of DOM quality are not routinely included as part of large-scale watershed monitoring programs and only a few comparisons have been made of the spectral properties of DOM over a wide range of aquatic ecosystems. One encouraging finding when considering cross-site comparisons of DOM is that Jaffe *et al.* [2008] showed that the results of spectroscopic analyses to quantify DOM quality were generally consistent across two laboratories analyzing the same broad set of samples, although a slight bias was found for more dilute samples. In addition, application of instrument specific correction factors has been shown to result in comparable fluorescence spectra allowing comparison of DOM properties collected on different analytical instruments, although the effectiveness of the correction varied by instrument [Jaffe *et al.*, 2008; Cory *et al.*, 2010].

The emphasis on quantifying and understanding patterns in DOM quality at the Boulder Creek site has set the stage for a broader, regional comparison of DOM quantity and quality among sites. Here our objective was to define the spatial variability in DOM quantity and quality among five forested CZO sites. We collected stream samples at regular intervals over 1 year from each of the sites, which are situated in a diversity of geologic and climatic settings across North America. To best facilitate characterization of DOM quality through spectral measurements; we used consistent sampling, storage, and laboratory analysis methods among the sites.

We use the cross-site DOM data collected in this study, along with information from published literature, to develop a conceptual model about ecosystem processes influencing surface water DOM at regional scales. For example, spatial variability in acidic atmospheric deposition that contributes to soil acidification and in-stream water quality data are interpreted in the context of a conceptual model presented below. Given the spatial extent of this study, specific ecosystem processes influencing DOM quantity and quality are not quantified. Rather, relationships between rates of atmospheric deposition and water quality conditions are interpreted in the context of processes identified in previous studies to provide a first look at the role of atmospheric sulfur (S) and nitrogen (N) deposition and calcium (Ca) and magnesium (Mg) concentrations as contributing to spatial variability in DOM composition among watersheds representing a diversity of environmental conditions. This approach provides a foundation from which detailed, site-specific studies can quantify temporally and spatially variable watershed processes.

There are many factors that might affect the regional variation of DOM. The pH and ionic strength of surface waters and catchment soils influence DOM solubility as well as the molecular weight distribution among the myriad organic molecules comprising DOM. Atmospheric deposition of S and N results in soil acidification and increased soil solution ionic strength. Following the implementation of the 1990 Title IV Amendment of the Clean Air Act, decreases in S deposition, most notably in the northeastern U.S., have been observed over time [Lynch *et al.*, 2000; Driscoll *et al.*, 2001]. Multiple studies have suggested alterations to soil pH and changes in soil solution ionic strength influence the transport of DOM to surface waters [Galloway, 1995; Monteith *et al.*, 2007; Evans *et al.*, 2008, 2012; Hruška *et al.*, 2009; Ekstrom *et al.*, 2011]. For example, through spectroscopic analysis of archived samples collected from lakes in the northeastern US as part of a long-term monitoring program, it has been shown that decreased atmospheric deposition of S resulted in increased release of terrestrially derived (as indicated by lower fluorescence index values) DOM from the catchment [SanClements *et al.*, 2012]. Similarly, Ekstrom *et al.*, [2011] showed that low S additions contributed to flushing of soil water DOM with higher molecular weight, greater aromaticity, and greater hydrophobicity, as compared to soil water DOM in high S addition treatments. In a pH-manipulation experiment of surface waters, DOM had a larger hydrodynamic diameter and absorbed more light at high pH as compared to under low pH conditions [Pace *et al.*, 2012]. The concentration of divalent cations such as Ca and Mg also influence DOM solubility and molecular weight. For example, Ca and Mg have been shown to neutralize charges on humic substances in soils, resulting in



**Figure 1.** Conceptual diagram showing relationships between inorganic constituents and DOM quality and transport in watersheds. Previous studies have identified atmospheric deposition of S and N and the presence of divalent cations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) as contributing to decreased solubility and transport of high molecular weight terrestrially derived (low FI) DOM. In turn, there is selective downstream transport of microbially derived DOM (high FI). While not an exhaustive list of processes that influence DOM quality and transport, these processes provide examples of drivers of critical zone function, including atmospheric, terrestrial, and aquatic ecosystem forcings that interact to influence stream water DOM.

decreased solubility of the humic fraction of the DOM [Hayes and Swift, 1978]. Aiken and Malcolm [1987] observed a suppression of the solubility of high molecular weight DOM by Ca and Mg in river ecosystems representing diverse sources of DOM.

A conceptual diagram of the potential relationships between atmospheric deposition, soil pH, divalent cation concentrations, and DOM quality and transport is presented in Figure 1. This diagram hypothesizes that increased atmospheric deposition of S and N contributes to soil acidification, which coupled with the presence of divalent cations, results in decreased solubility and transport of high molecular weight, more chromophoric fractions of terrestrially derived DOM to streams. The response of DOM quantity and quality to changes in soil pH driven by atmospheric deposition of S and N may occur over a longer time scale relative to the response to the presence of Ca and Mg, which may be more instantaneous. The aggregate effects of these processes result in selective downstream transport of DOM derived from microbial biomass in soils or from microbial phototrophs in streams. While these processes are important drivers of DOM quality and transport, it is important to note that many other processes, not represented in this diagram also influence the concentration and composition or chemical quality of DOM in aquatic ecosystems. These include climatic conditions, hydrological flow paths, rates of primary productivity, photochemical processes, soil type, and geology [Cory et al., 2007; Miller et al., 2009; Fellman et al., 2010; Inamdar et al., 2011, 2012; Helton et al., 2015; Parr et al., 2015].

## 2. Materials and Methods

### 2.1. Sample Sites and Sample Collection

Five upland streams that drain small forested watersheds (Table 1 and Figure S1) situated within Critical Zone Observatories [White *et al.*, 2015] are the focus of this study, as further described in Supporting Information. Surface water samples were collected from each stream during nonstormflow conditions at approximately monthly intervals for a 1 year period beginning in spring/summer 2009. Only four of the monthly samples from the Boulder Creek site were analyzed for spectroscopic properties due to high iron (Fe) concentrations (>0.5 mg/L) in many of the samples which did not render them appropriate for spectral measurements (details provided below). These five CZO watersheds represent a diversity of biomes, ranging from a low elevation tropical site to high elevation, subalpine sites, and fall along a gradient of atmospheric deposition of S and N. Annual atmospheric wet and dry deposition of S and inorganic N data during 2009 were obtained from the nearest National Atmospheric Deposition Program National trends Network sampling locations (NADP-NTN; <http://nadp.sws.uiuc.edu/ntn/>) for wet deposition, and the Environmental Protection Agency Clean Air Status and Trends Network (CASTNET; <http://www2.epa.gov/castnet>) for dry deposition. Dry deposition data were not available for the Luquillo site. Total (wet + dry) S deposition rates were low (~35 Mol/ha/yr) at the Southern Sierra and Boulder Creek sites, compared with higher rates of S deposition at the other three sites (~220–270 Mol/ha/yr; Table 1). Total N deposition rates were also low at the Southern Sierra (286 Mol/ha/yr) and Boulder Creek (180 Mol/ha/yr) sites, as well as at the Luquillo site (150 Mol/ha/yr – wet deposition only), relative to the Shale Hills (403 Mol/ha/yr) and Christina River (496 Mol/ha/yr) sites. Details on the locations of atmospheric deposition monitoring stations are provided in Table S1 of Supporting Information.

All water samples were collected in precombusted 250 ml amber glass bottles, kept cold, and shipped immediately to the Pennsylvania State University for laboratory analyses. Upon arrival, approximately 100 ml were filtered through 0.7 μm, 47 mm precombusted Whatman GF/F glass fiber filters, and the filtrate was stored at 4°C until analyses. Filtration in the laboratory—as opposed to in the field—allowed for consistency in the staff, filtering approach, and filter types used among sites. All samples were analyzed for DOC as a measure of DOM concentration, and spectral absorbance and fluorescence as measures of organic matter composition. Samples were also analyzed for other parameters, including total dissolved Ca, Mg, Fe, S, and N.

