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Clearing the waters: Evaluating the need for site-specific field fluorescence corrections based on turbidity measurements

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Abstract

In situ fluorescent dissolved organic matter (fDOM) measurements have gained increasing popularity as a proxy for dissolved organic carbon (DOC) concentrations in streams. One challenge to accurate fDOM measurements in many streams is light attenuation due to suspended particles. Downing et al. (2012) evaluated the need for corrections to compensate for particle interference on fDOM measurements using a single sediment standard in a laboratory study. The application of those results to a large river improved unfiltered field fDOM accuracy. We tested the same correction equation in a headwater tropical stream and found that it overcompensated fDOM when turbidity exceeded ~ 300 formazin nephelometric units (FNU). Therefore, we developed a site-specific, field-based fDOM correction equation through paired in situ fDOM measurements of filtered and unfiltered streamwater. The site-specific correction increased fDOM accuracy up to a turbidity as high as 700 FNU, the maximum observed in this study. The difference in performance between the laboratory-based correction equation of Downing et al. (2012) and our site-specific, field-based correction equation likely arises from differences in particle size distribution between the sediment standard used in the lab (silt) and that observed in our study (fine to medium sand), particularly during high flows. Therefore, a particle interference correction equation based on a single sediment type may not be ideal when field sediment size is significantly different. Given that field fDOM corrections for particle interference under turbid conditions are a critical component in generating accurate DOC estimates, we describe a way to develop site-specific corrections.

Field-deployable, in-stream fDOM sensors can provide high-frequency estimates of DOC concentration (Downing et al. 2009; Pellerin et al. 2012; Carpenter et al. 2013; Goldman et al. 2014; Mast et al. 2015). However, the field fDOM signal can be diminished by attenuation of suspended particles if present at high enough concentrations (e.g., Saraceno et al. 2009). If near-synchronous increases in turbidity occur along with DOC concentrations, for example during a high flow event, particle interference could lower the apparent magnitude and shift the timing of the fDOM peak, resulting in erroneous DOC flux estimates and process interpretations (e.g., Saraceno et al. 2009). In situ filtration can remove sensor bias imparted by particle interference, but can be prohibitively expensive and therefore impractical for long-term, high-frequency DOC monitoring.

In the past few years, several studies have presented unfiltered in situ fDOM data (e.g., Wilson et al. 2013; Ganju et al. 2014; Crawford et al. 2015; Sobczak and Raymond 2015; Watras et al. 2015; Oestreich et al. 2016). While the aforementioned studies were conducted in systems that experience low turbidity, where turbidity interference of fDOM is expected to be minimal or non-existent, few studies have developed turbidity-based correction factors for the most widely utilized, peak-C (humic-like DOM) fDOM sensors (Saraceno et al. 2009; Downing et al. 2012; Lee et al. 2015). Though Saraceno et al. (2009) and Downing et al. (2012) used a reference material (International Humic Substances Society Elliott silt loam (ESL), http://www.humicsubstances.org/sources.html) rather than local sediments, the laboratory ESL-based corrections greatly improved the accuracy of fDOM as a proxy for DOC in both an agriculturally impacted slough in California and the Connecticut River, suggesting applicability across a range of river types. Lee et al. (2015) developed a site-

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specific correction factor based on local stream sediment in the laboratory, and applied it to in situ sensor measurements which improved field data accuracy. While Khamis et al. (2015) developed turbidity correction equations for tryptophan-like fluorescence sensors centered at lower wavelengths than the fDOM sensors used here, they documented signal attenuation when turbidity exceeded 200 FNU.

The transmission of light through water is altered by both the physical and chemical properties of the constituents in the sample. Suspended particles attenuate light through the combined effects of absorbance and scattering processes (Mobley 1994). Absorption occurs when light energy is converted into non-radiant energy by exciting an electron from a ground state to a higher energy orbital in particulates and dissolved constituents. Absorbed energy is then released through multiple competing pathways that include non-radiative thermal pathways and the re-release of light energy in the form of fluorescence. Scattering is a process by which photons are redirected in multiple directions, primarily by particles. Turbidity, a measurement of the light scattering at a specific angle, typically 90°, is often positively correlated with the concentration of suspended particles in a water sample, and is thus used interchangeably for suspended sediment concentration.

