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Comparison of UV/Vis and FDOM sensors for in situ monitoring of stream DOC concentrations

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Abstract

Optical measurements using ultra-violet/visible (UV/Vis) spectrophotometric sensors and fluorescent dissolved organic matter (FDOM) sensors have recently been used as proxies of dissolved organic carbon (DOC) concentrations of streams and rivers at high temporal resolution. Despite of the merits of the sensors, temperature changes and particulate matter in water can interfere the sensor readings, over- or under-estimating DOC concentrations. However, little efforts have been made to compare responses of the two types of the sensors in natural conditions. We conducted both laboratory experiments and in situ monitoring with a UV/Vis sensor and a FDOM sensor during the three storm events in the fall of 2012 and the spring of 2013 in a forest stream in Korea in order to compare their performance. Laboratory experiments using the Suwannee River natural organic matter, humic acid, and fulvic acid demonstrated strong linear relationships between both the sensor signals and measured DOC concentrations with $R^2 \geq 0.98$. Although temperature compensation might not be needed for the UV/Vis sensor, it was sensitive to relativley small changes in turbidity. In contrast, the FDOM sensor was insenstive to relatively low turbidity while the FDOM sensor outputs decreased significantly as temperature increased, requiring temperature compensated FDOM (e.g. FDOM_{20} for 20 °C) for in situ monitoring of DOC. The results suggest that both sensors can be employed as a proxy for stream DOC concentrations after temperature and turbidity compensation in a forest stream where terrestrially derived humic-like materials are dominant components.

1 Introduction

Dissolved organic carbon (DOC), which is a dominant form of organic carbon in many streams and rivers, plays significant roles in aquatic systems. Riverine DOC is the energy source for heterotrophs (Raymond and Bauer, 2000), protects living organisms from UV light (Morris et al., 1995), and affects metal availability (Di Toro et al., 2001).

High riverine DOC concentrations can also lower the quality of drinking water by increasing trihalomethane (THM) formation potential during water treatment (Hur et al., 2014; Xie, 2004). Thus, many studies on DOC concentrations have been conducted at a variety of spatial scales such as streams draining from small watersheds to major rivers from large basins (Aitkenhead and McDowell, 2000; Jeong et al., 2012; Oh et al., 2013).

Studies on DOC release from forest ecosystems showed a close relationship between carbon export and hydrology, representing an important role of discharge on DOC loads (Jeong et al., 2012; Pellerin et al., 2012; Raymond and Saiers, 2010). Stream DOC load increased as water discharge increased, and thus it was observed that DOC released during storm events accounted for a substantial amount of total carbon export from an ecosystem (Hinton et al., 1997; Raymond and Saiers, 2010; Yoon and Raymond, 2012). Considering that a large variation in water discharge during the heavy rainfall could result in large variation in daily as well as annual DOC loads, monitoring stream carbon concentrations with high temporal resolution during storm events is necessary (Jollymore et al., 2012). This is valid especially in Asian monsoon regions including Korea (Kim et al., 2013) where more than 50 % of annual precipitation (an average of 1320 mm from 1981 to 2010) is concentrated during summer months (Korea Meteological Administration, www.kma.go.kr). Measurements of DOC concentrations with low temporal resolution (e.g. weekly or monthly) cannot fully capture DOC changes that typically last for just a few hours during a storm event in small streams, resulting in large uncertainty of estimating DOC loads (Jollymore et al., 2012). Thus, optical sensors have been used to achieve high-resolution in situ monitoring of DOC concentrations (Etheridge et al., 2014; Jollymore et al., 2012; Koehler et al., 2009; Pellerin et al., 2012; Strohmeier et al., 2013).

Two types of optical sensors have been used frequently for this purpose; the ultraviolet/visible (UV/Vis) spectrophotometer (Etheridge et al., 2014; Jeong et al., 2012; Jollymore et al., 2012; Strohmeier et al., 2013) and the fluorescent dissolved organic matter (FDOM) sensor (Pellerin et al., 2012; Saraceno et al., 2009; Watras et al., 2011).

