

Photochemical production of dissolved organic carbon from resuspended sediments

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Abstract

A series of controlled photolysis experiments using simulated sunlight was conducted in the presence and absence of estuarine bottom sediments to address the role of sediment resuspension on dissolved organic carbon (DOC) cycling in estuarine and coastal waters. In 0.2- μm -filtered estuarine water samples with no added sediment, DOC concentrations decreased from 0.4 to 3 $\mu\text{mol L}^{-1} \text{h}^{-1}$ as a result of photooxidation. When 0.2- μm -filtered water samples with the addition of 1–2 grams of estuarine sediment per liter were irradiated, DOC was produced at rates of 3 to 150 $\mu\text{mol L}^{-1}$ DOC per gram dry sediment. Photoproduction of DOC from resuspended sediments increased in direct proportion to the percent organic carbon content of the added sediment. High-energy ultraviolet light was the most effective for photodegrading DOC in filtered samples and for photoproducing DOC from resuspended sediments. Photosynthetically active radiation (PAR; 400–700 nm) did not significantly degrade DOC in filtered water. However, PAR did produce half as much DOC from resuspended sediments in organic-rich regions of the estuary relative to full spectrum sunlight irradiations. The photoproduction of DOC from resuspended sediments, calculated for the top 1 m of coastal waters, resulted in fluxes that were significantly larger than benthic and riverine fluxes of DOC. Photoproduction from resuspended sediments therefore represents an episodically significant but previously unrecognized source of DOC to estuarine and coastal ecosystems receiving large sediment plumes.

Estuarine sediments are naturally resuspended and mobilized by wind-driven, wave-induced water movement as well as tidal and riverine currents. Anthropogenic sources of resuspended sediments in estuaries include dredging, bow waves, propeller wash, and bottom-trawling fishing devices. In the typically shallow waters of estuaries, sediment-water interactions are a fundamental, yet commonly neglected, set of processes that can significantly impact a host of important biogeochemical processes, such as trace-metal mobilization, nutrient and organic carbon (OC) cycling, and release of anthropogenic contaminants (Komada and Reimers 2001; Komada et al. 2002; Koelmans and Prevo 2003).

Sediment resuspension may affect OC concentrations in natural waters by dispersion of pore waters enriched in dissolved organic carbon (DOC) into overlying waters or by desorption or displacement of organics bound to disturbed sediments (Komada et al. 2002; Koelmans and Prevo 2003). Numerous studies have documented that organic matter is closely, and sometimes reversibly, associated with particles in river and estuarine systems (Hedges and Keil 1999). Resuspension and physical reworking of these sediments may significantly impact their remineralization rates (Aller 1998; Sun et al. 2002;

Arzayus and Canuel 2004) and could alter the partitioning of organics between the dissolved and particulate phases. For example, Komada and Reimers (2001) found DOC increased during resuspension of estuarine and inner-shelf sediments in bottom waters, primarily due to desorption of mineral-bound OC. The fraction of easily releasable OC was only a small fraction ($\leq 0.3\%$) of sedimentary particulate organic carbon (POC), but was correlated to POC content (Komada and Reimers 2001). Koelmans and Prevo (2003) found that DOC was produced during laboratory simulations of resuspension events of lake and river sediments containing varying levels of organic matter. It was suggested that a significant fraction of particulate carbon could be mobilized from the sediments within a few weeks of incubation.

Although these studies demonstrate the importance of dark release of DOC from resuspended sediments, they do not address the potentially significant role that photochemical transformations could play in the mobilization of DOC from sediments newly exposed to sunlit surface waters. Recently, Mayer et al. (2006) demonstrated the loss of POC in suspended sediments from the Mississippi River system after relatively long-term (>24 h total) exposure to simulated sunlight and inferred the progressive production of DOC from light-exposed sediments. Given the frequency of resuspension episodes and shallow depths in estuaries, the introduction of resuspended bottom sediments into the photic zone is a ubiquitous occurrence, although the magnitude and significance of DOC produced by light exposure remain poorly understood.

The potential photoreactivity of particle-bound organics may produce dissolved photoproducts, analogous to the production of low-molecular-weight photoproducts during sunlight irradiation of dissolved organic matter (Kieber et al. 1990; Wetzel et al. 1995; Opsahl and Benner 1998).

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Photochemical interactions could also impact the partitioning of organics between the solid and solution phases in several ways. For example, Miller and Zepp (1979a) showed that photolysis rates of several aquatic pollutants were enhanced in the presence of suspended sediments due to the increased diffusiveness of light. Other studies indicate that the photoreactivity of hydrophobic organics can be altered when adsorbed to suspended sediments relative to the dissolved phase and that light screening may reduce the photoreactivity of more soluble, less hydrophobic organics (Miller and Zepp 1979b; Zepp and Schlotzhauer 1981).

The goal of this work was to explore the role of photochemical processes on sediment-water interactions by examining DOC production and loss in the presence and absence of light. The relative importance of photochemical processes as a source of DOC in estuarine and coastal waters was also evaluated. This information better clarifies the roles of light and sediment resuspension on the biogeochemistry and cycling of carbon in estuarine environments.

