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 with 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 to critical interferences such as temperature and turbidity. The performance of a UV/VIS sensor and an FDOM sensor was compared in both laboratory experiments and *in situ* monitoring during three storm events in a forest stream in Korea. Although the UV/VIS sensor did not require temperature compensation in laboratory experiments using the forest stream water, its deviations from the DOC concentrations measured with a TOC analyzer increased linearly as turbidity increased. In contrast, the FDOM sensor outputs decreased significantly as temperature or turbidity increased, requiring temperature and turbidity compensation for *in situ* monitoring of DOC concentrations. The results suggest that temperature compenstation is relatively straightforward but turbidity compensation may not be simple because attenuation of lights by particles can significantly reduce the sensitivity of the sensors in highly turbid waters. Shifts in composition of fluorophores need to be also carefully tracked using periodically collected samples since light absorbance and fluorescence can vary as the concentrations of dominant fluorophores change.

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 concentration ([DOC]) can also lower the quality of drinking water by increasing trihalomethane formation potential during water treatment (Hur et al., 2014; Xie, 2004). Thus, many studies on [DOC] 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 can 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 South Korea (Kim et al., 2013) where more than 50% of annual precipitation (an average of 1,320 mm from 1981 to 2010) is concentrated during summer months (Korea Meteological Administration, www.kma.go.kr). Measurements of stream [DOC] 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] (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 ultra-violet/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] and light absorption has been used to provide algorithms that convert UV/VIS absorbance to [DOC] (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 as a proxy to monitor [DOC] in fresh water systems (Downing et al., 2012; Wilson et al., 2013).

Although the two types of sensors have been employed to monitor [DOC] 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 and iron) commonly observed in most 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 with 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] by 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], to our knowledge, there is no study directly comparing the performance of the two types of sensors (Table 1). The sensors may have their own strengths and weaknesses as a proxy to monitor stream [DOC], and thus, the objective of this study is to compare the performance of UV/VIS and FDOM sensors as a proxy for [DOC] using laboratory experiments and *in situ* measurements in a temperate forest stream.

Table 1

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^{TM}, 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 unit of output [DOC] 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 used to collect optical data of the sensors either every minute during laboratory experiments or every five minutes during *in situ* monitoring. Turbidity and temperature sensors were included in the UV/VIS sensor, and thus the water temperature and turbidity data were collected together with the proxy of [DOC]. 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 Hach 2100P Portable Turbidimeter (Hach Company, Loveland, USA).

In order to examine the feasibility of using the UV/VIS and FDOM sensors as a proxy to estimate [DOC], three reference materials from the International Humic Substances Society (IHSS, http://www.humicsubstances.org) were tested; 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] examined were 0 to 5.1 mg L^{-1}, 0 to 2.1 mg L^{-1}, and 0 to 4.1 mg L^{-1} for SRNOM, SRHA, and SRFA, respectively. The [DOC] was measured with Shimadzu-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] measured by the Shimadzu analyzer are presented as "lab DOC" in this article. Accuracy of the Shimadzu analyzer was verified by analyzing quality check (QC) solution (ERA, Colorado, USA) at a concentration similar to the sample [DOC]. The measurement error for a QC (4.8 mg L^{-1}) was 3% on average and < 0.1 mg L^{-1} for the other QC (0.5 mg L^{-1}).

2.2 Temperature and turbidity correction

During the laboratory experiments, UV/VIS and FDOM sensors were submerged in a 10 L glass beaker containing 10 L of DI with black-covered books lying below it to minimize light reflection. The stock solution prepared with the IHSS standards was added to the beaker so that the final [DOC] of the solutions were within the ranges between 0 and 5.1 mg L^{-1}. In order to simulate field conditions, about 20 L of stream water was used for temperature and turbidity correction. The stream water had been collected from a forest watershed as detailed in the next section (2.3) at peak discharge using precombusted 2 L glass bottles when the typhoon, "NAKRI" hit South Korea on August 2nd in 2014, and was kept frozen before the experiment. The [DOC] of the thawed and fitered (GF/F) stream water was 3.4 mg L^{-1} and was used to test effects of temperature on UV/VIS and FDOM sensors over 6 – 26^{o}C.

An artificial turbid stream water was also prepared by adding 270 g of soils collected from the study site (see 2.3) in 10 L of the stream water, extracting DOC from the soils for about 48 hours to preclude additional organic matter dissolved from the soil (Downing et al., 2012; Jeong et al., 2012). The soils were collected from the study watershed at 0-15 cm depth, air-dried, and sieved (< 2 mm) before use. The lab DOC of the resulting solution was 12.3 mg L^{-1} which was used to prepare a series of solution of different lab DOC from 1.1 to 10.5 mg L^{-1} by mixing with DI to evaluate temperature effects on the sensor readings.

Linear regression between UV/VIS sensor and temperature was used to estimate the temperature correction factor for UV/VIS sensor outputs, $r_{UV, T}$ (Eq. 1). Since the difference in slopes of the UV sensor against temperature was not statistically significant (Fig. 2d), the mean of the two slopes (α) was used to calculate the UV/VIS sensor outputs at 20°C (UV/VIS_{20}) (Eq. 1).

$$UV/VIS_{20} = UV/VIS_m + \alpha\,(20 - T_m) \qquad \text{(Eq. 1)}$$

where T_m is the temperature at which UV/VIS sensor outputs were measured (UV/VIS_m).

The temperature compensation of the FDOM sensor was conducted following the method of Watras et al. (2011).

$$FDOM_{20} = FDOM_m / [1 + \rho(T_m - 20)] \qquad \text{(Eq. 2)}$$

where $FDOM_{20}$ is a predicted FDOM at 20°C, $FDOM_m$ is the measured FDOM at temperature (T_m), ρ is temperature coefficient (°C^{-1}), and T is temperature (°C) (Eq. 2).

