Biogeosciences, 13, 583–595, 2016
www.biogeosciences.net/13/583/2016/
doi:10.5194/bg-13-583-2016

Biogeosciences Open Access EGU

Colored dissolved organic matter in shallow estuaries: relationships between carbon sources and light attenuation

W. K. Oestreich[1,2], N. K. Ganju[3], J. W. Pohlman[3], and S. E. Suttles[3]

[1]Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA, USA
[2]Department of Civil and Environmental Engineering, Northwestern University, Evanston, IL, USA
[3]US Geological Survey Woods Hole Coastal and Marine Science Center, Woods Hole, MA, USA

Correspondence to: N. K. Ganju (nganju@usgs.gov)

Received: 17 April 2015 – Published in Biogeosciences Discuss.: 18 May 2015
Revised: 8 December 2015 – Accepted: 14 January 2016 – Published: 2 February 2016

Abstract. Light availability is of primary importance to the ecological function of shallow estuaries. For example, benthic primary production by submerged aquatic vegetation is contingent upon light penetration to the seabed. A major component that attenuates light in estuaries is colored dissolved organic matter (CDOM). CDOM is often measured via a proxy, fluorescing dissolved organic matter (fDOM), due to the ease of in situ fDOM sensor measurements. Fluorescence must be converted to CDOM absorbance for use in light attenuation calculations. However, this CDOM–fDOM relationship varies among and within estuaries. We quantified the variability in this relationship within three estuaries along the mid-Atlantic margin of the eastern United States: West Falmouth Harbor (MA), Barnegat Bay (NJ), and Chincoteague Bay (MD/VA). Land use surrounding these estuaries ranges from urban to developed, with varying sources of nutrients and organic matter. Measurements of fDOM (excitation and emission wavelengths of 365 nm ($\pm$5 nm) and 460 nm ($\pm$40 nm), respectively) and CDOM absorbance were taken along a terrestrial-to-marine gradient in all three estuaries. The ratio of the absorption coefficient at 340 nm (m^{-1}) to fDOM (QSU) was higher in West Falmouth Harbor (1.22) than in Barnegat Bay (0.22) and Chincoteague Bay (0.17). The CDOM : fDOM absorption ratio was variable between sites within West Falmouth Harbor and Barnegat Bay, but consistent between sites within Chincoteague Bay. Stable carbon isotope analysis for constraining the source of dissolved organic matter (DOM) in West Falmouth Harbor and Barnegat Bay yielded $\delta^{13}C$ values ranging from -19.7 to -26.1 ‰ and -20.8 to -26.7 ‰, respectively. Concentration and stable carbon isotope mixing models of DOC (dissolved organic carbon) indicate a contribution of ^{13}C-enriched DOC in the estuaries. The most likely source of ^{13}C-enriched DOC for the systems we investigated is *Spartina* cordgrass. Comparison of DOC source to CDOM : fDOM absorption ratios at each site demonstrates the relationship between source and optical properties. Samples with ^{13}C-enriched carbon isotope values, indicating a greater contribution from marsh organic material, had higher CDOM : fDOM absorption ratios than samples with greater contribution from terrestrial organic material. Applying a uniform CDOM : fDOM absorption ratio and spectral slope within a given estuary yields errors in modeled light attenuation ranging from 11 to 33 % depending on estuary. The application of a uniform absorption ratio across all estuaries doubles this error. This study demonstrates that light attenuation coefficients for CDOM based on continuous fDOM records are highly dependent on the source of DOM present in the estuary. Thus, light attenuation models for estuaries would be improved by quantification of CDOM absorption and DOM source identification.

1 Introduction

Benthic primary production in estuaries, including those along the Atlantic coast of the United States, is typically dominated by seagrass (Heck et al., 1995). Furthermore, seagrass acts as an ecosystem engineer in temperate coastal ecosystems via habitat provision and nutrient cycling (Ehlers et al., 2008). Recent anthropogenic nutrient loading to these ecosystems due to industrial and agricultural development has caused a loss of seagrass density. This occurs as eutroph-

Published by Copernicus Publications on behalf of the European Geosciences Union.

ication creates water column algal blooms and increases benthic algae populations (Burkholder et al., 2007; Hauxwell et al., 2003). These algal processes reduce penetration of the light necessary for survival of seagrasses (Kennish et al., 2011). As anthropogenic impacts on coastal ecosystems compound with increasing urbanization of coastal zones (McGranahan et al., 2007), it is important to understand the factors controlling light attenuation in the estuarine water column.

Four main factors attenuate light in the water column: water itself, non-algal particulate material, phytoplankton, and colored dissolved organic matter (CDOM; Kirk, 1994). Proxies are typically used to quantify these factors in situ: depth, turbidity, chlorophyll *a* fluorescence, and fluorescing dissolved organic matter (fDOM), respectively (Ganju et al., 2014). The use of fDOM as a proxy for the CDOM component is widespread due to the ease of measuring in situ fluorescence. However, variability in the CDOM : fDOM absorption ratios observed both between and within numerous aquatic systems (Clark et al., 2004; Del Castillo et al., 1999; Hoge et al., 1993) confounds using fDOM alone to quantify absorbance. Quantifying and understanding what controls the relationship between fDOM and CDOM is required to accurately model light attenuation and seagrass viability in estuaries. CDOM also has great importance for its utility as a tracer (Stedmon et al., 2003; Del Castillo et al., 1999), its major role in photochemistry (Mopper et al., 2015), its effects on biological production (Coble, 2007), and remote sensing relevance (Nelson and Siegel, 2013).

Estuaries are transition zones between freshwater and marine systems where DOM from a variety of sources mixes (Raymond and Bauer, 2001). The major sources of DOM to estuaries are typically terrestrial DOM from riverine inputs, oceanic DOM from phytoplankton, and tidal marsh DOM from emergent and submergent marsh vegetation (Peterson et al., 1994). Both seagrass and macroalgae can also contribute DOM in these systems (Barron et al., 2014; Pregnall, 1983). Marine and terrestrial DOM exhibit different structural characteristics (Harvey et al., 1983) that are reflected in the optical properties of CDOM (Helms et al., 2008; De Souza Sierra et al., 1994). Additionally, photodegradation is a major sink for CDOM (Mopper et al., 2015; Kouassi and Zika, 1992), and must also be considered when discussing CDOM and light attenuation. Due to its role in attenuating light in the water column, measurement of CDOM and enhanced understanding of its source-dependent optical properties are important for modeling light availability in estuaries.

The goal of this study is to improve the understanding of light attenuation in the estuarine water column by characterizing the optical properties and sources of CDOM in three diverse estuaries located along the mid-Atlantic US margin: West Falmouth Harbor (MA), Barnegat Bay (NJ), and Chincoteague Bay (MD, VA). Our objectives are to quantify the CDOM : fDOM absorption ratio, establish absorption spectral slopes for use in light models (Gallegos et al., 2011), determine the sources of CDOM in these estuaries, and identify variation in the CDOM : fDOM absorption ratio as a function of source.

2 Site descriptions

2.1 West Falmouth Harbor

West Falmouth Harbor is a small (0.7 km^2), groundwater-fed estuary on the western shore of Cape Cod, Massachusetts (Fig. 1b). The harbor has a mean depth of approximately 1 m, and is connected to Buzzard's Bay by a 3 m deep, 150 m wide channel. Residence time in the harbor is approximately 1 day (Hayn et al., 2014). Tidal range is 1.9 m during spring tides and 0.7 m during neap tides, with tidal currents at the mouth approaching 0.5 $m\,s^{-1}$. The dominant source of freshwater and nutrients is groundwater. Land use surrounding the harbor is largely residential, with influence from a legacy wastewater plume within the aquifer (Ganju et al., 2012). Plant coverage in surrounding wetlands is variable, but *Spartina alterniflora* and *Spartina patens* tend to dominate, with some lesser coverage by *Juncus gerardii* and forbs such as *Salicornia* spp., *Limonium carolinianum*, and *Solidago sempervirens* (Buchsbaum and Valiela, 1987). *Zostera* spp. eelgrass is also present in the harbor (Del Barrio et al., 2014).