Materials and methods

Study site and sampling—Sediment and water samples were collected seasonally from two sites in the Cape Fear River estuary (CFRE) located in southeastern North Carolina. The Cape Fear River drains the largest river basin in the state of North Carolina (Fig. 1). In the estuarine portion of the river near Wilmington, North Carolina, two coastal plain rivers, the Black and Northeast Cape Fear Rivers, contribute darkly colored, organic-rich freshwater to the river. Concentrations of DOC range from $\geq 1,000 \mu\text{mol L}^{-1}$ in freshwaters to $\sim 200 \mu\text{mol L}^{-1}$ near the estuary mouth (Avery et al. 2003; Shank et al. 2004). Seawater sources include the Atlantic Ocean and the Atlantic Intracoastal Waterway at the seaward end of the estuary. In general, the estuary is well mixed vertically because of the relatively short water residence time and rapid flow. Water depths in the estuary range from 1–2 m near the margins to ~ 10 –15 m in the main channel.

The two sampling sites included an upper estuarine station with typically low salinity (5–15) and a lower estuarine station with typically high salinity (25–35). For one experiment sediment samples and overlying water were collected from stations located over the normal salinity gradient of the estuary (M23, M35, M42, M54, M61). Sampling locations and hydrographic parameters in bottom waters of each station are shown in Figure 1 and Table 1, respectively.

Sediment samples were collected with a box corer in water depths of at least 5 m. Three subsamples were taken from the upper 2–3 cm of the stainless-steel box core and stored in sealed polyethylene cups at 4°C in the dark. Samples of overlying bottom water were collected with an air-operated double-diaphragm plastic pump and Kynar® tubing. Water samples were stored in 12.5-L fluorinated high-density polyethylene (FLPE) carboys at in situ temperatures and were protected from light exposure. Additional water samples were filtered on site through in-

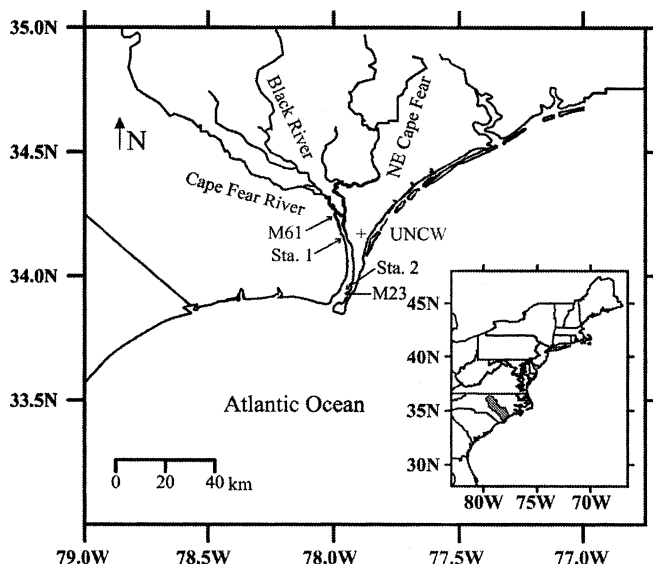


Fig. 1. Map of the Cape Fear River estuary, North Carolina, showing sampling locations. Stations M35, M42, and M54 are omitted for clarity but are approximately equally spaced between stations M23 and M61.

line 1.2- μm polypropylene and 0.2- μm polyethersulfone filter cartridges (Meissner) and were stored in FLPE containers. All plastic bottles, tubing, and filtration equipment were extensively acid washed to prevent contamination (Shank et al. 2004).

Photochemical resuspension experiments—Suspensions were prepared at concentrations of 1–2 g L⁻¹, which are relevant to disturbed environments (Shi et al. 2003) using bottom sediments and overlying water at each site. At each site, three polyethylene cups were filled with surface sediment (2–3 cm depth) from the box core, and they were homogenized into one sample using a Teflon®-coated stir rod. Controlled photolysis experiments were performed with 0.2- μm -filtered water, unfiltered water, and 0.2- μm -filtered water plus added sediment. Subsamples of water and sediment were apportioned into six 500-mL quartz flasks, and two aliquots were stored for analysis of initial DOC concentrations. Three quartz flasks were enclosed in black plastic bags to serve as dark controls. The three light-exposed flasks were placed in a constant-temperature water bath (set at ambient estuarine temperature) and irradiated in simulated sunlight for 9 h using a Spectral Energy™ solar simulator (1 kW Xe arc light source) with an AM1 filter to remove wavelengths not found in the solar spectrum. Light measurements were made with an Ocean Optics S2000 fiber-optic spectrophotometer equipped with a CC-3-UV cosine collector or an IL1700 radiometer equipped with factory calibrated detectors for ultraviolet (UV) B, UVA, and photosynthetically active radiation (PAR; 400–700 nm). At the end of the irradiation, the three light-exposed flasks and three dark controls were filtered separately through Meissner 0.2- μm polyethersulfone acid-washed capsule filters and analyzed for DOC.

Table 1. Sampling dates, stations, hydrographic parameters for bottom waters and organic content of sediments. The April 2003 sampling took place during a period of very high river flow, hence salinities were close to zero.