UV/Vis sensors use the range of ultraviolet and visible light wavelengths (e.g. 220 to 720 nm) to rapidly scan absorbance of UV/Vis light by molecules in the water and estimate concentration of the molecules based on the Beer–Lambert law. Strong correlation between DOC concentration and light absorption has been used to provide algorithms that convert UV/Vis absorbance to DOC concentrations (Jollymore et al., 2012). FDOM sensors measure intensity of fluorophores, molecules absorbing UV light and reemitting light at longer wavelengths. Streams and rivers containing terrestrial DOC have many fluorophores and thus, FDOM sensors can be used to monitor DOC concentrations in fresh water (Downing et al., 2012; Wilson et al., 2013).

Although the two types of sensors have been employed to monitor DOC concentrations in various systems, several factors such as pH, turbidity, inorganic matters, and temperature could limit the use of both sensors. While the effects of pH and inorganic materials (e.g. nitrate, iron) commonly observed in most of natural watersheds are negligible (Weishaar et al., 2003), change of water temperature and increased turbidity could reduce the accuracy of the sensor readings (Downing et al., 2012). Fluorescence decreases as temperature increases, which is known as thermal quenching (Watras et al., 2011), and particles significantly attenuate or interfere detection of UV/Vis and FDOM sensors (Downing et al., 2012; Jeong et al., 2012). While in situ fluorescence measurements in filtered streamwater can provide a reliable proxy of stream DOC concentration overcoming interference due to particles, filter clogging has been reported to result in data loss during the later monitoring phase (Saraceno et al., 2009).

Although the UV/Vis and FDOM sensors have been used widely to estimate stream and river DOC concentrations, there is no study directly comparing the performance of the two types of sensors. The sensors may have their own strengths and weaknesses to monitor stream DOC concentration, and thus, the objectives of this study are to compare and contrast the performance of UV/Vis and FDOM sensors using laboratory experiments and in situ measurements in a temperate forest stream.

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◂◂ | ▸▸
◂ | ▸
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

2 Methods

2.1 Optical measurements using a UV/Vis and an FDOM sensor

Laboratory experiments and in situ measurements were conducted with a UV/Vis sensor (carbo::lyser™, s::can Messtechnik GmbH, Austria) and an FDOM sensor (cyclops-7, Turner Designs, USA). The UV/Vis sensor used in this study has two beams for auto-calibration and a 5 mm optical path length which is fitted to measurement ranges of 1–150 mg L^{-1} for TOC and 0.5–75 mg L^{-1} of DOC (Jeong et al., 2012; Waterloo et al., 2006). It scans light absorbance from 220 to 720 nm and the sensor uses standardized spectral algorithms called "global calibration" to estimate the concentrations of organic carbon. DOC concentrations are estimated by compensating absorbance by particles from that of TOC on the basis of mathematical fitting derived from absorbance measurements at the multiple turbidity-related wavelengths in the visible range between 450 and 650 nm (Jeong et al., 2012). Since post-measurement correction can considerably increase the accuracy of the UV/Vis sensor, the output DOC concentration of the sensor before the post-measurement correction was expressed as RU (relative unit).

The FDOM sensor uses LED (light emitting diode) as a light source, and the sensor uses the single excitation/emission pair, 325 nm/470 nm, with 120 and 60 nm excitation/emission band pass, respectively. Fluorescence intensity was normalized with quinine sulfate standards and expressed as quinine sulfate equivalent (QSE) in parts per billion. Quinine sulfate standards from 0 to 100 ppb were prepared to calibrate the FDOM sensor by diluting 1000 ppm of quinine sulfate stock solution which was made by dissolving 1.21 g of quinine sulfate dihydrates in 1 L of 0.5 M sulfuric acid.

A data logger (CR1000, Campbell science, USA) was programmed to collect optical data by FDOM sensor every 30 s, and data by UV/Vis sensor every 5 min. Turbidity and temperature sensors were included in the UV/Vis sensor, and thus the water temperature and turbidity data were collected together with DOC concentrations at 5 min-intervals. The temperature and turbidity sensors inside the UV/Vis sensor were tested using an independently calibrated temperature sensor (HOBO U12 stainless temperature data logger, Onset Computer Corporation, USA) and a turbidity sensor (Cyclops-7, Turner Designs, USA).