2.2 Barnegat Bay

The Barnegat Bay–Little Egg Harbor estuary is a back-barrier system along the New Jersey Atlantic coast (Fig. 1c). The estuary is approximately 70 km long, 2–6 km wide, and 1.5 m deep. Bay and ocean water exchange occurs at three inlets: the Point Pleasant Canal at the northern limit, Barnegat Inlet in the middle of the barrier island, and Little Egg Inlet at the southern limit. Limited exchange through these inlets leads to a spatially variable residence time exceeding 30 days in some locations (Defne and Ganju, 2014). For the purpose of this study, sites north of Barnegat Inlet are referred to as "North Barnegat Bay", while sites parallel to and south of Barnegat Inlet are referred to as "South Barnegat Bay". Tides are semidiurnal and range from < 0.1 to 1.5 m, and current velocities range from < 0.5 to 1.5 $m\,s^{-1}$ (Kennish et al., 2013; Ganju et al., 2014); there is also a pronounced south-to-north gradient in tidal range and flushing (Defne and Ganju, 2014). While the land surrounding the northern portion of the bay is developed with mixed urban–residential land use, the area south of Barnegat Inlet is less developed and retains much of the original marsh (Wieben and Baker, 2009). The salt marshes south of Barnegat Inlet are dominated by *Spartina alterniflora* (Olsen and Mahoney, 2001). Freshwater inputs are largest at the northern end of the bay due to the Toms River, Metedeconk River, and Cedar Creek (US EPA, 2007).

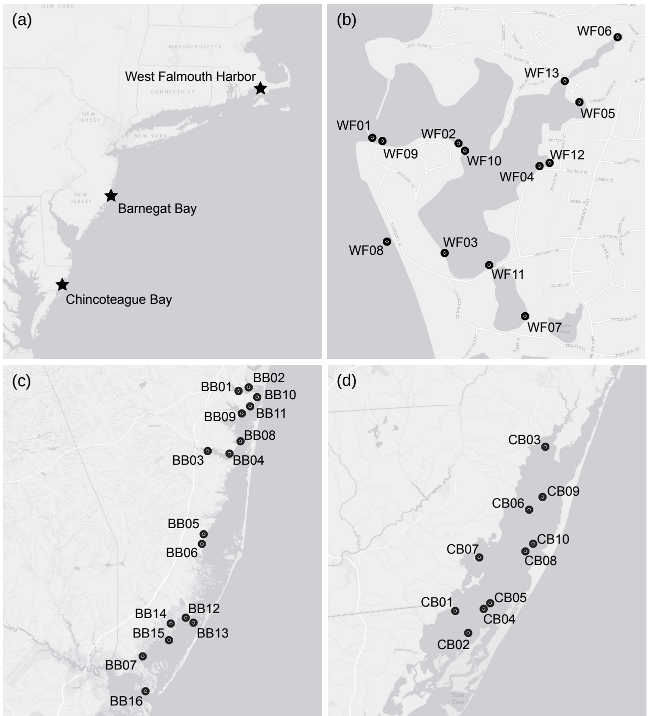

Figure 1. (a) Location of US Atlantic Coast estuaries investigated in this study. Sample locations within **(b)** West Falmouth Harbor, **(c)** Barnegat Bay, and **(d)** Chincoteague Bay.

2.3 Chincoteague Bay

Chincoteague Bay is along the Atlantic coast of the Delmarva Peninsula (Fig. 1d). This estuary has an area of 355 km^2 and an average depth of 2 m. The watershed surrounding Chincoteague Bay is 487 km^2, and consists of 36 % forest, 31 % agricultural development, 25 % wetlands, and 8 % urban development (Bricker et al., 1999). Vegetation in the wetland portion is dominated by *Spartina alterniflora*, much like South Barnegat Bay (Keefe and Boynton, 1973). Tide range averages 0.5 m, and residence time has been estimated at 8 days (Bricker et al., 1999). The bay is connected to the ocean via two inlets: Ocean City Inlet in the north and Chincoteague Inlet in the south (Allen et al., 2007). Historically, Chincoteague Bay has been marked by extensive seagrass coverage and higher water quality, especially compared to other more developed and less well-flushed bays on the Atlantic coast (Wazniak et al., 2004).

3 Methods

3.1 Fluorescence measurements

Sampling sites were approached by both land (WF01-WF13, BB01-BB07) and sea (BB08-BB16, CB01-CB10). Sampling occurred from 25 June 2014 to 17 July 2014 (Table 1). Either a bucket (sites approached on foot) or 1 L Nalgene sampling bottle (sites approached by boat) was rinsed with native water and then used to collect a surface water sample. A pre-calibrated YSI EXO 2 multisonde, measuring fDOM, temperature, salinity, pH, turbidity, chlorophyll *a* fluorescence, blue-green algae fluorescence, and dissolved oxygen concentration, was placed in each sample. Excitation and emission wavelengths for the fluorescing dissolved organic matter sensor were 365 nm ($\pm$5 nm) and 460 nm ($\pm$40 nm), respectively. Measurements of each parameter were collected at 1 s intervals for approximately 60 s and averaged. For sites approached on foot, the YSI EXO was deployed immediately; for sites approached by boat, the YSI EXO was deployed later on land (in concurrence with absorbance measurements, as described below).

Temperature, turbidity, and inner filter effects (IFEs) have been shown to alter fluorescence measurements (Baker, 2005; Downing et al., 2012). For this reason, we corrected fluorescence measurements to account for temperature, turbidity, and IFEs, according to Downing et al. (2012).

3.2 Absorbance measurements

A 60 mL syringe was used to draw a water sample from these buckets for absorbance measurements. Fifteen milliliters of this sample was filtered through a 0.2 µm inorganic membrane filter into a 5 cm path length cuvette. Absorbance measurements were recorded in 20 nm increments over the range of 340–440 nm (West Falmouth Harbor) or 340–720 nm (Barnegat Bay and Chincoteague Bay). Spectral slope was calculated over both the entire 340–720 nm range and the 340–440 nm range for Barnegat Bay and Chincoteague Bay to allow for direct comparison to West Falmouth Harbor and other studies (e.g., Huang and Chen, 2009; Del Castillo et al., 1999). The estimated photometric accuracy of the spectrophotometer was 0.003 absorbance units. Offsets from zero were determined for the West Falmouth Harbor CDOM spectra by running a blank sample (Milli-Q water) at 440 nm (the high end of the recorded spectrum). For Barnegat Bay and Chincoteague Bay, offsets from zero were determined by running a blank sample before measurement at each wavelength (340–720 nm). Absorbance measurements were converted to Naperian absorption coefficients as follows:

$$a(\lambda) = 2.303A(\lambda)/l, \quad (1)$$

where $A(\lambda)$ is the absorbance at 340 nm, l is the cell length in meters (0.05 m for this study), and $a(\lambda)$ is the absorption coefficient (Green and Blough, 1994). Absorbance values at 340 nm were the highest across the range scanned, so 340 nm was chosen as the absorbance wavelength for calculating the absorption coefficient. Spectral slopes were calculated by plotting the natural log of absorption coefficient against wavelength. Due to use of the natural log, non-positive absorption coefficients were discarded to calculate

Table 1. Sampling sites and procedures.

Estuary	No. of sites	Site IDs	Isotope Analysis (Y/N)	Date
West Falmouth Harbor, MA	13	WF01-WF13	Yes	25 June 2014
Barnegat Bay, NJ	16	BB01-BB16	Yes	14–15 July 2014
North Barnegat Bay (BB-N)	8	BB01-BB04; BB08-BB11	Yes	14–15 July 2014
South Barnegat Bay (BB-S)	8	BB05-BB07; BB12-BB16	Yes	14–15 July 2014
Chincoteague Bay, MD/VA	10	CB01-CB10	No	17 July 2014

spectral slope, as described in Eq. (2) (Bricaud et al., 1981):

$$S = \ln(a(\lambda)/a(r))(r-\lambda), \quad (2)$$

where λ is wavelength, r is a reference wavelength, $a(\lambda)$ is absorption coefficient at a given wavelength, $a(r)$ is absorption coefficient at the reference wavelength, and S is the spectral slope. The value of S shows the rate at which absorption decreases with increasing wavelength (Green and Blough, 1994). This parameter can be used to predict absorption coefficients across the spectrum based on absorption at one reference wavelength (Bricaud et al., 1981).

