Optical in-situ sensors capture dissolved organic carbon (DOC) dynamics after prescribed fire in high-DOC forest watersheds


ADepartment of Civil and Environmental Engineering, University of California, Berkeley, CA, 760 Davis Hall, 94720, USA.
BDepartment of Environmental Engineering and Earth Science, Clemson University, 342 Computer Court, Anderson, SC, 29625, USA.
CBiogeochemistry and Environmental Quality, Clemson University, 177 Hobcaw Road, Georgetown, SC, 29440, USA.
DDepartment of Environmental Engineering, Marmara University, Istanbul, Turkey.
EDepartment of Science, Southern New Hampshire University, 2500 North River Road, Manchester, NH, 031006 USA.
FCenter for Forsted Wetland Research, USDA Forest Service, 3734 Highway 402, Cordesville, SC, 29434, USA.
GCorresponding author. Email: achow@clemson.edu

Abstract. Fires alter terrestrial dissolved organic carbon (DOC) exports into water, making reliable post-fire DOC monitoring crucial. We evaluated DOC optical sensors in a pair of burned and unburned first-order watersheds at the Santee Experimental Forest, in the coastal plain forests of South Carolina, and the receiving second-order watershed during four post-fire storm DOC pulses. Median DOC concentrations were 30 and 23 mg L\(^{-1}\) in the burned and unburned watersheds following the first post-fire storm. Median DOC remained high during the second and third storms, but returned to pre-fire concentrations in the fourth storm. During the first three post-fire storms, sensor DOC load in the burned watershed was 1.22-fold higher than in the unburned watershed. Grab samples underestimated DOC loads compared with those calculated using the in-situ sensors, especially for the second-order watershed. After fitting sensor values with a locally weighted smoothing model, the adjusted sensor values were within 2 mg L\(^{-1}\) of the grab samples over the course of the study. Overall, we showed that prescribed fire can release DOC during the first few post-fire storms and that in-situ sensors have adequate sensitivity to capture storm-related DOC pulses in high-DOC forest watersheds.

Additional keywords: first-order watershed, forest management, prescribed burn, Santee Experimental Forest, South Carolina.

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Introduction

Increased frequency of severe wildfires threatens water resources in forested regions globally (Scholze et al. 2006; Westerling et al. 2006; Emelko and Sham 2014) and the use of prescribed fires has been promoted as an option to reduce fuel loads and wildfire risk (Boer et al. 2009). Periodic controlled burns can reduce understory vegetation density and competition with desired species (Wade et al. 1989; Mutch 1994). Indigenous peoples in North America have long used controlled burns (Ryan et al. 2013) and the United States (US) Forest Service has used prescribed fires in the US south-east extensively during the 20th century (Wade et al. 1989; Fairchilds and Trettin 2006).

Forest ed watersheds provide drinking water to more than 180 million people in the USA (Sedell et al. 2000; Stein et al. 2005). Wildfires can influence water quality in forested watersheds (Smith et al. 2011; Emelko and Sham 2014; Khan et al. 2015), as precipitation runoff mobilises debris, sediment, organic matter, and nutrients (Nyman et al. 2011), with effects that may last for years (Smith et al. 2011). As the mobility of
these sediments is increased, so is the transport of dissolved organic matter (DOM) (Raymond and Saiers 2010; Smith et al. 2011; Revchuk and Suffet 2014). Compared with wildfires, prescribed fires are expected to have moderate effects on water resources. Prescribed fire in experimental plots decreased soluble DOM compared with unburned plots in coastal South Carolina (Tsai et al. 2015), but increased DOM was found in soils burned in a prescribed fire event in a south-western Georgia wetland (Battle and Golladay 2003). These conflicting post-fire DOM results need to be further evaluated in more watershed studies.

Potential for post-fire increases in stream DOC is a concern for drinking water supply because it is a precursor for disinfection by-products formed during water treatment (Writer et al. 2014; Majidzadeh et al. 2015; Tsai et al. 2015; Hohner et al. 2016). Moreover, elevated post-fire DOM can simulate growth of noxious algal blooms (Gill 2004; Smith et al. 2011), which are known to have adverse human health effects.

Systematic grab samples are the most common approach used for monitoring stream DOC, but their regular sampling intervals often miss storm-related pulses (Mast et al. 2016) that may be crucial to post-fire DOC export. In-situ optical sensors that rely on proxy ultraviolet-visible light (UV-Vis) measurements have the potential to track sudden DOC changes and have applications in remote forest watersheds with logistical or safety challenges (Jeong et al. 2012; Pellerin et al. 2012; Lee et al. 2015; Blaen et al. 2016; Hohner et al. 2016; Mast et al. 2016). Fluorescence-based sensors have effectively characterised fluctuating DOC concentrations during snowmelt (Pellerin et al. 2012) and after storms (Jeong et al. 2012) in low DOC streams, but may fail to provide accurate measurements in streams with excess of 12 mg L\(^{-1}\) of DOC (Mast et al. 2016).