In order to examine the feasibility of using the UV/Vis and FDOM sensors to estimate DOC concentrations, three reference materials from the International Humic Substances Society (IHSS, http://www.humicsubstances.org) were used; the Suwannee River natural organic matter (SRNOM: 2R101N), the Suwannee River humic acid standard II (SRHA: 2S101H), and the Suwannee River fulvic acid standard I (SRFA: 1S101F). Stock solution of each reference material was made by dissolving 500 mg of SRNOM, and 100 mg of the other materials in 100 mL volumetric flask with deionized water (DI), respectively, followed by filtration through glass fiber filter (GF/F, Whatman; nominal pore size 0.7 µm). The range of DOC concentrations examined were 0 to 10.0, 0 to 2.0, and 0 to 4.0 $\mathrm{mg\,L^{-1}}$ for SRNOM, SRHA, and SRFA, respectively. The DOC concentrations were measured with Shimadzu-$\mathrm{V_{CPH}}$ TOC analyzer (Shimadzu Corporation, Japan) based on high temperature combustion method measuring non-purgeable organic carbon in acidified samples (∼ pH 2). Unless specified, the filtered DOC concentrations measured by the Shimadzu analyzer are presented as "lab DOC" in this article. Accuracy of the Shimadzu analyzer was verified by including quality check solutions (ERA, Colorado, USA) at a concentration similar to the sample DOC concentrations.

2.2 Temperature and turbidity correction

The effects of temperature on UV/Vis and FDOM sensors were tested over the range from 0 to 26.5 °C. The three reference solutions and an artificial stream water were prepared for the purpose. During the laboratory experiments, UV/Vis and FDOM sensors were submerged in a 10 L glass beaker containing 10 L of DI with black books lying below it to minimize light reflection. Then, 4–56 mL of stock solution prepared with the IHSS standards was added to the beaker so that the final DOC concentrations of the solutions were within the ranges between 0 and 10 $\mathrm{mg\,L^{-1}}$.

The artificial stream water was prepared by mixing leaves and soils collected from the study site (see Sect. 2.3) with DI, extracting DOC from the materials for about 48 h (Downing et al., 2012). The extracted water was filtered through glass fiber filter (GF/F, Whatman, USA) and used to test temperature effects on sensor readings. The sensor outputs were recorded as temperature changed and 50 mL of aliquots were collected from the beaker to measure lab DOC. Solutions were continuously stirred with magnetic bar during the experiments. The temperature compensation of the FDOM sensor was conducted following the method of Watras et al. (2011) in which the equation below was used.

$$\mathrm{FDOM}_{20} = \mathrm{FDOM}_\mathrm{m}/[1+\rho(T_\mathrm{m}-T_{20})] \quad (1)$$

where FDOM_{20} is predicted FDOM at 20 °C, FDOM_m is FDOM at a measured temperature (T_m), ρ is temperature coefficient (°C^{-1}), and T is temperature (°C).

In order to examine turbidity effects on the optical sensors, soil particles were added to the artificial stream water. The soils were collected from the study watershed at 0–15 cm depth, air-dried, and sieved (< 2 mm) before use. About 30 g of soils were mixed with DI and stayed for more than 48 h to preclude additional organic matter dissolved from the soil (Downing et al., 2012; Jeong et al., 2012). The soils were gradually added to the 10 L of glass beaker containing the artificial stream water so that turbidity increased stepwise from 0 to ~ 50 NTU, and aliquots were collected at each turbidity followed by filtration with GF/F filter for lab DOC measurements. The range of turbidity was selected after examination of the in situ turbidity of the forest stream (see 2.3) although this range of turbidity was about an order of magnitude smaller than those of other experiments (Downing et al., 2012; Jeong et al., 2012).

2.3 In situ measurements of the sensors in a forest stream

The UV/Vis, FDOM, and temperature sensors were deployed in a 2nd order stream from a forested watershed, “Bukmoongol watershed” (BW; 35.0319° N, 127.6050° E) in

Mt. Baekwoon located in Gwangyang city, Korea. The watershed is 33.3 ha in size and composed of 70 % of coniferous and 30 % of deciduous forests. Major tree species are *Pinus densiflora*, *Pinus rigida*, *Cryptomeria japonica*, *Pinus taeda*, and *Carpinus laxiflora*. Mean annual temperature is 14.4°C and mean annual precipitation is 1531 mm (1981–2010) in Suncheon (Korea Meteological Administration, www.kma.go.kr) which is located about 21 km away from Mt. Baekwoon. Bedrock is mainly composed of granite and partially gneiss, and sandy loam and clay loam comprise much of its soil (Park et al., 2000).