The turbidity of the solution was measured using aliquots and the sensor readings of the artificial turbid water were recorded every minute while the solution was continuously stirred with magnetic bar during the experiments. The sensor outputs of the turbid water were compared with those of the filtered water to calculate the r_p (Eqs. 3 and 4) (Downing et al., 2012). The maximum turbidity of the solution was 973.3 NTU to cover most extreme events in streams and rivers (Downing et al., 2012; Jeong et al., 2012; Kim et al., 2013).

$$r_{UV,\,p} = (UV/VIS_m) / (UV/VIS_f) \qquad \text{(Eq. 3)}$$

$$r_{FDOM,\,p} = FDOM_m / FDOM_f \qquad \text{(Eq. 4)}$$

where UV/VIS_m and $FDOM_m$ are measured sensor outputs, and UV/VIS_f and $FDOM_f$ are the sensor outputs of filtered solution by GF/F filters. Given that the slope of UV/VIS outputs against lab DOC were not statistically different (Jeong et al., 2012), $r_{UV,\,p}$ can be calculated using linear interpolation for any turbidity of any lab DOC. Thus, the raw sensor outputs were corrected for temperature and turbidity using the following equations.

$$UV/VIS_{20,p} = [\, UV/VIS_m + \alpha\,(20 - T_m)\,] / r_{UV,\,p} \qquad \text{(Eq. 5)}$$

$$FDOM_{20,p} = [\, FDOM_m / [1 + \rho(T_m - 20)]\,] / r_{FDOM,\,p} \qquad \text{(Eq. 6)}$$

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 ^{o}N, 127.6050 ^{o}E) in Mt. Baekwoon located in Gwangyang city, South 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^{o}C and mean annual precipitation is 1,531 mm (1981-2010) in the weather station located in Suncheon (Korea Meteological Administration, www.kma.go.kr), ~20 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 sensors as a [DOC] proxy were examined during three storm events, October 27-28th and November 10-11th in 2012, and April 23-24th 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 with the sensor head facing the streambed to minimize setteling of particles 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 1,088 data points were filtered off when they were larger than [mean + 3 standard deviation] from consecutive measurements for 1 hour, 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 hours 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 exhibited 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 significantly different from those of SRNOM and SRFA (Fig. 1a), and the slope of FDOM signals of SRFA was significantly different from those of SRNOM and SRHA (Fig. 1b).

$SUVA_{254}$ (specific UV absorbance at 254 nm) of the SRHA (1S101H) was higher than those of the SRFA (1S101F) and the SRNOM (1R101N) indicating that SRFA and SRNOM contain more non-UV absorbing carbon (Alberts and Takács, 2004). In contrast, relative fluorescence intensities of SRFA were higher than those of the SRHA (1S101H) and SRNOM (1R101N) (Alberts and Takács, 2004). This suggests that the reliability of the UV/VIS and FDOM sensors can 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 periodically collected samples is warranted.

Fig. 1.

3.1.2 Temperature effects on optical measurements

The UV/VIS sensor outputs showed little variability with temperature change (slope: 0.009 to -0.004, R^2: 0.22 to 0.54, $p < 0.01$) in SRNOM, SRHA, and SRFA solutions (Fig. 2a) as well as in the forest stream water (Fig. 2d; slope: 0.001 to 0.002 RU $^oC^{-1}$, R^2: 0.03 to 0.04, $p < 0.01$). The slopes of the UV/VIS sensor outputs against temperature were less than 0.01 RU $^oC^{-1}$, indicating that the effect of temperature on UV/VIS sensor was negligible. Even if temperature of the forest stream water increased by 20^{o}C, the sensor outputs would increase only by ~0.03 RU, which is less than 1% of sensor readings of the forest stream (Fig. 2d). Therefore, it may be advantageous to use the UV/VIS sensor in remote areas with a large 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^{o}C to ~25^{o}C (Jeong et al., 2012).

In contrast, FDOM signals can be significantly affected by temperature changes 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 the FDOM sensor with temperature in the reference materials as well as in the the whole range of DOC concentrations from 1.1 to 10.5 mg L^{-1} of the forest stream (slope: -0.17 to -2.07 (ppb QSE) $^{o}C^{-1}$, R^2: 0.97 to 0.99, $p<0.001$), decreasing by ~1.4% in ppb QSE per 1^{o}C increase (Fig. 2b, 2e). This result is consistent with the former studies showing that FDOM signals decreased by an average of 0.8-1.5% per 1^{o}C increase over the range from ~1 to 25^{o}C (Downing et al., 2012; Watras et al., 2011).

A study on fluorescence of wetland-dominated lakes demonstrated that slope of the fluorescence against temperature increased as concentration decreased (Watras et al., 2011) and the same pattern was observed in this study (Fig. 2e). Temperature coefficent, ρ ($^{o}C^{-1}$) was estimated to be -0.017 ± 0.004 (mean ± SD) for the solutions of lab DOC from 1.1 to 10.5 mg L^{-1} at 20^{o}C. Given that the extent of thermal quenching is related to the exposure of the fluorophores to the heat source (Baker, 2005), the concentration of fluorophores can increase as [DOC] increases, and thus more fluorophores in high DOC concentrations are prone to thermal quenching as temperature increases. This suggests that temperature compensation of FDOM sensor outputs would be critical especially for water of relatively 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 compared to humic-like or fulvic-like fluorohphores (Baker, 2005). Thus, it warrants a further study if the accuracy of the FDOM sensor decreases in a water containing high amounts of tryptophan-like compounds.

These results suggest that the FDOM sensor requires a temperature compensation to correctly estimate [DOC], especially in streams where [DOC] is relatively high and temperature varies a lot. After the temperature compensation, $FDOM_{20}$ did not change significantly as temperature increased (Fig. 2c, f), demonstrating that a proper temperature compensation allows the FDOM sensor to be used as a proxy of [DOC] in the streams that are also continously monitored for water temperature.

Fig. 2.