**Table 1.** Watershed Characteristics for the Five CZO Study Sites (ND = No Data)

CZO Location	Drainage Area (km <sup>2</sup> )	Elevation Range (m)	Annual Mean Discharge (m <sup>3</sup> /s)	Mean Annual Precipitation (mm/yr)	Mean Annual Temperature (°C)	Dominant Vegetation	Bedrock	Atmospheric Inorganic Nitrogen Wet/Dry Deposition (Mol/ha/yr)	Atmospheric Sulfur Wet/Dry Deposition (Mol/ha/yr)	References
Southern Sierra, CA	1.0	1790–2115	0.007	1450	8.6	Oak, pine, mixed conifers	Granite, Granodiorite	234/38	31/5	Johnson <i>et al.</i> [2011], Hunsaker <i>et al.</i> [2012a], Hunsaker and Neary [2012b], Riebe and Granger [2013], Hahn <i>et al.</i> [2014], <a href="http://criticalzone.org/sierra/data/">http://criticalzone.org/sierra/data/</a>
Boulder Creek, CO	2.6	2446–2737	0.02	519	5.1	Pine, mixed conifer	Granodiorite, biotite gneiss	141/39	28/6	Anderson <i>et al.</i> [2011], Gabor <i>et al.</i> [2014], <a href="http://criticalzone.org/boulder/data/">http://criticalzone.org/boulder/data/</a>
Shale Hills, PA	0.08	256–310	0.001	1050	9.5	Deciduous and evergreen	Shale	299/104	140/128	Jin <i>et al.</i> [2011], West <i>et al.</i> [2013], <a href="http://criticalzone.org/shale-hills/data/">http://criticalzone.org/shale-hills/data/</a>
Christina River, DE	0.12	77–108	ND	1205	12	Mixed deciduous	Pelitic gneiss and schist	376/120	136/83	Inamdar <i>et al.</i> [2011, 2012], <a href="http://metosrv2.umd.edu/~climate/">http://metosrv2.umd.edu/~climate/</a>
Luquillo, PR	2.6	375–1050	0.29	4380	24	Tropical	Basalt, volcaniclastics	150/ND	247/ND	McDowell and Asbury [1994], <a href="http://luq.lternet.edu/">http://luq.lternet.edu/</a>

## 2.2. Laboratory Methods

All water quality samples collected from the CZO sites were analyzed at the Pennsylvania State University. Concentrations of DOC and total dissolved N (TDN) were measured using a Shimadzu TOC-VCPH high-temperature carbon/N analyzer in the Department of Ecosystem Science and Management Water Quality Lab, using the catalytic oxidation/NDIR method (for DOC) and chemiluminescence method (for N), following methods for DOC analyses put forth by the US Geological Survey [Bird *et al.*, 2003]. The detection limits for DOC were 0.015 mgC/L, and for TDN were 0.015 mgN/L. C : N was calculated as the ratio of DOC to TDN concentration. Concentrations of total dissolved Ca, Mg, Fe, and S were analyzed via inductively coupled plasma atomic emission spectroscopy at Pennsylvania State's Agricultural Analytical Services Lab. Fe is a strong absorber and was analyzed to screen for samples where high iron concentrations may interfere with spectral analysis (described below).

Absorbance spectra were measured on a Shimadzu UV-1800 UV-Visible spectrophotometer in the Department of Ecosystem Science and Management Water Quality Lab at the Pennsylvania State University. Absorbance was measured every 1 nm from 190 nm to 1100 nm using a 3 ml quartz cuvette with a 1 cm path length. Specific ultraviolet absorbance ( $SUVA_{254}$ ) was calculated as the ratio of the decadic absorption coefficient at 254 nm to the DOC concentration [Weishaar *et al.*, 2003]. Aromaticity of DOC increases as  $SUVA_{254}$  values increase. Innerfilter corrections are inadequate for removing innerfilter effects that occur during the collection of fluorescence spectra of highly absorbing samples [Ohno, 2002; Miller *et al.*, 2010]. Therefore, highly absorbing samples were diluted such that absorbance at 254 nm was less than 0.2 prior to fluorescence analyses. Similarly, high Fe concentrations can influence absorbance, and subsequently fluorescence measurements [Weishaar *et al.*, 2003; Poulin *et al.*, 2014], and samples with Fe concentrations greater than 0.5 mg/L were not analyzed for absorbance or fluorescence.

Three-dimensional fluorescence spectra were measured using a Fluoromax-4 fluorometer in a 1 cm path length quartz cuvette in the Department of Ecosystem Science and Management Water Quality Lab at the Pennsylvania State University. Emission scans of quinine sulfate were collected monthly and instrument-corrected using the instrument-specific emission correction file. The corrected scan was compared with the National Institute of Standards and Technology (NIST) reference spectra for quinine sulfate to verify the effectiveness of the instrument-specific emission correction file in removing instrument bias. A lamp scan, cuvette check, and water Raman scan were collected daily to ensure stable instrument function. Blank (deionized water) and sample scans were collected in ratio (S/R) mode, bandwidth was 5 nm for excitation and emission, and spectra were collected over an excitation range of 240–450 nm, at a 10 nm interval, and an emission range of 300–600 nm, at a 2 nm interval. Fluorescence spectra were corrected in Matlab following the recommendations of Cory *et al.*, [2010] as follows: water Raman scans, blanks, and samples were instrument corrected using the instrument-specific excitation and emission correction files, samples were innerfilter corrected [McKnight *et al.*, 2001], samples and blanks were normalized to the area under the water Raman curve, and samples were blank subtracted. Fluorescence spectra of Pony Lake fulvic acid and Suwannee River fulvic acid, which are available from the International Humic Substances Society (IHSS; <http://www.humicsubstances.org/>), and serve as microbial and terrestrial end-member fulvic acids, respectively, were collected and corrected as described above on a monthly basis to ensure that the spectra were invariant over time and similar to those reported by Cory *et al.* [2010].

Fluorescence index (FI) values were calculated as the ratio of the fluorescence intensity at an emission of 470 nm to the intensity at 520 nm at an excitation wavelength of 370 nm [McKnight *et al.*, 2001; Cory *et al.*, 2010]. Larger FI values are indicative of DOM derived from a variety of microbial sources including heterotrophic activity in soils and benthic or planktonic microbial sources which are autochthonous sources to surface waters (hereafter "microbially derived" DOM); whereas lower values are indicative of DOM derived from vascular plant material and soils which are allochthonous sources to surface waters (hereafter "terrestrially derived" DOM). Corrected excitation emission matrices (EEMs) were fit to the 13 component Cory and McKnight [2005] parallel factor analysis (PARAFAC) model. Fitting EEMs to this existing PARAFAC model enables the resolution of a more diverse suite of fluorescence components than may be possible by building a PARAFAC model unique to these study sites which may have limited variation. The presence of fluorescent components in the sample EEMs not captured by the diversity of components in the Cory and McKnight [2005] model would be expected to appear as peaks in residual EEMs [Cawley *et al.*, 2012]. PARAFAC model fit was assessed by investigation of residual EEMs (i.e., the difference between the measured and PARAFAC

modeled EEMs). Samples with residual EEMs that had absolute values of fluorescence intensities less than 10% of measured intensities were determined to be fit well by the model [Mladenov *et al.*, 2008], and were retained for further analyses. Two of the 69 samples fit to the PARAFAC model had residuals with intensities greater than 10% of measured intensities, and were not retained for further analyses. The percent amino acid-like and quinone-like fluorescence was calculated as the sum of Fmax values, as percents, of components 8 and 13 (amino acid-like fluorophores) and components 2, 4, 5, 7, 9, 11, and 12 (quinone-like fluorophores).

### 2.3. Statistical Analyses

The nonparametric Wilcoxon rank-sum test [Wilcoxon, 1945] was used to compare differences in concentrations of Ca, Mg, S, DOC, and TDN, as well as C : N, SUVA<sub>254</sub>, FI, %amino acid-like fluorescence, and %quinone-like fluorescence among each of the five stream sites. To identify the relative importance of water quality variables among CZO stream sites, a principal components analysis (PCA) was run on DOC, TDN, Ca, Mg, and S concentration data, C : N, SUVA<sub>254</sub>, and FI, values, and %amino acid-like and %quinone-like fluorescence using the PRIMER package [Clarke and Gorley, 2006]. All data were fourth-root transformed and standardized to a mean of zero and standard deviation of one to down-weight the influence of water quality variables with high absolute values [Clarke and Warwick, 2001]. Linear regression analyses between total (wet + dry) combined S and N deposition and average DOC and FI were used to represent the longer time scale response of DOM quantity and quality to atmospheric deposition of S and N. The rationale for combining S and N deposition is that the relevance of these constituents to DOM biogeochemistry in this study is as an acid. In contrast to the longer time scale response of DOM quantity and quality to atmospheric deposition of S and N, DOM response to stream chemistry is expected to occur over shorter time scales. For this reason, linear regression analyses including all samples collected at each site (as opposed to average values) were used to assess the relationships between DOM quantity and quality and the combined molar concentrations of Ca and Mg. Similar to the rationale described above for combining S and N deposition, Ca and Mg were combined given that they are expected to impact DOM biogeochemistry in the same way.

