

Long-Term Experimental Acidification Drives Watershed Scale Shift in Dissolved Organic Matter Composition and Flux

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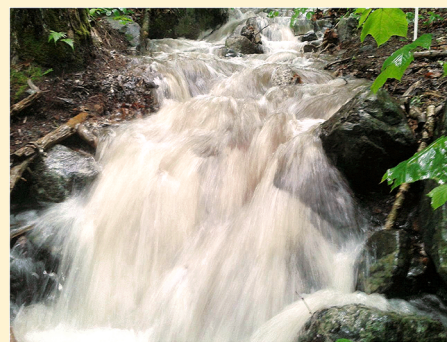
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S Supporting Information

ABSTRACT: Over the last several decades dissolved organic carbon concentrations (DOC) in surface waters have increased throughout much of the northern hemisphere. Several hypotheses have been proposed regarding the drivers of this phenomenon including decreased sulfur (S) deposition working via an acidity-change mechanism. Using fluorescence spectroscopy and data from two long-term (24+ years at completion of this study) whole watershed acidification experiments, that is, the Bear Brook Watershed in Maine (BBWM) and Fernow Experimental Forest in West Virginia (FEF) allowed us to control for factors other than the acidity-change mechanism (e.g., differing vegetation, shifting climate), resulting in the first study we are aware of where the acidity change mechanism could be experimentally isolated at the whole ecosystem and decadal scales as the driver of shifts in DOM dynamics. The multidecadal record of stream chemistry at BBWM demonstrates a significantly lower DOC concentration in the treated compared to the reference watershed. Additionally, at both BBWM and FEF we found significant and sustained differences in stream fluorescence index (FI) between the treated and reference watersheds, with the reference watersheds demonstrating a stronger terrestrial DOM signature. These data, coupled with evidence of pH shifts in upper soil horizons support the hypotheses that declines in S deposition are driving changes in the solubility of soil organic matter and increased flux of terrestrial DOC to water bodies.



INTRODUCTION

The declines in ambient sulfur (S) deposition associated with The Clean Air Act (CAA) of 1970 and subsequent Title IV Amendment of the CAA in 1990 drove declines in S deposition across the United States, with declines commonly exceeding 50% in the northeastern United States.^{1–4} Over the same period, there has been a noted increase in dissolved organic carbon (DOC) concentrations (a proxy for dissolved organic matter) in many lakes and streams of the Northern Hemisphere.^{5–12} A number of drivers have been hypothesized for the observed increase in DOC concentrations including climate warming, elevated nitrogen (N) deposition, changing hydrology, increased atmospheric CO₂, and declining S deposition via an acidity-change mechanism.¹³ The acidity change mechanism derives from the relationship between soil organic matter (SOM) solubility and soil solution pH; that is, SOM solubility decreases with decreasing pH via hydrogen ions resulting in increased protonation of carboxylic functional groups, neutralization of negative charge, and less hydrophilic organic matter.^{14–18} Thus, elevated acid deposition that lowers soil pH should reduce SOM solubility and suppress fluxes of DOM from soils to lakes and streams. Conversely, significant

reductions in ambient acid deposition could decrease soil acidity and lead to increased SOM solubility and increased fluxes of terrestrial DOM to water bodies, with a range of implications for their chemical and physical properties.^{2,6,13,19}

A number of studies^{5,12,21,22} have linked increased DOC concentrations in water bodies across the northern hemisphere to reductions in S deposition via the described acidity-change mechanism. The acidity change mechanism can be evaluated by chemical characterization of DOM to determine if an increase in plant/soil derived DOM has occurred. Previous work by SanClements et al., 2012²¹ calculated the FI on archived water samples from nine lakes in Maine to retrospectively trace increasing DOC concentrations to terrestrial sources and correlate them to decadal declines in S deposition over the period 1993–2009. Specifically, it was found that lakes that had experienced an increase in DOC also experienced decreasing

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SO_4^{2-} and FI, whereas lakes in the study that had no demonstrable DOC increase did not.

To date, the evidence in support of the acidity-change hypothesis is largely reliant upon long-term monitoring data and correlative inference from sites where multiple potential drivers (e.g., climate, hydrology) are simultaneously changing and confounding the ability to isolate acidity as the sole driver of DOC increases across much of the Northern Hemisphere.^{20,21}

Here we use data from long-term (24+ years at completion of this study) whole watershed acidification experiments, that is, The Bear Brook Watershed in Maine (BBWM) and Fernow Experimental Forest (FEF) in West Virginia (Figure 1) to