3.1.3 Turbidity effects on optical measurements

The UV/VIS sensor outputs increased as turbidity increased, and thus, $r_{UV,p}$ had a positive linear relationship over 0 to ~1000 NTU of turbidity (slope: 0.0006, R^2: 0.98, $p<0.001$), resulting in ~70% increase in UV/VIS sensor signals at 1000 NTU of the forest stream water (Fig. 3). The slope of $r_{UV,p}$ against turbidity was slightly higher (0.0009) over the range of 0 – 100 NTU of turbidity, suggesting that $r_{UV,p}$ was more sensitive in relatively low turbidity. However, the change in $r_{UV,p}$ was only ~10% even at 100 NTU for the forest stream water.

Fig. 3

In contrast, FDOM outputs decreased exponentially, as turbidity increased from 0 to ~1000 NTU. Values of $r_{FDOM,p}$ also changed exponentially in the whole range of turbidity and decreased linearly at low turbidity (Fig. 3c, d, $p<0.001$). About 34% of FDOM signals were attenuated at ~100 NTU and 84% of FDOM signals at ~1000 NTU, which was similar with the results by Downing et al. (2012). Although about 80% to 90% FDOM signals were attenuated at ~1000 NTU using the Elliott Soil (IHSS standard), the attenuation of FDOM signals was just 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), soils with different particle compositions may result in different attenuation effect.

Turbidity can increase >1000 NTU during strong storms in upstream forested watersheds in South Korea although turbidity was lower than 1000 NTU throughout the year in most streams and rivers (Kim et al., 2013). Given the strong dependency of DOC esimation on turbidity in the UV/VIS sensor and exponential decrease of FDOM outputs due to increased turbidity, compensation for turbidity is a critical step for the sensors to be used as a proxy for [DOC]. This could be even more critical in streams with relatively high slopes under Asian monsoon climates. Since stream turbidity can be a function of size of particles and soil mineralogy of a watershed (Hur and Jung, 2009), site-specific compensation for turbidity is necessary.

3.2 In situ measurements of UV/VIS and FDOM sensors

The UV/VIS and FDOM sensors followed the changes of [DOC] in the three storms (Fig. 4) in which water temperature ranged from 8.2 to 13.8^{o}C. The precipitation of the three storm events were 40.5, 19.5, and 56.0 mm, respectively, which increased turbidity only up to ~30 NTU. Since the variation of temperature and turbidity was relatively small, the in-situ data of the sensors corrected for temperature and turbidity (Eqs. 5 & 6) were similar to the raw singals of the sensors except the temperature corrected FDOM signals (Fig. 4).

While the UV/VIS signals did not change significantly after temperature and turbidity corrections, the FDOM signals decreased after temperature correction because water temperature was consistently lower than the reference temperature of 20^{o}C with negligible change for turbidity correction (Fig. 4). The correlation coefficient of linear regression between $FDOM_{corr}$ (temp + turb) and lab DOC (R^2 = 0.95) was higher than that between UV/VIS_{corr} (temp + turb) signals and lab DOC (R^2 = 0.62) (Fig. 5). The relatively low R^2 of the UV/VIS sensor was due to the two outliers of storm 1. We postulate that the UV/VIS sensor outputs are sensitive to turbidity sensor outputs within the system since both of them appear tightly connected in “global calibration.”

Fig. 4

Fig. 5

The three storm events were not strong in terms of precipitation intensity and did not capture large variation of temperature and turbidity in the field and this is a limitation of this study. However, this can be also interpreted that the sensors can be employed to provide reliable, high resolution data for base flow conditions. Although it is demonstrated that the sensors can be compensated for temperature and turbidity to be used as a proxy of [DOC], there are several other factors that should be considered for successful application of the sensors in the field.

The sensors use absorbance and fluorescence of lights by DOM, and thus the DOM with the optical properties may not represent the entire DOM pools although fluorophores correlate well with diverse, known compounds in other riverine environments (Stubbins et al., 2014). The single excitation and emission pair that the FDOM sensor used in this study (Table

1) estimates the intensity of fluorescence of humic-like DOM (Stedmon and Markager, 2005). If the dominant DOM 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 stream [DOC]. However, considering that ~80% of stream DOC released from the forested watershed were terrestrial humic components estimated by PARAFAC analysis (unpublished data), the FDOM sensor can be effectively employed as a proxy of [DOC] after temperature and turbidity correction. Nontheless, comparison with [DOC] of periodically collected samples would be still necessary since the proportion change of chromophores and fluorophores in humic materials during intensive storms could result in changes in sensor outputs.

Although we tested two specific models of UV/VIS and FDOM sensors, multiple models are available and we did not address variability of many sensors or variability within a model line. Sensor-specific as well as site-specific calibration would be necessary to use the sensors as a proxy of [DOC] considering that each sensor reacts differently to a range of temperature and turbidity. For example, four types of FDOM sensors showed different attenuation ratio to changes of turbidity although they all showed increasing trends of attenuation with increased turbidity (Downing et al., 2012). FDOM sensors with open path responded strongly to turbidity changes than that with close path (Downing et al., 2012).

Inner filter effect (IFE) could be a problem in obtaining correct fluorescence data of stream water if the stream has relatively high [DOC] with high aromaticity. However, a study highlighted that common rivers and streams have minor IFE effects by dissolved organic matter (Downing et al., 2012). It is unlikely that FDOM signals need to be compensated for IFE in the forest stream where [DOC] was less than 3 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 (Etheridget et al., 2013). Algae which commonly occur in lakes or large rivers during summer in South Korea could interfere light path of optical sensors. Although algae were not observed in the study site, the surface of the sensor need to be cleaned periodically because it could be still coated by inorganic materials. The UV/VIS sensor 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 field check may still need to be decided depending on site characteristics.