The performance of the sensors was examined during three storm events, 27–28 October and 10–11 November in 2012, and 23–24 April in 2013. Both sensors were submerged in the water next to each other in a ponding basin of a U-shaped weir. UV/Vis sensor was deployed vertical to the stream flow and compressed air cleaned the sensor head right before the measurements to prevent from sediment accumulation. FDOM sensor was deployed with its head down to the streambed to minimize light reflection. Two aberrant UV/Vis data points out of a total of 1088 data points were filtered off when they were larger than [mean + 3 stand deviation] from consecutive measurements for 1 h, which could be due to stochastic disturbances of leaves or debris (Jeong et al., 2012). The two outliers were replaced with average of neighboring two data points.

During the in situ deployment of the sensors, discrete stream water samples were collected every 1 to 4 h from the start to the end of each event. Samples were frozen immediately after sampling, and transported on ice to the laboratory. Then, they were filtered through GF/F filter and lab DOC concentrations were measured to compare with the sensor outputs. The DOC concentrations of several frozen samples were compared to those of refrigerated samples and the difference was less than 0.1 mg L^{-1} ($p = 0.46$). Linear regression models were used to estimate relationships between sensor outputs and lab DOC. Statistical analyses were conducted with R statistical program (http://www.r-project.org/), and considered significant when $p < 0.05$.

3 Results and discussion

3.1 Laboratory experiments

3.1.1 Sensor signals vs. lab DOC of reference materials

Laboratory experiments of UV/Vis and FDOM sensors on SRNOM, SRHA, and SRFA demonstrated strong linear relationships between the sensor signals and lab DOC (R^2: 0.98 to 1, $p < 0.01$) although the slopes were not identical among the dissolved organic materials (Fig. 1). The slope of UV/Vis signals of SRHA was statistically different from those of SRNOM and SRFA (Fig. 1a), and the slope of FDOM signals of SRFA was statistically different from those of SRNOM and SRHA (Fig. 1b).

SUVA_{254} (specific UV absorbance at 254 nm) of Suwannee River Standard Humic Acid (1S101H) was higher than those of Suwannee River Standard Fulvic Acid (1S101F) and Suwannee River Natural Organic Matter (1R101N) indicating that SRFA and SRNOM contained more non-UV absorbing carbon (Alberts and Takács, 2004). In contrast, relative fluorescence intensities of SRFA was higher than those of the humic acid (1S101H) and natural organic matter (1R101N) (Alberts and Takács, 2004). This suggests that the reliability of the UV/Vis and FDOM sensors could be dependent on the proportion of light-absorbing functional groups in DOC and degree of charge-transfer interactions between the electron donor (e.g. hydroxy benzene) and acceptor (e.g. quinoid) groups (Del Vecchio and Blough, 2004).

Humic acids and fulvic acids are the major fraction of DOC in natural waters that are ubiquitously found in nature (Del Vecchio and Blough, 2004), covering about 60 % of aquatic DOC in a 1 : 3 ratio between humic acid and fulvic acid in the median freshwater (Perdue and Ritchie, 2014). Although the DOC composition could remain relatively constant across seasons, slightly increased fluorescence per unit absorbance was reported in a forest stream in northeastern US (Wilson et al., 2013). Since stream and riverine DOC composition can be shifted following storms (Fellman et al., 2009), comparison of monitored sensor signals with lab DOC of regularly (e.g. weekly) collected samples is warranted.

3.1.2 Temperature effects on optical measurements

The UV/Vis sensor showed little variability with temperature change (slope: −0.009 to −0.04 RU °C^{-1}, R^2: 0.22 to 0.54) indicating that the effect of temperature on UV/Vis sensor was minimal (Fig. 2a). Therefore, it is advantageous to use a UV/Vis sensor in remote areas with temperature fluctuation (Jollymore et al., 2012). For example, the UV/Vis sensor was used for continuous monitoring of DOC in a forest stream where stream temperature varied from near 0 to ∼ 25 °C (Jeong et al., 2012).