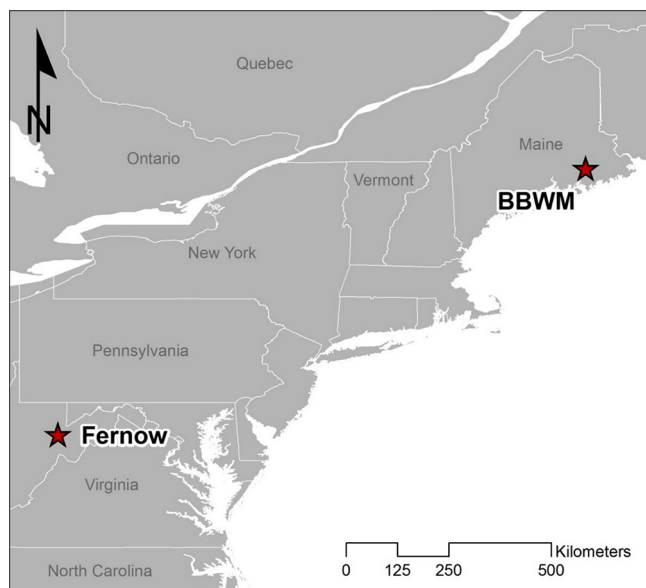


Figure 1. Locations of the Bear Brook Watershed in Maine and Fernow Experimental forest in West Virginia. Both are long-term (24+ years at time of study) paired whole watershed acidification experiments. We used these sites to isolate and test the acidity change mechanism as a driver of increased dissolved organic matter fluxes from soils to streams.

isolate and test the acidity change mechanism as a driver of shifts in stream DOM dynamics in two forested catchments in the eastern United States. Both BBWM and FEF are paired whole watershed experiments, each with a reference watershed that has experienced substantial ambient declines in S deposition and a treated/acidified watershed receiving periodic ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) additions since 1989.²³ The small paired watershed approach provides a powerful experimental tool for testing ecosystem response²⁴ and also provides a unique backdrop for this work by controlling for drivers other than the acidity-change mechanism (e.g., differing vegetation, shifting climate) within BBWM and FEF.

We used fluorescence spectroscopy to calculate the fluorescence index (FI) of streamwater and soil extracts to trace the origins of DOM in streams draining both the treated and reference watersheds at BBWM and FEF. The FI provides valuable information regarding the source and composition of DOM; higher FI values (i.e., 1.7–1.9) are indicative of autochthonous microbial DOM and lower FI values (i.e., 1.2–1.5) of DOM derived from terrestrial sources (Figure 2).^{25,26} This study utilizes a similar strategy as that employed by

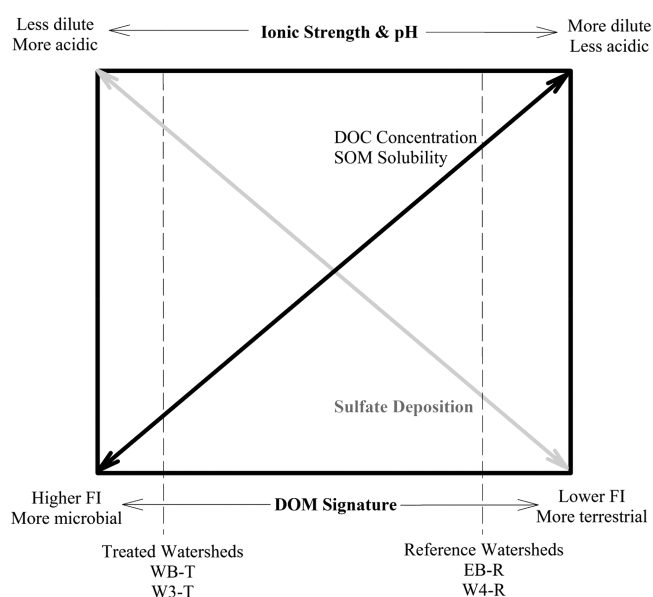


Figure 2. Modified from SanClements et al., 2012.²¹ Conceptual depiction of the relationship between the acidity change mechanism and the fluorescence signature and source of DOM. Decreasing pH and increasing ionic strength would result in decreased solubility of soil organic matter, decreased flux of DOC to streams, and a higher FI signature.

SanClements et al., 2012,²¹ (i.e., long-term records in conjunction with fluorescence spectroscopy to make inference about not only trends in DOC concentration, but also the composition and source of these DOM). However, unlike previous work, this is the first we are aware of that combines this analytical approach at sites where the acidity change mechanism could be experimentally isolated at the whole ecosystem and decadal scales as the driver of shifts in DOM dynamics.

MATERIALS AND METHODS

Site and Sample Descriptions. The Bear Brook Watershed in Maine (BBWM), (44°52' N, 68°06'), is a long-term, paired watershed acidification experiment. East Bear (EB-R) comprises 11.0 ha and serves as the reference watershed, West Bear (WB-T) is the treated watershed and is similar in size at 10.3 ha. Both watersheds are drained by first order streams.

Over the period 1989–2012 at BBWM ambient mean annual wet S deposition was 4.2 kg ha⁻¹ and ranged from 2.0 kg ha⁻¹ to 6.9 kg ha⁻¹. There was a significant negative correlation between time and S deposition at BBWM, with S deposition decreasing between 1989 and 2012. Mean annual wet-only N deposition at BBWM was 3.3 kg ha⁻¹. In addition to ambient deposition, WB-T has been treated bimonthly with ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) at 28.8 kg S ha⁻¹ yr⁻¹ and 25.2 kg N ha⁻¹ yr⁻¹ since November 1989.²⁷ Mean annual precipitation is 1320 mm yr⁻¹.²³ Soils in both watersheds are coarse-loamy, mixed, frigid Typic Haplorthods formed from till averaging ~1 m in thickness.²⁸ Bedrock is primarily quartzite and gneiss with granitic intrusions. At the time of this study vegetation was similar in both watersheds with higher elevations dominated by red spruce (*Picea rubens* Sarg.) and balsam fir (*Abies balsamea* L.); lower elevations were dominated by northern hardwoods, predominantly declining American beech (*Fagus grandifolia*