## 3. Results

### 3.1. Spatial Variability in Water Quality

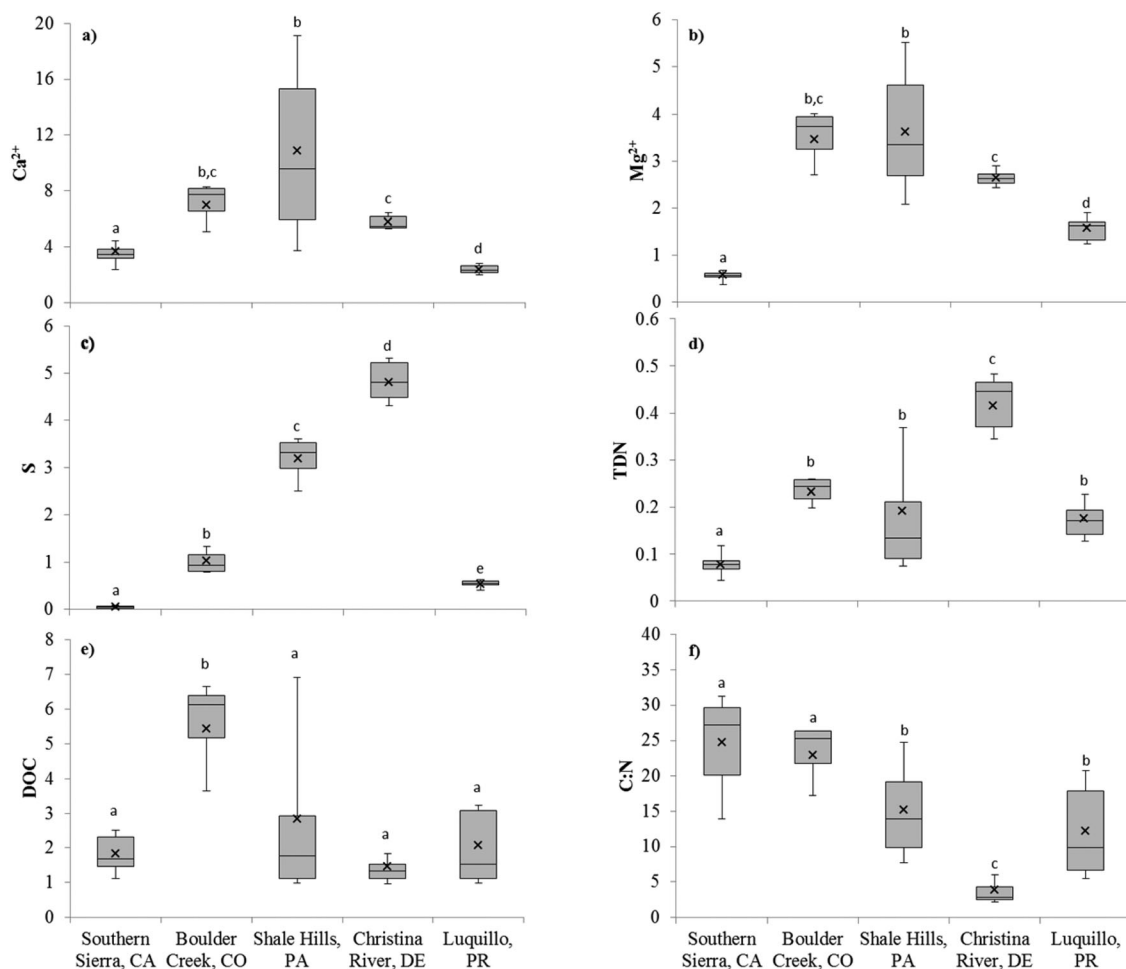
Concentrations of Ca and Mg had nearly identical relative patterns among sites (Figures 2a and 2b). Ca and Mg were highest at the Shale Hills site (average concentrations of  $10.9 \pm 6.1$  and  $3.6 \pm 1.3$  mg/L, respectively); followed by the Boulder Creek and Christina River sites. The Luquillo and Southern Sierra sites had the lowest Ca and Mg concentrations. S concentrations increased about 2 orders of magnitude along a west to east gradient for the four sites in the continental U.S. (Southern Sierra, Boulder Creek, Shale Hills, Christina River; Figure 2c).

S concentrations were lowest at the Southern Sierra site (average of  $0.05 \pm 0.03$  mg/L), followed by Luquillo (average of  $0.5 \pm 0.1$  mg/L), Boulder Creek (average of  $1.0 \pm 0.3$  mg/L), Shale Hills (average of  $3.2 \pm 0.5$  mg/L), and Christina River (average  $4.8 \pm 0.5$  mg/L, Figure 2c). A weaker, but similar pattern was observed for TDN concentrations (Figure 2d). TDN concentrations were significantly greater at the Christina River site (average of  $0.42 \pm 0.08$  mg/L) compared with the other sites. The Boulder Creek, Shale Hills, and Luquillo sites had intermediate TDN concentrations (averages of  $0.23 \pm 0.03$ ,  $0.19 \pm 0.16$ , and  $0.18 \pm 0.05$  mg/L, respectively) and there were no statistically significant differences among these three sites. The Southern Sierra site had significantly lower concentrations of TDN (average of  $0.08 \pm 0.03$  mg/L) compared with the other sites.

Average DOC concentrations ranged from  $1.5 \pm 0.6$  mg/L at the Christina River site to  $5.4 \pm 1.9$  mg/L at the Boulder Creek site (Figure 2e). DOC concentrations were significantly greater at the Boulder Creek site compared with the other four sites, among which there were no statistically significant differences. The Southern Sierra and Boulder Creek sites had significantly greater C : N ratios (averages of  $24.6 \pm 7.0$  and  $22.8 \pm 5.8$ , respectively) compared with the other sites (Figure 2f). These high ratios were driven by low TDN concentrations at the Southern Sierra site and high DOC concentrations at the Boulder Creek site. The Shale Hills and Luquillo sites had intermediate C : N ratios (averages of  $15.1 \pm 6.5$  and  $12.1 \pm 6.6$ , respectively), which were significantly greater than the C : N ratios at the Christina River site (average of  $3.8 \pm 2.2$ ).

There was little among-site variability in the aromaticity of the DOC. Average SUVA<sub>254</sub> values ranged from  $3.6 \pm 0.8$  L/mgC\*m at the Christina River site to  $4.3 \pm 1.0$  L/mgC\*m at the Luquillo site (Figure 3a), and there

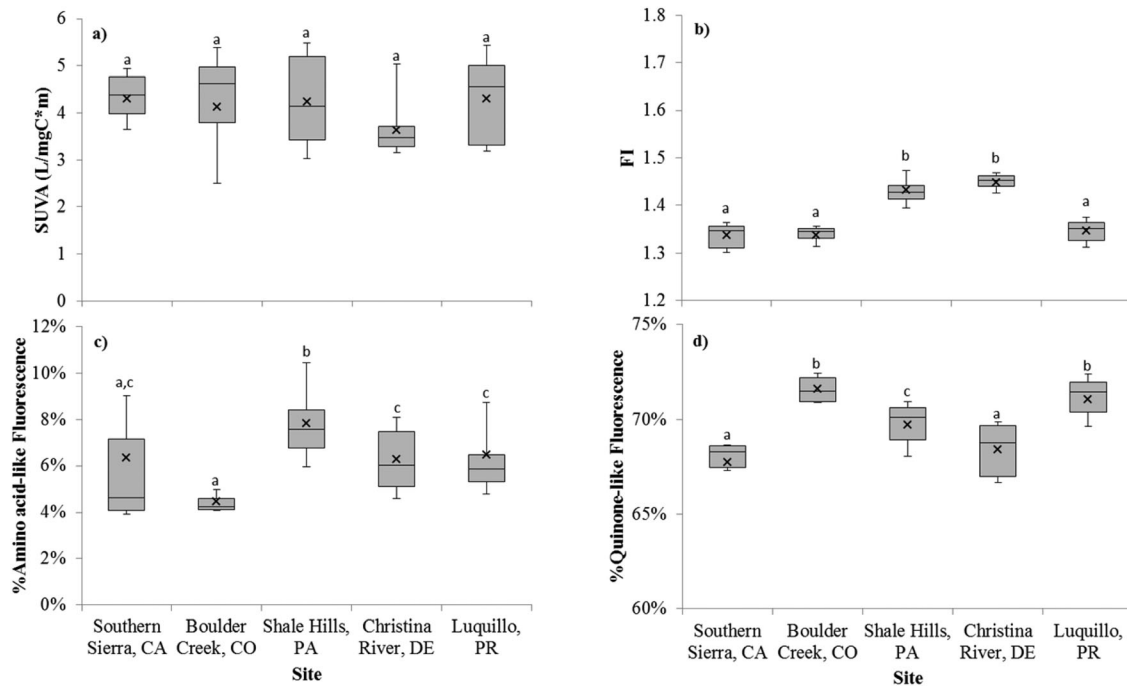




**Figure 2.** Box plots for (a) calcium, (b) magnesium, (c) sulfur, (d) total dissolve nitrogen, (e) dissolved organic carbon, and (f) the ratio of carbon to nitrogen. All concentrations are in mg/L. Horizontal lines represent median values, crosses represent average values, boxes represent the 25th and 75th percentiles and error bars represent the 10th and 90th percentiles. Statistically significant differences among sites are indicated by lower case letters ( $p < 0.05$ ).

