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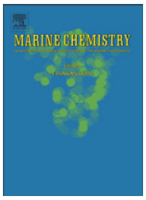

# Influence of organic matter source and diagenetic state on photochemical release of dissolved organic matter and nutrients from resuspendable estuarine sediments

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ABSTRACT

Presently there is a paucity of knowledge regarding the influence of sedimentary organic matter (SOM) source and diagenetic state on photolytic fluxes of dissolved organic matter and nutrients from sediments likely to be resuspended during high energy events such as storms. Here we present data on the photochemical release of dissolved organic carbon (DOC), total dissolved nitrogen (TDN), dissolved organic nitrogen (DON), $NH_4^+$, and $PO_4^{3-}$ from the fine fraction of sediments obtained along an estuarine gradient, coupled with analyses of biogeochemical and molecular indicators of SOM source. Photochemical release of DOC and $PO_4^{3-}$ was significantly higher than dark controls at all sites. DOC photorelease from fine (<ca. 10–20 μm) sediments was ten times higher than previous studies that used bulk sediment in suspensions. The magnitude, stoichiometry, and speciation of nutrients and dissolved organic matter released during sediment photolysis appear to be influenced by a combination of SOM source and diagenetic processing. Release of DOC and $PO_4^{3-}$ was higher at upstream sites, where sediments were dominated by relatively unaltered terrestrially-derived SOM. In contrast, TDN, DON, and $NH_4^+$ releases were higher at downstream sites, which exhibited more degraded organic matter of both terrestrial and aquatic origin. The ratio of inorganic nutrients released was low at all sites ($NH_4^+$: $PO_4^{3-}$ ~1–7) suggesting that SOM photolysis may be relatively more important as a source of inorganic P than N. Our results also demonstrate that SOM is broadly photolabile and that previous studies may underestimate photolytic release of DOC from the fine fraction of sediments.

## 1. Introduction

Recent studies have demonstrated that marine and estuarine resuspended sediments release dissolved organic carbon (DOC), dissolved organic nitrogen (DON), $NH_4^+$, and $PO_4^{3-}$ upon exposure to simulated sunlight (Mayer et al. 2006; Kieber et al. 2006, Southwell et al. 2010). These studies suggest that this process constitutes an episodic yet potentially significant input of nutrients and organic matter into surface waters, possibly augmenting nutrient availability. The inorganic nutrients from sediment photolysis are likely to be quickly recycled, especially as they are released in or near the euphotic zone (Southwell et al. 2010). Furthermore, evidence from photodegradation of algal detritus indicates dissolved organic matter (DOM) released from this source is biologically labile (Mayer et al., 2009a). Photolysis of resuspended sediments is therefore a potentially important pathway for dissolution, degradation, and remineralization of sedimentary organic matter (SOM), which could stimulate primary and secondary production in surface waters.

Significant photolytic release of DOC has been measured in sediments ranging from freshwater riverine sites to continental shelf sediments (Kieber et al. 2006, Riggsbee et al. 2008, Southwell et al. 2010), suggesting that SOM is broadly photolabile. Mayer et al. (2009a) reported preferential release of fresh (bomb $^{14}C$-enriched) organic matter upon exposure of resuspended sediments to continuous light for 68–70 h. Changes in chemical indicators of SOM source during these irradiations suggest that both marine and terrestrial organic matter are photolabile to some extent.

These earlier studies establish the potential importance of photochemical processes in the recycling of particulate carbon and nutrients but they do not adequately address the environmental controls and mechanistic aspects of this phenomenon. The goal of the present study was to more fully evaluate the role organic matter source plays in the release of dissolved organic carbon and nutrients from sediments along an estuarine gradient under environmentally relevant conditions. We present measurements of photolytic release of DOC, DON, $PO_4^{3-}$, $NH_4^+$, and $NO_3^-$ plus $NO_2^-$ (hereafter $NO_x^-$) from size-fractionated (<ca. 10–20 μm) sediments from the Cape Fear River Estuary (CFRE), North Carolina, USA. These measurements were coupled with analyses of sediment organic carbon content, $\delta^{13}C$ values, and extractable *n*-alkanes as indicators of source and relative diagenetic state of SOM. This is important in a hydrodynamically

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complex system such as the CFRE, in which multiple organic matter sources are likely and sediment deposition and transport may be spatially and temporally variable. The results are discussed in the context of influences of SOM composition on photolytic fluxes and the potential implications of inorganic nutrient release and nutrient element stoichiometry for primary productivity in surface waters.