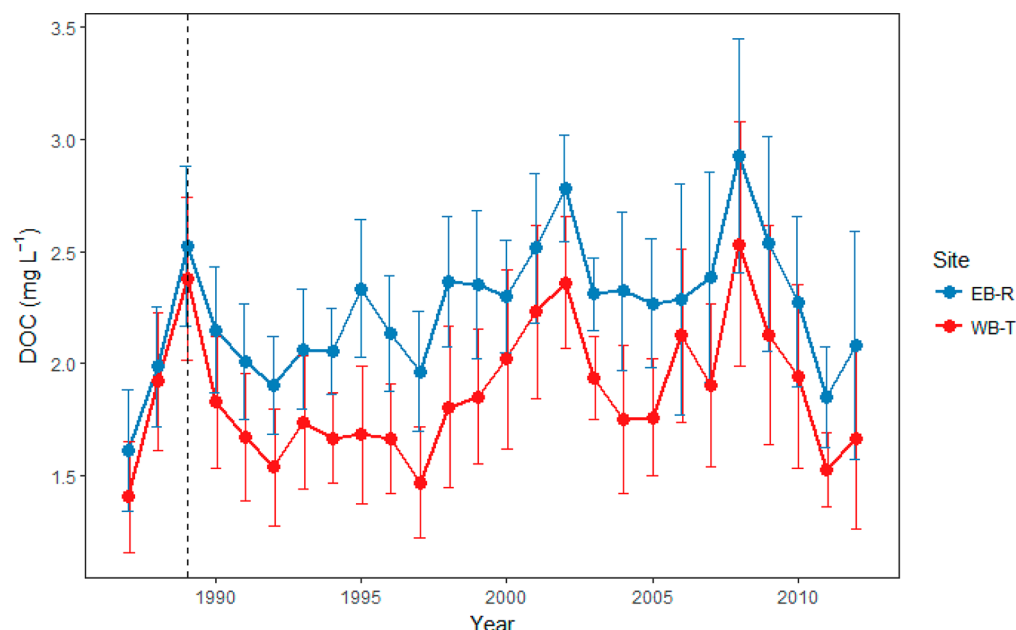


Figure 3. Time series of mean annual DOC data from East Bear (EB-R) and West Bear (WB-T) watersheds. The dashed vertical line indicates the onset of treatment by ammonium sulfate in the West Bear watershed. Mean DOC concentrations were significantly higher in EB-R than WB-T following onset of treatment ($P < 0.05$) when treated as pre- and post-treatment groups.

Ehrh.), sugar maple (*Acer saccharum* Marsh.), and red maple (*Acer rubrum* L.).²⁷

The Fernow Experimental Forest (FEF) is located in the Appalachian Mountains of north-central West Virginia and includes a paired whole watershed acidification experiment. Over the period 1989–2012 ambient mean annual wet S deposition was 8.0 kg ha^{-1} and ranged from 3.7 kg ha^{-1} to 13.9 kg ha^{-1} at FEF. There was a significant negative correlation between time and S deposition at FEF. Mean annual wet only N deposition at FEF was 5.6 kg ha^{-1} and ranged from 8.0 kg ha^{-1} to 2.8 kg ha^{-1} . At FEF, Watershed 4 (W4-R) serves as the reference watershed while Watershed 3 (W3-T) receives ambient deposition and has been treated three times per year with $(\text{NH}_4)_2\text{SO}_4$ at a rate of $40.6 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ and $35.4 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ since January 1989. Mean annual temperature has been 8.8°C and mean annual precipitation has been 1470 mm .²³ Soils in both watersheds are loamy-skeletal, mixed, active, mesic Typic Dystrochrepts formed in colluvium (poorly sorted rock fragments carried downslope by gravity) and residuum (in place weathering of underlying rock) overlying quartzose sandstone and shale²⁹ and the watersheds were not glaciated during the Wisconsin ice age. The dominant overstory vegetation consisted of American Beech (*Fagus grandifolia* Ehrh.), black cherry (*Prunus serotina* Ehrh.), red maple (*Acer rubrum* L.), and red oak (*Quercus rubra* L.).³⁰

Additional information regarding collection, processing, and analysis of data collected as part of the BBWM and FEF long-term records can be found in Fernandez et al. 2010 and references therein.

Sample Collection and Preprocessing. Water samples from BBWM (EB-R and WB-T) and FEF (WS4-R and WS3-T) were collected from just above the V-notch weirs installed in each of the watersheds. Samples were collected on a biweekly basis when possible, but were sometimes limited by environmental conditions (freezing or drought) or personnel availability. Water samples from BBWM and FEF were collected in precombusted amber glass bottles and placed in

coolers for transport (BBWM) or shipped (FEF) to the University of Maine Sawyer Environmental Chemistry Laboratory where they were filtered through precombusted (450°C for 6 h) 47 mm Whatman GF/F filters. Filtered samples were then transferred to fresh precombusted amber glass bottles and stored at 4°C in the dark until shipped to the University of Colorado for spectroscopic analysis. Samples were analyzed within 2 weeks of filtration. Soil samples from BBWM were tented and air-dried, sieved through a 2 mm sieve, and extracted using a Milli-Q water ratio of 10:1 on an orbital shaker for 1 h. The pH of samples ranged from 2.4 to 4.7. After shaking, extracts were decanted and filtered through precombusted (450°C for 12 h) 47 mm Whatman GF/F filters.