In contrast, FDOM signals can be significantly affected by temperature because the temperature increase is likely to return an excited electron to its ground state by radiationless decay, resulting in reduced fluorescence emission intensity (Watras et al., 2011). We observed strong negative correlations of FDOM sensor with temperature (slope: −0.28 to −0.69 ppb QSE °C^{-1}, R^2: 0.93 to 0.99, $p < 0.001$), decreasing by about 1.4 % in ppb QSE per 1 °C increase (Fig. 2b). This result is consistent with the former studies showing that FDOM signals decreased by an average of 0.8–1.5 % °C^{-1} increase over the range from ∼ 1 to 25 °C (Downing et al., 2012; Watras et al., 2011). The slight difference in the slopes of the four materials (Fig. 2b) can be due to the difference in concentration as indicated by a study on fluorescence of wetland-dominated lakes as a function of temperature where slope of the fluorescence against temperature increased as concentration decreased (Watras et al., 2011). The extent of thermal quenching is related to the exposure of the fluorophores to heat source (Baker, 2005). The concentration of fluorophores can increase as DOC concentration increases, and thus more fluorophores in high DOC concentrations are prone to thermal quenching as temperature increases. This suggests that temperature compensation would be critical especially for relativley high DOC concentrations.

The degree of thermal quenching is also dependent on the components of DOC such that tryptophan-like fluorophores exhibit strong thermal quenching properties com-

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

pared to humic-like or fulvic-like fluorohphores (Baker, 2005). Thus it should be also investigated if the concentrations of tryptophan-like components can vary significantly when the FDOM sensor is deployed in a water system.

These results suggest that FDOM sensor need temperature compensation to correctly estimate DOC concentrations, especially in places where DOC concentration is relativley high and temperature variation can be large. After the temperature compensation, the estimated FDOM at 20 °C (FDOM_{20}) did not change significantly as temperature increased (Fig. 2c) demonstrating the great potential of FDOM sensor for continuous monitoring of DOC in the fields with temperature data loggers.

3.1.3 Turbidity effects on optical measurements

The UV/Vis sensor had a propensity for increased DOC (RU) as turbidity increased (Fig. 3a). The UV/Vis sensor was designed with auto-compensation for turbidity but DOC concentrations was over-estimated as turbidity increased (Jeong et al., 2012). The UV/Vis sensor over-estimated lab DOC of about 2 $\text{mg}\,\text{L}^{-1}$ by more than 10 times in water of turbidity > 1000 NTU (Jeong et al., 2012). The effects of turbidity on the UV/Vis sensor were still observable in the low range of turbidity from 0 to 50 NTU (Fig. 3a). In this range of turbidity, the slopes of the UV/Vis sensor outputs and turbidity were both positive, 0.056 and 0.018 NTU^{-1}, for the solutions of lab DOC of 3.1 and 5.2 $\text{mg}\,\text{L}^{-1}$, respectively (Fig. 3a), suggesting that the UV/Vis sensor can be highly sensitive to relatively low turbidity.

In contrast, FDOM_{20} of the DOC solutions did not change significantly (lab DOC of 3.1 $\text{mg}\,\text{L}^{-1}$) or slightly decreased (lab DOC of 5.2 $\text{mg}\,\text{L}^{-1}$) as turbidity increased from 0 to ~ 50 NTU (Fig. 3b). A study on turbidity effects on FDOM signals using the Elliott Soil (IHSS standard) sample demonstrated 80 to 90 % attenuation of FDOM signals at ~ 1000 NTU (Downing et al., 2012). However, the attenuation of FDOM signals quickly decreased to about 10–20 % at turbidity less than 50 NTU (Downing et al., 2012). Considering that the slope of light attenuation vary with the particle size distribution (Boss et al., 2001), different particle compositions of soils used in the experiment could result in different attenuation effect.

Turbidity can increase over 100 NTU during strong storms (e.g. typhoons) when daily rainfall is larger than 100 mm day^{-1} and thus a calibration process over a large range of turbidity may be required (Downing et al., 2012; Saraceno et al., 2009). However, our results indicated that turbidity correction for the FDOM sensor may not be necessary in BW stream during the study period when the DOC concentration was lower than 3 mg L^{-1} with turbidity less than 50 NTU.