Date	Location	Salinity	Temp (°C)	% O ₂ saturation	% OC sediments	DOC (μmol L ⁻¹)
Mar 2002	Sta. 1 (34°06.969'N, 77°56.253'W)	9.7	12	84.0	1.5±0.4	664±7
Jul 2002	Sta. 1 (34°06.969'N, 77°56.253'W)	25.1	27	85.0	3.4±0.4	395±4
Nov 2002	Sta. 1 (34°06.969'N, 77°56.253'W)	14.0	17	76.0	5.7±0.2	562±2
Mar 2003	Sta. 1 (34°06.969'N, 77°56.253'W)	2.6	11	78.0	8.4±0.3	379±9
Jun 2003	Sta. 1 (34°06.969'N, 77°56.253'W)	1.7	24	70.5	11.7±0.5	669±1
Mar 2002	Sta. 2 (33°57.395'N, 77°57.060'W)	22.2	11	91.0	2.6±1	391±8
Jul 2002	Sta. 2 (33°57.395'N, 77°57.060'W)	31.8	27	89.9	0.4±0.09	224±6
Nov 2002	Sta. 2 (33°57.395'N, 77°57.060'W)	14.5	17	84.5	1.5±0.2	292±2
Mar 2003	Sta. 2 (33°57.395'N, 77°57.060'W)	19.0	12	90.0	7.7±0.1	652±2
Jun 2003	Sta. 2 (33°57.395'N, 77°57.060'W)	6.3	24	82.3		478±1
Apr 2003	Sta. M23 (33°56.736'N, 77°58.175'W)	0	15	94.1	1.4±0.05	388±4
Apr 2003	Sta. M35 (4°02.045'N, 77°56.366'W)	0	15	85.3	3.5±0.3	393±1
Apr 2003	Sta. M42 (34°05.410'N, 77°56.013'W)	0	15	81.4	2.8±0.3	381±3
Apr 2003	Sta. M54 (34°08.390'N, 77°56.757'W)	0	15	79.4	3.8±0.6	384±6
Apr 2003	Sta. M61 (34°11.626'N, 77°57.435'W)	0	15	80.3	5.5±0.6	391±2

Dissolved organic carbon—Dissolved organic carbon was determined on acidified water samples with a Shimadzu TOC 5000 carbon analyzer equipped with an ASI 5000 autosampler. This instrument and techniques were previously used in conjunction with an Equatorial Pacific Ocean DOC methods intercomparison study and were found to generate very low instrumental blanks (Sharp et al. 1995). Borosilicate glass sample vials were cleaned prior to use by thoroughly rinsing with Milli-Q water and muffle at 550°C for 2 h or more to remove organic material. Each sample was injected at least three times with the average and standard deviation of those measurements reported. The detection limit for this instrument was 5 μM with a relative standard deviation of ≤3% (Avery et al. 2004).

Percent organic carbon and water content—Sediments used for solar simulator experiments were analyzed for organic carbon and water loss. Drying dishes were muffled at 550°C and stored in a desiccator to prevent water absorption. Triplicate samples were prepared with approximately 3 g of wet sediment per dish. Samples were dried at 60°C overnight, cooled in a desiccator, and reweighed for water loss measurement. The dried samples were muffled at 550°C to determine percentage mass loss due to organic matter in the sediment. These values were divided by the conversion factor of 1.7 to give %OC (ISO 10694 and BS7755 1995) with an average precision of ~12%. As a comparison, 15 samples taken throughout the CFRE were analyzed for %OC by combustion and CHN analysis after acid digestion to remove carbonates. Both methods had comparable precision and results were well correlated ($R^2 = 0.904$). The combustion method was chosen for the muddy-to-sandy, low-carbonate sediments of the CFRE because the larger sample size of this method (grams) provided more reliable results and better captured the heterogeneous nature of the sediments compared to the CHN analysis, which utilized milligram quantities.

Data analysis—Experimental effects were analyzed using one-, two-, or three-way analysis of variance (ANOVA) as appropriate. Data from each set of experiments were initially analyzed for normality (Kolmogorov-Smirnov test) and equal variances (Levene median test) using Sigma Stat (v. 2.03; SPSS, Inc.). For data sets that failed the normality test ($p < 0.001$) but passed the variance test, we chose to apply parametric ANOVA due to its relative robustness (Zar 1984). Parametric ANOVA and post-hoc Tukey pairwise multiple comparisons were performed using Sigma Stat. Data sets that failed both tests were analyzed using nonparametric ANOVA employing ranked data; post-hoc comparisons were made using the Kruskal-Wallis H statistic at the 95% confidence level (SYSTAT 10.2, SYSTAT Software, Inc.).

Results and discussion

Water and sediment irradiations with simulated sunlight—A series of controlled photolysis experiments was conducted using estuarine water in the presence and absence of natural sediments in order to understand the influence of sediment resuspension on DOC cycling in estuaries and coastal waters. Given the depth of sampling and the very high PAR attenuation coefficients ($3.9 \pm 1.4 \text{ m}^{-1}$ in the upper estuary to $1.9 \pm 0.8 \text{ m}^{-1}$ in the lower estuary; Mallin et al. 1999), the sampled bottom sediments had little if any benthic microalgal primary productivity that would significantly contribute to observed DOC changes. In addition, the experiments utilizing 0.2-μm-filtered water would exclude virtually all phytoplankton and bacteria that could influence DOC concentrations through photosynthesis, uptake, or cell lysis.