Spectroscopy. Following initial processing soil and water samples were analyzed for UV-absorbance using an Agilent 8453 UV-spectrophotometer in a 1 cm quartz cuvette over the wavelength range 190–1100 nm. Samples with absorbances greater than 0.3 at 254 nm (A_{254}) were diluted with Milli-Q water until within the range of 0.1–0.2 at A_{254} to limit inner-filter effects during collection of excitation emission matrices (EEMs).³³ EEMs were collected using a Fluoromax-3 fluorometer by Horiba Jobin Yvon Inc. over an excitation range of 240–450 nm in 10 nm increments, whereas emission was monitored from 300 to 560 nm in 2 nm increments. All scans were corrected for instrument specific bias using manufacturer supplied correction factors for both excitation and emission wavelengths, corrected for inner-filter effects using UV-vis absorbance scans, normalized to the area under the instrument corrected Raman curve at emission 350 nm and blank subtracted using corrected EEMs of daily Milli-Q blanks analyzed over the same wavelengths as samples.^{27,31,32}

The FI was calculated for all corrected EEMs as the ratio of emission intensity wavelength of 470 nm to the emission intensity at 520 nm at an excitation wavelength of 370 nm.^{25,26} The FI is primarily a measure of DOM source (i.e., terrestrial versus microbial) and is generally correlated with aromaticity of

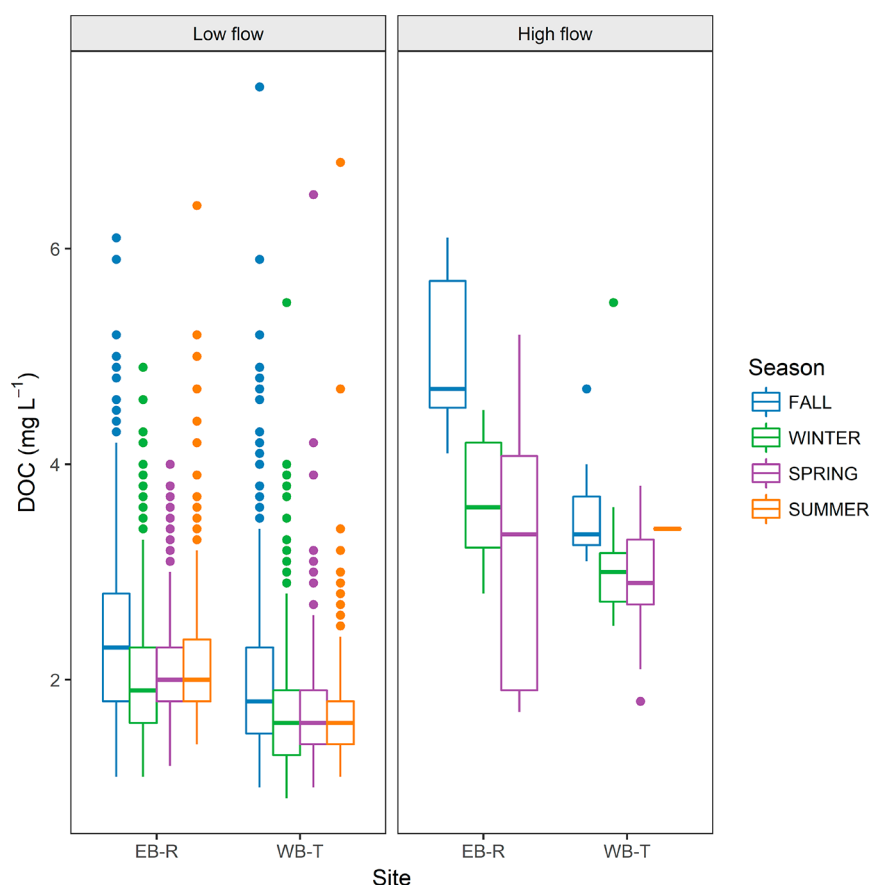


Figure 4. Boxplots of DOC data for East Bear and West Bear watersheds binned by season and flow. Here we display median values and interquartile ranges. The interquartile range is the difference between Q3 and Q1 and describes the middle 50% of values. The separation of DOC export between EB-R and WB-T is at its greatest during periods of high flow in fall.

humic materials.²⁶ In addition, the FI is strongly correlated with the relative proportions of two semiquinone like fluorophores (i.e., components SQ1 and SQ2) identified in the Cory and McKnight Global PARAFAC model.²⁶ Component SQ1 is associated with plant litter and soil derived material while SQ2 is associated with microbial sources. As DOM becomes increasingly microbial in its origin the contribution of SQ2 increases along with the FI value, and conversely, the FI will decrease with increasing terrestrial contributions.