3.2 In situ measurements of UV/Vis and FDOM sensors

The UV/Vis and FDOM sensors followed the changes of DOC concentrations in the three storms (Fig. 4) in which water temperature ranged from 8.2 to 13.8 °C. The precipitation of the three storm events were 40.5, 19.5, and 56.0 mm, respectively, which increased turbidity only up to ~ 10 NTU, and thus turbidity effect was assumed to be negligible (Fig. 3). The correlation coefficient of linear regression between FDOM$_{20}$ and lab DOC ($R^2 = 0.93$) was higher than that between UV/Vis signals and lab DOC ($R^2 = 0.62$) (Fig. 5). Although turbidity compensation would be necessary for large storm events, this suggests that the FDOM sensor was sensitive even at relatively low concentrations of DOC and has a great potential to monitor DOC concentrations in the forest stream.

In contrast, the UV/Vis sensor was less accurate in estimating DOC concentration (Figs. 4 and 5) although POC and turbidity outputs can be also provided by the sensor. Whereas about 50 % of FDOM signal can be attenuated at ~ 200 FTU of turbidity (Downing et al., 2012), the UV/Vis sensor can significantly overestimate stream DOC concentration of high turbidity unless post-measurement correction was made (Jeong et al., 2012). Estimated DOC concentration by the UV/Vis sensor increased by ~ five times as turbidity increased from 0 to ~ 1000 NTU for the water of DOC concentration of 2 mg L^{-1} in a forest stream in Korea (Jeong et al., 2012). The monitored three storms were not strong in terms of rainfall intensity resulting in relatively low turbidity. However, turbidity compensation can be the most critical step for the sensors to be employed for monitoring of stream DOC concentrations during summer monsoon because of the strong dependence of the sensor outputs on turbidity.

The sensors use optical properties of DOC, especially humic materials. The single excitation and emission pair (325 nm/470 nm) that the FDOM sensor used in this study estimates the intensity of fluorescence of humic-like DOM (Stedmon and Markager, 2005). If the dominant DOC composition of water sample reacts to different excitation and emission pair, for example, tryptophan-like components which absorbs at 280 nm and emits at 344 nm of wavelength (Stedmon and Markager, 2005), the FDOM sensor may underestimate DOC concentrations. However, considering that ~ 80 % of stream DOC released from the forested watershed were terrestrial humic components estimated by PARAFAC analysis (unpublished data), the optical sensors could be effectively employed for monitoring of DOC at the study site. Nontheless, comparison with DOC concentrations of regular (e.g. weekly) grab samples would be still warranted since the proportion change of chromophores and fluorophores in humic materials during intensive storms could result in changes in sensor outputs.

Although inner filter effect (IFE) could be a problem in obtaining correct fluorescence data of stream water if it has relatively high DOC concentrations with high aromaticity, a study highlighted that common rivers and streams have minor IFE effects by dissolved organic matters (Downing et al., 2012). Furthermore, considering that IFE effects could be significant only in streams or rivers with relatively high DOC concentrations, it is unlikely that FDOM signals need to be compensated for IFE in the forest stream where the DOC concentration was less than 3 $\mathrm{mg\,L^{-1}}$.

Maintaining clean surface of light sources of the sensors during long-term monitoring is an important practical consideration ensuring data quality since particles can cause light absorption or scattering. Algae which commonly occur in lakes or large rivers during summer in Korea could interfere light path of optical sensors. Although alga were not observed in the study site, the surface of the sensor need to be cleaned regularly because it could be still coated by inorganic materials. The UV/Vis sensor

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

uses air bubbles to prevent accumulation of particles in the light beam path and some advanced FDOM sensors have auto-cleaning wiper. However, the frequency of manual field check may still need to be decided depending on site characteristics.

4 Conclusions

A variety of organic compounds can absorb UV/Visible light and reemit light at longer wavelength and this optical property can be used to monitor stream DOC concentrations by UV/Vis and FDOM sensors. Terrestrially derived humic materials have many fluorophores and thus UV/Vis and FDOM sensors have a strong potential to be used for continuous monitoring of DOC concentrations in streams of forested watersheds. However, temperature and turbidity compensation using site-specific information may be needed to reduce the error in monitoring DOC concentrations. Shifts in composition of fluorophores need to be also carefully tracked since light absorbance and fluorescence can vary as the concentrations of dominant fluorophores change. Nonetheless, the credibility as well as continuity of the field DOC data may improve significantly if combined with field based calibration process due to the recent advances in sensor technology as well as wireless remote on-line connection.