This paper addresses particle scattering effects on the fDOM sensor that is most widely used for continuous fDOM monitoring. While the effects of shape, color, and chemical composition play a role in particle scattering, their overall effect is small in comparison to particle size for mineral sediments (Gippel 1995; Storlazzi et al. 2015). For the same mass, small particles attenuate light more efficiently than larger ones (van de Hulst 1957). In addition, the attenuation spectrum is sensitive to particle size; smaller particles attenuate shorter (i.e., UV-blue) wavelengths more intensely than longer (i.e., red-IR) wavelengths (e.g., Boss et al. 2001). Therefore, the degree of fDOM signal bias is expected to depend on changes in particle size with respect to the concentration of particles as indicated by turbidity. If a correction equation is developed using a single sediment type, corrections applied to a suspension with substantially different particle size may be inaccurate.

The objective of this work was to follow up on the closing discussion in Downing et al. (2012), which cautioned that different sediment types may require turbidity-based, particle interference correction equations with a different magnitude. To this end, we tested the applicability of the turbidity correction factor, r_p, in Eq. 3 in Downing et al. (2012) (hereafter referred to as Elliot silt loam (ESL) correction) for two, multi-week periods in a tropical headwater stream with flashy streamflow and associated changes in particle concentrations. We also outline strategies to correct fDOM measurements made in turbid waters when site specific corrections are not immediately available.

Materials and procedures

In situ optical and discharge data were collected at the U.S. Geological Survey gauging station (USGS site 50075000) on the Río Icacos, a flashy sediment-laden tropical stream in the Luquillo Experimental Forest in northeastern Puerto Rico (Shanley et al. 2011; Stallard and Murphy 2012). The Río Icacos watershed is underlain by the Río Blanco quartz diorite that is characterized by medium- to coarse-grained plagioclase, quartz, amphibole, and minor biotite (Seiders 1971). Overlying soils consist of very deep and poorly drained inceptisols, which are typically sandy to loamy in texture and are composed of quartz, weathered biotite, kaolinite, and other clays (Murphy et al. 2012 and references therein).These soils are mainly derived from the upper parts of the saprolite weathering profile and are typically mobilized during landslides (Dosseto et al. 2014).

We made concurrent filtered and unfiltered fDOM measurements following the approach outlined in Saraceno et al. (2009) during two periods in 09–13 July 2014 and 14–27 August 2014, with each period covering multiple storm events with elevated turbidity. We developed a site-specific turbidity correction equation based on data collected during the August period. We then applied the correction equation to unfiltered fDOM data for the July period.

Filtered and unfiltered fDOM were measured using a pair of Turner Designs (Sunnyvale, California, U.S.A.) Cyclops-7 (C7) CDOM sensors manufactured in 2012 and operated at 10x gain setting. Optical specifications for the excitation and emission filters used in the C7 CDOM (hereafter referred to as fDOM) sensor are 325 nm with a full-width at half maximum (FWHM) of 120 nm and 470 nm with a FWHM of 60 nm, respectively (Turner Designs 2016). The filtered fDOM data provided a reference signal with no particle interference in which to evaluate fDOM particle correction equation performance.

Water was delivered from the stream to the filtration system using a 12V DC submersible pump that was triggered by the controller via a solid state relay. The pump was submerged in the stream at the same depth and adjacent to the unfiltered sensors approximately 0.5 m above the stream bed. Stream water was filtered using a 0.2 μm polyethersulfone (PES) hollow-fiber cartridge filter, part number 279-20-029 (Mintech, Minneapolis, Minnesota, U.S.A.). A new, clean filter was installed prior to each sampling period. Due to the lack of mechanical wiping in the filtered fDOM flow cell, the filtered fDOM sensor face was manually cleaned with optical lens paper at the time of filter installation. The fDOM sensor flow cell (part number 2100-608, Turner Designs, Sunnyvale, California, U.S.A.) is constructed out of gray colored water resistant Delrin© plastic and was fitted with 3/8″ poly-propylene barbed fittings to interface black 3/8″ Tygon© 3603 tubing.