Statistical Analysis. All statistical analyses were conducted using R version 3.4.0. Concentrations of DOC in EB-R and WB-T were analyzed to detect experimentally induced changes in stream DOC concentrations at the decadal scale. Prior to conducting statistical analyses the data set was cleaned and merged in a series of steps: duplicate entries were removed from the data set; observations below the reporting limit were removed (0.5 mg L^{-1}); and data were broken into two groups: “pretreatment” and “treatment”. The pretreatment group comprises EB-R and WB-T DOC data from October 1, 1986 to October 31, 1989, whereas the treatment group includes EB-R and WB-T DOC data and runs from November 1, 1989 through December 16, 2012. East Bear and West Bear DOC data (pretreatment and treatment) were compared to one another via Kruskal–Wallis tests as the data were not normally distributed. DOC data from BBWM were further scrutinized to identify potential relationships among DOC, discharge rate, and seasonality. East Bear and West Bear DOC data were binned by

season and flow rate intervals: $(0, 85) \text{ L min}^{-1}$, and $(85, 500) \text{ L min}^{-1}$ and box plots were generated.

RESULTS AND DISCUSSION

Effect of Experimental Acidification on DOM Composition and Flux. Prior to the onset of treatment at BBWM in 1989, the EB-R and WB-T watersheds were very similar in their chemical budgets and had virtually identical hydrographs.²⁷ Figure 3 depicts mean annual DOC values for EB-R and WB-T over the period 1986 to 2012. We evaluated DOC concentrations in stream samples collected from EB-R and WB-T prior to the onset of treatment in 1989 (i.e., between 1986 and 1989; $n = 403$) and found no statistical difference in DOC concentrations between the EB-R and WB-T streams. A comparison of samples collected following the onset of treatment ($n = 4696$) in WB-T revealed significantly greater ($p < 0.05$) DOC concentrations in EB-R (2.2 mg C L^{-1}) versus WB-T (1.7 mg C L^{-1}), suggesting that shifts in acid loading via treatment have resulted in a detectable suppression of DOC concentrations within the treated stream. An evaluation of the standard error of the means for individual years of EB-R and WB-T revealed interesting patterns about the evolution of treatment effects on DOC concentrations (Figure 3). The treatment did not appear to enhance the effect over time, but rather resulted in an immediate shift in 1990 to suppressed DOC concentrations in WB-T. This pattern persisted consistently (with the exception of 2000 and 2001) through 2005. From 2005 through 2012 we see less frequent significant

differences on an annual basis (only 2007 and 2011). It may be that decreasing differences are driven by the ambient decline in S and N at BBWM or the result of emergent biogeochemical trends. It should also be noted that the annual sample size for stream DOC declined beginning in 2000 which may have reduced the statistical ability to detect differences.

In testing hypotheses around the acidity change mechanism it is important to note that treatment in WB-T is via $(\text{NH}_4)_2\text{SO}_4$ and therefore consider the contributions of S and N to acidification, versus the role of N as a nutrient in driving these differences in DOC. A synthesis of data from 12 long-term North American and European field experiments (including BBWM) found responses in DOC to N additions were determined by the form of N applied and its influence on soil acidity. At those sites where N additions decreased soil acidity, DOC increased. Nitrogen additions with an acidifying effect typically resulted in DOC decreases. Collectively, the authors interpreted this as evidence that N deposition is unlikely to be the sole driver of rising DOC, but rather a potential contributor to the acidity change mechanism.²⁰

Investigations into the effect of seasonality and flow-rate on in-stream DOC concentration and source (as reflected in FI) provide additional insights regarding the role of soil characteristics and flow-paths on spatial and temporal patterns of DOC in temperate forested watersheds. Analysis of stream DOC concentrations at BBWM by watershed, flow, and season revealed that DOC concentrations in both EB-R and WB-T were generally greater in samples collected during high streamflow (i.e., defined as $85.01\text{--}500\text{ L min}^{-1}$ in this study) versus low streamflow (i.e., $<85.01\text{ L min}^{-1}$ in this study) (Figure 4). Regardless of watershed or flow, DOC concentrations were greatest in the autumn following leaf off and the associated addition of fresh litter to the system. The greatest differences in stream DOC concentrations between EB-R and WB-T occurred under high flow during fall where EB-R concentrations were $\sim$ twice those in WB-T. An analysis of in-stream litter processing at BBWM by Simon et al., 2010 found that acidity and N additions had little effect on the breakdown rates of litter. Additionally, a study by Kenlan et al. 2009,³⁴ while able to detect significant higher diversity in EB-R, found no significant differences in understory biomass between the treated and reference watersheds. The lack of significant difference in rates of in-stream litter processing and understory biomass suggest the elevated DOC in EB-R during high flow events is sourced from soil rather than the result of in-stream processes, a notion supported by the FI data in Figures 5 and 6 and the evolution of FI signatures during precipitation events displayed in Figure 7.