In 0.2-μm-filtered CFRE samples with no added sediment, the most significant differences occurred between light and dark treatments (three-way parametric ANOVA, $p < 0.001$). DOC concentrations in the light-exposed samples were significantly different from dark controls,

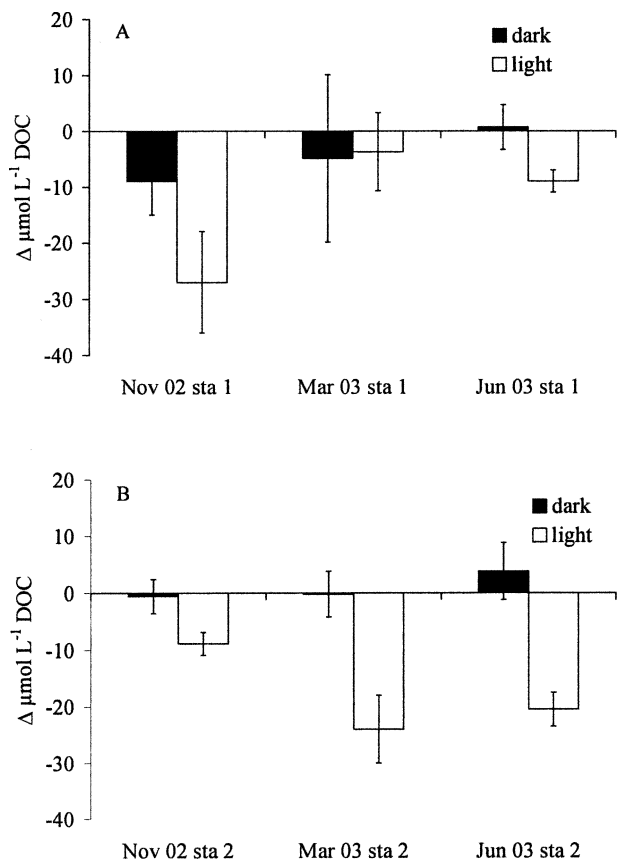


Fig. 2. Average change (Δ) in DOC concentrations ($\mu\text{mol L}^{-1}$) for 0.2- μm -filtered Cape Fear River estuary samples incubated in the presence and absence of simulated sunlight for 9 h relative to initial values. Error bars represent \pm one standard deviation based on three replicates for each treatment. A = Sta. 1, B = Sta. 2.

showing decreases ranging from 4 to 27 $\mu\text{mol L}^{-1}$ after 9 h of irradiation or 0.4 to 3 $\mu\text{mol L}^{-1} \text{h}^{-1}$ (Fig. 2). These decreases most likely reflect photochemical conversion of dissolved organic to dissolved inorganic carbon (DIC). The variability in the DOC loss in light-exposed flasks did not qualitatively correlate with initial DOC concentrations and most likely resulted from the heterogeneity of the DOC in this highly variable estuarine system. Net changes in DOC concentrations, calculated by subtracting the change in the dark controls from the change in the light-exposed samples, decreased in 5 of the 6 samples, with the net losses ranging from 8 to 24 $\mu\text{mol L}^{-1}$.

These results are consistent with earlier studies that also demonstrated that DOC is very photoreactive and can be photochemically degraded in coastal ecosystems into DIC, including CO_2 and CO (Miller and Zepp 1995; Gao and Zepp 1998; Zepp 2002). Photodegradation plays an important role in the cycling of carbon within the ocean, both by complete photooxidation of OC to DIC and by photoproduction of low-molecular-weight substrates, which subsequently can be microbially degraded (Amon and Benner 1996; Opsahl and Benner 1998; Mopper and Kieber 2000).

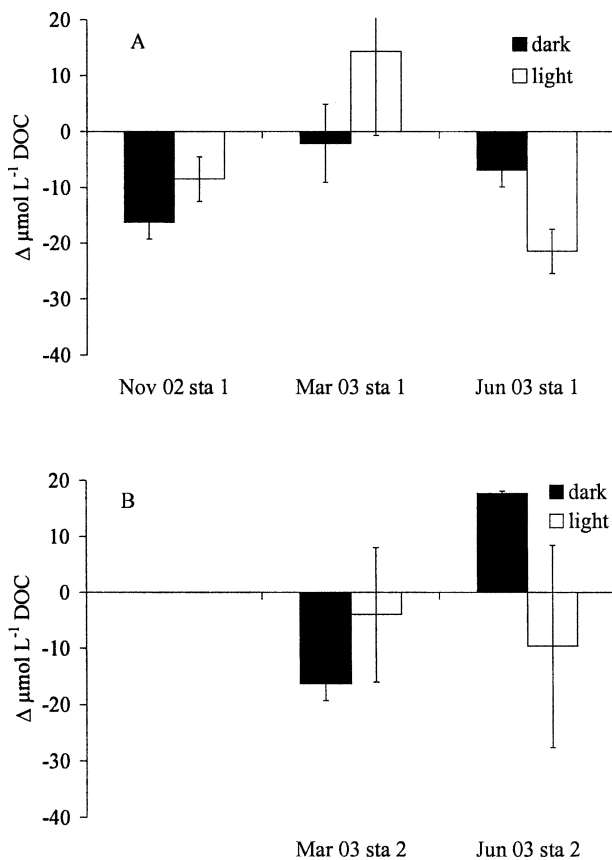


Fig. 3. Average change (Δ) in DOC concentrations ($\mu\text{mol L}^{-1}$) for unfiltered Cape Fear River estuary samples incubated in the presence and absence of simulated sunlight for 9 h relative to initial values. Error bars represent \pm one standard deviation based on three replicates for each treatment. A = Sta. 1, B = Sta. 2.

