# Effects of sunlight on the production of dissolved organic and inorganic nutrients from resuspended sediments

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**Abstract** A series of laboratory-based and field experiments was conducted to address the effects of sunlight-exposed resuspended sediments on dissolved nutrient fluxes in two different water bodies. In suspensions of tidal creek sediments in 0.2 μm-filtered creek water, measurable increases in dissolved nutrients occurred after only 2 h of exposure to simulated sunlight. During a 6-h irradiation, nutrient release rates for total dissolved nitrogen (TDN) and phosphate were $2.2 \pm 0.5$ (standard error; S.E.) $\mu mol\ g^{-1}\ h^{-1}$ and $0.09 \pm 0.005\ \mu mol\ g^{-1}\ h^{-1}$ (S.E.), compared to no significant changes in dark controls. The majority of nitrogen was released as dissolved organic nitrogen (87% on average) with lesser amounts of ammonium (13%). Continental shelf sediments resuspended in unfiltered seawater also released phosphate and TDN when exposed to sunlight, suggesting that this process can occur in a variety of marine and estuarine environments. The source material for inorganic nutrients appears to be associated with sediments rather than dissolved organic matter, as no significant changes in nutrient concentrations occurred in experiments with 0.2 μm-filtered creek water or seawater alone. Results suggest that photoproduction of dissolved nutrients from resuspended sediments could be an episodically significant and previously unrecognized source of dissolved organic and inorganic nutrients to coastal ecosystems. This process may be especially important for continental margins where episodic resuspension events occur, as well as in regions experiencing high riverine sediment fluxes resulting from erosion associated with deforestation and desertification.

## Introduction

The coastal zone, including tidal creeks, estuaries and nearshore oceanic environments, represents a critical transition between marine and terrestrial ecosystems. These areas are under increasing pressure from commercial development that often results in significant increases in sediment (Saenger et al. 2008) and nutrient loading (Mallin et al. 2004). Nutrient dynamics in such coastal zones are complex and are subject to seasonal, tidal, meteorological, and anthropogenic forcing (Wolaver et al. 1984; Mallin et al. 2004). Sediment–water interactions in these typically shallow waters influence a variety of biogeochemical processes, including mobilization of trace metals, nutrients, organic carbon, and anthropogenic contaminants (Simon 1989; Komada and Reimers 2001; Koelmans

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and Prevo 2003). Mobilization of coastal sediments is commonly caused by a combination of natural forces, such as local rainfall, tidal, and wind forcing, (Voulgaris and Meyers 2004) and anthropogenic factors such as boat wakes, terrestrial runoff, and coastal development (Posey et al. 2002; Saenger et al. 2008). Wind-induced resuspension can be especially important in shallow coastal environments that have a large fetch. For example, Booth et al. (2000) determined that relatively modest multi-directional winds of 4 cm s$^{-1}$ were sufficient to resuspend 50% of surface sediments in the Barataria Basin, Louisiana. Allison et al. (2005) have also shown considerable resuspension with subsequent redistribution and deposition of 1–5 cm of sediment after the passage of Hurricane Lili over the Louisiana shelf. These studies demonstrate that sediments along river dominated margins are susceptible to episodic sediment mobilization events such as frontal passages, flood events, and hurricanes.

Recent studies have demonstrated that photodegradation of particulate organic matter (POM) associated with resuspended sediments engenders episodically large fluxes of dissolved organic carbon (DOC) upon exposure to simulated sunlight (Mayer et al. 2006; Kieber et al. 2006). Mayer et al. (2006) demonstrated that particulate organic carbon (POC) in suspended sediments from the Mississippi River system decreased after long-term exposure (6 h day$^{-1}$ for 7–9 days) to simulated sunlight. Kieber et al. (2006) reported increases of DOC from 3 to 150 μM in suspensions of estuarine sediments after 9-h exposures to simulated sunlight. Photoproduction of DOC from resuspended sediments in this latter study calculated for the top 1 m of coastal waters resulted in episodic fluxes which were significantly larger than benthic and riverine fluxes of DOC combined.

These earlier studies are significant because they demonstrate the importance of sunlight on the biogeochemistry of resuspended estuarine sediments. The goal of the present study was to determine if dissolved nitrogen and phosphorus species are also produced during the photolysis of resuspended sediments. Increases in water column nutrient concentrations and primary productivity after sediment resuspension events have previously been interpreted as the redistribution of porewater nutrients and/or adsorbed ammonium (Simon 1989; Ogilvie and Mitchell 1998). Morin and Morse (1999) suggested that release of adsorbed $NH_4^+$ from estuarine

sediments during resuspension events may be similar in magnitude to benthic fluxes. A recent study by Riggsbee et al. (2008) demonstrated the significance of photochemistry on the production of dissolved organic nitrogen (DON) acting on freshwater riverine sediments collected from an inland site in central North Carolina. Extrapolations through the water column produced significant nitrogen fluxes (40 μM m$^{-2}$ day$^{-1}$) due to sediment resuspension similar to those observed during 1.5 year floods.