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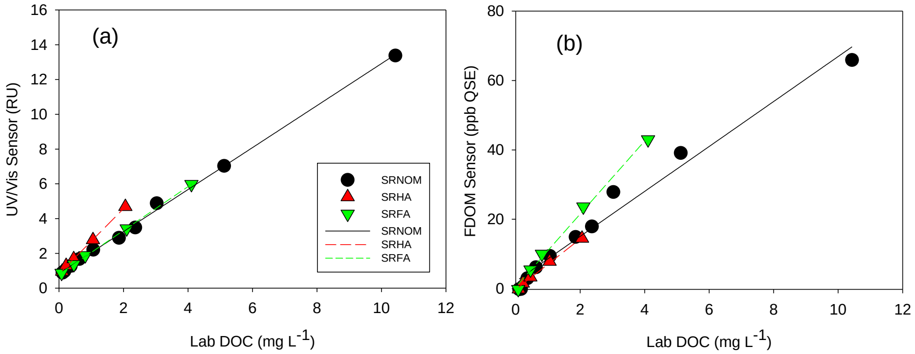

Figure 1. Relationship between **(a)** UV/Vis (RU: relative units), and **(b)** FDOM sensor readings and DOC concentrations measured by Shimadzu TOC analyzer (lab DOC) of IHSS reference materials (SRNOM, SRHA, and SRFA) at water temperature between 17 and 19 °C. The R^2 of the linear regression lines were 0.98 to 1.00.

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
◀◀
▶▶
◀
▶
Back
Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

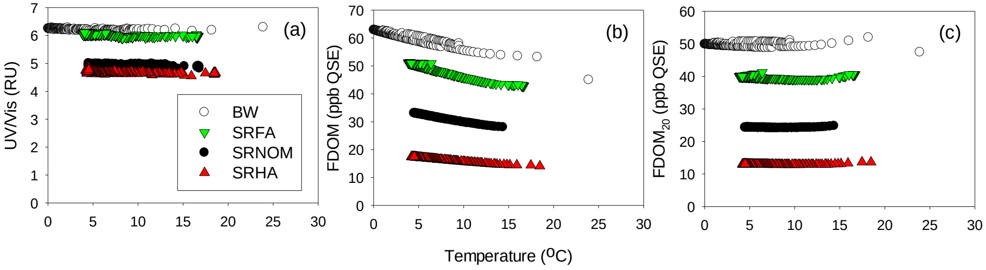

Figure 2. Relationship between **(a)** UV/Vis (RU: relative units), **(b)** FDOM, and **(c)** FDOM$_{20}$ (FDOM signals compensated for 20 °C) and temperature. The FDOM$_{20}$ was estimated following the method of Watras et al. (2011). The lab DOC concentrations of the BW, SRFA, SRNOM, SRHA were 5.2, 4.1, 3.0, and 2.1 mg L^{-1}, respectively.

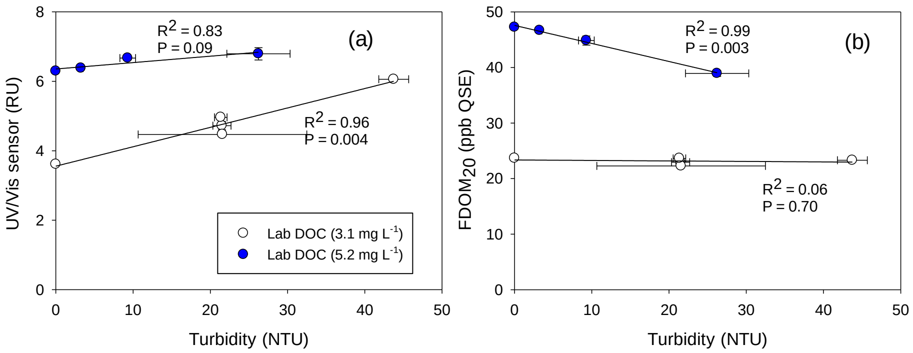

Figure 3. Relationship between **(a)** UV/Vis sensor outputs (RU: relative units) and turbidity, and **(b)** $FDOM_{20}$ (FDOM compensated for 20 °C) and turbidity. The error bars are standard errors.