When the same water samples presented in Figure 2 were irradiated without prior filtration (i.e., containing only ambient suspended matter), much more variable behavior was observed (Fig. 3). No attempt was made to normalize changes in DOC to the quantity of suspended material; however, suspended sediment concentrations in the CFRE were generally low, ranging from 1 to 30 mg L^{-1} (Mallin et al. 2000). Furthermore, it was not possible to differentiate between biological and nonbiological photoprocesses influencing DOC changes, although biological production in this light-limited system was generally very low (Mallin et al. 1999).

In these samples, there was variability in DOC changes upon irradiation—there was net production relative to dark controls in three samples and net destruction in the other two. This variability may have been the result of changes in the microbial community in the different samples or it may have been due to the heterogeneity of the particles and their sunlight exposure history in the estuary. Particles that have spent a significant amount of time in the estuarine photic zone may have already photoreleased their particle-bound DOC before being collected and further irradiated. This would result in a net loss of DOC upon irradiation because the primary photoprocess occurring in these samples would

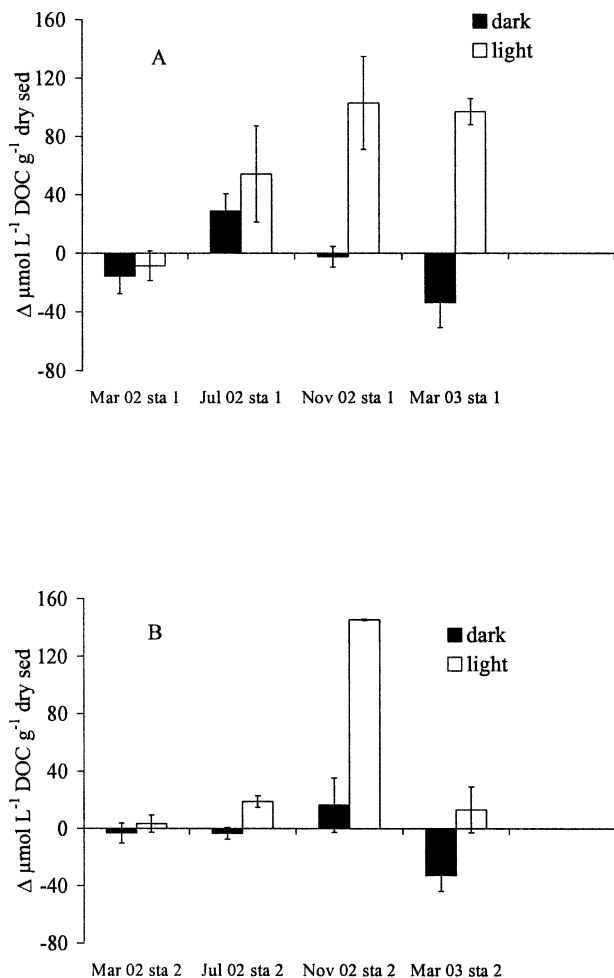


Fig. 4. Average change (Δ) in DOC concentrations ($\mu\text{mol L}^{-1} \text{g}^{-1}$ dry sediment) for 0.2- μm -filtered Cape Fear River estuary samples with 1–2 g L^{-1} added sediment incubated in the presence and absence of simulated sunlight for 9 h relative to initial values. Error bars represent \pm one standard deviation based on three replicates for each treatment. A = Sta. 1, B = Sta. 2.

be photoconversion of dissolved organic to dissolved inorganic carbon as discussed in Figure 2. Particles with relatively less sunlight exposure history may have more photolabile POC, which could be photooxidized to DOC resulting in net production relative to dark controls. The variable photochemical history of ambient estuarine particles may explain why late fall and early spring samples (November 2002 and March 2003) showed net production of DOC relative to dark controls (more photolabile POC), whereas summer samples (June 2003) showed net decreases in DOC despite being exposed to significantly more sunlight prior to collection.

The effect of resuspended sediments on DOC concentrations was evaluated by comparing irradiated samples in the presence and absence of sediments to dark controls. Changes in DOC concentrations were normalized to the amount of dry sediment added to each flask (Fig. 4). The water content of added sediments ranged from 22% to 55% by weight. Assuming 2,500 $\mu\text{mol L}^{-1}$ C as a pore water

DOC concentration, the amount of DOC added to the flasks from pore waters was less than 1% of initial DOC concentrations.

Changes in dissolved organic carbon concentrations in samples incubated in the dark in the presence of sediments were somewhat variable; there was loss of DOC in some cases and increases in others (Fig. 4). The increase of DOC in dark flasks most likely resulted from nonphotochemical release from sediments, part of which may have been microbially mediated. Koelmans and Prevo (2003) suggested that disturbance of sediments plays an important role in DOC formation when particulate carbon bound to sediments is mobilized and desorbed. These authors suspended sediments in various concentrations in lake and river waters from the Netherlands without controlling light conditions. They noted a decrease in POC during resuspension as POC was converted to DOC. Komada and Reimers (2001) performed similar experiments using water and sediments from the Hudson River estuary and adjoining shelf. They found that during resuspension, OC loosely bound to mineral surfaces was released to form DOC and that the greater the dilution of particles in the water column, the greater the release of the DOC.