3.3 Isotope analysis

At each site in West Falmouth Harbor and Barnegat Bay, water samples were collected for stable carbon isotope analysis of DOC (dissolved organic carbon). Chincoteague Bay was excluded due to logistical limitations. Thirty milliliters of the collected sample was filtered through a 0.2 µm inorganic membrane filter, collected in a 40 mL glass autosampler vial that had been baked at 450 °C for 4 h, and sealed with caps and Teflon-faced silicon septa that had been soaked and rinsed with 10 % (by volume) HCl. Additionally, trace metal grade 12N HCl (Sigma-Aldrich) was added to each isotope water sample to achieve pH < 2. The vials were then stored at 4 °C. Samples were analyzed by high-temperature combustion–isotope ratio mass spectrometry (HTC-IRMS) at the USGS-WHOI Dissolved Carbon Isotope Lab (DCIL), as described by Lalonde et al. (2014). The DCIL HTC-IRMS system consists of an OI 1030C total carbon analyzer and a Graden molecular sieve trap interfaced to a Thermo-Finnigan DELTAplus XP IRMS via a modified Conflo IV. The stable carbon isotope ratios are reported in the standard δ notation relative to Vienna Pee Dee Belemnite (VPDB) and are corrected by mass balance to account for the analytical blank, which was less than the equivalent of 15 µM DOC in the sample. By comparison, the sample DOC concentrations ranged from 60.7 to 581 µM. Thus the blank correction was always less than 25 % of the sample concentration. The analytical precision of the δ^{13}C analysis was less than 0.3 ‰. DOC concentration was calculated using a standard curve consisting of four potassium hydrogen phthalate (KHP) calibration standards quantified as the integrated volt-seconds (Vs) of the mass-44 peak on the IRMS (Lalonde et al., 2014). Peak areas were corrected for analytical blanks determined from ultrapure lab water injections.

Salinity and δ^{13}C values for freshwater and marine end-members from West Falmouth Harbor and Barnegat Bay were used to construct isotope mixing models for the estuaries (Kaldy et al., 2005). Marine and freshwater end-members are defined as the most and least saline samples collected at each estuary. Because of the number of samples clustered near the highest salinity for each estuary, marine end-members were checked with geographic location. For West Falmouth Harbor, the site chosen as marine end-member (WF01) was taken from the mouth of the harbor where the estuary connects to Buzzard's Bay. For Barnegat Bay, the site of highest salinity (BB13) was taken from the middle of Little Egg Harbor in South Barnegat Bay. However, a more geographically intuitive marine end-member would be site BB16, near Little Egg Inlet. The only slightly lower salinity at this site (29.69 psu) as compared to BB13 (30.08 psu), along with the geographic location of BB16 at an oceanic inlet, makes BB16 a more appropriate marine end-member. Therefore, end-members used in the conservative mixing models were as follows: WF06 (freshwater), WF01 (marine), BB01 (freshwater), and BB16 (marine). The conservative mixing models (Kaldy et al., 2005) were constructed as

$$C_{\text{mix}} = fC_R + (1-f)C_O, \quad (3)$$

where C_{mix} is the calculated concentration for use in the mixing model, C_R and C_O are freshwater and marine end-member DOC concentrations, respectively, and f is the fraction of freshwater calculated from salinity:

$$f = (S_O - S_{\text{M}})/(S_O - S_R), \quad (4)$$

where S_{M} is measured salinity at a specific site, and S_R and S_O are freshwater and marine end-member salinities, respectively. These calculations lead to the modeled isotope ratio of each sample as

$$\delta_{\text{mix}} = [fC_R\delta_R + (1-f)C_O\delta_O]/C_{\text{mix}}, \quad (5)$$

where all subscripts and variables are the same as described for Eqs. (3) and (4).

3.4 Carbon-normalized CDOM

In addition to the stable carbon isotope analysis, a "carbon-normalized CDOM" (C-normalized $CDOM_{340}$) was calculated for each sample as

$$\text{C-normalized CDOM}_{340} = A(\lambda)/\text{DOC}, \quad (6)$$

where DOC is dissolved organic carbon concentration ($mg\,L^{-1}$) and $A(\lambda)$ is decadic light absorbance at 340 nm (m^{-1}). This C-normalized $CDOM_{340}$ is comparable to specific ultraviolet absorbance (SUVA), a measure proven to correlate strongly with DOC aromaticity (Weishaar et al., 2003). While SUVA is typically calculated at 254 nm, the C-normalized $CDOM_{340}$ calculated here provides a similar measure while accommodating this study's minimum absorbance measurement wavelength of 340 nm.

4 Results

4.1 Spectral slopes

The estuary-wide average spectral slope (over the range 340–440 nm) for West Falmouth was steeper than for Barnegat and Chincoteague, with S_{avg} equal to 0.021, 0.016, and 0.018, respectively (Table S1). At West Falmouth Harbor, spectral slope ranged from 0.013 to 0.044, with a standard deviation of 0.010. At Barnegat Bay, S ranged from 0.011 to 0.019, with a standard deviation of 0.002. At Chincoteague Bay, S ranged from 0.014 to 0.023, with a standard deviation of 0.003. Spectral slope values for Barnegat and Chincoteague were slightly steeper over the range 340–440 nm as compared to S calculated over the range 340–720 nm (Table S1 in the Supplement).

4.2 Fluorescence measurements (fDOM)

At West Falmouth, fDOM ranged from 0.63 to 10.21 QSU, with a standard deviation of 2.57 QSU. At Barnegat Bay, fDOM ranged from 12.06 to 84.40 QSU, with a standard deviation of 20.82 QSU. At Chincoteague Bay, fDOM ranged from 11.15 to 49.49 QSU, with a standard deviation of 10.95 QSU. Values observed for fDOM were within ranges reported for similar estuaries and coastal waters (Callahan et al., 2004; Clark et al., 2002; Green and Blough, 1994). Sites at West Falmouth and Barnegat Bay represented a freshwater to seawater gradient, with salinity ranging from 0.13 to 31.28 psu at West Falmouth and 3.41–30.08 psu at Barnegat. At Chincoteague Bay, salinity ranged from 25.88 to 31.85 psu. A complete salinity gradient was not sampled at Chincoteague due to the relatively high salinity found throughout the main basin of the bay, and low freshwater input. fDOM correlated inversely with salinity (Fig. 2), as expected because riverine input is typically the main external source of DOM. However, the slope and strength of the fDOM–salinity relationship differed both between and within estuaries. The steepest relationship (most rapidly decreasing fDOM signal with increasing salinity) was observed at Chincoteague Bay and in South Barnegat Bay. These two areas displayed a similar fDOM–salinity relationship; fDOM and salinity showed a slightly less negative relationship at North Barnegat Bay, and even less negative at West Falmouth Harbor.

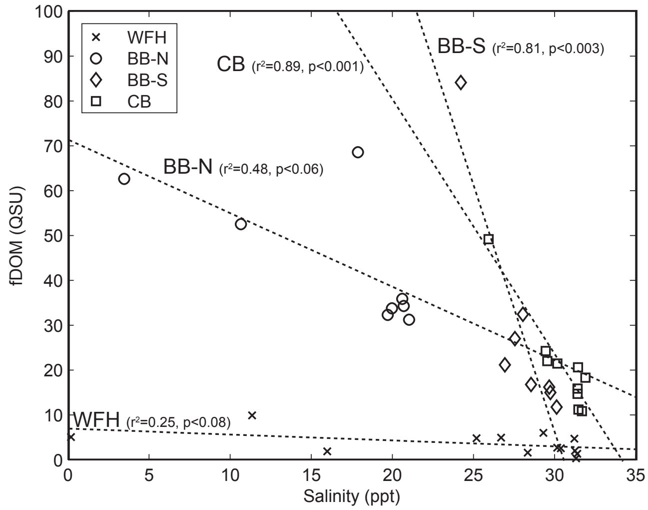

Figure 2. Fluorescence measurement versus salinity for all sample sites at West Falmouth Harbor (WFH), North Barnegat Bay (BB-N), South Barnegat Bay (BB-S), and Chincoteague Bay (CB). Dashed lines indicate the best linear fits to the data, with associated r^2 and p value.

4.3 CDOM absorption and CDOM : fDOM ratios

At West Falmouth, $a(340)$ ranged from 0.92 to 5.07 m^{-1}, with a standard deviation of 1.02 m^{-1}. At Barnegat Bay, $a(340)$ ranged from 0.97 to 14.97 m^{-1}, with a standard deviation of 3.99 m^{-1}. At Chincoteague Bay, $a(340)$ ranged from 1.84 to 8.38 m^{-1}, with a standard deviation of 1.86 m^{-1} (Table 2). The ratio between $a(340)$ and fDOM differed both between and within estuaries, as expected (Table S1; Fig. 3). The mean ratio of $a(340)$ to fDOM was relatively higher in West Falmouth Harbor (1.22) than in Barnegat Bay (0.22) and Chincoteague Bay (0.17). There were two significant outliers at Barnegat Bay: BB01, which had a lower absorption coefficient (0.97 m^{-1}) than expected based on its higher fDOM value (69.92 QSU), and BB15, which showed a much higher absorption coefficient (14.97 m^{-1}) than expected based on its lower fDOM value (16.50 QSU). West Falmouth also demonstrated substantial variability in $a(340)$: fDOM ratio between sites. Chincoteague Bay, however, showed a highly consistent ratio.