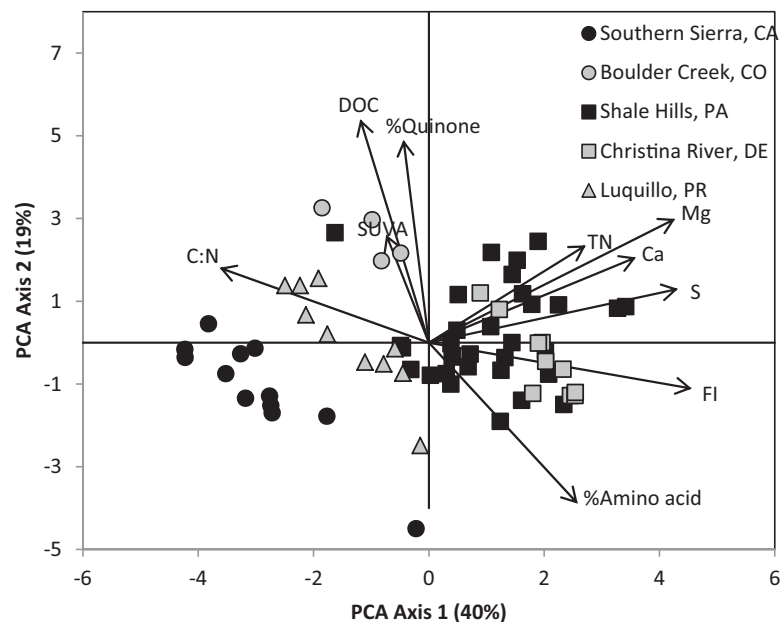
were no significant differences in  $SUVA_{254}$  values among sites. FI values were greatest at the Shale Hills and Christina River sites (averages of  $1.43 \pm 0.04$  and  $1.45 \pm 0.02$ , respectively), indicating a source of microbially derived DOM compared with the other sites which had lower FI values, reflective of dominant sources of terrestrially derived DOM (Figure 3b). FI values at the Southern Sierra (average of  $1.34 \pm 0.03$ ), Boulder Creek ( $1.34 \pm 0.03$ ), and Luquillo ( $1.35 \pm 0.03$ ) sites were significantly less than the FI values at the Shale Hills and Christina River sites by approximately 0.1 units, which is generally indicative of a difference in DOM source [McKnight *et al.*, 2001]. The percent of amino acid-like fluorescence was lowest at the Boulder Creek site (average  $4 \pm 1\%$ ) and greatest at the Shale Hills site (average of  $8 \pm 2\%$ ; Figure 3c). The other sites had intermediate average percent contributions of amino acid-like fluorescence ( $6 \pm 4\%$  at the Southern Sierra site, and  $6 \pm 2\%$  at the Christina River and Luquillo sites). The percent of quinone-like fluorescence was greatest at the Boulder Creek and Luquillo sites (averages of  $72 \pm 1\%$  and  $71 \pm 1\%$ , respectively), intermediate at the Shale Hills site (average of  $70 \pm 1\%$ ), and lowest at the Southern Sierra and Christina River sites (averages of  $68 \pm 2\%$  and  $68 \pm 1\%$ , respectively).

There were clear differences in the PCA scores among the five study sites (Figure 4). The first and second axes of the PCA accounted for 40 and 19%, respectively, of the variance in water quality conditions. Despite the fact that only 59% of the variance in the data is explained by these two axes, the PCA results show that sites tend to group together in the PCA plot. All of the Southern Sierra samples had negative scores on axis 1 and negative or slightly positive scores on axis 2, and were inversely related to Ca, Mg, TDN, and S. The Boulder Creek samples also had negative scores on axis 1, but positive scores on axis 2, where there were



**Figure 3.** Box plots for (a) specific ultraviolet absorbance at 254 nm, (b) the fluorescence index, (c) percent of amino acid-like fluorescence, and (d) percent of quinone-like fluorescence. Horizontal lines represent median values, crosses represent average values, boxes represent the 25th and 75th percentiles and error bars represent the 10th and 90th percentiles. Statistically significant differences among sites are indicated by lower case letters ( $p < 0.05$ ).

strong positive weightings of DOC, SUVA, and %quinone-like fluorescence. Shale Hills and Christina River samples had positive scores on axis 1 and both positive and negative scores on axis 2, and were positively related to Mg, Ca, S, TDN, FI, and %amino acid-like fluorescence, and negatively related to C : N. The Luquillo samples had negative scores on axis 1 and both positive and negative scores on axis 2, and were positively related to C : N, but inversely related to FI and % amino acid-like fluorescence. Those sites with negative



**Figure 4.** Principal components analysis (PCA) scores for the 10 water quality variables included in the study. Arrows represent the weighting and direction of eigenvectors for each water quality variable.

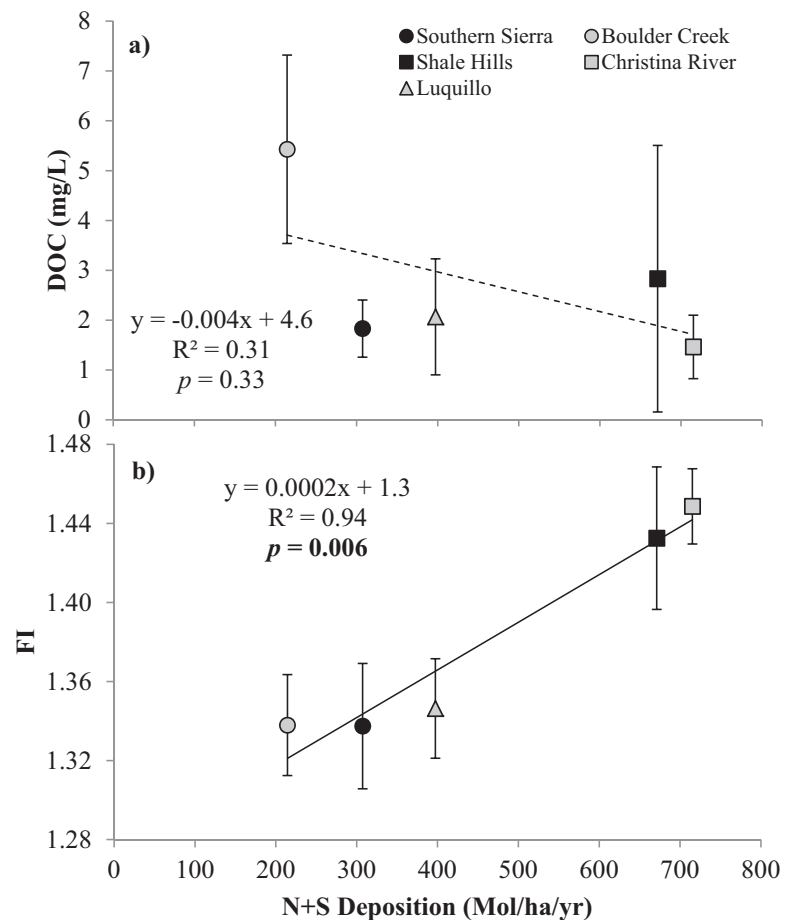
axis 1 scores—Southern Sierra, Boulder Creek, and Luquillo—are sites that had low rates of atmospheric N deposition (Table 1).

### 3.2. Relations Between Atmospheric Deposition of S and N and DOC Quantity and Quality

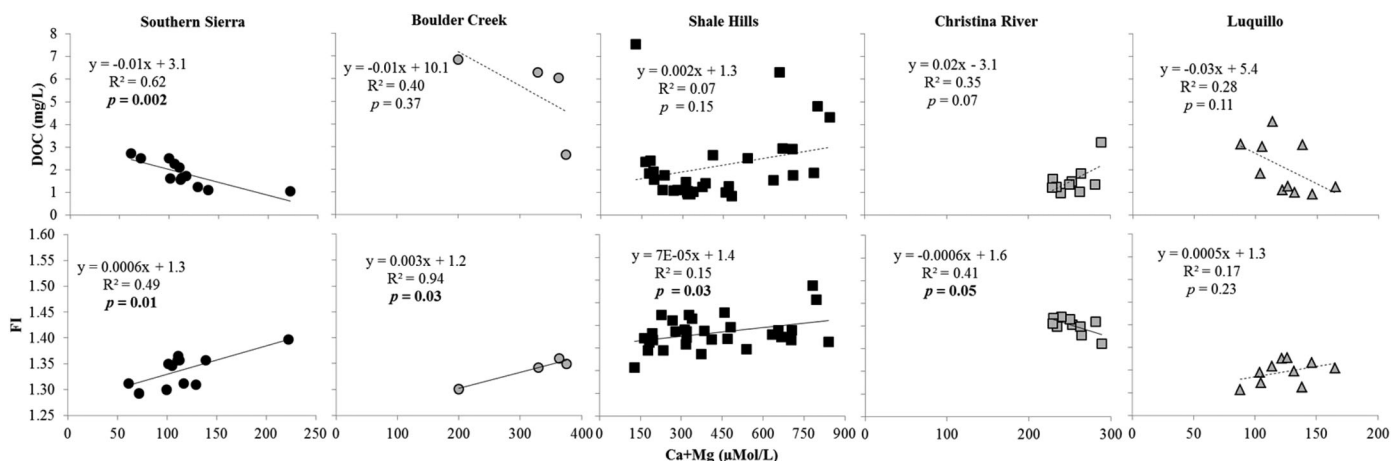
To represent the response of DOM quantity and quality to soil acidification driven by atmospheric deposition of S and N, which is expected to occur over years to decades, the relationships between total (wet + dry) combined annual S and N deposition and DOC and FI were investigated (Figure 5). DOC was generally lower at sites with higher rates of combined S and N deposition, although the relationship is statistically insignificant ( $p = 0.30$ ). The exception to this pattern is the Southern Sierra site, where there was a low deposition rate and low average DOC concentration. Deviation from the inverse relationship between atmospheric deposition of S and N and DOC may be driven by watershed characteristics such as low soil organic matter content limiting the supply of DOC and/or sorption of S to DOM or trace metals. In contrast, FI was generally greater at sites with higher rates of deposition ( $p = 0.006$ ). This indicates that a greater fraction of stream water DOM was microbially derived at sites with high rates of S and N deposition.