## 2. Methods

*Study site and sampling*—The Cape Fear River drains the largest river basin in North Carolina (Fig. 1). In general, the estuary is well mixed vertically, with relatively short water residence time because of the rapid river flow (Mallin et al. 1999). The sampling sites in our study, Horseshoe Bend (HB), M54, M35, and M23, correspond to long-term water quality monitoring stations in the estuary (Mallin et al. 1999) and represent the extent of the normal salinity gradient in the estuary (Fig. 1). Previous work in the CFRE suggests that photochemical lability of surface sediments likely to be scoured during high energy events differs from the ambient particles present under normal flow conditions, possibly due to differences in composition and previous light exposure history (Kieber et al. 2006) Because our goal was to mimic conditions in a high energy resuspension event (e.g., hurricane), we collected and isolated the fine fraction of bottom sediments rather than particulate matter from the water column. The sediments were then crudely size fractionated to obtain only the fine material likely to stay in suspension for a substantial amount of time.

Sediment samples were collected in February 2009 with a grab sampler in water depths of at least 5 m. Sediment was taken from the upper 2–3 cm of the grab sample and dispensed into two Kapak™ (Kapak Corp.) bags, which were sealed and stored in dark coolers at ambient temperatures while in transit. Upon returning to the lab, one bag from each site was stored at 4 °C for photolysis experiments (which occurred within two months) and one bag was stored at −20 °C for analysis of hydrocarbons. Seawater used in resuspensions was obtained from Wrightsville Beach, North Carolina in 4-L high density polyethylene (HDPE) bottles and filtered with 0.2 μm polyethersulfone (Supor™; Gelman Sciences) the day prior to the irradiation experiment. Seawater was chosen as a suspension medium in order to mimic rapid offshore transport of sediment during a high energy resuspension event. All plastic, quartz, and glassware were washed in 10% HCl and Milli-Q deionized water ($\geq 18\ \mathrm{M\Omega\,cm^{-1}}$; Millipore Corp.) Glass and quartz items were also combusted overnight at 450 °C, and glass fiber filters were combusted for 2 h at 450 °C.