4 Conclusions and Implications

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] by UV/VIS and FDOM sensors. The credibility as well as continuity of the field DOC data may improve significantly due to the recent advances in sensor technology as well as wireless remote on-line connection if combined with field based calibration process. 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] in streams of forested watersheds. However, the results shown in this study suggest that temperature and turbidity compensation using site-specific and sensor-specific information is critical to reduce inaccurate sensor responses to large temporal fluctuations of temperature and turbidity, particularly during strong storm events when turbidity can increase by a few orders of magnitude. While the sensor compensation for temperature is relatively straightforward, that for turbidity is not simple because turbidity can be affected by particle size and soil mineralogy. More than 80%

of lights can be attenuated at turbidity >1,000 NTU in FDOM sensor. Although refined calibration with quantified particle size distribution may improve the accuracy of the sensors as a [DOC] proxy, the results suggest that the use of the optical sensors needs caution especially for turbid waters (e.g. > ~400 NTU) where sensitivity of the sensors quickly decreases due to attenuation of lights. We speculate that the same problem can occur to the UV/VIS sensor although $r_{UV,p}$ did not saturate within ~1000 NTU. The linear $r_{UV,p}$ could be possibly because the sensor outputs were already adjusted within the sensor by "global calibration." Sensors connected to a filtration system may still provide a proxy of [DOC] even in the highly turbid waters (Saraceno et al., 2009), however, clogging can hamper the wide application of the sensors. 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. Thus, analyses of UV/VIS and fluorescence spectra of periodically collected water samples are also recommended in addition to laboratory [DOC] measurement for the use of the sensors as a [DOC] proxy.

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References

Aitkenhead, J. A. and McDowell, W. H.: Soil C:N ratio as a predictor of annual riverine DOC flux at local and global scales, Global Biogeochemical Cycles, 14, 127-138, 2000.

Alberts, J. J. and Takács, M.: Total luminescence spectra of IHSS standard and reference fulvic acids, humic acids and natural organic matter: comparison of aquatic and terrestrial source terms, Org Geochem, 35, 243-256, 2004.

Baker, A.: Thermal fluorescence quenching properties of dissolved organic matter, Water Research, 39, 4405-4412, 2005.

Boss, E., Pegau, W.S., Gardner, W.D., Zaneveld, J.R.V., Barnard, A.H., Twardowski, M.S., Chang, G.C., Dickey, T.D., 2001. Spectral particulate attenuation and particle size distribution in the bottom boundary layer of a continental shelf. Journal of Geophysical Research: Oceans 106, 9509-9516.

Del Vecchio, R. and Blough, N. V.: On the origin of the optical properties of humic substances, Environmental Science & Technology, 38, 3885-3891, 2004.

Di Toro, D. M., Allen, H. E., Bergman, H. L., Meyer, J. S., Paquin, P. R., and Santore, R. C.: Biotic ligand model of the acute toxicity of metals. 1. Technical basis, Environmental Toxicology and Chemistry, 20, 2383-2396, 2001.

Downing, B. D., Pellerin, B. A., Bergamaschi, B. A., Saraceno, J. F., and Kraus, T. E. C.: Seeing the light: The effects of particles, dissolved materials, and temperature on in situ measurements of DOM fluorescence in rivers and streams, Limnology and Oceanography-Methods, 10, 767-775, 2012.

Etheridge, J.R., Birgand, F., Burchell, M.R., Smith, B.T., 2013. Addressing the Fouling of In Situ Ultraviolet-Visual Spectrometers Used to Continuously Monitor Water Quality in Brackish Tidal Marsh Waters. Journal of environmental quality 42, 1896-1901.

Etheridge, J. R., Birgand, F., Osborne, J. A., Osburn, C. L., Burchell, M. R., II, and Irving, J.: Using in situ ultraviolet-visual spectroscopy to measure nitrogen, carbon, phosphorus, and suspended solids concentrations at a high frequency in a brackish tidal marsh, Limnology and Oceanography-Methods, 12, 10-22, 2014.

Fellman, J. B., Hood, E., Edwards, R. T., and D'Amore, D. V.: Changes in the concentration, biodegradability, and fluorescent properties of dissolved organic matter during stormflows in coastal temperate watersheds, Journal of Geophysical Research-Biogeosciences, 114, 2009.

Hinton, M. J., Schiff, S. L., and English, M. C.: The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments, Biogeochemistry, 36, 67-88, 1997.

Hur, J., Hang Vo-Minh, N., and Lee, B.-M.: Influence of upstream land use on dissolved organic matter and trihalomethane formation potential in watersheds for two different seasons, Environmental Science and Pollution Research, 21, 7489-7500, 2014.

Hur, J. and Jung, M. C.: The effects of soil properties on the turbidity of catchment soils from the Yongdam dam basin in Korea, Environmental Geochemistry and Health, 31, 365-377, 2009.

Jeong, J. J., Bartsch, S., Fleckenstein, J. H., Matzner, E., Tenhunen, J. D., Lee, S. D., Park, S. K., and Park, J. H.: Differential storm responses of dissolved and particulate organic carbon in a mountainous headwater stream, investigated by high-frequency, in situ optical measurements, Journal of Geophysical Research-Biogeosciences, 117, 2012.

Jollymore, A., Johnson, M. S., and Hawthorne, I.: Submersible UV-Vis spectroscopy for quantifying streamwater organic carbon dynamics: Implementation and challenges before and after forest harvest in a headwater stream, Sensors, 12, 3798-3813, 2012.

Kim, J.-K., Jung, S., Eom, J.-s., Jang, C., Lee, Y., Owen, J. S., Jung, M.-S., and Kim, B.: Dissolved and particulate organic carbon concentrations in stream water and relationships with land use in multiple-use watersheds of the Han River (Korea), Water International, 38, 326-339, 2013.

Koehler, A. K., Murphy, K., Kiely, G., and Sottocornola, M.: Seasonal variation of DOC concentration and annual loss of DOC from an Atlantic blanket bog in South Western Ireland, Biogeochemistry, 95, 231-242, 2009.

Morris, D. P., Zagarese, H., Williamson, C. E., Balseiro, E. G., Hargreaves, B. R., Modenutti, B., Moeller, R., and Queimalinos, C.: The attentuation of solar UV radiation in lakes and the role of dissolved organic carbon, Limnology and Oceanography, 40, 1381-1391, 1995.