Table 2. Light attenuation model parameters and ensuing errors arising from usage of estuary-wide mean values. Note reduced number of significant figures for reporting of spectral slope as compared to Table S1.

Estuary	Mean CDOM : fDOM ratio (range)	Mean spectral slope (range)	Mean light attenuation error (range)
West Falmouth Harbor, MA	1.2 (0.50–4.3)	0.03 (0.01–0.05)	15 % (0–52 %)
Barnegat Bay, NJ	0.23 (0.01–0.96)	0.01 (0.01–0.02)	33 % (0–220 %)
Chincoteague Bay, MD/VA	0.17 (0.16–0.19)	0.01 (0.01–0.02)	11 % (0.01–28 %)

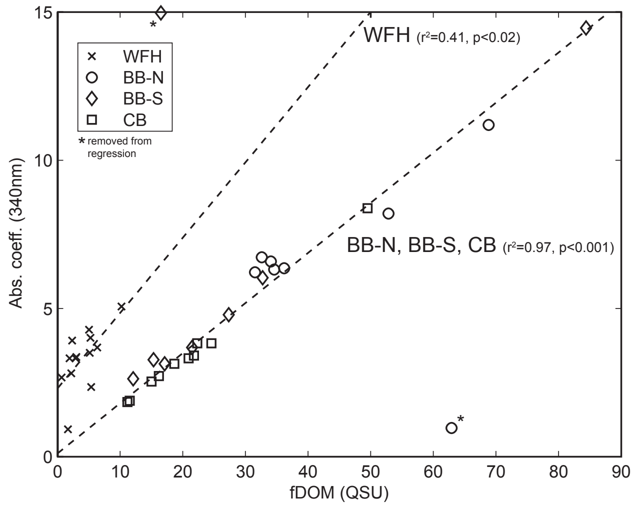

Figure 3. Absorption coefficient at 340 nm versus fluorescence measurement for all sampling sites at West Falmouth Harbor (WFH), North Barnegat Bay (BB-N), South Barnegat Bay (BB-S), and Chincoteague Bay (CB). Dashed lines indicate the best linear fit to the data, with associated r^2 and p value. Two outliers (indicated by asterisks) removed from the regressions for Barnegat Bay.

4.4 Stable carbon isotope analysis

The observed isotope–salinity relationship at West Falmouth Harbor and Barnegat Bay had numerous δ^{13}C values well outside the range predicted by concentration and isotopic conservative mixing models (Table S2; Figs. 4a and 5a), which suggests an additional DOM source from within the estuaries (discussed further in Sect. 5.3). For West Falmouth Harbor, end-members of the conservative mixing model had δ^{13}C values of −23.0 and −26.1 ‰. The observed δ^{13}C data, however, ranged from −19.7 to −26.1 ‰, six of which were more ^{13}C-enriched samples than the modeled range. For Barnegat Bay, end-members of the conservative mixing model had δ^{13}C values of −22.1 and −26.7 ‰. The observed δ^{13}C data ranged from −20.8 to −26.7 ‰, four of which were more ^{13}C-enriched than the modeled range. The two points from North Barnegat Bay falling well above the model (Fig. 5a) correspond to sites BB04 and BB09. The two points from South Barnegat Bay falling well above the model correspond to sites BB12 and BB14. These ^{13}C-enriched samples from Barnegat were all taken from areas near significant stretches of marsh along the western edge of Barnegat Bay. Furthermore, these samples all fall above the concentration-based mixing model for Barnegat Bay (Fig. 5b). Spatial representation of δ^{13}C values at Barnegat Bay (Fig. 5c) shows significantly less negative δ^{13}C values in South Barnegat Bay compared to North Barnegat Bay.

4.5 Comparison of isotopic signature and fDOM-CDOM absorption ratio

Comparison of the isotopic and optical analyses suggests a correlation between δ^{13}C signature and fDOM-CDOM absorption ratio (Fig. 6). For both West Falmouth Harbor and Barnegat Bay, the more ^{13}C-enriched samples also had a higher absorption coefficient per unit fluorescence. This trend is highlighted by the extremes of the data set, with the most ^{13}C-enriched sample (WF02) displaying the highest CDOM : fDOM absorption ratio, and the least ^{13}C-enriched sample (BB01) displaying the lowest CDOM : fDOM absorption ratio. Furthermore, West Falmouth Harbor samples had both higher CDOM : fDOM absorption ratios (−0.032, natural log scale, average) and ^{13}C enrichment (δ^{13}C average of −22.4 ‰) as compared to Barnegat Bay (−1.75 and −23.4 ‰, respectively).

5 Discussion

5.1 Absorption coefficient and spectral slope ranges

Absorption coefficients for West Falmouth and Chincoteague were comparable to those reported for other estuaries and coastal waters (Chen et al., 2003; Green and Blough, 1994). Absorption coefficients for Barnegat Bay were somewhat higher, but within the range reported by Green and Blough (1994). Likewise, all values observed for spectral slope were within ranges reported for similar estuaries and coastal waters (Keith et al., 2002; Green and Blough, 1994), despite differences in the range over which spectral slope was calculated (400–550 nm for Keith et al., 2002; 290 nm to wavelength of absorption detection limit for Green and Blough, 1994). At Barnegat Bay and Chincoteague Bay, the range of calculated spectral slopes was quite small (Table S1). At West Falmouth Harbor, however, there was sig-

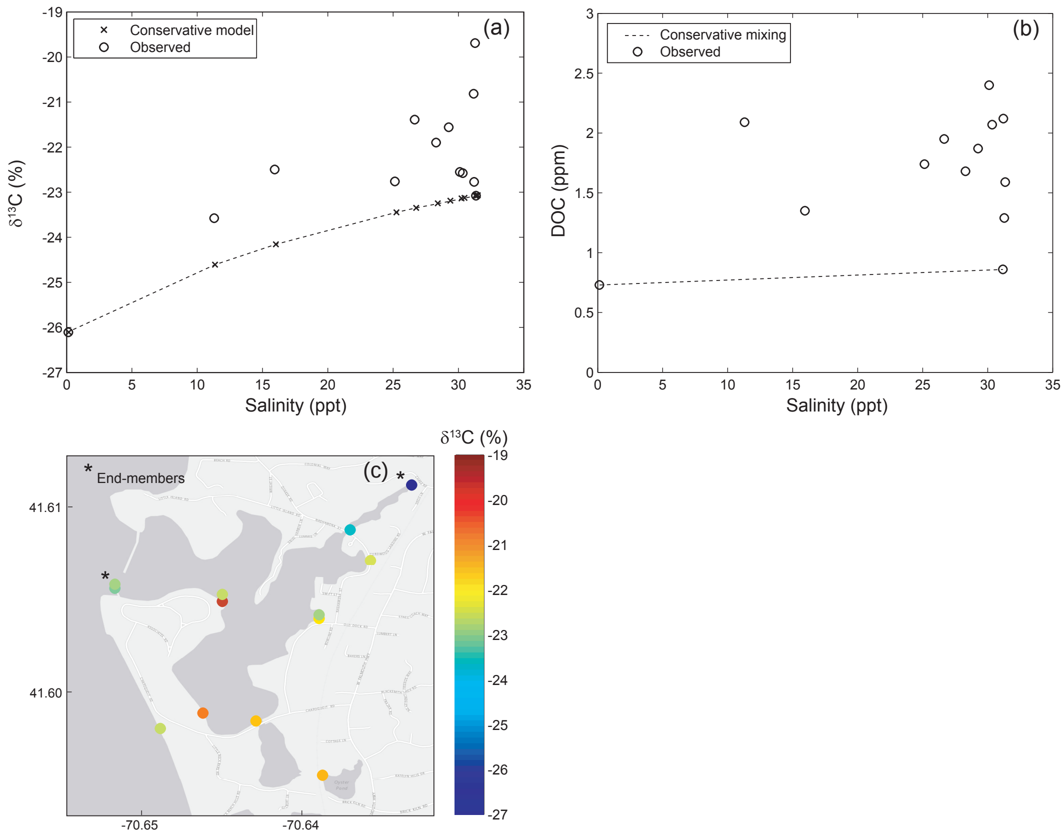

Figure 4. (a) Measured δ^{13}C-DOC values and salinity for West Falmouth Harbor are plotted against an isotopic conservative mixing model for location. Deviations from the model suggest contributions of DOC ^{13}C-enriched relative to the assumed end-members. **(b)** Measured DOC concentration and salinity for West Falmouth Harbor are plotted along with a line of concentration-based conservative mixing between end-members. Data points with concentrations greater than those predicted by conservative mixing indicate addition of DOM to the system. **(c)** Spatial plot of isotopic signatures measured at West Falmouth Harbor. Asterisks indicate assumed end-members.

nificantly more variability in spectral slope. West Falmouth Harbor is a relatively dynamic system with multiple freshwater point sources and unique mixing characteristics (Ganju et al., 2012). Considering the dramatic influence that variable sources (aquatic vs. terrestrial) and alterations (e.g., microbial and photodegradation) have on the optical properties of DOM (Spencer et al., 2009; Helms et al., 2008; De Souza Sierra et al., 1994), the variability in spectral slopes observed at West Falmouth Harbor may be attributable to the physical complexity and short residence time of this estuary. More specifically with respect to source, previous studies have shown that DOM comprised of primarily fulvic acids has steeper spectral slopes than DOM comprised of primarily humic acids (Carder et al., 1989). Considering the physical complexity and variety of point sources at West Falmouth Harbor, variable organic matter composition and spectral slope is not surprising.