C7 fDOM measurements were converted to parts per billion (ppb) of quinine sulfate equivalents (QSE) (1 QSE = 1 ppb quinine sulfate dihydrate in 0.1N H_2SO_4) using a five point calibration curve that covered the range from 0 to 300 ppb QSE, following Downing et al. (2012). fDOM data were temperature compensated following Watras et al. (2011) at a reference temperature of 25°C. While fully correcting fDOM data requires also correcting for the inner filter effect (IFE), here we are only interested in the effects of particle interference. We did not make a correction for the IFE as laboratory absorbance data across a suitable range was not available for this time period. Turbidity was measured using a Turner Designs (Sunnyvale, California, U.S.A.) Cyclops-7 (C7) turbidity sensor manufactured in 2012 and was operated at a 1x gain setting in order to cover the range of turbidity encountered at the site. The turbidity sensor was calibrated to formazin nephelometric units (FNU) using sensor-specific GFS Chemicals (Columbus, Ohio, U.S.A.) AMCO Clear turbidity standards up to 1000 FNU. C7 sensor data were logged by a Campbell Scientific Ltd. (Logan, Utah, U.S.A.) CR1000 datalogger and controller as described in Pellerin et al. (2012). The unfiltered fDOM and turbidity sensor faces were wiped prior to each measurement using a Zebra-Tech Ltd. model Hydro-Wiper –J (Nelson, New Zealand).

To account for deployment differences (one sensor in the stream, and one in a filtered flow cell on the bank), the unfiltered and filtered fDOM sensors were inter-calibrated during a period of low turbidity (FNU < 10) base flow, when particle interference was assumed to be negligible ($r^2 > 0.99$; data not shown) (Saraceno et al. 2009). In order to purge stagnant sample water and to account for any lag time between unfiltered and filtered fDOM measurements, we sampled both fDOM sensors within 1 min following a 2 min filter flush period.

We computed the fraction of filtered fDOM signal lost due to particle interference for each hourly sample based on the relative percent difference between the filtered and unfiltered fDOM values. We then generated a site-specific correction equation by fitting the fraction of filtered fDOM recovered as a function of turbidity for the August 2014 deployment using non-linear damped least squares minimization. The best fit was achieved using an exponential decay model of the form: $y = A * \exp^{(-b*\mathrm{Turbidity})} + c$ (Fig. 1). To evaluate correction performance, the root mean square error (RMSE) was calculated using the residuals of the linear relationship between filtered fDOM and the unfiltered and corrected fDOM signals for the July period. All statistical analysis was carried out using the Statsmodels (version 0.6.1) package in Python (version 2.7.11) (Oliphant 2007).

In order to understand the effect of particle size on fDOM correction performance, we collected bank and bed sediment samples from Río Icacos on 13 August 2014 just after a storm event. The sediment samples were oven dried overnight at 105°C, cleaned of visible organic debris, screened at 1 mm, and split using a Quantachrome Instruments (Boynton Beach, Florida, U.S.A.) sieving riffler prior to analysis. We

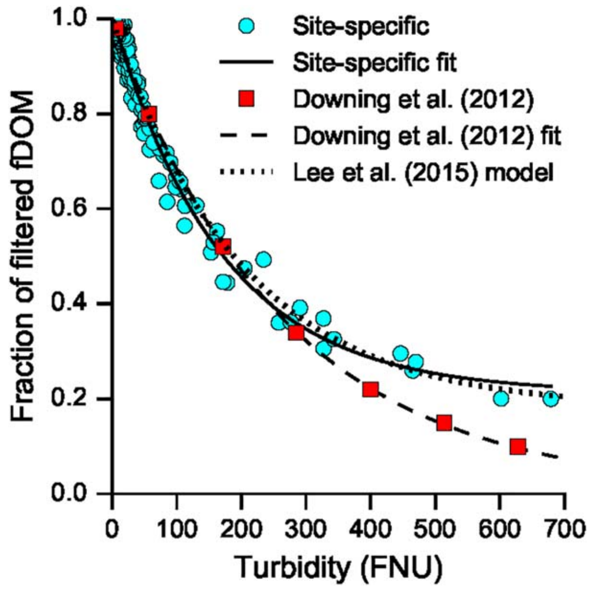

Fig. 1. Fraction of fDOM recovered (in unfiltered water vs. filtered water) as a function of turbidity at Río Icacos for the August 2014 study period (teal circles, solid line), compared to the analogous relation for Elliott Silt Loam determined in the laboratory by Downing et al. (2012) (red squares, dashed line, RMSE = 2.84) and the model developed by Lee et al. (2015) (dotted line).