### 3.3. Relations Between Divalent Cations and DOC Quantity and Quality

In contrast to the longer time scale response of DOM quantity and quality to soil acidification driven by atmospheric deposition of S and N, DOM response to stream chemistry, in particular Ca and Mg, is expected to occur over shorter time scales. For this reason, all samples collected at each site (as opposed to average values) were used to assess the relationship between DOM quantity and quality and combined concentrations of Ca and Mg (Figure 6). DOC was inversely related to Ca+Mg and positively related to FI at the Southern Sierra ( $p = 0.002$  for DOC and  $p = 0.01$  for FI), Boulder Creek ( $p = 0.37$  for DOC and  $p = 0.03$  for FI), and



**Figure 5.** Plots of total (wet + dry) N and S deposition versus average (a) DOC and (b) fluorescence index (FI). Error bars represent one standard deviation. Solid lines of best fit represent statistically significant relationships ( $p < 0.05$ ), whereas dashed lines of best fit represent nonstatistically significant relationships. Note that only wet deposition data are available for the Luquillo site.



**Figure 6.** Plots of calcium and magnesium versus DOC concentration and fluorescence index (FI) for all samples from each site. Solid lines of best fit represent statistically significant relationships ( $p < 0.05$ ), whereas dashed lines of best fit represent nonstatistically significant relationships. Note the variable ranges on the x axes.

Luquillo ( $p = 0.11$  for DOC and  $p = 0.23$  for FI) sites, indicating a greater contribution of microbially derived DOM during times of greater Ca + Mg concentrations. Ca + Mg was positively related to DOC at the Shale Hills ( $p = 0.15$ ) and Christina River ( $p = 0.07$ ) sites, while Ca + Mg was positively related to FI at Shale Hills ( $p = 0.03$ ) and negatively related to FI at the Christina River ( $p = 0.05$ ). The range in Ca + Mg concentrations at the Shale Hills site was greater than the ranges observed at the other four sites, with peak concentrations twice that seen at the other sites. This may be a reflection of the greater solubility of the underlying Shale bedrock at the Shale Hills site (Table 1). It is also possible that buffering capacity at this site was high enough to maintain neutral to basic pH.

## 4. Discussion

### 4.1. Among-Site Variation in Stream Water DOM Quantity and Quality

This analysis of water quality conditions and relations among water quality constituents observed at five CZO sites provide insights into the role of overall drivers of critical zone function, including atmospheric, terrestrial, and aquatic ecosystem forcings. Streams occupy a relatively small area compared to the non-aquatic compartments of a watershed (e.g., atmosphere, soil, terrestrial vegetation, and underlying geology). However, because they are at the lowest point in watersheds, surface waters serve as excellent integrators and indicators of processes taking place in other watershed compartments [Williamson *et al.*, 2008]. For example, in-stream S and TDN concentrations may be reflective of atmospheric deposition and/or terrestrial and aquatic biogeochemical processes, whereas the variability in Ca and Mg concentrations among sites are likely indicative of differences in lithology and weathering processes. Among-site variation in deposition rates and biogeochemical and weathering processes directly influence the concentrations of these inorganic constituents; which in turn, can control the source and quality of DOM (Figure 1).

Patterns in stream water N and S concentrations may reflect regional differences in rates of atmospheric deposition and watershed retention. For example, the discrepancy between relatively high rates of atmospheric N deposition (272 Mol/ha/yr at Southern Sierra and 404 Mol/ha/yr at Shale Hills; Table 1) and low stream water TDN concentrations (average of 0.08 mg/L at Southern Sierra and 0.19 mg/L at Shale Hills; Figure 2d) at the Southern Sierra and Shale Hills sites suggests that watershed retention of N may be a dominant control on stream water quality at these sites. Of the water quality constituents investigated, average S concentrations had the greatest range among sites—Southern Sierra (0.05 mg/L), Boulder Creek (1.02 mg/L), Shale Hills (3.19 mg/L), Christina River (4.81 mg/L), and Luquillo (0.54 mg/L) (Figure 2c). The increase in S concentrations along a west-east gradient for the four sites in the continental US is related to regional differences in rates of atmospheric sulfate deposition, with total sulfate deposition rates during 2009 of 36, 34, 368, and 219 Mol/ha/yr at the Southern Sierra, Boulder Creek, Shale Hills, and Christina River sites, respectively (Table 1). The Luquillo site, which had low in-stream S concentrations (average of 0.54 mg/L), had a 2009 wet deposition rate of 247 Mol/ha/yr. This discrepancy between the high deposition rate and low in-

stream concentrations at the Luquillo site indicates that the atmospherically deposited sulfate may be retained in the terrestrial environment. The nonconservative nature of sulfate at Luquillo is consistent with previous investigations of the fate of atmospherically deposited sulfate in a Puerto Rican watershed [McDowell and Asbury, 1994; Peters *et al.*, 2006]. Potential processes contributing to these observed patterns include sorption to DOM or to weathering-derived aluminum and iron oxides [Shanley, 1992].

Analysis of among-site variation in stream water quality identifies the two sites in the northeastern US as being distinct from the other sites. PCA results show that the DOM at the Shale Hills and Christina River sites has a higher proportion of microbially derived DOM, a high contribution of amino acid-like fluorescence, and low C : N. Soil and surface waters with high amino acid-like fluorescence and low C : N have been shown to be positively correlated with bioavailable DOC [Fellman *et al.*, 2008, 2009; Hood *et al.*, 2009; Petrone *et al.*, 2011]. The low C : N ratios at the northeastern sites, possibly driven by higher rates of atmospheric N deposition (Table 1), suggest that the microbially derived DOM may be more bioavailable, as low C : N ratios have been shown to support higher bacterial growth efficiencies [Hunt *et al.*, 2000]. In turn, the bioavailability of surface water DOM influences energy transfer through the aquatic food web.

#### 4.2. Atmospheric Deposition and Ca and Mg as Controls on DOM Quantity and Quality

The negative correlations between atmospheric deposition of S and N and DOC concentration and positive correlations between S and N and FI (Figure 5) provide further insight into DOM processing in terrestrial compartments of watersheds. Specifically, these results suggest that sites with high rates of atmospheric S and N deposition tend to have lower concentrations of DOC, with relatively more microbially derived DOC than sites with lower rates of atmospheric deposition, which have higher DOC concentrations and more terrestrially derived DOC. This cross-site pattern is consistent with the within-site trends of increased delivery of terrestrially derived DOC to surface waters in Maine in response to declining rates of atmospheric sulfate deposition reported by SanClements *et al.* [2012]. While our results do not provide a picture of temporal change in atmospheric deposition-DOM dynamics, they do suggest that the same atmospheric deposition and watershed biogeochemical processes shown to influence temporal variability in DOM reported by SanClements *et al.* [2012] may underlie or contribute to regional differences in water quality patterns among CZO sites.

In addition to highlighting the potential importance of regional differences in atmospheric deposition-DOM dynamics, this study also identifies divalent cations as potentially important controls on organic matter stream chemistry. Previous investigations have demonstrated that divalent cations act to suppress the solubility of high molecular weight DOM [Aiken and Malcolm, 1987; Hayes and Swift, 1978]. The observed negative relationship between Ca + Mg and DOC and positive relationship between Ca + Mg and FI at the Southern Sierra, Boulder Creek, and Luquillo sites (Figure 6) is consistent with the conceptual diagram presented in Figure 1. That is, the presence of Ca and Mg results in a decrease of the solubility and transport of terrestrially derived DOM, and the selective transport of microbially derived DOM in surface waters. This result is also consistent with previous studies that have demonstrated that terrestrially derived DOM is generally composed of higher molecular weight DOM than DOM derived from microbial phototrophs [McKnight *et al.*, 2001]. There was also a weak positive relationship between Ca + Mg and FI at Shale Hills. However, at both this site and the Christina River site there were positive relationships between Ca + Mg and DOC. These two sites have significantly greater FI values than the other three sites (Figure 3), suggesting that much of the DOC is microbially derived, and thus less likely to be influenced by terrestrial processes, as compared to the other sites that have a greater proportion of terrestrially derived DOM.