5.2 Variability in fDOM–salinity relationship

The inverse relationship between fDOM and salinity observed for these three estuaries is consistent with other estuarine studies (Clark et al., 2002; Green and Blough, 1994). Differing slopes of the inverse relationships suggests the freshwater DOM sources vary between and within estuaries. This is due to differences in organic matter composition and fluorescence between the freshwater sources (Stedmon et al., 2003; Parlanti et al., 2000). South Barnegat Bay and Chincoteague Bay display a similar fDOM–salinity relationship, while South Barnegat Bay and North Barnegat Bay show a divergent relationship. South Barnegat Bay and Chincoteague Bay also have geographic and land use similarities with less development and extensive *Spartina alterniflora*-dominated marshes (Wieben and Baker, 2009; Olsen and Mahoney, 2001; Keefe and Boynton, 1973), whereas North Barnegat Bay is much more developed (Wieben and Baker, 2009). Furthermore, North and South Barnegat Bay appear to have different organic matter sources (determined via isotope analysis; see Sect. 5.3). This information considered together

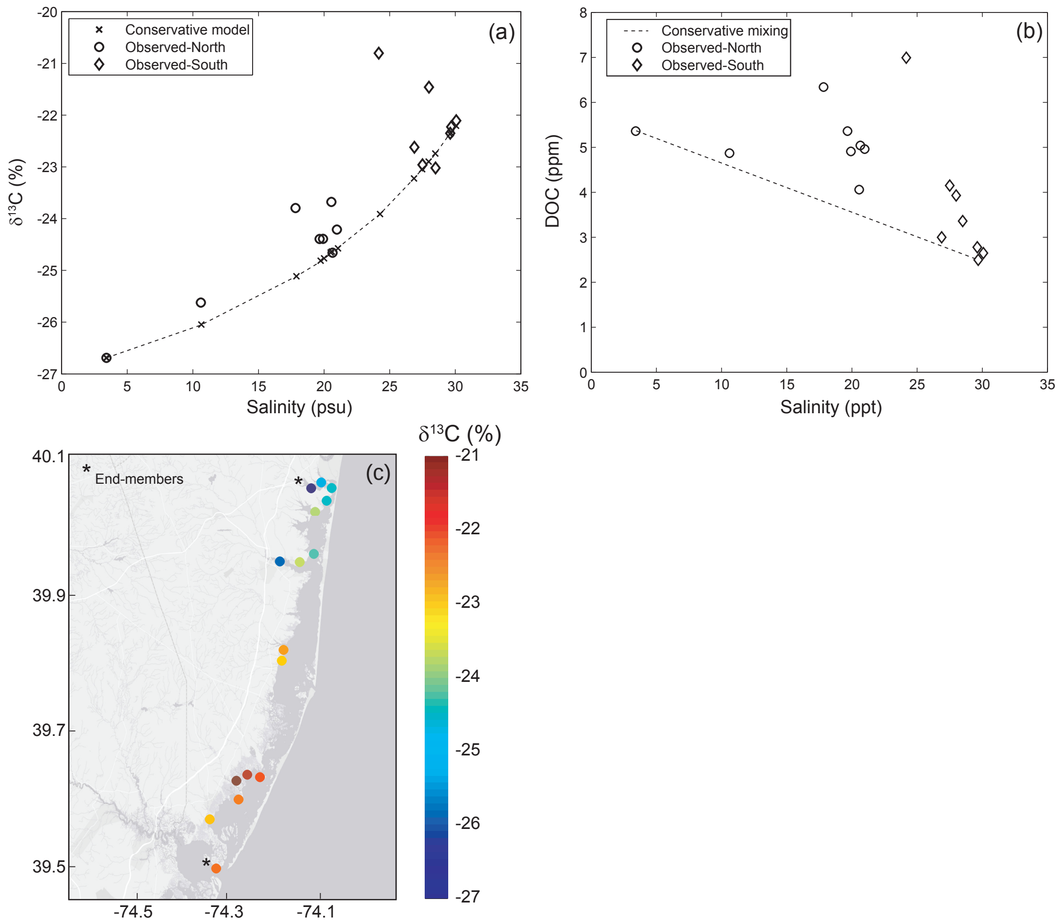

Figure 5. (a) Measured δ^{13}C-DOC values and salinity for both North and South Barnegat Bay are plotted against an isotopic conservative mixing model for location. Deviations from the model suggest contributions of DOC that is distinct from the assumed end-members. **(b)** Measured DOC concentration and salinity for Barnegat Bay are plotted along with a line of concentration-based conservative mixing between end-members. Data points with concentrations greater than those predicted by conservative mixing indicate addition of DOM to the system. **(c)** Spatial plot of isotopic signatures measured at Barnegat Bay. Asterisks indicate assumed end-members.

supports the idea of differing organic matter sources due to various inputs affecting fluorescence properties. As for the variability seen within West Falmouth Harbor, this is again likely attributable to the relatively low fluorescence signals observed throughout the estuary, along with the variety of freshwater inputs to this complex system.

5.3 Evidence for internal DOM sources

The disparity between observed δ^{13}C values and those predicted by conservative mixing models (Figs. 4a and 5a) suggests an additional DOM source within the estuaries. Previous studies of DOC in eastern US estuaries have suggested a marine end-member δ^{13}C value of -24 to -22 ‰, and a freshwater end-member δ^{13}C of -28 to -26 ‰ (Peterson et al., 1994). Observed values falling above the mixing model and approaching much more ^{13}C-enriched values than the defined marine end-member are likely due to the influence of DOC from *Spartina* spp. cordgrass in nearby salt marshes. Analysis of DOC *Spartina* spp. by past studies has indicated a δ^{13}C signature of about -16.4 to -11.7 ‰ (Komada et al., 2012; Chmura and Aharon, 1995). The tendency of values from this study towards this ^{13}C-enriched signature, in combination with knowledge of *Spartina* coverage around the sites differing from conservative mixing models, suggests a DOM source derived from *Spartina* cordgrass. The influence of this end-member is particularly notable in South Barnegat Bay (specifically sites BB12 and BB14), where *Spartina* coverage is extensive (Olsen and Mahoney, 2001), and the δ^{13}C of the DOC is -21.6 and -20.9 ‰ for BB12 and BB14, respectively. Although *Spartina* coverage in North Barnegat Bay is not as extensive as in South Barnegat Bay, the sites with DOC δ^{13}C values that are more enriched than the conservative mixing model for North Barnegat Bay (BB04 and BB09) were taken from inland sampling locations, specifically the north bank of the lower Toms River and Reedy Creek, where stands of *Spartina* are present.

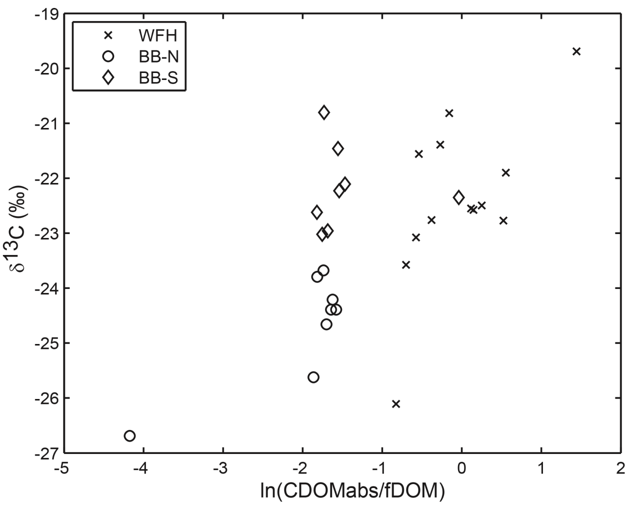

Figure 6. Isotopic signature versus CDOM absorption coefficient (340 nm) divided by fluorescence for all sites at West Falmouth Harbor (WFH), North Barnegat Bay (BB-N), and South Barnegat Bay (BB-S). CDOM absorption coefficient per unit fluorescence presented on natural log scale.