Earlier studies of stream DOC (Moeller et al. 1979) do not adequately characterise conditions in high-DOC streams, such as those found in the eastern half of North America (Spencer et al. 2013). Given predictions for increased DOC in North America and in North and Central European streams (Delpia et al. 2009; Jiménez Cisneros et al. 2014), analysis of high-DOC streams will help elucidate the future state of US watersheds.

We studied DOC concentration changes in a prescribed burned first-order watershed in coastal South Carolina following post-fire storm events. We compared DOC concentrations with an adjacent unburned first-order watershed and determined the load contributions of the burned watershed into a receiving second-order watershed. Our objectives were to (1) evaluate the effectiveness of an optical in-situ sensor for capturing changes in DOC concentration following prescribed fire in high-DOC streams (10–20 mg L\(^{-1}\)), (2) estimate DOC load export after post-fire storms and (3) determine the amount of DOC load from the burned watershed exported to the receiving second-order watershed.

**Methods**

**Study sites**

The Santee Experimental Forest, South Carolina, consists of paired first-order watersheds and a receiving secondary watershed (Fig. 1). One of the first-order watersheds covers 1.55 km\(^2\) and has been burned using prescribed fires on 2–4-year intervals since the 1960s. The other first-order watershed covers 1.6 km\(^2\) and has been unburned since 1968 (Richter et al. 1984; Amaty and Trettin 2007; Coates 2017; USDA Forest Service 2017). The first-order watersheds converge in a second-order watershed that covers 5 km\(^2\) and is also regularly monitored. The Santee Experimental Forest is characterised by pines in the uplands and riparian hardwoods in the bottomlands that regenerated after Hurricane Hugo in 1989 (Harder et al. 2007; Dai et al. 2013). The burned watershed is dominated by loblolly pine (Pinus taeda) and the unburned and second-order watersheds contain a combination of oaks and loblolly and longleaf (P. palustris) pines (Amaty and Trettin 2007; Harder et al. 2007). Riparian soils are moderately drained sandy loams over poorly drained clay subsoils (Harder et al. 2007; Dai et al. 2013).

The US Forest Service performed the most recent prescribed fire in 16 April, 2016 in the burned watershed using aerial ignition. A post-fire survey determined that 77% of the burned watershed exhibited moderate- and 22% experienced...
low-severity burn effects (Napper et al. 2009). The prescribed fire coincided with the beginning of a dry period that resulted in no streamflow until early June.

**Sampling and analyses**

**Grab samples and DOC analyses**

Duplicate water samples were collected at the three stream gauges biweekly between January and November 2016 in pre-rinsed amber glass 1-L bottles. Samples were refrigerated (4°C) immediately after collection, filtered with 0.45-μm prewashed Supor polyether sulfone membranes (PALL Corp., Port Washington, NY, USA) and analysed within 1 week. DOC was measured with a Shimadzu organic carbon analyser model TOC-VCHS (Shimadzu Corp., Kyoto, Japan) with a limit of quantification of 0.1 mg L⁻¹. UV-Vis spectral scans (200–700 nm) were recorded with a Varian Cary 50 (Agilent Technologies, Santa Clara, CA, USA) spectrophotometer with accuracy of ±0.07 absorbance units. We determined the absorbance at 254 nm (UV254) and calculated the 254/360 nm ratio (E2/E3) and spectral slope ratio (SSR) between the absorption spectra slope 275–295 nm divided by the 350–400 nm slope for the collected spectra. The last two parameters are known to positively correlate with the average molecular size of DOM (Helms et al. 2008).

**In-situ DOC sensor**

Optical Carboxylse II sensors (range 0–150 mg L⁻¹ DOC; turbidity 0–1400 Formazin Turbidity Units) (S-CAN, Vienna, Austria) were installed at each watershed sampling gauging station and powered by solar panels. The sensors recorded UV-Vis absorbance between 220 and 720 nm, which then passed through a proprietary algorithm that outputs DOC. The sensors were initialised using a single DOC concentration from each watershed following the specifications of the manufacturer (Jollymore et al. 2012). We compared the DOC analysis of grab samples with sensor readings every 14 days to adjust for changes in turbidity and DOM aromaticity that were not captured by the initial instrument calibration to refine sensor reading to better represent local conditions. We adjusted sensor values by subtracting the measurement error (the difference between paired grab sample DOC concentrations and the sensor reading of the closest timepoint) from them. Measurement errors were fitted to a locally estimated scatterplot smoothing (LOESS) function (span = 0.3) in R (see Fig. S1 in Supplementary Material available online; and Text S1 R-code for sensor correction in the burned watershed example) (Cleveland et al. 1992; R Development Core Team 2017). We used a locally weighted regression approach developed for temporally fluctuating environmental phenomena that integrates randomness associated with storms and drought. (Erlandsson et al. 2008; Hirsch et al. 2010; Kisi and Ozkan 2017; Taufik et al. 2017).