Oh, N. H., Pellerin, B. A., Bachand, P. A. M., Hernes, P. J., Bachand, S. M., Ohara, N., Kavvas, M. L., Bergamaschi, B. A., and Horwath, W. R.: The role of irrigation runoff and winter rainfall on dissolved organic carbon loads in an agricultural watershed, Agriculture Ecosystems & Environment, 179, 1-10, 2013.

Park, J.-H., Woo, B.-M., Kim, O.-R., Ahn, H.-C., and Kim, J.-S.: The effects of timber harvesting on soil chemical ingredients and stream water quality, The Korean Journal of Ecology, 23, 9-15 (In Korean with English abstract), 2000.

Pellerin, B. A., Saraceno, J. F., Shanley, J. B., Sebestyen, S. D., Aiken, G. R., Wollheim, W. M., and Bergamaschi, B. A.: Taking the pulse of snowmelt: in situ sensors reveal seasonal, event and diurnal patterns of nitrate and dissolved organic matter variability in an upland forest stream, Biogeochemistry, 108, 183-198, 2012.

Perdue, E. M. and Ritchie, J. D.: Dissolved organic matter in freshwaters. In: Treatise on Geochemistry, Holland, H. D. and Turekian, K. K. (Eds.), Elsevier, Netherlands, 2014.

Raymond, P. A. and Bauer, J. E.: Bacterial consumption of DOC during transport through a temperate estuary, Aquatic Microbial Ecology, 22, 1-12, 2000.

Raymond, P. A. and Saiers, J. E.: Event controlled DOC export from forested watersheds, Biogeochemistry, 100, 197-209, 2010.

Ryder, E., Jennings, E., de Eyto, E., Dillane, M., NicAonghusa, C., Pierson, D.C., Moore, K., Rouen, M., Poole, R., 2012. Temperature quenching of CDOM fluorescence sensors: temporal and spatial variability in the temperature response and a recommended temperature correction equation. Limnology and Oceanography: Methods 10, 1004-1010.

Saraceno, J. F., Pellerin, B. A., Downing, B. D., Boss, E., Bachand, P. A. M., and Bergamaschi, B. A.: High-frequency in situ optical measurements during a storm event: Assessing relationships between dissolved organic matter, sediment concentrations, and hydrologic processes, Journal of Geophysical Research-Biogeosciences, 114, 11, 2009.

Stedmon, C. A. and Markager, S.: Resolving the variability in dissolved organic matter fluorescence in a temperate estuary and its catchment using PARAFAC analysis, Limnology and Oceanography, 50, 686-697, 2005.

Strohmeier, S., Knorr, K. H., Reichert, M., Frei, S., Fleckenstein, J. H., Peiffer, S., and Matzner, E.: Concentrations and fluxes of dissolved organic carbon in runoff from a forested catchment: insights from high frequency measurements, Biogeosciences, 10, 905-916, 2013.

Waterloo, M. J., Oliveira, S. M., Drucker, D. P., Nobre, A. D., Cuartas, L. A., Hodnett, M. G., Langedijk, I., Jans, W. W. P., Tomasella, J., de Araujo, A. C., Pimentel, T. P., and Estrada, J. C. M.: Export of organic carbon in run-off from an Amazonian rainforest blackwater catchment, Hydrol. Process., 20, 2581-2597, 2006.

Watras, C. J., Hanson, P. C., Stacy, T. L., Morrison, M., Mather, J., Hu, Y. H., and Milewski, P.: A temperature compensation method for CDOM fluorescence sensors in freshwater, Limnology and Oceanography-Methods, 9, 296-301, 2011.

Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R., and Mopper, K.: Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon, Environmental Science & Technology, 37, 4702-4708, 2003.

Wilson, H. F., Saiers, J. E., Raymond, P. A., and Sobczak, W. V.: Hydrologic drivers and seasonality of dissolved organic carbon concentration, nitrogen content, bioavailability, and export in a forested New England stream, Ecosystems, 16, 604-616, 2013.

Xie, Y. F.: Disinfection Byproducts in Drinking Water: Formation, Analysis, and Control, Lewis Pulbishers, Boca Raton, FL, 2004.

Yoon, B. and Raymond, P. A.: Dissolved organic matter export from a forested watershed during Hurricane Irene, Geophysical Research Letters, 39, 2012.

Figure captions

Fig. 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 standard reference materials (SRNOM, SRHA, and SRFA) at water temperature between 17 and 19^oC. The R^2 of the linear regression lines were 0.98 to 1.00.

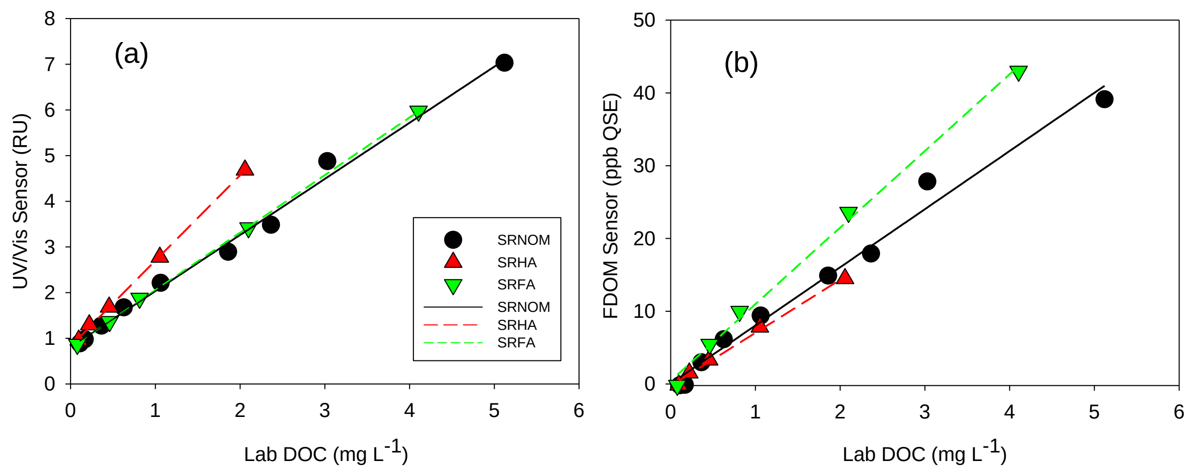
Fig. 2. Plots of UV/VIS (RU: relative units), FDOM, and $FDOM_{20}$ (FDOM signals compensated for 20^oC) against temperature for the IHSS standard reference materials (SRFA, SRNOM, and SRHA) (a, b, c), and for the forest stream water (d, e, f). The lab DOC of SRFA, SRNOM, and SRHA were 4.1, 3.0, and 2.1 mg L^{-1}, respectively, and the seven lines in (e) and (f) represent lab DOC of 10.5, 7.2, 5.2, 3.4, 2.1, 1.1, and 0 mg L^{-1} from top to bottom, respectively. All of slopes were statistically significant ($p < 0.01$) except (c) the three lines of $FDOM_{20}$ ($p > 0.36$) and (f) lab DOC of 3.4 mg L^{-1} ($p = 0.09$).