In conjunction with analysis of the long-term DOC record at BBWM (DOC concentrations were not measured regularly at FEF and therefore only FI values from FEF are discussed here) we used fluorescence spectroscopy to calculate the fluorescence index (FI) of stream samples collected from BBWM and FEF between 2010 and 2013. FI values provide reliable information about the source and quality of DOM and have been used to identify and link catchment processes; higher FI values ($\sim 1.7\text{--}1.9$) are reflective of autochthonous microbial sources, whereas lower values ($\sim 1.2\text{--}1.5$) are indicative of DOM derived from terrestrial sources (higher plants).^{26,35} Thus, the FI allows us to further test hypotheses about the acidity-change mechanism as a driver of DOC patterns in these streams. According to the acidity change mechanism, WB-T and W3-T should demonstrate a decrease in export of terrestrial DOM following more

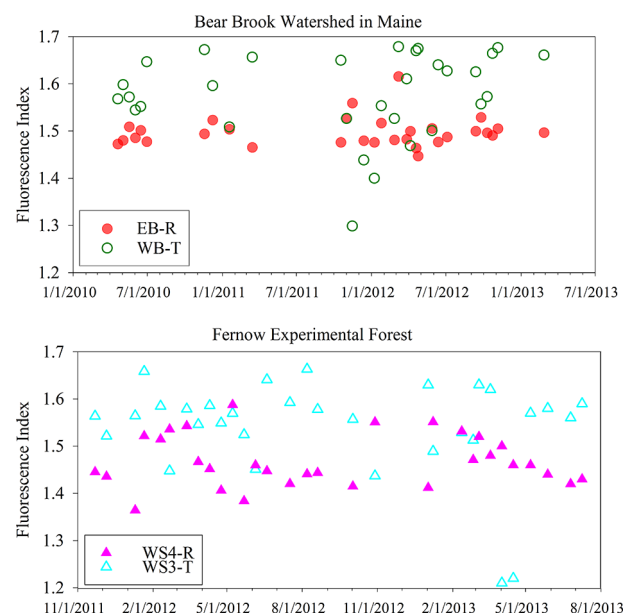


Figure 5. Fluorescence index values from the treated and reference watersheds at BBWM and FEF. Samples were collected between 2011 and 2013. In both plots the treated watershed is designated by solid triangles and the reference watershed open circles. At BBWM and FEF the reference watersheds had significantly lower ($p < 0.05$) FI values indicating a greater contribution of DOM sourced from terrestrial sources.

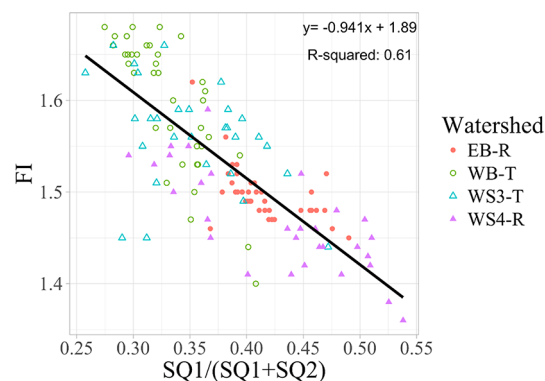


Figure 6. Fluorescence index as a function of the ratio of PARAFAC components SQ1 (C5) over the sum of SQ1 and SQ2 (C7). Samples with lower FI have greater amounts of SQ1 relative to SQ2. At both BBWM and FEF the reference watersheds reflect this trend suggesting the shifts in FI are dictated by shifts in the composition of specific DOM components.

than two decades of experimental acidification (Figure 2). This increased terrestrial signature should be detectable as a higher FI in WB-T relative to EB-R and W3-T relative to W4-R. At BBWM and FEF the treated watersheds exhibit consistent and significant greater FI values following 24 years (at the time of this study) of experimental acidification (additions of $(\text{NH}_4)_2\text{SO}_4$) (Figure 5). Specifically, streamwater from the treated watersheds (WB-T and W3-T) has significantly higher ($p < 0.05$) FI values than those from their untreated counterparts, confirming a decreased terrestrial DOM contribution with acidification. Conversely, the significantly lower FI values in EB-R relative to WB-T and W4-R relative to W3-T indicate increased contributions of DOM derived from soils in the reference watersheds at both BBWM and FEF. To ensure