The effect of simulated sunlight on changes in DOC concentrations caused by sediment resuspension in Cape Fear estuarine water was also evaluated. Filtered water samples with added sediment showed significant increases in DOC in light-exposed samples relative to dark controls (three-way nonparametric ANOVA, $p < 0.001$). Increases ranged from 3 to 150 $\mu\text{mol L}^{-1}$ or 1.5 to 75 $\mu\text{mol DOC g}^{-1}$ dry sediment in the 500-mL flask (Fig. 4). In samples that showed increases in both light-exposed and dark controls, increases in the light were always larger. The photochemical flux was also considerably larger than dark DOC production rates from six surface sediments within the Hudson River Estuary and Inner New York Bight, which ranged from 0.7 to 3.8 $\mu\text{mol DOC g}^{-1}$ dry sediment, although direct comparison to this latter study should be made with caution because significantly higher concentrations of resuspended sediment (100 g L^{-1}) with different organic carbon contents were used (Komada and Reimers 2001).

There was a significant seasonal difference ($p < 0.001$) reflected in the much larger DOC production observed at both stations in November 2002 relative to the spring and summer periods. The source of this difference is not known, but may reflect a higher reactivity of sediment-bound organic matter during this period.

The results presented in Figure 4 suggest that decomposition of POC and production of DOC in these sediments occurs via a light-mediated process. These results are clearly much different than the net losses of DOC that usually occur when 0.2- μm -filtered samples without added sediment are irradiated with simulated sunlight and in which DOC concentrations in dark controls are relatively stable (Fig. 2). Thus, the degree of conversion of sediment OC to DOC depicted in Figure 4 should be viewed as a net change since there is concurrent photooxidation of DOC during irradiation and possibly microbial degradation of the photoproduct DOC. The bioavailability of the DOC

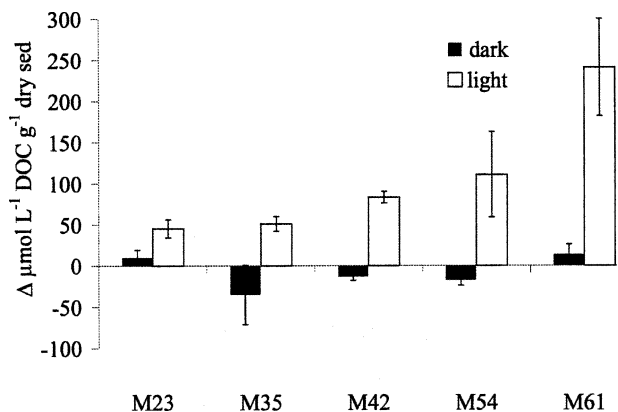


Fig. 5. Average change (Δ) in DOC concentrations ($\mu\text{mol L}^{-1} \text{g}^{-1}$ dry sediment) for 0.2- μm -filtered Cape Fear River estuary samples with 1–2 g L^{-1} added sediment collected from each site incubated in overlying bottom water from that site in the presence and absence of simulated sunlight for 9 h relative to initial values. Station M23 is near the mouth, and station M61 is at the upper end of the estuary. Error bars represent \pm one standard deviation based on three replicates for each treatment.

produced from sediments and particles is currently under investigation in our laboratory.

To examine the effect of organic carbon (a function of sediment texture) on DOC photoproduction from resuspended sediments, a second set of irradiation experiments was conducted from five sites (stations M61, M54, M42, M35, M23), which were equally spaced along the estuary between M61 and M23 and spanned a wide range of sediment organic carbon content (Table 1). In 0.2- μm -filtered water samples with added sediments exposed to light, there was a significant release of DOC relative to their dark controls (two-way parametric ANOVA, $p < 0.001$; Fig. 5). The magnitude of photoproduced DOC increased from the lower (M23) to upper estuary (M61) and was significantly related to organic carbon content ($p < 0.001$). Dark controls showed small and variable DOC changes upon storage with no discernible pattern along the estuarine gradient.

The mechanistic reasons behind the gradually increasing DOC photoproduction from the lower portion to the upper reaches of the estuary observed in Figure 5 most likely reflect the gradient of sediment OC concentration and composition along the estuary. This is demonstrated by the linear relationship between increases in DOC after irradiation of sediment suspensions and the OC content of the sediments from the five sampling sites (Fig. 6). These results indicate that the greater photoproduction of DOC observed at M61 relative to M23 results from the approximately five times greater %OC in the fine-grained upper estuarine sediments, which in turn may be related to the grain size and surface area of the sediment (Keil et al. 1994; Mayer 1994), as well as the strength of the association between the particles and photolabile organic matter.