Fig. 3. Relationships between (a, b) $r_{UV,p}$ and turbidity, and those between (c, d) $r_{FDOM20,p}$ and turbidity for the forest stream water (lab DOC = 12.3 mg L^{-1}). Note that the graphs (b) and (d) were drawn for turbidity less than 120 NTU only to establish a regression equation for turbidity correction of in-situ monitoring of the forest stream.

Fig. 4. *In situ* UV/VIS and FDOM sensor outputs of raw data, corrected for temperature at 20^oC (UV/Vis_{corr} (Temp) and $FDOM_{corr}$ (Temp)), and corrected for temperature at 20^oC and turbidity (UV/Vis_{corr} (Temp + Turb) and $FDOM_{corr}$ (Temp + Turb)), compared with lab DOC. The precipitation of three storm events were (a, b) 40.5, (c, d) 19.5, and (e, f) 56.0 mm.

Fig. 5. Comparison between lab DOC of the three storm events (Fig. 4) and (a) UV/VIS and (b) FDOM sensor outputs corrected for temperature at 20^{o}C and turbidity.

Figures



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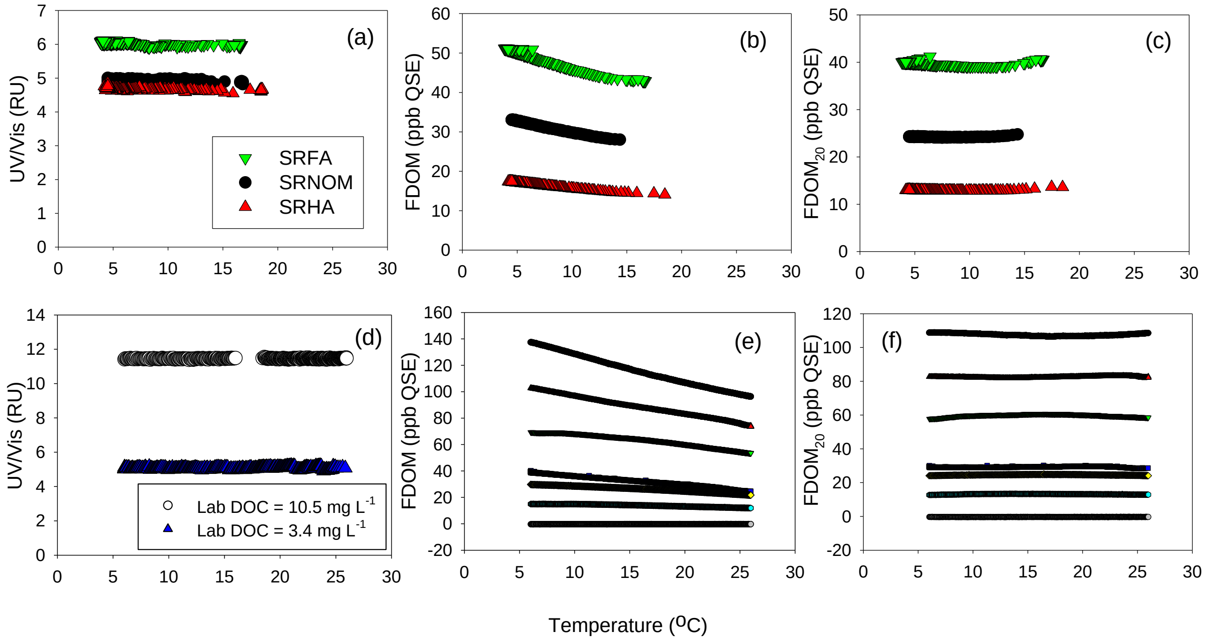