**Statistical analysis**

We compared DOC measured from grab samples to uncorrected and LOESS adjusted sensor data. We combined data from all three watersheds to compare agreement among the laboratory DOC measurements and both types of sensor values across a wide range of DOC concentrations and flow conditions. To see how well the sensor data could predict DOC values we evaluated goodness of fit with two-sample Kolmogorov–Smirnov tests (α ≤ 0.05) conducted with the ‘stats’ package in R (Warnes et al. 2019) between grab samples and both of the sensor values. We defined DOC accuracy for the sensor values as ±2 mg L⁻¹ for the mean of differences between grab samples and sensor. To calculate the mean of differences, a Bland–Altman analysis was used (Bland and Altman 1986; Watson and Petrie 2010).

Based on sensor DOC peaks (Fig. 2), we established the following analysis periods: pre-fire (1–19 April), post-fire storms Number 1 (1–30 June), Number 2 (1–15 July), Number 3 (16 July–2 August) and Number 4 (3–15 August). We evaluated data normality for each period and watershed with the Shapiro–Wilk test and found some periods not to be normally distributed (see Table S1 in Supplementary Material). We compared median corrected DOC sensor values for the burned and unburned watersheds within the discrete pre- and post-fire storm periods with Wilcoxon rank sum tests.

We calculated the DOC load (kg carbon per time period) for each pre- and post-fire period based on grab and sensor DOC concentrations (mg L⁻¹) and stream flow (L s⁻¹) from each gauging station. We estimated the difference in DOC load based on periodic grab samples compared with continuous sensor data for the sum of the first three storms after the prescribed burn. To calculate the grab DOC load in days without grab DOC concentrations, we used linear interpolation between the two closest grab DOC concentration timepoints to estimate the DOC concentration for that day.

We evaluated whether turbidity, UV254, E2/E3 or SSR was related to measurement error with Pearson linear correlations using the ‘GGally’ package (Schloerke et al. 2018) in R for pre- and post-fire storms. The third and fourth post-fire storms were grouped because only two grab samples were taken during the fourth storm. We considered the correlation was strong when the absolute value of the Pearson correlation coefficient (r) was greater than 0.5.

**Results and Discussion**

**General trends and seasonal variability of DOC**

The DOC concentrations in all watersheds were higher during the growing season (July–November) (Fig. 2). The unburned and second-order watersheds had a higher pre-fire mean DOC (15–20 mg L⁻¹) than the burned watershed (10–12 mg L⁻¹). These ranges were consistent with data collected in these sites since 2003 (USDA Forest Service 2017). Because of the drought conditions, streamflow ceased in all three watersheds from late April until June (see Fig. S2 in Supplementary Material). Resurgence of streamflow was associated with DOC peaks of
A similar pattern of increased DOC has been reported following dry periods in 30 small rivers in eastern USA (Raymond and Saiers 2010).

Prescribed fire effects on DOC, optical parameters and turbidity

The majority of organic matter transport after forest fires occurs during the first few high-intensity rainstorms (Gill 2004; Writer et al. 2014). Median adjusted sensor DOC concentrations were higher in the burned watershed (30 mg L$^{-1}$) compared with the unburned watershed (23 mg L$^{-1}$) during the first post-fire storm (Fig. 3). However, the Wilcoxon rank sum test did not show significant differences in DOC distribution ($P = 0.24$). Median adjusted sensor DOC concentration increased 13 mg L$^{-1}$ above the pre-fire baseline in the burned watershed, but only increased 3 mg L$^{-1}$ in the unburned watershed. The burned watershed median adjusted sensor DOC remained higher than the unburned one in the next two storm events and showed significant differences in DOC distribution between both watersheds (Wilcoxon rank sum test post-fire storm Number 2 $P = 0.004$, storm Number 3 $P = 0.002$). This difference was not evident during the fourth post-fire storm and median DOC differed by only 2 mg L$^{-1}$ (Wilcoxon ran sum test $P = 0.573$). In the second-order watershed, the first storm increased median DOC by 19–23 mg L$^{-1}$ above the pre-fire baseline and the increase oscillated between 16 and 23 mg L$^{-1}$ in the subsequent storms.