Whereas light-exposed flasks displayed a regular increase of DOC with %OC of the sediments, no similar relationship was observed in dark samples (Figs. 5, 6). This is in contrast to earlier studies, where dark DOC release

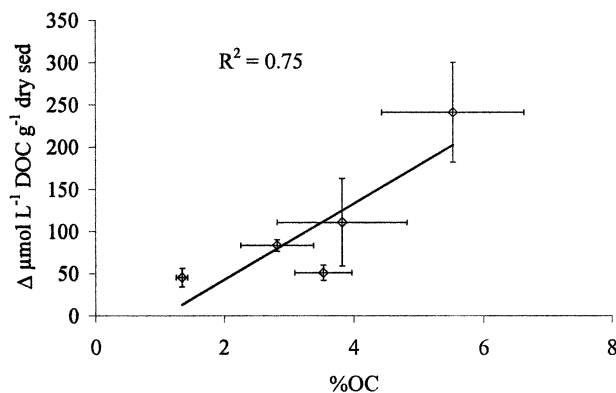


Fig. 6. Average change (Δ) in DOC concentrations ($\mu\text{mol L}^{-1} \text{g}^{-1}$ dry sediment) in samples from Figure 5 plotted as a function of the % organic carbon content of the added sediments. Error bars represent \pm one standard deviation based three replicates for each treatment.

generally increased with increasing OC of the resuspended sediments (Koelmans and Prevo 2003). Komada and Reimers (2001) found that the POC content of the high-density ($>1.9 \text{ g mL}^{-1}$) sediment fraction, containing most of the mineral-bound OC, was the best predictor of OC release during resuspension. Sunlight irradiation may promote mobilization of a more strongly bound OC fraction that is not exchangeable on short time scales in the absence of light.

Effect of irradiation wavelength—The effect of irradiation wavelength on the photochemical production of DOC from resuspended sediments of the CFRE was also evaluated. This has important ramifications with respect to the depth at which photochemical release of DOC from resuspended sediments occurs. In the optically thick, highly turbid waters of the Cape Fear River estuary, the depth to which PAR penetrates is approximately 1.3 m in the upper estuary at station M61 and 2.4 m near the mouth at station M18. In contrast, penetration of high-energy UV light ($\lambda < 400 \text{ nm}$) is typically $<30 \text{ cm}$ in the CFRE (R.F. Whitehead, unpubl. data). In optically clearer estuarine and shelf waters, including those that receive many major river plumes, penetration of both UV and PAR wavelengths would be significantly greater.

A filtered CFRE sample collected from station M61 in April 2003 was exposed to three different light regimes. One portion was exposed to full spectrum sunlight, one portion to PAR only, and a third was used as a dark control. The concentration of DOC in each aliquot was measured initially and after 5 h (Fig. 7). In the sample exposed to full spectrum light, there was a decrease in DOC concentration similar to what was observed in the filtered water samples presented in Figure 2 (one-way parametric ANOVA, $p = 0.001$). In filtered water with no added sediment irradiated with PAR light only or those placed in the dark, DOC concentrations were variable but not statistically different from initial concentrations ($p > 0.05$). This suggests that high-energy UVA and UVB wavelengths are the most effective at photooxidizing DOC in filtered CFRE water, whereas wavelengths in the

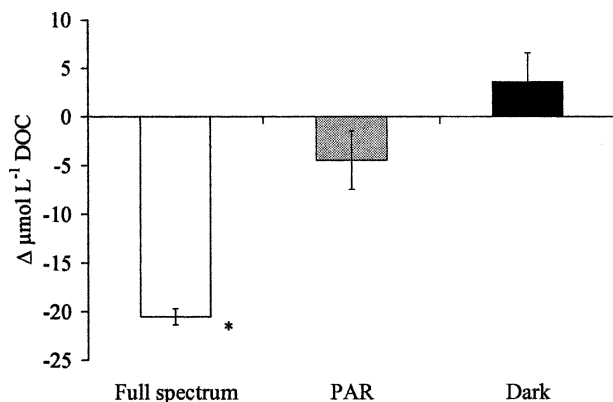


Fig. 7. Average change (Δ) in DOC concentrations for 0.2- μm -filtered M61 Cape Fear River estuarine water (April 2003) incubated in the presence and absence of simulated full spectrum sunlight and PAR for 9 h relative to initial values. Error bars represent \pm one standard deviation based on three replicates for each treatment; * represents statistically significant changes.

PAR region of the solar spectrum have little or no effect on DOC photodegradation.

To determine the effect of wavelength on the photoproduction of DOC from resuspended sediments, the same water sample used for the experiment described above was exposed in an analogous set of light treatments except natural CFRE sediments from stations M61, 1, and 2 were added prior to irradiation. Changes in DOC concentrations were determined relative to initial concentrations and were normalized to the amount of added sediment (Fig. 8). There were no significant differences detected between treatments at all three stations (two-way nonparametric ANOVA, $p \geq 0.015$) due largely to the lack of effects at stations 1 and 2. Results from station M61 alone indicate significant differences between full spectrum, PAR, and dark treatments (one-way parametric ANOVA, $p < 0.001$). This indicates that both PAR and full spectrum light had a significant impact on photoproduction of DOC from resuspended sediments at station M61, in contrast to what was observed in the filtered water sample without sediment, in which PAR had little or no impact on photodegradation of DOC. The degree of DOC production from PAR in the organic-rich sediments of station M61 was approximately half the quantity produced in full spectrum light. The results of Figures 7 and 8 indicate that high-energy UVA and UVB light is most effective for photodegradation of DOC into DIC (Fig. 7) and photoproduction of DOC from resuspended sediments containing bound OC (Fig. 8). The results also indicate that PAR is ineffective at photodegradation of DOC but is effective at photoproduction of DOC from resuspended sediments, particularly those that are organic-rich, such as at station M61. The broad spectral response of DOC photoproduction is consistent with results reported by Mayer et al. (2006), who found that POC decreased in suspensions of Atchafalaya River sediments exposed for 33 h total (6 h d^{-1}) under various light filters. Approximately half of their total observed POC loss occurred with visible light and the remaining half under UV wavelengths (Mayer et al. 2006).