However, the observed ^{13}C enrichment could also be attributed to *Zostera* eelgrass, which has been shown to exhibit a ^{13}C-enriched signature (Hemminga and Mateo, 1996). For this reason, the aforementioned samples falling well above the conservative mixing models cannot necessarily be considered a result of *Spartina* influence. However, a comparison of site locations to known seagrass and *Spartina* wetland coverage can yield some indication of the most likely source of ^{13}C-enriched DOC. Seagrass coverage maps (Lathrop and Haag, 2011) and maps of estuarine intertidal wetland coverage (United States Fish and Wildlife Service, 2015) for Barnegat Bay show intertidal wetland coverage and no seagrass coverage for sites BB09, BB12, and BB14. Site BB04 is characterized by neither type of coverage, but its inland location places it much closer to known intertidal wetland coverage (US Fish & Wildlife Service, 2015). This geographic comparison indicates *Spartina* as the more likely additional end-member at Barnegat Bay, though *Zostera* influence is still possible. Considering the movement of water and potential for mixing during residence in the estuary, this geographic analysis is by no means definitive, but does provide some insights.

For West Falmouth Harbor, sites falling well above the conservative mixing model (WF02, WF03, WF04, WF05, WF07, WF11) were compared to known seagrass (Del Barrio et al., 2014) and intertidal wetland (US Fish & Wildlife Service, 2015) coverage for West Falmouth Harbor. For sites WF03, WF05, WF07, and WF11, there is known intertidal wetland coverage and no known *Zostera* coverage. For site WF02, there is both intertidal wetland coverage and *Zostera* coverage, whereas WF04 corresponds to neither *Spartina* nor *Zostera*. This comparison yields a less clear picture of DOC sources, but this is to be expected considering the aforementioned complexity of surrounding land uses, potential DOC inputs, and limited mixing at West Falmouth Harbor. Furthermore, spatial representation of δ^{13}C values at West Falmouth Harbor (Fig. 4c) show ^{13}C-depleted samples in the northeastern corner of the harbor, the location of a freshwater culvert discharging groundwater (Ganju, 2011). On the whole, the conservative mixing models used in this study may not be appropriate for a system as complex as West Falmouth Harbor. Unlike the clear indication of a third end-member from the mixing model for Barnegat Bay, one could envision a more complex system with multiple additional end-members for West Falmouth Harbor (Fig. 4a and b).

5.4 Potential influence of photodegradation

We also considered the potential influence of photodegradation on the samples with DOC that was ^{13}C-enriched in comparison to the conservative mixing model. Irradiation experiments have shown that riverine DOC becomes ^{13}C-enriched by $\sim$ 3.5 ‰ and concentrations decrease by as much as 45 % over 57 days as a result of photodegradation (Spencer et al., 2009), suggesting the possibility that the aforementioned ^{13}C-enriched samples are photodegraded terrestrial DOM. This is unlikely for samples from West Falmouth Harbor, given the very short residence time of this estuary ($\sim$ 1 day; Hayn et al., 2014). For Barnegat Bay, however, the influence of photodegradation is possible. Sites BB12 and BB14 are in areas with residence time of $\sim$ 10 days, while sites BB04 and BB09 are in areas with residence time of $\sim$ 15–20 days (Defne and Ganju, 2014). These residence times are within the time frame over which photodegradation effects on δ^{13}C have previously been observed (Spencer et al., 2009), which could also influence the ^{13}C-enriched signatures observed for these samples. However, the relative lack of ^{13}C enrichment observed at other Barnegat Bay sites with even longer residence times (e.g., BB03 and BB07; Defne and Ganju, 2014) implies that photodegradation alone likely does not explain the ^{13}C-enriched signatures found for certain Barnegat Bay samples. Furthermore, and most convincing, the concentration-based mixing model for Barnegat Bay (Fig. 5b) demonstrates a net input of DOC into the estuary. DOC concentrations that exceed the conservative concentration-based mixing model indicate a source of DOC within the estuary. If the samples were affected by photodegradation, one would expect a net loss of measured DOC within the estuary (e.g., Spencer et al., 2009).

Further insight into the possibility of photodegradation can be derived from the C-normalized $CDOM_{340}$ (Table S2). Carbon-normalized CDOM correlates strongly with sample aromaticity (Weishaar et al., 2003), which one would expect to decrease as a result of photodegradation (Hood et al., 2005). However, C-normalized $CDOM_{340}$ (and thus aromaticity) is not significantly lower for the potentially photodegraded terrestrial DOM samples as compared to other terrestrial DOM samples such as BB01 and BB03 (Table S2). This lack of a drop in aromaticity does not support the possibility that the ^{13}C-enriched samples from Barnegat Bay are photodegraded terrestrial DOM.

5.5 Variability in fDOM–CDOM absorption relationship

The variability between fDOM and CDOM absorption in these estuaries was expected based on the results of previous studies (Clark et al., 2004; Del Castillo et al., 1999; Hoge et al., 1993). West Falmouth Harbor in particular showed a different absorption coefficient to fDOM ratio as compared to the general trend for Barnegat and Chincoteague Bays (Fig. 3). We ascribe this difference to groundwater inputs, which have been shown to have lower CDOM (Shen et al., 2015; Chen et al., 2010; Huang and Chen, 2009) and are substantial in West Falmouth Harbor (Ganju, 2011). Additionally, the extremes of CDOM variability in this study can be explained by differing DOC sources within the estuaries. While the relatively uniform CDOM–fDOM relationship for Barnegat Bay results in clustering of Barnegat Bay samples (Fig. 6), this relationship is highlighted by both the Barnegat Bay outliers and the higher $CDOM_{abs}$: fDOM observed for the more ^{13}C-enriched samples at West Falmouth Harbor. Points such as the outliers at Barnegat Bay are indicative of how the CDOM–fDOM relationship can be altered in an estuary with such diverse sources and transport mechanisms. This assertion of variable CDOM–fDOM relationship depending on source is supported by the findings of Tzortziou et al. (2008), which suggested that marsh-exported DOC has a lower fluorescence per unit absorbance as compared to humic DOC originating from a freshwater source. For the two extreme outliers, ^{13}C-enriched DOC (likely *Spartina* source) was associated with a lower fluorescence per unit absorbance. ^{13}C-depleted DOC (terrestrial source) was associated with a higher fluorescence per unit absorbance. While other studies have focused on differences in the fluorescence–absorbance relationship as a function of molecular weight (Belzile and Guo, 2006; Stewart and Wetzel, 1980), the combination of CDOM optical and isotopic analyses presented here provide a connection between CDOM source and optical characteristics, as suggested by Tzortziou et al. (2008).

The effects of in situ processing on absorption properties of DOM must also be considered here. In particular, photodegradation is known to reduce the absorbance of light by DOM (Spencer et al., 2009; Kouassi and Zika, 1992). Therefore, observations of higher fluorescence per unit absorbance could be a result of photochemical effects. However, the ^{13}C-enriched DOC samples discussed here exhibit lower fluorescence per unit absorbance than expected. This trend provides additional evidence refuting the aforementioned possibility that the ^{13}C-enriched samples from Barnegat Bay are photodegraded terrestrial DOM (Sect. 5.4).

5.6 Ramifications for light attenuation modeling

The variability in fDOM optical properties between and within estuaries has important consequences for light attenuation models. Continuous estimates of light attenuation are possible with continuous proxy measurements of turbidity (for sediment), chlorophyll *a* fluorescence, and fDOM (Gallegos et al., 2011), but Ganju et al. (2014) found that light models can be highly sensitive to the CDOM–fDOM relationship, specifically in Barnegat Bay. We applied the light model of Gallegos et al. (2011) to the individual measurements of turbidity, chlorophyll *a* fluorescence, and fDOM collected in this study. We explored two cases to calculate light attenuation: (1) use of the individual point CDOM : fDOM ratio and spectral slope from measurements and (2) use of an estuary-wide average CDOM : fDOM ratio and spectral slope (model parameters related to sediment particles and chlorophyll were held constant to values reported in Ganju et al., 2014). Variation in the DOM properties led to average light attenuation errors ranging from 11 to 33 % (Table 2), with individual site errors over 200 % at sites with the highest deviation from the estuary mean (site BB01, at the landward end of Barnegat Bay). This suggests that constraining optical properties of the DOM pool is critical for light modeling, and that high variability within an estuary may confound use of spatially constant parameters.