used a Beckman Coulter (Brea, California, U.S.A.) model LS 13 320 Laser Diffraction Particle Size Analyzer to generate particle size distributions across the range of 0.017–2000 μm.

Results and discussion

The fraction of filtered fDOM signal recovered decreased exponentially as turbidity increased (Fig. 1). Interestingly, the site-specific field data and laboratory-based ESL data (Downing et al. 2012) were nearly indistinguishable at turbidity values less than 300 FNU (Fig. 1). Above 300 FNU, however, the field and ESL data diverge, with the ESL signal diminishing more steeply and asymptotically toward zero with increasing turbidity. The field-based experiment, in contrast, indicated greater signal recovery at high turbidities, and the fitted curve asymptotes toward a signal recovery fraction of 0.22, rather than zero. A similar empirical fit with an asymptote of 0.18 was presented by Lee et al. (2015) using field sediment in a laboratory experiment (Fig. 1). The divergence of the ESL and site-specific curves clearly indicates that at high turbidity, the Río Icacos sediment transmits more light in the fDOM relevant wavelengths (UV-A to blue) than the ESL, underscoring the need for a site-specific correction equation. Compared to the ESL correction (RMSE = 2.84), the site-specific correction improves considerably (RMSE = 0.77) on the uncorrected fDOM signal (RMSE = 4.32). While the ESL correction is an improvement over the raw signal, it significantly overestimates fDOM above 300 FNU turbidity (Fig. 2b). In comparison, the

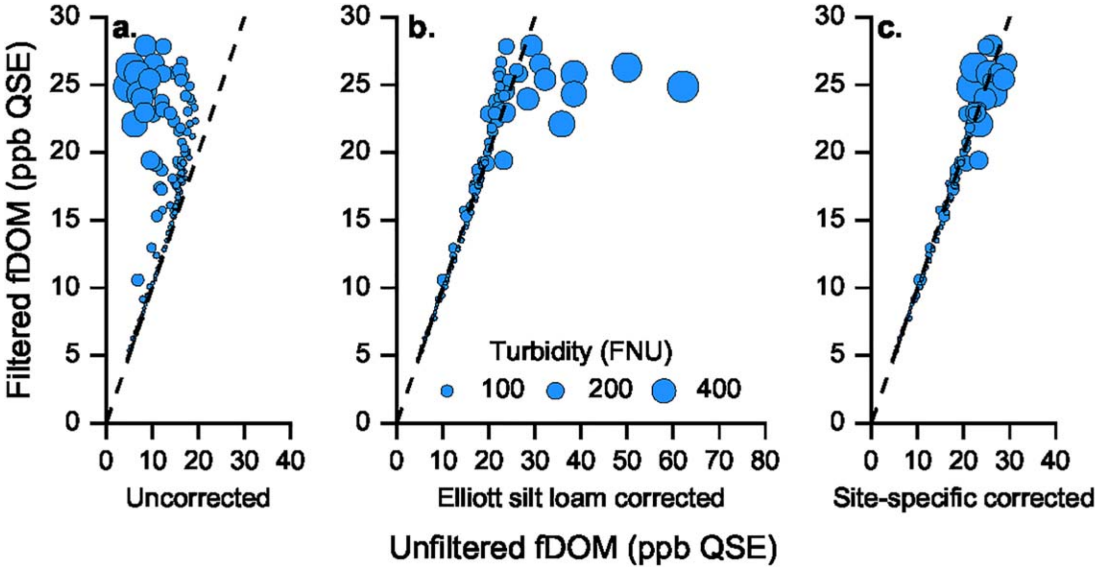

Fig. 2. Filtered fDOM concentration vs. (**a**) raw, uncorrected fDOM (RMSE = 4.32), (**b**) laboratory-based Elliott silt loam (ESL) corrected fDOM (RMSE = 2.84), and (**c**) site-specific corrected fDOM data (RMSE = 0.77) based on unfiltered/filtered comparison for August, 2014 storm events at Río Icacos. Bubble size is proportional to turbidity magnitude. The 1 : 1 agreement lines (dashed) are shown for reference. Data in all plots were corrected for water temperature bias.