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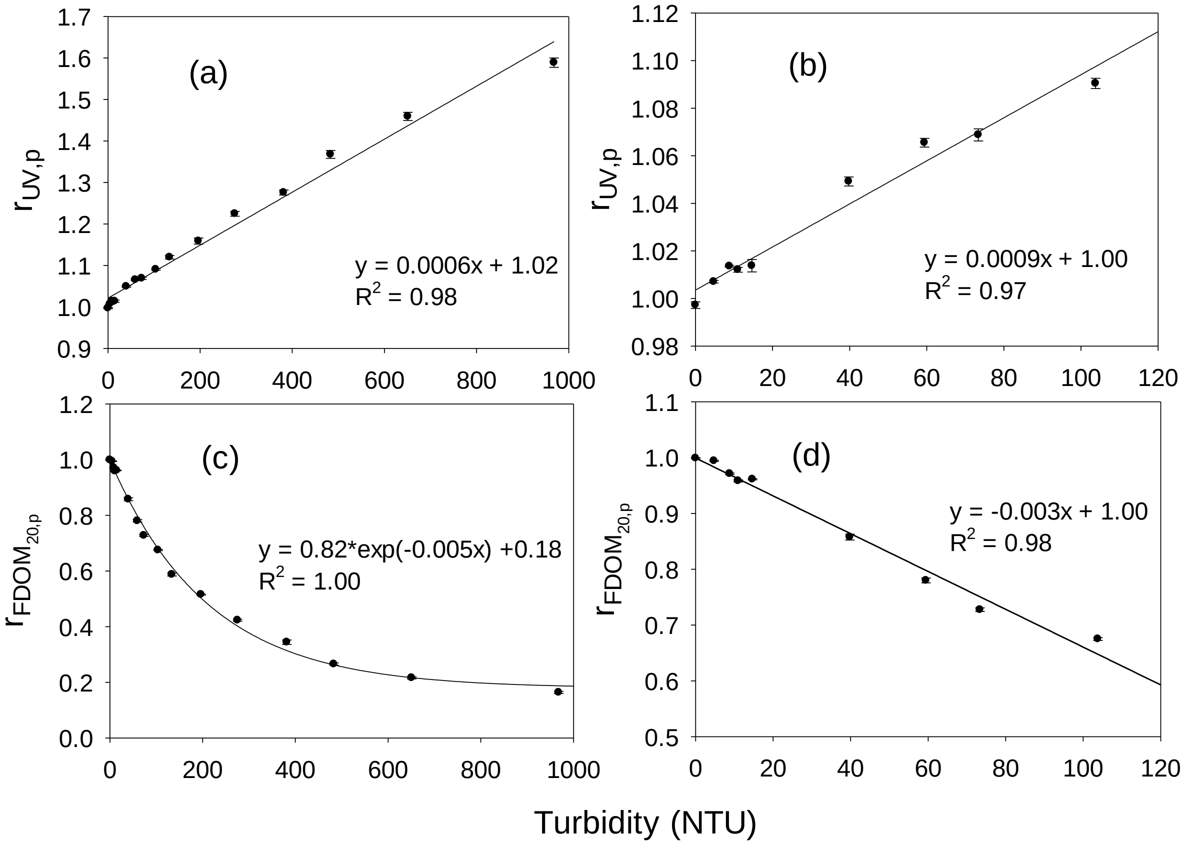

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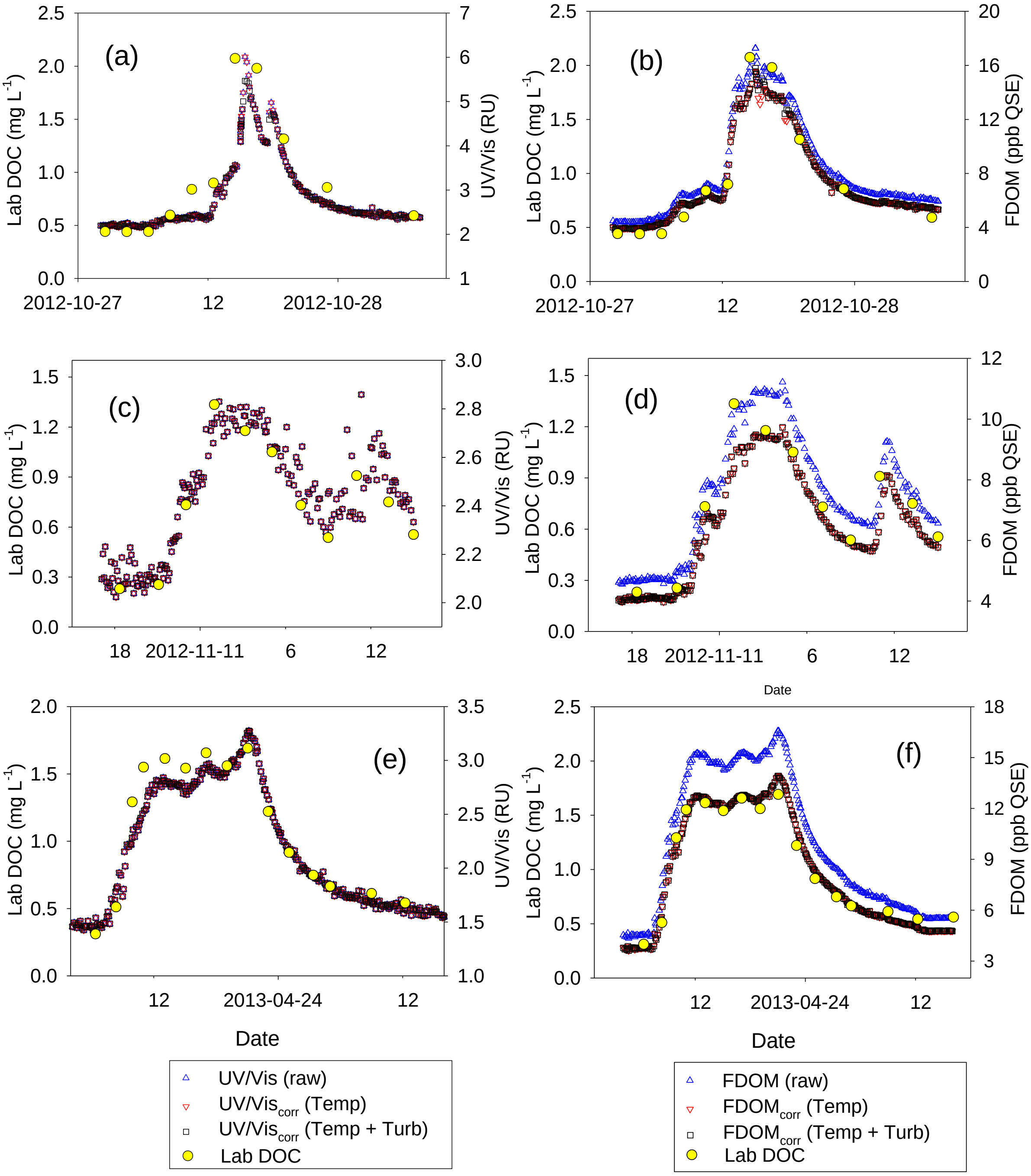