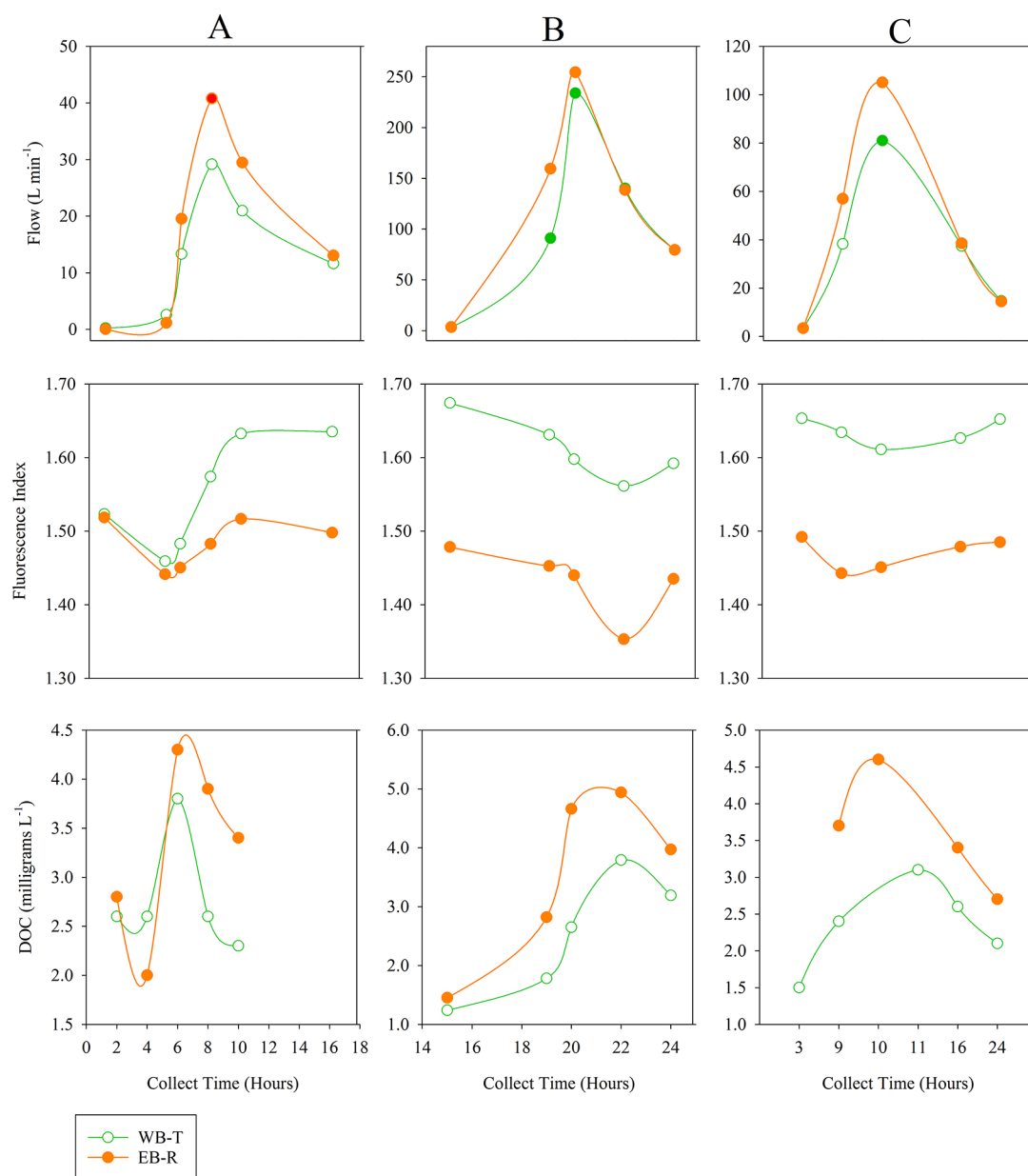


Figure 7. Panels A, B, and C represent individual precipitation events at BBWM that were sampled as part of this study. Each panel displays the evolution of the FI and streamflow in the treated and reference watersheds throughout the event.

shifts in FI were resulting from changes in the composition of DOM we conducted PARAFAC modeling and compared the FI to the ratio of components C5 (SQ1) and the sum of C5 and C7 (SQ1 + SQ2) from the Cory McKnight PARAFAC model (Figure 6). As noted in Cory and McKnight 2005, the FI should function as a ratio of these quinone-like components. We found that SQ1 and SQ2 varied consistently with the FI and that the treated and reference watersheds separated out as a function of the ratio between these two components. While we do see variation in the composition of individual EEMs (see Supporting Information (SI) Figure S1) the shifts in those components were not consistent or correlated with FI.

Humification index values (see SI) demonstrated less consistent trends than those of the FI, and are likely reflective of variation in H:C ratios within DOM as opposed to the source itself. The detectable difference in FI and DOM source between the treated and reference watersheds at BBWM and

FEF provides strong experimental whole ecosystem evidence in support of the acidity change mechanism in driving shifts in the mobilization of DOM from soils to streams in these ecosystems.

Evolution of DOM Signature during Precipitation Events. We opportunistically sampled three precipitation events at BBWM as a means of linking in-stream DOM patterns to terrestrial flow paths. Numerous studies have demonstrated that within catchments of first order streams (including BBWM), high flows reflect the properties of surface and near surface soils, whereas base flow is reflective of deeper soils^{36–38} in these headwater catchments. Columns A, B, and C in Figure 7 each depict a separate precipitation event during which samples were collected along the rising and falling limbs of the hydrograph and analyzed for FI and DOC.

Panel A displays streamflow and FI from a precipitation event occurring on October 15th, 2010 at BBWM. This event

followed a long dry period at BBWM where streamflow had been reduced to nearly zero (i.e., 0.2 L s^{-1}) and therefore was likely representative of base flow and deep soil characteristics. Just prior to this event, following a period of sustained minimal flows, FI values from EB-R and WB-T had converged at 1.5 indicating that DOM in both streams had a similar composition and source no longer reflective of the acidification treatments in WB-T. However, with the onset of precipitation and subsequent increase in streamflow, there is an initial and slight decrease in the FI signature of both streams, likely reflecting an initial pulse of DOM from near-stream soils. As streamflow continues to increase along the rising limb of the hydrograph from 0.2 L s^{-1} to a peak of 40.8 L s^{-1} , the EB-R and WB-T stream FI signals diverge to reflect the consistent differences seen in samples collected during sustained flows at BBWM between 2010 and 2013 (Figures 4 and 6). This shift in FI with increasing streamflow suggests a shift in flow paths where in-stream DOM is increasingly reflecting the whole watershed treatments.