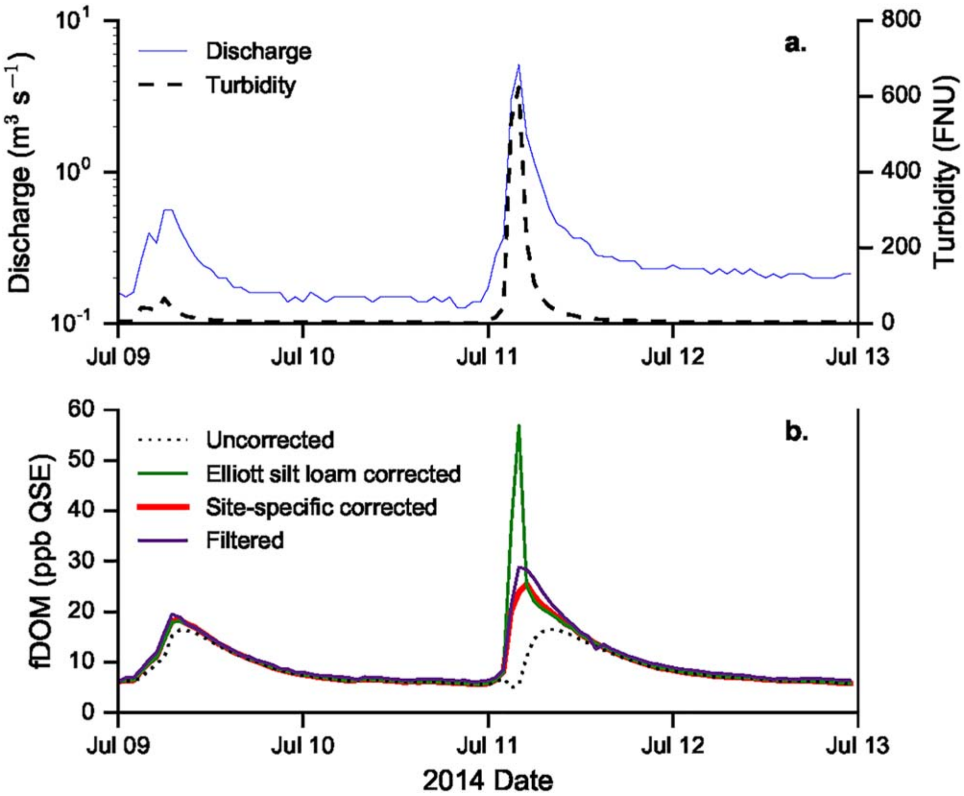

Fig. 3. Application of fDOM correction equations to unfiltered fDOM time series at the Río Icacos during July 2014. (**a**) Discharge (blue) and turbidity (black dashed). (**b**) Uncorrected (black dashed), Elliott silt loam (ESL) – corrected (green), and site-specific corrected fDOM (violet), with filtered fDOM (heavy red) provided for reference. All fDOM series were corrected for water temperature bias.