6 Conclusions

This study shows that the CDOM absorption–fDOM relationship is variable both between and within West Falmouth Harbor, Barnegat Bay, and Chincoteague Bay, and depends upon DOM source. DOM that was ^{13}C-enriched (higher δ^{13}C values) also had a higher absorption coefficient per unit fluorescence. Additionally, fDOM–salinity relationship was variable between and within these estuaries. The exception here was the lack of variability in these relationships within Chincoteague Bay. Future work in relation to this study might involve a stable carbon isotope analysis at Chincoteague Bay similar to the analysis carried out here for West Falmouth Harbor and Barnegat Bay. Results of such an analysis could further elucidate the effects of DOM source on the CDOM : fDOM ratio. Finally, spectral slopes for use in light models were consistent between and within Barnegat and Chincoteague Bays, with more variability observed at West Falmouth Harbor.

The Supplement related to this article is available online at doi:10.5194/bg-13-583-2016-supplement.

Author contributions. W. K. Oestreich executed the sampling strategy and analyzed data. N. K. Ganju and J. W. Pohlman designed the experiment and assisted in data interpretation. S. E. Suttles assisted in designing and executing the sampling strategy. All authors contributed to the drafting of the manuscript.

Acknowledgements. Funding was provided by the Woods Hole Oceanographic Institution Summer Student Fellowship Program and the USGS Coastal and Marine Geology Program. Thanks to Brian Bergamaschi of the US Geological Survey California Water Science Center for input on fDOM corrections. Thanks to the Rutgers University Marine Field Station, in particular Tom Malatesta and Roland Hagan, for field support at Barnegat Bay. Thanks also to Nicholas Nidzieko of the University of Maryland Horn Point Laboratory for field support at Chincoteague Bay. Patrick Dickhudt and Wally Brooks provided assistance with instrument preparation and running of stable carbon isotope analysis samples, respectively. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the US Government.

Edited by: G. Herndl

References

Allen, T. R., Tolvanen, H. T., Oertel, G. F., and McLeod, G. M.: Spatial characterization of environmental gradients in a coastal lagoon, Chincoteague Bay, Estuar. Coast., 30, 959–977, 2007.

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

Barron, C., Apostolaki, E. T., and Duarte, C. M.: Dissolved organic carbon fluxes by seagrass meadows and macroalgal beds, Front. Mar. Sci., 1, 42, doi:10.3389/fmars.2014.00042, 2014.

Belzile, C. and Guo, L.: Optical properties of low molecular weight and colloidal organic matter: Application of the ultrafiltration permeation model to DOM absorption and fluorescence, Mar. Chem., 98, 183–196, 2006.

Bricaud, A., Morel, A., and Prieur, L.: Absorption by dissolved organic matter of the sea (yellow substance) in the UV and visible domains, Limnol. Oceanogr., 26, 43–53, 1981.

Bricker, S. B., Clement, C. G., Pirhalla, D. E., Orlando, S. P., and Farrow, D. R. G.: National Estuarine Eutrophication Assessment: Effects of Nutrient Enrichment in the Nation's Esuaries, NOAA, National Ocean Service, Special Projects Office and the National Centers for Coastal Ocean Science, Silver Spring, MD, 71 pp., 1999.

Buchsbaum, R. and Valiela, I.: Variability in the chemistry of estuarine plants and its effect on feeding by Canada geese, Oecologia, 73, 146–153, 1987.

Burkholder, J. M., Tomasko, D. A., and Touchette, B. W.: Seagrasses and eutrophication, J. Exp. Mar. Biol. Ecol., 350, 46–72, 2007.

Callahan, J., Dai, M., Chen, R. F., Li, X., Lu, Z., and Huang, W.: Distribution of dissolved organic matter in the Pearl River Estuary, China, Mar. Chem., 89, 211–224, 2004.

Carder, K. L., Steward, R. G., Harvey, G. R., and Orner, P. B.: Marine humic and fulvic acids: Their effects on remote sensing of ocean chlorophyll, Limnol. Oceanogr., 34, 68–81, 1989.

Chen, C., Shi, P., Yin, K., Pan, Z., Zhan, H., and Hu, Z.: Absorption coefficient of yellow substance in the Pearl River estuary, Proc. SPIE 4892, P. Soc. Photo-Opt. Ins., 215, 2003.

Chen, M., Price, R. M., Yamashita, Y., and Jaffe, R.: Comparative study of dissolved organic matter from groundwater and surface water in the Florida coastal Everglades using multi-dimensional spectrofluorometry combined with multivariate statistics, Appl. Geochem., 25, 872–880, 2010.

Chmura, G. L. and Aharon, P.: Stable carbon isotope signatures of sedimentary carbon in coastal wetlands as indicators of salinity regime, J. Coast. Res., 11, 124–135, 1995.

Clark, C. D., Jimenez-Morais, J., Jones II, G., Zanardi-Lombardo, E., Moore, C. A., and Zika, R. G.: A time-resolved fluorescence study of dissolved organic matter in a riverine to marine transition zone, Mar. Chem., 78, 121–135, 2002.

Clark, C. D., Hiscock, W. T., Millero, F. J., Hitchcock, G., Brand, L., Miller, W. L., Ziolkowski, L., Chen, R. F., and Zika, R. G.: CDOM distribution and CO_2 production on the Southwest Florida Shelf, Mar. Chem., 89, 145–167, 2004.

Coble, P. G.: Marine optical biogeochemistry: the chemistry of ocean color, Chem. Rev., 107, 402–418, 2007.

Defne, Z. and Ganju, N. K.: Quantifying the residence time and flushing characteristics of a shallow, back-barrier estuary: application of hydrodynamic and particle tracking models, Estuar. Coast., 38, 1719–1734, 1–16, doi:10.1007/s12237-014-9885-3, 2014.

Del Barrio, P., Ganju, N. K., Aretxabaleta, A. L., Hayn, M., Garcia, A., and Howarth, R. W.: Modeling future scenarios of light attenuation and potential seagrass success in a eutrophic estuary, Estuar. Coast Shelf S., 149, 13–23, 2014.

Del Castillo, C. E., Coble, P. G., Morell, J. M., Lopez, J. M., and Corredor, J. E.: Analysis of optical properties of the Orinoco River plume by absorption and fluorescence spectroscopy, Mar. Chem., 66, 35–51, 1999.

De Souza Sierra, M. M., Donard, O. F. X., Lamotte, M., Belin, C., and Ewald, M.: Fluorescence spectroscopy of coastal and marine waters, Mar. Chem., 47, 127–144, 1994.

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, Limnol. Oceanogr.-Methods, 10, 767–775, 2012.

Ehlers, A., Worm, B., and Reusch, T. B. H.: Importance of genetic diversity in eelgrass *Zostera marina* for its resilience to global warming, Mar. Ecol.-Prog. Ser., 355, 1–7, 2008.

Gallegos, C. L., Werdell, P. J., and McClain, C. R.: Long-term changes in light scattering in Chesapeake Bay inferred from Secchi depth, light attenuation, and remote sensing measurements, J. Geophys. Res., 116, C00H08, doi:10.1029/2011JC007160, 2011.

Ganju, N. K.: A novel approach for direct estimation of fresh groundwater discharge to an estuary, Geophys. Res. Lett., 38, L11402, doi:10.1029/2011GL047718, 2011.

Ganju, N. K., Hayn, M., Chen, S. N., Howarth, R. W., Dickhudt, P. J., Aretxabaleta, A. L., and Marino, R.: Tidal and groundwater fluxes to a shallow, microtidal estuary: Constraining inputs through field observations and hydrodynamic modeling, Estuar. Coast., 35, 1285–1298, doi:10.1007/s12237-012-9515-x, 2012.

Ganju, N. K., Miselis, J. L., and Aretxabaleta, A. L.: Physical and biogeochemical controls on light attenuation in a eutrophic, back-barrier estuary, Biogeosciences, 11, 7193–7205, doi:10.5194/bg-11-7193-2014, 2014.

Green, S. A. and Blough, N. V.: Optical absorption and fluorescence properties of chromophoric dissolved organic matter in natural waters, Limnol. Oceanogr., 39, 1903–1916, 1994.

Harvey, G. R., Boran, D. A., Chesal, L. A., and Tokar, J. M.: The structure of marine fulvic and humic acids, Mar. Chem., 12, 119–132, 1983.