Columns B and C of Figure 7 depict two additional events captured at BBWM in April and October of 2012. Both of these precipitation events began at considerably higher initial flows, (~ 3.2 - and $\sim 3.4 \text{ L s}^{-1}$ or 15–17 times the initial flow rate during the event in column A), which are more typical of streams throughout much of the year at BBWM. At these higher flows, EB-R and WB-T FI signals do not converge at any point, but rather mirror the FI record from sustained flows in Figure 4 (i.e., greater terrestrial signature in the reference watershed) throughout the entirety of the event, providing further evidence for the notion of flow playing an important role in the dynamics of the interplay between soil acidification and DOM.

There are some similarities in the way stream FI responds across all three events. Notably, in all events (columns A, B, and C) we see a consistent pattern of higher DOC values within EB-R in all but one sample. Both watersheds, across all three events, also exhibit a decline in FI values that coincides with peak DOC concentrations and is likely representative of the peak contributions of DOM from near surface soils and lateral flow in both watersheds.

Studies of the effects of experimental acidification on soil characteristics at BBWM during 1998 and again in 2006 found significant differences between the treated and reference watersheds in numerous parameters, including significantly lower pH in the upper soil horizons (i.e., O horizons and 0–5 cm of B horizons) of WB-T compared to EB-R.^{28,39} Similarly, we found significant differences in the FI of water extractable organic matter (WEOM) from BBWM soils sampled during 2012 (Figure 8). Specifically, we see significantly lower ($p < 0.05$) FI values in WEOM from soils in the 0–5 and 10–25 cm increments of the B horizon (zones of C accumulation in these Spodosols) in EB-R compared to WB-T (i.e., means of 1.4 and 1.5, respectively), mirroring patterns seen in streams at BBWM and FEF (Figures 5 and 7). While not dramatic, shifts of 0.10 on the FI scale are notable and when coupled with the patterns in stream DOC and FI support the idea that the differences in stream DOM originate in soils via the acidity-change mechanism.

Broader Implications. In aquatic systems, DOM influences biological, chemical, and physical processes including pH, nutrient availability, light penetration, mixing depth, thermal structure, and community structure.^{19,40,41} Additionally, the transport of DOM to waterbodies has important economic and

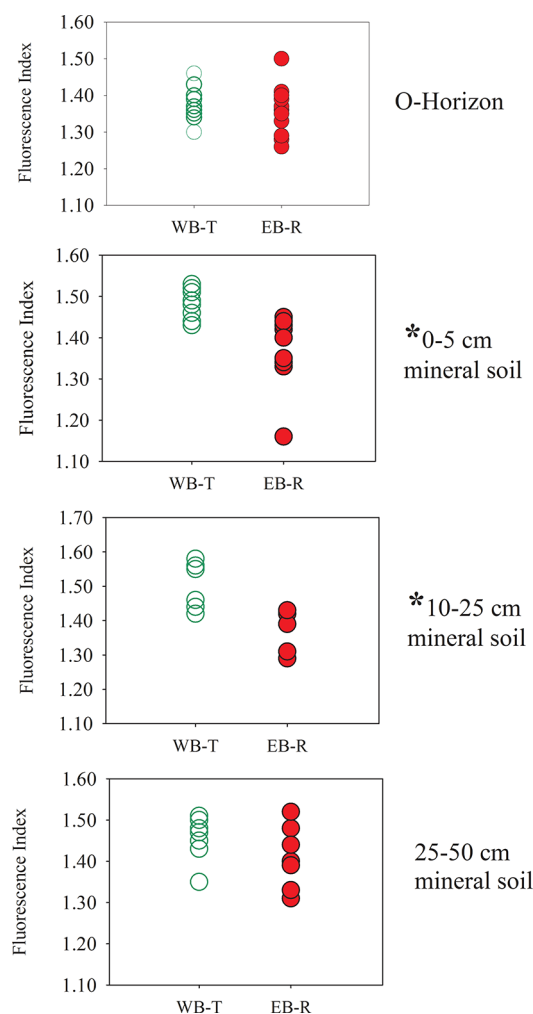


Figure 8. WEOM FI as a function of soil depth in the treated (WB-T) and reference (EB-R) watersheds at BBWM. The significant differences (denoted by asterisks) in the 0–5 cm and 10–25 cm increments, zones of high C accumulation in these Spodosols mirror those in seen in streams suggesting treatment effects on DOM may originate from within these depths in the soil.

health consequences for drinking water quality due to the potential generation of disinfection byproducts.^{42,43,40} In this study we combined specialized tools (i.e., fluorescence spectroscopy) capable of providing information about the source of DOM with experimental study sites to isolate and test the role of acidity as the driver of a widespread ecological phenomenon at the watershed and regional scales in eastern forests. This work shows that fluorescence spectroscopy can be used to identify underlying processes in subtle changes in terrestrial and aquatic C dynamics. More broadly, the reliance of this study and others on long-term empirical records of ecosystem function underscores the importance of long-term study sites in a changing chemical and physical climate. These results demonstrate that policies which alter acid deposition to temperate forested ecosystems may also drive changes in DOM cycling with subsequent consequences for a range of ecosystem processes.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b04499.

Additional figures and tables related to the humification index of streamwater at BBWM and Fernow as well as depictions of representative EEMs and the distribution of PARAFAC components in those EEMS. We also include annual solute chemistry from the EB and WB streams and fluorescence data generated via extractions of BBWM soils (PDF)

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Notes

The authors declare no competing financial interest.

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