The burned watershed showed a decrease in the 254/360 nm absorbance ratio (E2/E3) and SSR in the first three post-fire storms (see Fig. S3 in Supplementary Material). Lower E2/E3 ratio and SSR have been associated with lower molecular weight DOM (Helms et al. 2008). The decrease in these parameters in the first three post-fire storms was not observed in the unburned

Fig. 2. Dissolved organic carbon (DOC) monitored with grab samples and adjusted sensor data in (a) burned and (b) unburned first-order watersheds, as well as the (c) receiving second-order watershed. Grey areas show discharge normalised to watershed area. The dashed lines show the DOC periods for analysis (pre-fire baseline, post-fire storms 1–4). (*) Sensor installation dates. The discontinuity of sensor data between mid-April and late May is because there was no stream flow at the gauging station.
watershed, suggesting that the decrease in the molecular weight of DOM may have been caused by the prescribed burn. Smaller E2/E3 and SSR were also observed in the second-order watershed, indicating the delivery of lower molecular weight DOM from the burned watershed into the second-order watershed. Moreover, there were no clear trends for turbidity in the burned and unburned watersheds, but there was a gradual turbidity increase in the second-order watershed throughout the periods in our study (see Fig. S3 in Supplementary Material).

**DOC load export from burned watershed to second-order watershed**

Prescribed fire resulted in a higher DOC load in the post-fire storms compared with the unburned watershed (Fig. 4). Notably, the sum of the first three post-fire storms indicated a 22% increase in the DOC load in the burned watershed compared with the unburned watershed (burned 382.7 kg-C, unburned 311.5 kg-C). The fourth storm was not included in the calculation, given the similarity of the median DOC concentration between these watersheds (Fig. 3). To determine any downstream effect of the additional DOC load released from the burned watershed, we compared the relative contributions of the burned and unburned watersheds on the DOC load of the second-order watershed. In the post-fire storms, the burned and unburned DOC load contributions accounted for 60–98% of the second-order watershed mass transfer under pre-fire conditions and the first, second and fourth post-fire flush events (see Fig. S4 and Text S2 in Supplementary Material).

Unlike DOC loads calculated from continuous in-situ sensor data, loads calculated from grab samples fail to capture storm peaks. In the unburned and second-order watersheds, the DOC load calculated with the grab samples underestimated the load by 11.8 and 63.7%, respectively, although the grab samples only underestimated the DOC load by 3.1% in the burned watershed. However, grab samples missed five DOC peaks in the burned watershed and one or two peaks in the other watersheds (Fig. 2), so DOC load underestimates were not related to the number of storms missed.

**Sensor goodness of fit, accuracy and sensor error correlations**

The unadjusted sensor data differed statistically from the grab samples (two-sample Kolmogorov–Smirnov test D = 0.094, P = 0.895), but the adjusted sensor values did not (two-sample Kolmogorov–Smirnov test D = 0.88462, P < 2.2 × 10−16). The adjusted sensor data fell within 2 mg L−1 of grab sample DOC concentrations and thus met our accuracy threshold based on Bland–Altman analysis.

The parameters influencing sensor error were related to watershed order and individual storms, but not to the prescribed burn. Before the prescribed burn, turbidity strongly correlated with sensor error in both first-order watersheds whereas the UV-Vis parameters had stronger correlations with sensor error in the second-order watershed (Table 1). In the first post-fire storm, SSR had the strongest correlation with sensor error for all watersheds and turbidity did not have a strong correlation with sensor error. During the second post-fire storm, both turbidity and SSR had the strongest correlations with sensor error across the watersheds.
Conclusion

In-situ optical sensors corrected with grab sample data were found to be effective in recording rapid changes in DOC concentration following a prescribed burn in watersheds with high DOC levels. Our field study showed that the peak DOC concentration lasted for three post-fire storms in a burned first-order watershed. Moreover, an additional 22% of the DOC load was observed within that burned watershed over a 2-month period (during which the first three storms occurred). The DOC load estimated by grab samples underestimated the sensor load, especially in the second-order watershed (63.7%). The DOC load contributed by the burned watershed accounted for 67.5% of the DOC load in the second-order watershed. Although these are high-DOC systems, additional DOC from prescribed fire might challenge downstream water treatment in sudden pulses if they exceed a treatment design threshold for DOC. Therefore, downstream water utilities and water resource managers need to pay attention to DOC pulses in watersheds during post-fire precipitation events.

Conflicts of interest

The authors declare this study to be free of conflicts of interest. They also did not benefit from this study or collaborate with the manufacturer of the instruments and sensors used in this research.

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