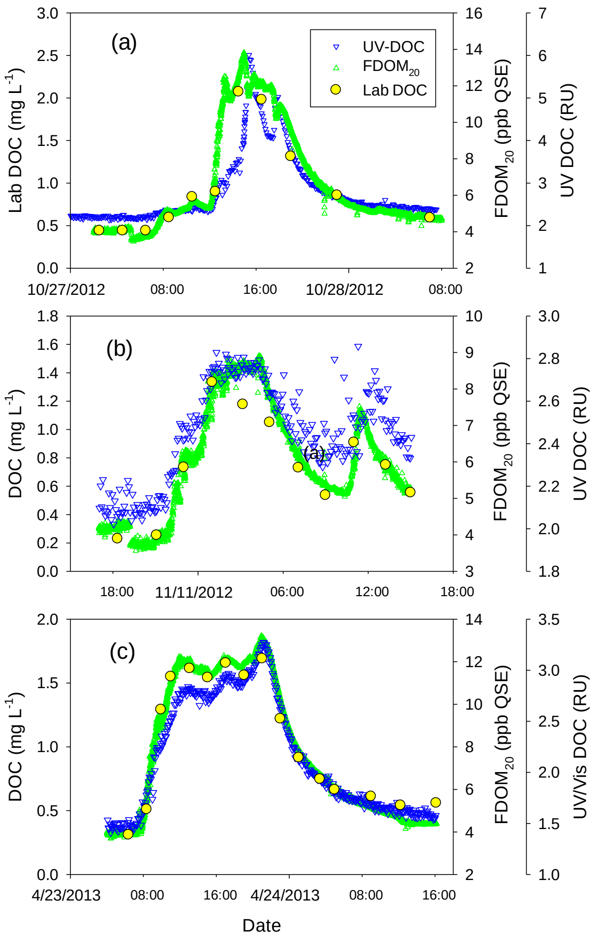

Figure 4. In situ $FDOM_{20}$ and UV/Vis sensor outputs during the three storm events of **(a)** 40.5, **(b)** 19.5, and **(c)** 56.0 mm of precipitations.

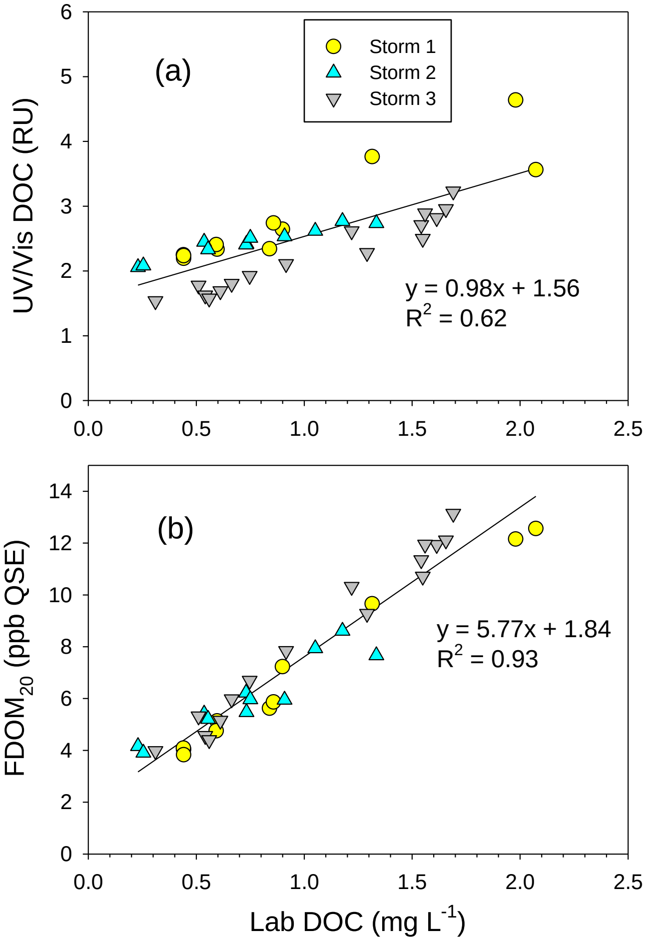

Figure 5. Comparison of the **(a)** UV/Vis sensor outputs and **(b)** $FDOM_{20}$ with lab DOC for the three storm events (Fig. 4).