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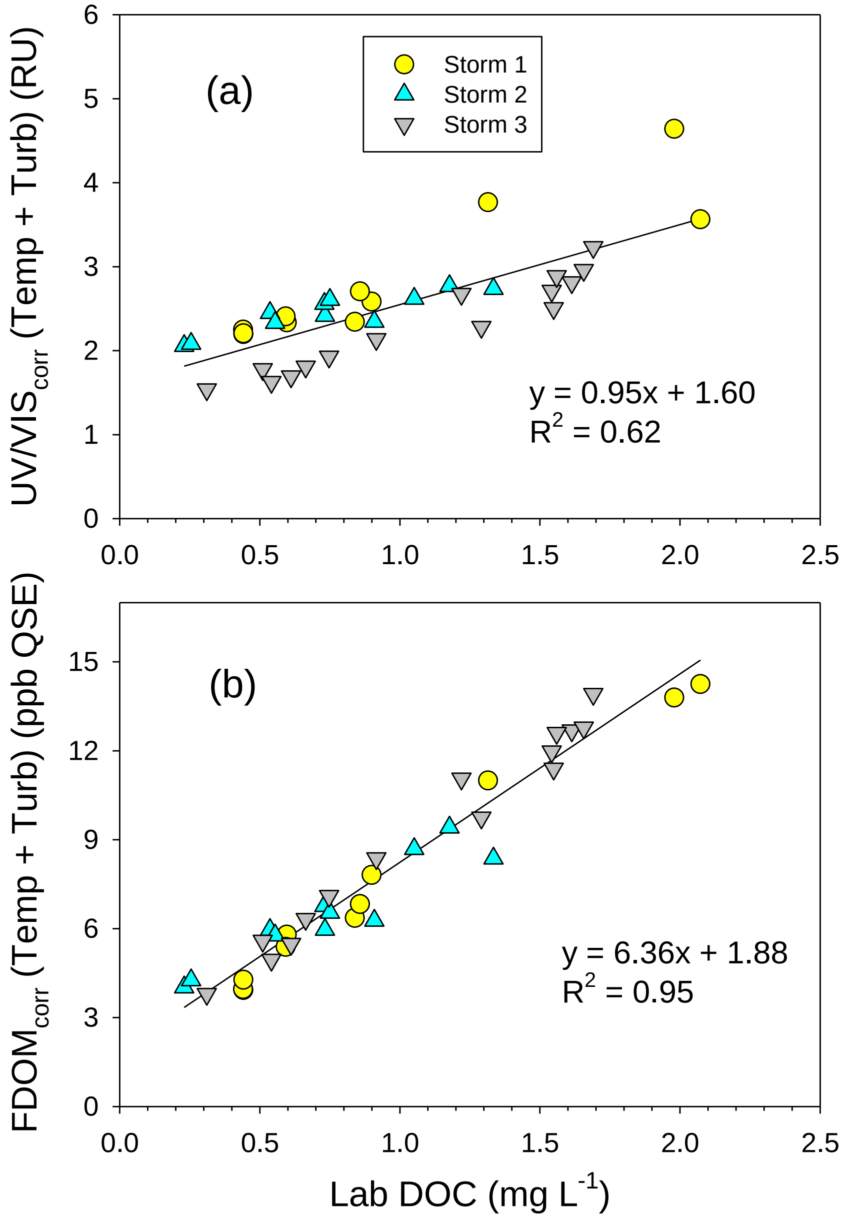

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Table 1. Previous studies using UV/VIS or FDOM sensors

Sensor type	Sensor model (Company name)	Wave lengths	Location	Study year	Purpose	Reference
UV/VIS	Carbo::lyser (s::can)	220-720 nm	Forested watershed, South Korea	2009-2010	[DOC] and [POC] monitoring	Jeong *et al.*, 2012
UV/VIS	Spectro::lyser (s::can)		Forested (harvested) watersehd, British Columbia, Canada	2010-2011	[DOC] monitoring	Jollymore *et al.*, 2012
UV/VIS	Spectro::lyser (s::can)	200-732 nm	Forested watershed, Germany	2010-2011	[DOC] monitoring	Strohmeier *et al.*, 2013
UV/VIS	Spectro::lyser (s::can)	220-742.5 nm	Brackish marsh, North Carolina, USA	2011	[DOC] monitoring	Etheridge *et al.*, 2014
FDOM	WETstar FDOM fluorometer (WETLabs)	Ex 370 nm/ Em 460 nm†	Agricultural watershed, California, USA	2008	Turbidity correction	Saraceno *et al.*, 2009
FDOM	C3 Fluorometer (Turner Designs); UV Fluorometer	Ex 340 nm/ Em 470 nm; Ex 370 nm/	Wetland-dominated lakes, Wisconsin, USA	2010	Temperature correction	Watras *et al.*, 2011

	(SeaPoint)	Em 440 nm‡				
FDOM	WETstar FDOM fluorometer (WETLabs)	Ex 370 nm/ Em 460 nm†	Forested watershed, Vermont, USA	2009	[DOC] monitoring	Pellerin *et al.*, 2012
FDOM	UV fluorometer (SeaPoint)	Ex 370 nm/ Em 440 nm‡	Inflows to a lake, Ireland	2010-2011	Temperature correction	Ryder *et al.*, 2012
FDOM	Fluorometer (Turner Designs, WETLabs, Sea Point)	Ex 340-370 nm/ Em 430-460 nm (four sensors)	The Connecticut River, Connecticut, USA	2010-2011	Temperature, color, & turbidity correction	Downing *et al.*, 2012
FDOM	Cyclops 7 (Turner Designs)		Bigelow brook, Massachusetts, USA	2009-2010	[DOC] monitoring	Wilson *et al.*, 2013
UV/VIS vs. FDOM	Carbo::lyser (s::can) vs. Cyclops 7 (Turner Designs)	220 - 720 nm (UV/VIS); Ex 325 nm/ Em 470 nm†	Forest stream, South Korea	2012-2013	UV/VIS vs. FDOM Sensor comparison	This study

†: Single excitation / emission wavelength pair, ‡: Center wavelength