#### 4.3. Future Applications and Recommendations

Processes impacting stream water DOM characteristics are varied and complex, and despite the fact that our observed relationships between atmospheric S and N deposition, Ca and Mg concentrations, and DOM quantity and quality are consistent with previous studies linking DOM response to atmospheric deposition and divalent cation concentrations (Figure 1), we acknowledge that other processes play a role. For example, time-variable streamflow has been shown to influence DOM quantity and quality [Hood *et al.*, 2006; Inamdar and Mitchell, 2006; Sebestyen *et al.*, 2008; Perdrial *et al.*, 2014; Bellmore *et al.*, 2015]. While the effects of hydrology on stream water quality cannot be ruled out, many of the effects of time-variable discharge on stream water quality were accounted for by collecting samples during nonstormflow conditions. Other processes that have been shown to contribute to variability in DOM biogeochemistry include microbial

processing of DOM [Wickland *et al.*, 2007], primary productivity [Stedmon and Markager, 2005; Miller *et al.*, 2009], and photochemical alteration of DOM [Cory *et al.*, 2007, 2014]. Groundwater residence times can also affect DOM quantity and quality. For example, it has been suggested that aromatic and humic DOM moieties are removed as water passes through the subsurface environment at the Christina River site [Inamdar *et al.*, 2011, 2012], and humic-like aromatic DOM decreased while labile DOM increased with increased residence time in an alluvial aquifer in Montana [Helton *et al.*, 2015]. The relative influence of independent effects of groundwater residence times on DOM and the selective transport of microbially derived DOM due to atmospheric deposition of S and N or the presence Ca and Mg warrants further attention. While we were not able to account for all possible processes contributing to within-site temporal variability in DOM quantity and quality, the observed relationships reported here demonstrate the utility of incorporating measures of DOM quality, obtained using consistent laboratory methods, into monitoring programs such as the CZO.

Ongoing changes in environmental conditions such as climate and land use have direct impacts on water quality conditions, including DOM quantity and quality; which in turn have implications for providing a safe supply of water for growing human populations. Therefore, there is an urgent need to understand ecosystem processes that interact to control DOM in surface waters. We demonstrate that the inclusion of regular measures of DOM quantity and quality as part of monitoring programs can be used to identify ecosystem conditions and potential processes as controls on DOM. Importantly, an analysis of stream water DOM across environmental gradients, such as the one presented here, can only be conducted where errors linked to inter-instrument comparisons do not play a large role, and long-term monitoring programs such as the Long Term Ecological Research program [Jaffe *et al.*, 2008] and Critical Zone Observatories facilitate such efforts.

Additional comparative studies of DOM biogeochemistry across climatic, hydrologic, or land use gradients are needed to identify and more fully understand the importance of a broad suite of atmospheric and terrestrial ecosystem processes that influence stream water quality conditions. The conceptual model presented here sets the stage for future detailed site-specific investigations of specific processes. To this end, we propose that regular collection of samples for DOM quantity and quality be included as part of existing or future monitoring programs. Application of the instrument correction factors documented in Cory *et al.* [2010] to spectral data, and comparisons of corrected scans of quine sulfate and reference humic substances to NIST and IHSS reference spectra, respectively will ensure that results from different laboratories are comparable. Coupling regular measures of DOM quantity and quality with detailed site-specific studies of ecosystem processes influencing DOM biogeochemistry at CZO and other long-term monitoring sites will provide insight into the complex relationships among climatic, physical, chemical, and biological conditions that contribute to stream water quality conditions.

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#### References

- Aiken, G. R., and R. L. Malcolm (1987), Molecular weight of aquatic fulvic acids by vapor pressure osmometry, *Geochim. Cosmochim. Acta*, *51*, 2177–2184, doi:10.1016/0016-7037(87)90267-5.
- Aiken, G. R., H. Hsu-Kim, and J. N. Ryan (2011), Influence of dissolved organic matter on the environmental fate of metals, nanoparticles, and colloids, *Environ. Sci. Technol.*, *45*, 3196–3201, doi:10.1021/es103992s.
- Anderson, S. P., R. S. Anderson, E.-L. S. Hinckley, P. Kelly, and A. Blum (2011), Exploring weathering and regolith transport controls on Critical Zone development with models and natural experiments, *Appl. Geochem.*, *26*, supplement, S3–S5, doi:10.1016/j.apgeochem.2011.03.014.
- Andrews, D. M., H. Loin, Q. Zhu, L. Jin, and S. L. Brantley (2011), Hot spots and hot moments of dissolved organic carbon export and soil organic carbon storage in the Shale Hills catchment, *Vadose Zone J.*, *10*, 943–954, doi:10.2136/vzj2010.0149.
- Battin, T. J., L. A. Kaplan, S. Findlay, C. S. Hopkinson, E. Marti, A. I. Packman, J. D. Newbold, and F. Sabater (2008), Biophysical controls on organic carbon fluxes in fluvial networks, *Nat. Geosci.*, *1*, 95–100, doi:10.1038/ngeo101.
- Battin, T. J., S. Lyssaert, L. A. Kaplan, A. K. Aufdenkampe, A. Richter, and L. J. Tranvik (2009), The boundless carbon cycle, *Nat. Geosci.*, *2*, 598–600, doi:10.1038/ngeo618.
- Beggs, K. M. H., R. S. Summer, and D. M. McKnight (2009), Characterizing chlorine oxidation of dissolved organic matter and disinfection by-product formation with fluorescence spectroscopy and parallel factor analysis, *J. Geophys. Res.*, *114*, G04001, doi:10.1029/2009JG001009.
- Bellmore, R. A., J. A. Harrison, J. A. Needoba, E. S. Brooks, and C. K. Keller (2015), Hydrologic controls of dissolved organic matter concentrations and quality in a semiarid artificially drained agricultural catchment, *Water Resour. Res.*, *51*, 8146–8164, doi:10.1002/2015WR016884.
- Bergamaschi, B. A., M. S. Fram, C. Kendall, S. R. Silva, G. R. Aiken, and R. Fujii (1999), Carbon isotopic constraints on the contribution of plant material to the natural precursors of trihalomethanes, *Org. Geochem.*, *30*, 835–842, doi:10.1016/S0146-6380(99)00066-2.
- Bird, S. M., M. S. Fram, and K. L. Crepeau (2003), Method of analysis by the U.S. Geological Survey California District Sacramento Laboratory—Determination of dissolved organic carbon in water by high temperature catalytic oxidation, method validation, and quality-control practices, *U.S. Geol. Surv. Open File Rep.*, 2003-366, 14 pp.