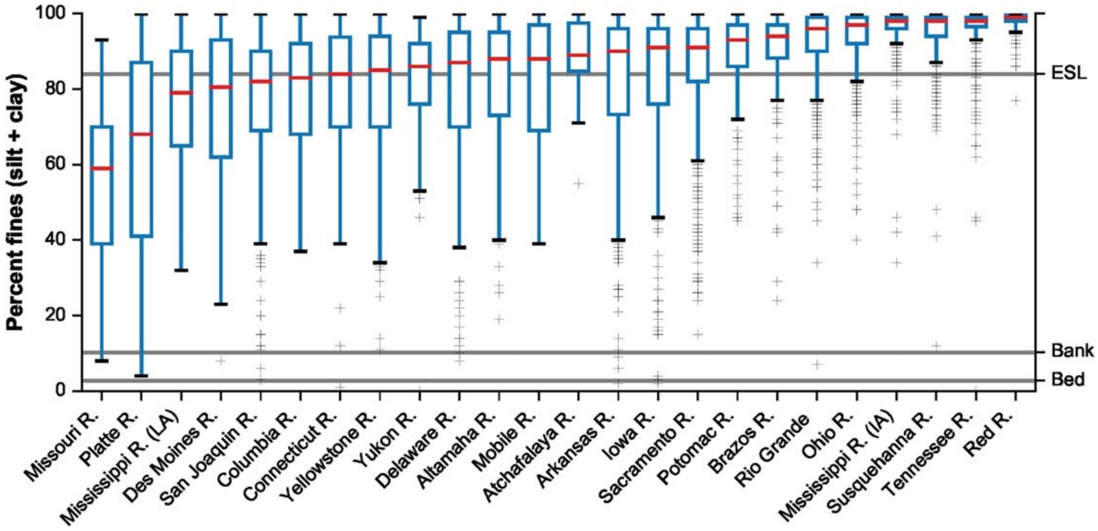

Fig. 4. Box and whisker plots of suspended particle size data from 24 rivers in the USGS NASQAN Coastal and Large River Subnetworks available through waterdata.usgs.gov. USGS Station numbers that corresposnd to site data are shown in Table S-1 in the Supporting Information. Percent fines represents the fraction of suspended sediment that is in the silt and clay fractions (< 62.5 μm). Red line is median value; boxes enclose the interquartile range (25th to 75th percentiles); box ends represent the 15 and 85 percentiles and crosses are outliers. Percent fines of Elliot silt loam (ESL), Río Icacos bed (Bed), and bank (Bank) sediments are also included for reference (solid horizontal lines).

site-specific correction obtains the average tendency of the filtered fDOM values, though there is still a moderate degree of scatter around the 1 : 1 line particularly at high turbidity (Fig. 2c).

In order to evaluate the performance of the site-specific equation, we applied both the ESL and the site-specific corrections to unfiltered fDOM data collected at Río Icacos across a set of storms during July 2014 (Fig. 3). In terms of discharge and turbidity, the July correction evaluation period encompassed one small (09 July) and one large (11 July) storm event (Fig. 3a). Turbidity did not exceed 100 FNU during the 09 July event and caused only a small fDOM signal loss. For this event, both correction equations performed equally well in matching the filtered signal, perhaps because streamflow was not sufficient to raise the median particle size significantly above that of the ESL (Fig. 3b). The 11 July event had a peak turbidity greater than 600 FNU (Fig. 1). At peak turbidity, the ESL overcompensated by nearly a factor of 2.5 compared to the site-specific correction (0.1 vs. 0.25) (Fig. 1). Accordingly, the ESL correction resulted in a positive fDOM spike, while the site-specific correction showed a more muted peak close to the filtered fDOM value. Note that the raw, uncorrected signal was yet more muted and had a delayed peak, even suggesting dilution just as filtered fDOM was peaking. The ESL correction captured the general nature of the system dynamics (increased fDOM in response to flow, with proper timing), but overestimated fDOM at peak turbidity (Fig. 3b).

Turbidity is dependent on both the concentration and the quality (size, chemical composition, and shape) of suspended sediment (e.g., Gippel 1995; Hatcher et al. 2000; Merten et al. 2014), with the particle size distribution having the greatest effect on turbidity after the concentration (Downing 2006). For example, per unit mass, silts and clays contribute greater scattering than sands (Baker and Lavelle 1984; Downing 2006; Merten et al. 2014). Thus, the same turbidity value could be attained from different grain size distributions. The scatter around the 1 : 1 line of fDOM data corrected using the site-specific correction (Fig. 2c) could arise from variation in suspended sediment size among events, and/or during individual events. While a limited number of storms was available in this study to explore inter and intra storm variation in sediment size, it could be useful to evaluate a large number of storms to characterize within and between storm variability in order to better understand turbidity based correction performance across a range of hydrologic conditions.