Here we present the first detailed study of the release of DON, dissolved inorganic nitrogen (DIN), and $PO_4^{3-}$ from the photolysis of estuarine and coastal sediments under environmentally relevant conditions. Several factors were manipulated in order to understand the mechanism of photorelease including autoclaving of sediments prior to irradiation, and irradiation of filtered and unfiltered water without sediments. The results are used to estimate areal photochemical fluxes nutrients from resuspended sediments and to compare them with other known sources of nutrients. Photolytic fluxes occurring in or near the euphotic zone as examined here could represent a significant and previously overlooked source of dissolved nutrients to coastal ecosystems receiving sediment plumes which could result in increased primary productivity.

## Methods

### Tidal creek experiments

Experiments were carried out using sediment collected from Bradley Creek in Wilmington, NC (34$\overset{\circ}{}$13′16.6″N, 77$\overset{\circ}{}$50′39.1″W). The top 1 cm of sediment was collected from the intertidal zone at low tide using a petri dish. One half of the petri dish was pressed into the sediment and a plastic plate was inserted beneath the dish to allow the sediment to be removed intact. Water was obtained from the same site in 4 l high density polyethylene (HDPE) bottles. All plastic, quartz, and glassware were washed in 10% HCl and Milli-Q deionized water ($\geq$18 MΩ cm$^{-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.

After returning to the lab, the sediment was homogenized by stirring with a metal spatula and stored in an HDPE container at 4°C. A portion

(approximately 20 ml) of the sediment was placed in a 40-ml glass vial and autoclaved at 120°C for 1 h. Creek water was filtered twice, first with GF/F filters (0.7 μm nominal pore size; Whatman) and then with 0.2 μm polysulfone (Supor; Gelman Sciences) filters, and stored at 4°C. Raw (not autoclaved) sediment was used the day after collection, and autoclaved sediment was used within 1 week of collection. Filtered creek water was used the day after collection.

Homogenized sediment was added to filtered creek water in proportions of approximately 2 g (wet weight) per liter, and was then completely resuspended by vigorous shaking. In order to exclude coarse sediment, the suspension was poured into a large graduated cylinder and allowed to settle for 5 min. The suspended material remaining in the top 20 cm, containing particles <30 μm (Jackson 1973), was then decanted into a 4-l HDPE carboy. The suspension was then shaken again and poured into four 250 ml quartz flasks with magnetic stir bars. The sediment that settled during the 5 min interval was filtered onto a tared 47 mm GF/F filter, dried, and weighed in order to determine the fraction of sediments that remained in suspension versus settling out.

After dispensing the suspension into the quartz flasks, a 50-ml aliquot was removed for an initial time point. Two flasks were then covered in aluminum foil to serve as dark controls. All four 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 1,000 watt 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, mid-summer solar spectrum at 40°N latitude. The 6 h exposure to simulated sunlight in our experiments should therefore equal the same light input as 1 day in midsummer at this latitude. We also performed irradiations on 0.2 μm filtered and unfiltered creek water in the absence of sediment additions using the above protocol.

Flasks were stirred using magnetic stir bars at the minimum speed necessary to maintain sediments in suspension. Experiments with sediment additions were sampled every 2 h, and experiments without sediment additions were sampled only at the initial and final time points. One 50-ml aliquot was removed from each flask and filtered using tared GF/F 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 total dissolved nitrogen (TDN) analyses, 4 ml was removed for analysis of $NH_4^+$, and the remaining 16 ml was frozen in 50-ml centrifuge tubes for analysis of $NO_3^-$ plus $NO_2^-$ (hereafter $NO_x^-$) and $PO_4^{3-}$. Analysis of TDN, $NO_x^-$, and $PO_4^{3-}$ usually occurred within 1 month, and $NH_4^+$ was measured immediately. The GF/F filters from the time point samples 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 and the volume of filtrate recorded. The filters were dried for 48 h at 40°C and weighed for determination of total suspended solids (TSS).

Shipboard experiments

Two experiments were carried out in June 2008 using surface and bottom sediments obtained from two continental shelf stations off southeastern North Carolina. Site 1 was located at 33̊ 50.777′N, 78̊ 02.338′W at a depth of 7.8 m, and Site 2 was located at 33̊ 50.149′N, 78̊03.167′W at a depth of 11 m. Surface sediments were collected in acrylic core barrels using an Ocean Instruments MC-8 multicorer and unfiltered surface waters (∼2 m depth) were pumped using an air-operated polyethylene pump and Kynar tubing into 50 l polyethylene carboy. The top 2 cm of the sediment core was collected by extrusion, homogenized by stirring, and used in photolysis experiments within several hours.