- Brantley, S. L., et al. (2016), Designing a suite of measurements to understand the critical zone, *Earth Surf. Dyn.*, *4*, 212–235, doi:10.5194/esurf-4-211-2016.
- Burns, M. A., H. R. Barnard, R. S. Gabor, D. M. McKnight, and P. D. Brooks (2016), Dissolved organic matter transport reflects hillslope to stream connectivity during snowmelt in a montane catchment, *Water Resour. Res.*, *52*, 4905–4923, doi:10.1002/2015WR017878.
- Cawley, K. M., K. D. Butler, G. R. Aiken, L. G. Larsen, T. G. Huntington, and D. M. McKnight (2012), Identifying fluorescent pulp mill effluent in the Gulf of Maine and its watershed, *Mar. Pollut. Bull.*, *64*, 1678–1687, doi:10.1016/j.marpolbul.2012.05.040.
- Chiou, C. T., R. L. Malcolm, T. I. Brinton, and D. E. Kile (1986), Water solubility enhancement of some organic pollutants and pesticides by dissolved humic and fulvic acids, *Environ. Sci. Technol.*, *20*, 502–508, doi:10.1021/es00147a010.
- Chow, A. T., K. K. Tanji, and S. Gao (2003), Production of dissolved organic carbon (DOC) and trihalomethane (THM) precursor from peat soils, *Water Res.*, *37*, 4475–4485, doi:10.1016/S0043-1354(03)00437-8.
- Clarke, K. R., and R. N. Gorley (2006), *PRIMER v6: User Manual/Tutorial*, Primer-E, Plymouth, U. K.
- Clarke, K. R., and R. M. Warwick (2001), *Change in Marine Communities: An Approach to Statistical Analysis and Interpretation*, 2nd ed., Primer-E, Plymouth, U. K.
- Cole, J. J., et al. (2007), Plumbing the global carbon cycle: Integrating inland waters in to the terrestrial carbon budget, *Ecosystems*, *10*, 171–184, doi:10.1007/s10021-006-9013-8.
- Cory, R. M., and D. M. McKnight (2005), Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter, *Environ. Sci. Technol.*, *39*, 8142–8149, doi:10.1021/es506962.
- Cory, R. M., D. M. McKnight, Y.-P. Chin, P. Miller, and C. L. Jaros (2007), Chemical characteristics of fulvic acids from Arctic surface waters: Microbial contributions and photochemical transformations, *J. Geophys. Res.*, *112*, G04551, doi:10.1029/2006JG000343.
- Cory, R. M., M. P. Miller, D. M. McKnight, J. J. Guerard, and P. L. Miller (2010), Effects of instrument-specific response on the analysis of fulvic acid fluorescence spectra, *Limnol. Oceanogr. Methods*, *8*, 67–78, doi:10.4319/lom.2010.8.0067.
- Cory, R. M., C. P. Ward, B. C. Crump, and G. W. Kling (2014), Sunlight controls water column processing of carbon in arctic fresh waters, *Science*, *345*, 925–928, doi:10.1126/science.1253119.
- Driscoll, C. T., G. B. Lawrence, A. J. Bulger, T. J. Butler, C. S. Cronan, C. Eagar, K. F. Lambert, G. E. Likens, J. L. Stoddard, and K. C. Weathers (2001), Acidic deposition in the northeastern United States: Sources and inputs, ecosystem effects, and management strategies, *Bioscience*, *51*, 180–198, doi: 10.1641/0006-3568(2001)051[0180:ADITNU]2.0.CO;2.
- Ekstrom, S. M., E. S. Kritzberg, D. B. Kleja, N. Larsson, P. A. Nilsson, W. Graneli, and B. Bergkvist (2011), Effect of acid deposition on quantity and quality of dissolved organic matter in soil-water, *Environ. Sci. Technol.*, *45*, 4733–4739, doi:10.1021/es104126f.
- Evans, C. D., et al. (2008), Does elevation nitrogen deposition or ecosystem recovery from acidification drive increased dissolved organic carbon loss from upland soil? A review of evidence from field nitrogen addition experiments, *Biogeochemistry*, *91*, 13–35, doi:10.1007/s10533-008-9256-x.
- Evans, C. D., et al. (2012), Acidity controls on dissolved organic carbon mobility in organic soils, *Global Change Biol.*, *18*, 3317–3331, doi: 10.1111/j.1365-2486.2012.02794.x.
- Fellman, J. B., D. V. D'Amore, E. Hood, and R. D. Boone (2008), Fluorescence characteristics and biodegradability of dissolved organic matter in forest and wetland soils from coastal temperate watersheds in southeast Alaska, *Biogeochemistry*, *88*, 169–184, doi:10.1007/s10533-008-9203-x.
- Fellman, J. B., E. Hood, D. V. D'Amore, R. T. Edwards, and D. White (2009), Seasonal changes in the chemical quality and biodegradability of dissolved organic matter exported from soils to streams in coastal temperate watersheds, *Biogeochemistry*, *95*, 277–293, doi:10.1007/s10533-009-9336-6.
- Fellman, J. B., E. Hood, and R. G. M. Spencer (2010), Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: A review, *Limnol. Oceanogr.*, *55*, 2452–2462, doi:10.4319/lo.2010.55.6.2452.
- Fisher, S. G., and G. E. Likens (1973), Energy flow in Bear Brook, New Hampshire: An integrative approach to stream ecosystem metabolism, *Ecol. Monogr.*, *43*, 421–439, doi:10.2307/1942301.
- Gabor, R. S., K. Eilers, D. M. McKnight, N. Fierer, and S. P. Anderson (2014), From the litter layer to the saprolite: Chemical changes in water-soluble soil organic matter and their correlation to microbial community composition, *Soil Biol. Biochem.*, *68*, 166–176, doi:10.1016/j.soilbio.2013.09.029.
- Galloway, J. N. (1995), Acid deposition: Perspectives in time and space, *Water Air Soil Pollut.*, *5*, 15–24, doi:10.1007/BF00483685.
- Hahn, W. J., C. S. Riebe, C. E. Lukens, and S. Araki (2014), Bedrock composition regulates mountain ecosystems and landscape evolution, *Proc. Natl. Acad. Sci. U. S. A.*, *111*(9), 3338–3343, doi:10.1073/pnas.1315667111.
- Hayes, M. H. B., and R. S. Swift (1978), The chemistry of soil colloids, in *The Chemistry of Soil Constituents*, edited by D. J. Greenland and M. H. B. Hayes, Wiley-Interscience, N. Y.
- Helton, A. M., M. S. Wright, E. S. Bernhardt, G. C. Poole, R. M. Cory, and J. A. Sanford (2015), Dissolved organic carbon lability increases with water residence time in the alluvial aquifer of a river-floodplain ecosystem, *J. Geophys. Res. Biogeosci.*, *120*, 693–706, doi:10.1002/2014JG002832.
- Hood, E., M. N. Gooseff, and S. L. Johnson (2006), Changes in the character of stream water dissolved organic carbon during flushing in three small watersheds, Oregon, *J. Geophys. Res.*, *111*, G01007, doi:10.1029/2005JG000082.
- Hood, E., J. Fellman, R. G. M. Spencer, P. J. Hernes, R. Edwards, D. D'Amore, and D. Scott (2009), Glaciers as a source of ancient and labile organic matter to the marine environment, *Nature*, *462*, 1044–1048, doi:10.1028/nature08580.
- Hruška, J., P. Krám, W. H. McDowell, and F. Oulehle (2009), Increased dissolved organic carbon (DOC) in Central European streams is driven by reductions in ionic strength rather than climate change or decreasing acidity, *Environ. Sci. Technol.*, *43*, 4320–4326, doi:10.1021/es803645w.
- Hunsaker, C. T., and D. G. Neary (2012b), Sediment loads and erosion in forest headwater streams of the Sierra Nevada, California, in *Revisiting Experimental Catchment Studies in Forest Hydrology*, edited by A. A. Webb et al., vol. 353, IAHS Publ., Oxfordshire, U. K.
- Hunsaker, C. T., T. W. Whitaker, and R. C. Bales (2012a), Snowmelt runoff and water yield along elevation and temperature gradients in California's southern Sierra Nevada, *J. Am. Water Resour. Assoc.*, *48*, 667–678, doi:10.1111/j.1752-1688.2012.00641.x.
- Hunt, A. P., J. D. Parry, and J. Hamilton-Taylor (2000), Further evidence of elemental composition as an indicator of the bioavailability of humic substances to bacteria, *Limnol. Oceanogr.*, *45*, 237–241, doi:10.4319/lo.2000.45.1.0237.
- Inamdar, S. P., and M. J. Mitchell (2006), Hydrologic and topographic controls on storm-event exports of dissolved organic carbon (DOC) and nitrate across catchment scales, *Water Resour. Res.*, *42*, W03421, doi:10.1029/2005WR004212.
- Inamdar, S., S. Singh, S. Dutta, D. Levia, M. Mitchell, D. Scott, H. Bais, and P. McHale (2011), Fluorescence characteristics and sources of dissolved organic matter for stream water during storm events in a forested mid-Atlantic watershed, *J. Geophys. Res.*, *116*, G03043, doi: 10.1029/2011JG001735.