While turbidity is measured as side scatter in the infrared, rather than attenuation in the ultraviolet-visible range, it is perhaps not surprising that two different suspended sediment distributions with the same turbidity would have varying degrees of fDOM quenching, as the shape of spectral attenuation is expected to vary with particle size (Boss et al. 2001). Particle size analysis revealed stark differences in the size distributions between the ESL and Río Icacos sediments (Supporting Information Fig. S-1). The ESL is characterized as a poorly sorted, medium silt while the Río Icacos bank and bed sediment are fine grained, moderately well sorted and medium grained, well sorted sands, respectively. The median particle size (D_{50}) for bank ($\sim$ 240 μm) and bed ($\sim$ 510 μm) sediment at Río Icacos was more than an order of magnitude larger than the ESL ($\sim$ 20 μm) (Supporting Information Fig.

S-1), and while these sediments are not necessarily reflective of the D_{50} of suspended particles during high flow events, they are at least suggestive that the sediment regime at Río Icacos differs markedly from ESL. Optical theory predicts a decrease in light attenuation with an increase in the median particle size (van de Hulst 1957) and both experimental (e.g., Baker and Lavelle 1984; Storlazzi et al. 2015) and observational (e.g., Bowers et al. 2009) work has shown this to be the case with natural sediments. Although we are unable to demonstrate a direct link between particle size and the fraction of fDOM attenuated for a given turbidity in this study, the stark difference in the median particle size of sediment from the Río Icacos and the Elliot Silt loam (Supporting Information Fig. S-1), is at least suggestive that particle size plays a role in fDOM attenuation. While turbidity is relatively easy to measure, turbidity measurements alone may not provide sufficient information to accurately quantify the degree of particle interference on fDOM, especially when particle size is variable (Downing 2006).

As in Downing et al. (2012), Lee et al. (2015) performed rigorous laboratory experiments to assess the interference of suspended sediment on fDOM. A key difference is that Lee et al. (2015) used native soils from the watershed where they did their field assessment. Using a lab-based turbidity correction equation, Lee et al. (2015) obtained a strong relation between DOC and turbidity corrected fDOM, albeit they observed low turbidity values of only ~ 30 FNU during their field trials, thus the lab-based turbidity correction was minimally tested. Nevertheless, like Downing et al. (2012), they cautioned that the variable effect of turbidity based on dynamic fluctuations in particle size could be problematic, especially during high-energy events such as we report here.

Many streams have consistently low turbidity, even at high flows, and in these systems fDOM can be a reliable and robust proxy for DOC, provided sensors are kept clean and temperature corrections are applied (Gannon et al. 2015). Where high turbidities occur, they are typically episodic, and fDOM will still be reliable during the intervening periods. Of course, the high-flow periods are typically of great interest from both a DOC flux and process interpretation standpoint, so particle interference is often greatest when accurate fDOM is most desired. If a local correction can be developed, it can greatly improve the accuracy of DOC concentration estimates, albeit with a modicum of uncertainty (Figs. 2c, 3b).

Comments and recommendations

Concurrent turbidity measurements are critical for correcting in situ stream fDOM data for particle interference. Lacking any additional information, the ESL correction (Downing et al. 2012) is a good starting point and depending on particle size, may perform very well under certain conditions ($D_{50} \sim 20$ μm) (Figs. 2, 3b). For example, discrete data on suspended sediment collected from several large rivers across the U.S. show that the median percentage of fine particles (e.g., < 62.5 μm) is generally comparable to ESL (Fig. 4), suggesting that an ESL-based correction may be adequate in many settings.

As demonstrated here, high levels of suspended particles as reflected by high turbidity can quench fDOM measurements, resulting in underestimates of fDOM. While more accurate than no correction at all, under- or over-corrected unfiltered fDOM data may adversely impact the potential of fDOM as a DOC concentration proxy. For example, application of the ESL correction to fDOM measurements at Río Icacos would result in significant overestimates of DOC flux, especially given that the ESL correction overestimated fDOM the most near peak discharge (Fig. 3).