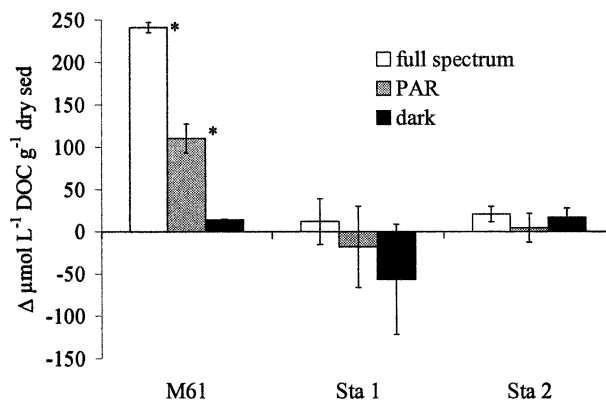


Fig. 8. Average change (Δ) in DOC concentrations ($\mu\text{mol L}^{-1} \text{g}^{-1}$ dry sediment) for 0.2- μm -filtered Cape Fear River estuary samples with 1–2 g L^{-1} added sediment collected from each site incubated in overlying bottom water from that site in the presence and absence of simulated full spectrum sunlight and PAR for 9 h relative to initial values. Error bars represent \pm one standard deviation based on three replicates for each treatment; * represents statistically significant changes.

Significance of photoproduced DOC in natural waters—Photoproduction of DOC occurs when sediment-laden waters are irradiated for extended periods in sunlit surface waters. Such exposure results from natural or anthropogenic resuspension by shipping operations, dredging, wind-driven waves, tides, and weather events in lakes, rivers, and estuaries. Exposure of large amounts of suspended sediment also occurs in persistent turbidity maxima in estuaries (Nichols and Biggs 1985) and in coastal waters receiving large river plumes, such as those associated with the Amazon and Mississippi Rivers (Nittrouer and DeMaster 1996; Wang et al. 2004). We used our measurements of photochemical production from resuspended sediments to estimate the quantitative importance of these processes as a source of DOC on an areal basis in the upper 1 m of coastal waters.

An approximate average DOC photoproduction rate from our experiments (0.1 mmol L^{-1} increase in 0.5 L of suspension per g dry sediment per 9 h irradiation, or 0.0056 $\text{mmol g}^{-1} \text{h}^{-1}$) applied to a modest suspended sediment concentration of 100 g m^{-3} would produce a flux of 0.56 $\text{mmol m}^{-2} \text{h}^{-1}$ in the top meter of surface water. Photochemical production from sediments can be compared to two other major sources of DOC to the ocean: benthic fluxes and riverine discharge. Measured benthic fluxes of DOC range from 0.004 to 0.088 $\text{mmol m}^{-2} \text{h}^{-1}$ in California continental margin sediments (Burdige et al. 1999) to 0.02–0.12 $\text{mmol m}^{-2} \text{h}^{-1}$ in estuarine sediments of Chesapeake Bay (Burdige and Homstead 1994). Riverine discharge integrated over the surface of the coastal ocean is estimated to be 0.04 $\text{mmol m}^{-2} \text{h}^{-1}$, calculated using a global riverine DOC discharge of $18 \times 10^{12} \text{ mol yr}^{-1}$ (Meybeck 1982) and an estimated marginal ocean area of $52 \times 10^6 \text{ km}^2$ (Stacey 1992).

Comparison of these fluxes suggests that photochemical production of DOC from resuspended sediments may be significantly larger than either riverine discharge or

sediment fluxes, even considering that photoproduction from particles only occurs during daylight hours, whereas riverine and sediment fluxes occur more continuously. The model calculation for DOC photoproduction from particles should be viewed with caution because it assumes a constant production rate with time, which may not be entirely accurate; this assumption is currently under investigation in our laboratory. Furthermore, it may somewhat overestimate production, since the model does not account for particle shading, advection, and settling, which would all occur in an estuary.

In a recent review, Dagg et al. (2004) emphasized the influence of physical and optical characteristics on transformations of material in the buoyant plumes of large rivers. As pointed out in previous studies, photolysis of dissolved organic material produces a variety of simpler substrates that can be utilized by phytoplankton and bacteria (Miller and Zepp 1995; Miller and Moran 1997; Moran and Zepp 1997). This photochemical stimulation, in addition to enhanced productivity due to higher optical clarity, can promote DOC production in river plumes. In the Mississippi River plume, Benner and Opsahl (2001) showed that nonconservative addition of DOC occurred at intermediate salinities. Our results imply that some fraction of this DOC may result from photolysis of particle-bound organic matter resulting in direct release of DOC or stimulation of bacterial and phytoplankton productivity with subsequent secondary release of DOC. Effective photoproduction occurs for organic-rich suspended sediments in the presence of both full spectrum sunlight and PAR, which penetrates more deeply into the water column. Even considering the extreme variability in optical properties and sediment concentrations, the data presented here demonstrate that sunlight interactions with resuspended organic-rich sediments represents a significant but previously unrecognized source of DOC to estuarine and coastal ecosystems.

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