- Inamdar, S., N. Finger, S. Sing, M. Mitchell, D. Levina, H. Bais, D. Scott, and P. McHale (2012), Dissolved organic matter (DOM) concentration and quality in a forested mid-Atlantic watershed, USA, *Biogeochemistry*, *108*, 55–76, doi:10.1007/s10533-011-9572-4.
- Jaffe, R., D. McKnight, N. Maie, R. Cory, W. H. McDowell, and J. L. Campbell (2008), Spatial and temporal variations in DOM composition in ecosystems: The importance of long-term monitoring of optical properties, *J. Geophys. Res.*, *113*, G04032, doi:10.1029/2008JG0000683.
- Jin L., D. M. Andrews, G. H. Holmes, H. Lin, and S. L. Brantley (2011), Opening the “Black Box”: Water chemistry reveals hydrological controls on weathering in the Susquehanna Shale Hills Critical Zone Observatory, *Vadose Zone J.*, *10*, 928–942, doi:10.2136/vzj2010.0133.
- Johnson, D. W., C. T. Hunsaker, D. W. Glass, B. M. Rau, and B. A. Roath (2011), Carbon and nutrient contents in soils from the Kings River Experimental Watersheds, Sierra Nevada Mountains, California, *Geoderma*, *160*, 490–502, doi:10.1016/j.geoderma.2010.10.019.
- Kraus, T. E. C., B. A. Bergamaschi, P. J. Hernes, D. Doctor, C. Kendall, B. D. Downing, and R. F. Losee (2011), How reservoirs alter drinking water quality: Organic matter sources, sinks and transformations, *Lake Reserv. Manage.*, *27*, 205–219, doi:10.1080/07438141.2011.597283.
- Lynch, J. A., V. C. Bowersox, and J. W. Grimm (2000), Changes in sulfate deposition in eastern USA following implementation of Phase I of Title IV of the Clean Air Act Amendments of 1990, *Atmos. Environ.*, *34*, 1665–1680, doi:10.1016/S135202310(99)00426-4.
- McDowell, W. H., and C. E. Asbury (1994), Export of carbon, nitrogen, and major ions from three tropical montane watersheds, *Limnol. Oceanogr.*, *39*, 111–125, doi:10.4319/lo.1994.39.1.0111.
- McIntyre, A. M., and C. Gueguen (2013), Binding interactions of algal-derived dissolved organic matter with metal ions, *Chemosphere*, *90*, 620–626, doi:10.1016/j.chemosphere.2012.08.057.
- McKnight, D. M., K. E. Bencala, G. W. Zellweger, G. R. Aiken, G. L. Feder, and K. A. Thorn (1992), Sorption of dissolved organic carbon by hydrous aluminum and iron oxides occurring at the confluence of Deer Creek with the Snake River, Summit County, Colorado, *Environ. Sci. Technol.*, *26*, 1388–1396, doi:10.1021/es00031a017.
- McKnight, D. M., E. W. Boyer, P. K. Westerhoff, P. T. Doran, T. Kulbe, and D. T. Andersen (2001), Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity, *Limnol. Oceanogr.*, *46*, 38–48, doi:10.4319/lo.2001.46.1.0038.
- Meyer, J. L., and R. T. Edwards (1990), Ecosystem metabolism and turnover of organic carbon along a blackwater river continuum, *Ecology*, *71*, 668–677, doi:10.2307.1940321.
- Miller, M. P., D. M. McKnight, S. C. Chapra, and M. W. Williams (2009), A model of degradation and production of three pools of dissolved organic matter in an alpine lake, *Limnol. Oceanogr.*, *54*, 2213–2227, doi:10.4319/lo.2009.54.6.2213.
- Miller, M. P., B. E. Simone, D. M. McKnight, R. M. Cory, M. W. Williams, and E. W. Boyer (2010), New light on a dark subject: Comment, *Aquat. Sci.*, *72*, 269–275, doi:10.1007/s00027-010-0130-2.
- Mladenov, N., P. Huntsman-Mapila, P. Wolski, W. R. L. Masamba, and D. M. McKnight (2008), Dissolved organic matter accumulation, reactivity, and redox state in ground water of a recharge wetland, *Wetlands*, *28*, 747–759, doi:10.1672/07-140.1.
- Monteith, D. T., et al. (2007), Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry, *Nature*, *450*, 537–540, doi:10.1038/nature06316.
- Ohno, T. (2002), Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter, *Environ. Sci. Technol.*, *36*, 742–746, doi:10.1021/es0155276.
- Pace, M. L., I. Reche, J. J. Cole, A. Fernandez-Barbero, I. P. Mazuecos, and Y. T. Prairie (2012), pH change induces shifts in the size and light absorption of dissolved organic matter, *Biogeochemistry*, *108*, 109–118, doi:10.1007/s10533-011-9576-0.
- Parr, T. B., C. S. Cronana, T. Ohno, S. E. G. Findlay, S. M. Smith, and K. S. Simon (2015), Urbanization changes the composition and bioavailability of dissolved organic matter in headwater streams, *Limnol. Oceanogr.*, *60*, 885–900, doi:10.1002/lno.10060.
- Perdrial, J. N., et al. (2014), Stream water carbon controls in seasonally snow-covered mountain catchments: impact of inter annual variability of water fluxes, catchment aspect and seasonal processes, *Biogeochemistry*, *118*, 273–290, doi:10.1007/s10533-013-9929-y.
- Peters, N. E., J. B. Shanley, B. T. Aulenbach, R. M. Webb, D. H. Campbell, R. Hunt, M. C. Larsen, R. F. Stallard, J. Troester, and J. F. Walker (2006), Water and solute mass balance of five small, relatively undisturbed watersheds in the U.S., *Sci. Total Environ.*, *358*, 221–242, doi:10.1016/j.scitotenv.2005.04.044.
- Petrone, K. C., J. B. Fellman, E. Hood, M. J. Donn, and P. F. Grierson (2011), The origin and function of dissolved organic matter in agro-urban coastal streams, *J. Geophys. Res.*, *116*, G01028, doi:10.1029/2010JG001537.
- Poulin, B. A., J. N. Ryan, and G. R. Aiken (2014), Effects of iron on optical properties of dissolved organic matter, *Environ. Sci. Technol.*, *48*, 10,098–10,106, doi:10.1021/es502670r.
- Riebe, C. S., and D. E. Granger (2013), Quantifying effects of deep and near-surface chemical erosion on cosmogenic nuclides in soils, saprolite, and sediment, *Earth Surf. Processes Landforms*, *38*, 523–533, doi:10.1022/esp.3339.
- Roberts, B. J., P. J. Mulholland, and W. R. Hill (2007), Multiple scales of temporal variability in ecosystem metabolism rates: Results from 2 years of continuous monitoring in a forested headwater stream, *Ecosystems*, *10*, 588–606, doi:10.1007/s10021-007-9059-2.
- SanClements, M. D., G. P. Oelsner, D. M. McKnight, J. L. Stoddard, and S. J. Nelson (2012), New insights into the source of decadal increases of dissolved organic matter in acid-sensitive lakes of the Northeastern United States, *Environ. Sci. Technol.*, *46*, 3212–3219, doi:10.1021/es204321x.
- Schindler, D. W., P. J. Curtis, S. E. Bayley, B. R. Parker, K. G. Beaty, and M. P. Stainton (1997), Climate-induced changes in the dissolved organic carbon budgets of boreal lakes, *Biogeochemistry*, *36*, 9–28, doi:10.1023/A:1005792014547.
- Scott, D. T., R. L. Runkel, D. M. McKnight, B. M. Voelker, B. A. Kimball, and E. R. Carraway (2003), Transport and cycling of iron and hydrogen peroxide in a freshwater stream: Influence of organic acids, *Water Resour. Res.*, *39*(11), 1308, doi:10.1029/2002WR001768.
- Sebestyen, S. D., E. W. Boyer, J. B. Shanley, C. Kendall, D. H. Doctor, G. R. Aiken, and N. Ohte (2008), Sources, transformations, and hydrological processes that control stream nitrate and dissolved organic matter concentrations during snowmelt in an upland forest, *Water Resour. Res.*, *44*, W12410, doi:10.1029/2008WR006983.
- Shanley, J. B. (1992), Sulfate retention and release in soils at Panola Mountain, Georgia, *Soil Sci.*, *153*, 499–508, doi:10.1097/00010694-199206000-00009.
- Shih, J. S., R. B. Alexander, R. A. Smith, E. W. Boyer, G. E. Schwarz, and S. Chung (2010), An initial SPARROW model of land use and in-stream controls on total organic carbon in streams of the conterminous United States, *U.S. Geol. Surv. Open File Rep.*, *2010-1776*, 22 pp.
- Stedmon, C. A., and S. Markager (2005), Tracing the production and degradation of autochthonous fractions of dissolved organic matter by fluorescence analysis, *Limnol. Oceanogr.*, *50*, 1415–1426, doi:10.4319/lo.2005.50.5.1415.
- Tranvik, L. J., et al. (2009), Lakes and reservoirs as regulators of carbon cycling and climate, *Limnol. Oceanogr.*, *54*, 2298–2314, doi:10.4319/lo.2009.54.6\_part\_2.2298.
- Volk, C. J., C. B. Volk, and L. A. Kaplan (1997), Chemical composition of biodegradable dissolved organic matter in streamwater, *Limnol. Oceanogr.*, *42*, 39–44, doi:10.4319/lo.1997.42.1.0039.



- Weishaar J. L., G. R. Aiken, B. A. Bergamaschi, M. S. Fram, R. Fujii, and K. Mopper (2003), Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon, *Environ. Sci. Technol.*, *37*, 4702–4708, doi:10.1021/es030360x.
- West, N., E. Kirby, P. Bierman, R. Slingerland, L. Ma, D. Rood, and S. L. Brantley (2013), Regolith production and transport at the Susquehanna Shale Hills Critical Zone Observatory: Part 2—Insights from meteoric  $^{10}\text{Be}$ , *J. Geophys. Res. Earth Surf.*, *118*, 1–20, doi:10.1002/jgrf.20121.
- White, T., et al. (2015), The role of Critical Zone Observatories in critical zone science, *Dev. Earth Surface Processes*, *19*, 15–78, doi:10.1016/B978-0-444-63369-9.00002-1.
- Wickland, K. P., J. C. Neff, and G. R. Aiken (2007), Dissolved organic carbon in Alaskan Boreal Forest: Sources, chemical characteristics, and biodegradability, *Ecosystems*, *10*, 1323–1340, doi:10.1007/s10021-007-9101-4.
- Wilcoxon, F. (1945), Individual comparisons by ranking methods, *Biometrics*, *1*, 80–83, doi:10.2307/3001968.
- Williamson, C. E., W. Dodds, T. M. Kratz, and M. A. Palmer (2008), Lakes and streams as sentinels of environmental change in terrestrial and atmospheric processes, *Front. Ecol. Environ.*, *6*, 247–254, doi:10.1890/070140.
- Yamashita, Y., and R. Jaffe (2008), Characterizing the interactions between trace metals and dissolved organic matter using excitation-emission matrix and parallel factor analysis, *Environ. Sci. Technol.*, *42*, 7374–7379, doi:10.1021/es801357h.