Hauxwell, J., Cebrián, J., and Valiela, I.: Eelgrass *Zostera marina* loss in temperate estuaries: relationship to land-derived nitrogen loads and effect of light limitation imposed by algae, Mar. Ecol.-Prog. Ser., 247, 59–73, 2003.

Hayn, M., Howarth, R., Marino, R., Ganju, N., Berg, P., Foreman, K., Giblin, A., and McGlathery, K.: Exchange of nitrogen and phosphorus between a shallow lagoon and coastal waters, Estuar. Coast. 37, 63–73, 2014.

Heck, K. L., Able, K. W., Roman, T. C., and Fahay, M. P.: Composition, abundance, biomass, and production of macrofauna in a New England estuary: Comparisons among eelgrass meadows and other nursery habitats, Estuaries, 18, 379–389, 1995.

Helms, J. R., Stubbins, A., Ritchie, J. D., Minor, E. C., Kieber, D. J., and Mopper, K.: Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter, Limnol. Oceanogr., 53, 955–969, 2008.

Hemminga, M. A. and Mateo, M. A.: Stable carbon isotopes in seagrasses: variability in ratios and use in ecological studies, Mar. Ecol.-Prog. Ser., 140, 285–298, 1996.

Hoge, F. E., Vodacek, A., and Blough, N. V.: Inherent optical properties of the ocean: Retrieval of the absorption coefficient of chromophoric dissolved organic matter from fluorescence measurements, Limnol. Oceanogr., 38, 1394–1402, 1993.

Hood, E., Williams, M. W., and McKnight, D. M.: Sources of dissolved organic matter (DOM) in a Rocky Mountain stream using chemical fractionation and stable isotopes, Biogeochemistry, 74, 231–255, 2005.

Huang, W. and Chen, R. F.: Sources and transformations of chromorphic dissolved organic matter in the Neponset River Watershed, J. Geophys. Res., 114, G00F05, 2009.

Kaldy, J. E., Cifuentes, L. A., and Brock, D.: Using stable isotope analyses to assess carbon dynamics in a shallow subtropical estuary, Estuaries, 28, 86–95, 2005.

Keefe, C. W. and Boynton, W. R.: Standing crop of salt marshes surrounding Chincoteague Bay, Maryland-Virginia, Chesapeake Science, 14, 117–123, 1973.

Keith, D. J., Yoder, J. A., and Freeman, S. A.: Spatial and temporal distribution of coloured dissolved organic matter (CDOM) in Narragansett Bay, Rhode Island: Implications for phytoplankton in coastal waters, Estuar. Coast Shelf S., 55, 705–717, 2002.

Kennish, M. J., Fertig, B. M., and Sakowicz, G. P.: Benthic macroalgal blooms as an indicator of system eutrophy in the Barnegat Bay-Little Egg Harbor estuary, Bulletin of the New Jersey Academy of Science, 56, 1–5, 2011.

Kennish, M. J., Fertig, B. M., and Sakowicz, G. P., In situ surveys of seagrass habitat in the northern segment of the Barnegat bay-Little Egg Harbor estuary, http://bbp.ocean.edu/Reports/2011Northernseagrasssurvey.pdf (last access: 8 February 2015), 2013.

Kirk, J. T. O.: Light and photosynthesis in aquatic ecosystems. Cambridge University Press, Cambridge and New York, 1994.

Komada, T., Polly, J. A., and Johnson, L.: Transformations of carbon in anoxic marine sediments: Implications from $\Delta^{14}C$ and $\delta^{13}C$ signatures, Limnol. Oceanogr., 57, 567–581, 2012.

Kouassi, K. M. and Zika, R. G.: Light-induced destruction of the absorbance property of dissolved organic matter in seawater, Toxicol Environ Chem, 35, 195–211, 1992.

Lalonde, K., Middlestead, P., and Gelinas, Y.: Automation of $^{13}C/^{12}C$ ratio measurement for freshwater and seawater DOC using high temperature combustion, Limnol. Oceanogr.-Methods, 12, 816–829, 2014.

Lathrop, R. G. and Haag, S.: Assessment of seagrass status in the Barnegat Bay – Little Egg Harbor Estuary: 2003 and 2009, CRSSA Technical Report #2011–01, Rutgers University, Grant F. Wilson Center for Remote Sensing and Spatial Analysis, New Brunswick, NJ, 2011.

McGranahan, G., Balk, D., and Anderson, B., The rising tide: assessing the risks of climate change and human settlements in low elevation coastal zones, Environ Urban, 19, 17–37, 2007.

Mopper, K., Kieber, D. J., and Stubbins, A.: Marine photochemistry of organic matter: processes and impacts, in: Biogeochemistry of Marine Dissolved Organic Matter 2nd ed; edited by: Hansell, D. A. and Carlson, C. A., Academic Press: Boston, 389–450, 2015.

Nelson, N. B. and Siegel, D. A.: The global distribution and dynamics of chromorphic dissolved organic matter, Annu. Rev. Mar. Sci., 5, 447–476, 2013.

Olsen, P. S. and Mahoney, J. B., Phytoplankton in the Barnegat Bay-Little Egg Harbor estuarine system: Species composition and picoplankton bloom development, J. Coastal Res., 32, 115–143, 2001.

Parlanti, E., Worz, K., Geoffroy, L., and Lamotte, M.: Dissolved organic matter fluorescence spectroscopy as a tool to estimate biological activity in a coastal zone submitted to anthropogenic inputs, Org. Geochem., 31, 1765–1781, 2000.

Peterson, B. J., Fry, B., Hullar, M., Saupe, S., and Wright, R.: The distribution and stable carbon isotopic composition of dissolved organic carbon in estuaries, Estuaries, 17, 111–121, 1994.

Pregnall, A. M.: Release of dissolved organic carbon from the estuarine intertidal macroalga *Enteromorpha prolifera*, Mar. Biol., 73, 37–42, 1983.

Raymond, P. A. and Bauer, J. E.: DOC cycling in a temperate estuary: A mass balance approach using natural ^{14}C and ^{13}C isotopes, Limnol. Oceanogr., 46, 655–667, 2001.

Shen, Y., Chapelle, F. H., Strom, E. W., and Benner, R.: Origins and bioavailability of dissolved organic matter in groundwater, Biogeochemistry, 122, 61–78, 2015.

Spencer, R. G. M., Stubbins, A., Hernes, P. J., Baker, A., Mopper, K., Aufdenkampe, A. K., Dyda, R. Y., Mwamba, V. L., Mangangu, A. M., Wabakanghazi, J. N., and Six, J.: Photochemical degradation of dissolved organic matter and dissolved lignin phenols from the Congo River, J. Geophys. Res., 114, G03010, doi:10.1029/2009JG000968, 2009.

Stedmon, C. A., Markager, S., and Bro, R.: Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy, Mar. Chem., 82, 239–254, 2003.

Stewart, A. J. and Wetzel, R. G.: Fluorescence : absorbance ratios-a molecular-weight tracer of dissolved organic matter, Limnol. Oceanogr., 25, 559–564, 1980.

Tzortziou, M., Neale, P. J., Osburn, C. L., Megonigal, J. P., Nagamitzu, M., and Rudolf, J.: Tidal marshes as a source of optically and chemically distinctive colored dissolved organic matter in the Chesapeake Bay, Limnol. Oceanogr., 53, 148–159, 2008.

United States Environmental Protection Agency: National estuary program coastal condition report, Chapter 3: Northeast national estuary program coastal condition, Barnegat Bay National Estuary Program, http://www.epa.gov/owow/oceans/nepccr/index.html (last access: 17 January 2015), 2007.

United States Fish and Wildlife Service National Wetlands Inventory, Ecological Services: Wetlands Mapper, http://www.fws.gov/wetlands/data/mapper.HTML, last access: 8 February 2015.

Wazniak, C., Hall, M., Cain, C., Wilson, D., Jesien, R., Thomas, J., Carruthers, C., and Dennison, W.: State of the Maryland coastal bays, Maryland Department of Natural Resources, Maryland Coastal Bays Program, and University of Maryland Center for Environmental Science, Integration, and Application Network, Annapolis, MD, http;//www.mdcoastalbays.org/archive/2004/MCB-State-Bay-2004.pdf (last access: 21 January 2015), 2004.

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, Environ. Sci. Technol., 37, 4702–4708, 2003.

Wieben, C. M. and Baker, R. J.: Contributions of nitrogen to the Barnegat Bay-Little Egg Harbor Estuary: Updated loading estimates, 19 p., Chapter prepared for the Barnegat Bay Partnership State of the Bay Technical Report, 2009.