More detailed experiments that evaluate the role of particle compositional variability on fDOM interference may also be carried out to improve our ability to make fDOM corrections for particle interference in situ. Ideally these experiments would focus on the impact of the most important factors related to light transmission through a turbid water sample, including sediment size (Hill et al. 2011), color (e.g., Storlazzi et al. 2015), and refractive index (e.g., Boss et al. 2001). Once quantified, the different factors that contribute to fDOM interference could then be incorporated into a multi-component correction equation. While a multi-component equation may still not be universally applicable, it is a potential improvement over a turbidity-only based correction.

Downing et al. (2012) found that correction factor magnitudes based on ESL varied among fDOM sensors produced by different manufacturers, attributing these to differences in sensor design (wavelength and geometry). Thus, it is important to use the same model sensor in the field as used during the development of the fDOM correction equation. Differences in turbidity sensor design such as wavelength and scattering angle as well as sensitivity may also contribute to correction equation coefficient variability. If the same turbidity sensor cannot be used, an inter-calibration between turbidity sensors should be carried out on sediment representative of site conditions. These factors need to be considered when swapping or replacing sensors, even if operated under similar water quality conditions at the same site.

In situ measurements that estimate particle size, such as optical laser diffraction (e.g., Mikkelsen et al. 2006), spectral beam attenuation (e.g., Boss et al. 2001), spectral backscattering (e.g., Slade and Boss 2015), or acoustical methods (e.g., Topping and Wright 2016) could be incorporated into a correction equation in order to overcome the limitations imposed by a turbidity-only based correction. For example, an equation based on continuous measurements of particle size (direct or indirect) could then account for temporal changes in particle size that may occur during events (Fig. 4). However, in lieu of adding a new and often costly sensor, one could leverage existing deployments by augmenting in situ data collection approaches, such as collecting high frequency "burst" turbidity data (e.g., > 20 measurements at 1 Hz that are logged for each measurement interval) that could be used to quantify variability in particle size. For example, burst attenuation and backscatter data have been successfully inverted to particle size using the variance to mean ratio in the laboratory (Briggs et al. 2013). The application of this approach to field side-scatter based turbidity data has yet to be shown, but could easily be investigated given the widespread use of turbidity sensors in monitoring programs.

Another cost-effective approach to developing a site-specific correction would be to develop an equation from discrete samples that are presumably already part of a study design. In general, the approach would be to measure fDOM in these discrete samples in the laboratory before and following filtration at 0.2 μm. Paired with the turbidity value of the unfiltered sample, one could calculate the fraction of fDOM lost due to particle interference. If the resulting dataset is representative of the range of turbidity and fDOM encountered in the stream, this relation can be used to derive an empirical, site-specific correction equation that could be applied to in situ unfiltered fDOM data.

The costs of these different approaches vary, however, and the specific method used likely depends on temporal and financial constraints. Using grab samples is likely the most cost effective approach, while executing numerous laboratory experiments represents the most labor and cost intensive method to characterize the varying effects of sediment characteristics on fDOM interference. Depending on site accessibility and logistics, the initial cost of equipment and installation of a side by side filtration field experiment is likely in the range of several thousand U.S. dollars. The total cost of a side by side experiment would rise with deployment time, as filters, pumps, and tubing are consumed during the course of study.

Conclusions

Correction for particle interference is critical for accurate determination of in-stream fluorescent dissolved organic matter. Application of a generic turbidity-based correction equation is a good first step, but it should be tested and a local equation developed if feasible. At a test stream in Puerto Rico, we developed a local correction based on concurrent measurements of filtered and unfiltered streamwater. A laboratory-derived correction equation based on Elliot Silt Loam (ESL) performed well at the test stream until turbidity exceeded 300 FNU, after which this correction overestimated fDOM. The difference in performance between the laboratory-based ESL correction equation and our site-specific, field-based correction equation likely arose from differences in particle size between the ESL sediment and local stream sediment in this study. This finding suggests that particle interference corrections based on a single sediment type may not be suitable when the particle size distribution in the stream of interest is significantly different. A cost-effective empirical correction equation can be developed through paired field observations and measured laboratory determinations of filtered fDOM on discrete samples.

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Conflict of Interest

None declared.

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