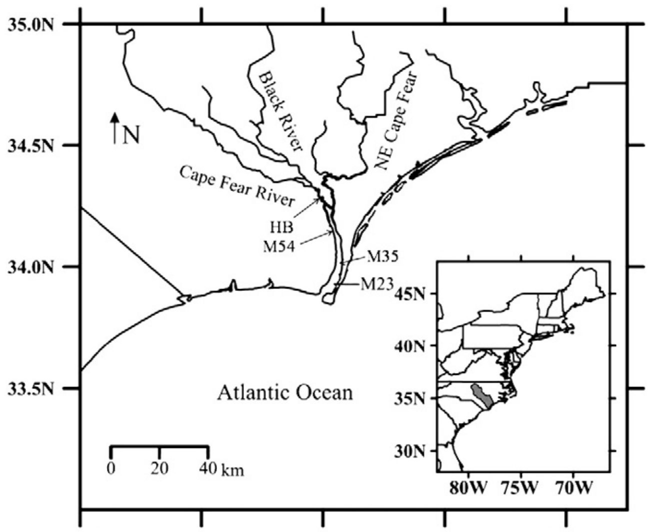

**Fig. 1.** Map of the Cape Fear River Estuary and sampling sites.

*Nutrient release experiments*—The sediment sample was homogenized by stirring with a metal spatula and 10–20 g (wet weight) was added to 4 L of filtered seawater water, then completely resuspended by vigorous shaking. In order to exclude coarse sediment, the suspension was allowed to settle for 40 min. The suspended material remaining in the top 20 cm, containing the fine particles (<ca. 10–20 μm, depending on density; Jackson 1973), was then siphoned into another 4-L HDPE bottle. The sediment that settled was discarded. The suspension of fines was then shaken again and poured into six 250-mL round-bottom quartz flasks (maximum depth 7 cm) containing magnetic stir bars. Separate settling experiments were performed to determine the percentage of bulk sediment that remained in the top 20 cm of the suspension.

After dispensing the suspension into the quartz flasks, a 50-mL aliquot was removed for an initial time point and the flasks were refilled with suspension mixture. Three flasks were then covered in aluminum foil to serve as dark controls. All six flasks were placed in a constant temperature (25 °C) water bath and irradiated using a solar simulator (Spectral Energy solar simulator LH lamp housing with a 1000 W Xe arc lamp) equipped with a sun lens diffuser and an AM1 filter to remove wavelengths not found in the solar spectrum. Irradiance measurements in our laboratory show that the solar simulator irradiance spectrum closely mimics the measured midday, midsummer solar spectrum at 40°N latitude. The 6-h exposure to simulated sunlight in our experiments should therefore equal the same light input as one day in midsummer at this latitude.

Flasks were stirred using magnetic stir bars at the minimum speed necessary to maintain sediments in suspension. At the end of the 6-h irradiation, one 50-mL aliquot was removed from each flask and filtered using tared GF/F (Whatman) filters. The first 10 mL of filtrate was discarded. Of the remaining 40 mL of filtrate, 20 mL was dispensed into glass scintillation vials and spiked with 50 μL of 6 M HCl for dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) analyses, 4 mL was removed for analysis of $NH_4^+$, and the remaining 16 mL was frozen in 30-mL HDPE bottles for analysis of $NO_3^-$ plus $NO_2^-$ (hereafter $NO_X^-$) and $PO_4^{3-}$. Analyses of DOC, TDN, $NO_X^-$, and $PO_4^{3-}$ usually occurred within one month, and $NH_4^+$ was measured immediately. The GF/F filters from the initial and final time points were frozen (−20 °C) and subsequently lyophilized and weighed for determination of POC and PON concentrations by CHN analysis after vapor acidification (Hedges and Stern 1984). At the end of the experiment, the remaining sediment-water mixture was filtered on tared 47-mm GF/F filters, rinsed with deionized water, and the volume of filtrate recorded. These filters were lyophilized and weighed for determination of total suspended solids (TSS).

*Stable carbon isotopic analysis*—Bulk stable carbon isotopic compositions of the sediments were measured on acidified samples using the same method for the elemental analysis described above. The measurement was performed on a Thermo Flash EA coupled online to a Thermo Delta V by a Conflo interface. The values are reported as $\delta^{13}C = [(R_{sample} - R_{std})/R_{std}] * 1000$, where R equals the $^{13}C/^{12}C$ ratio.

*Extractable alkanes*—Sediment was thawed and homogenized by stirring with a metal spatula. The sediment was resuspended and the fine fraction was collected as described above, except that higher sediment concentrations (~0.5–1 g $L^{-1}$) were used in order to obtain enough material for molecular analysis. The suspension was stirred in the dark for 6 h and then filtered using tared, combusted Whatman GF/F filters. The filters were frozen, then lyophilized and weighed.

*Analytical*—Ammonium measurements were made using the *o*-phthalaldehyde (OPA) fluorometric method described by Holmes et al. (1999), which was modified to reduce the volume of sample and reagent (2 mL of sample and 4 mL of OPA reagent). Samples from each flask were analyzed in duplicate. Samples were incubated in the dark for 3–5 h and analyzed on a Turner Designs Trilogy fluorometer. Standards