Approximately 4 ml of homogenized sediment was placed into 1.5 l of unfiltered seawater in a 5 l polyethylene container. After vigorous mixing, the suspension was allowed to settle 6 cm for 3 min to remove sand and coarse silt (>20 μm; Jackson 1973). The remaining suspension was quickly decanted into four Teflon-stoppered quartz tubes. In addition, four tubes were filled with unfiltered water containing no sediment and two were filled with 0.2 μm (Supor) filtered water. Half of the tubes for each treatment were wrapped in aluminum foil and served as dark controls. All tubes were attached to a plastic frame and submersed in a shallow plastic pool filled with

flowing seawater to maintain ambient temperature. Tubes were incubated for 7 and 8 h, respectively, for the two experiments, with periodic rotation of samples to maintain full sunlight exposure. Both experiments took place under mostly sunny, bright skies: integrated UVA/UVB radiation for the two experiments was $2.41 \times 10^2$ and $2.76 \times 10^2$ W cm$^{-2}$, respectively. After irradiation, suspensions were syringe-filtered through 0.2 μm Supor membranes housed in 47-mm polypropylene housings (Swinnex, Millipore Corp.) into 50 ml polypropylene centrifuge tubes (for nutrients) and precombusted 40 ml amber glass vials (for TDN and DON) under a clean hood supplied with HEPA filtered air. Filtration apparatus and centrifuge tubes were acid-washed to minimize contamination. Samples were stored frozen (−20°C) until analysis.

## 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 Horiba FluoroLog fluorometer. Standards made from NH$_4$Cl and samples for evaluation of background fluorescence and matrix effects (Holmes et al. 1999) were prepared and analyzed in the same manner as the samples.

Concentrations of TDN were analyzed by high temperature combustion (HTC) using a Shimadzu TOC 5050A total organic carbon analyzer coupled to an Antek 9000 N TDN analyzer equipped with an ASI 5000 autosampler (Kieber et al. 2005). Dissolved nutrients (NO$_x^-$ and PO$_4^{3-}$) were analyzed colorimetrically on a Technicon autoanalyzer. For the determination of DON, aliquots from the TDN sample vials were analyzed for NH$_4^+$ on the same day. DON was then calculated as TDN—NO$_x^-$–NH$_4^+$. All samples were analyzed in duplicate.

## Statistical treatment

Differences between experimental treatments were analyzed using standard least squares regression in JMP 7.0.1, including main effects for light, presence of sediment, interaction between sediment and light (sediment + light), filtered versus unfiltered water, and autoclaved versus raw, as appropriate. Tidal creek experiments for raw sediment, autoclaved sediment, and no sediment were analyzed independently. For these time course experiments, nutrient fluxes were calculated using linear regression of TSS-normalized concentration versus time, using concentration values from individual flasks. Statistical significance of fluxes was determined using an *F*-test of the slope of the individual regression lines (Zar 1984). Because of the small number of replicates, the two experiments with continental shelf sediments were analyzed together, with site included as an additional effect in the statistical model. Apparent photochemical fluxes were calculated as the difference between light and dark treatments, divided by the exposure time. Unless otherwise noted, all uncertainties are reported in terms of ±1 standard deviation (SD). Results with *p* values <0.05 are considered significant.

## Results

### Tidal creek

The in situ TSS (before filtration or sediment additions) in the Bradley Creek water used in this experiment was $14 \pm 2$ mg l$^{-1}$. Of the bulk sediment initially resuspended, 25 and 27% (for raw and autoclaved sediment, respectively) settled out in the initial 5 min settling period. The TSS concentration in the quartz flasks was $410 \pm 30$ ($n = 4$) mg l$^{-1}$ for the experiment with raw sediment and $340 \pm 20$ ($n = 4$) mg l$^{-1}$ for the experiment with autoclaved sediment. The carbon and nitrogen compositions of the initial resuspension mixture, determined from filters, are shown in Table 1. Changes in POC and PON content of the raw sediment over the course of the experiment were not significant, which is expected given the amount of TDN released represents only 3–5% of the starting particulate N (Tables 1 and 2).

Experiments without added sediment showed little or no change in nutrient concentrations. No significant changes in dissolved inorganic nutrients occurred in our photolysis experiments with filtered creek water only (Figs. 1b and 2b) or for dark controls of unfiltered creek water (Figs. 1a and 2a).

**Table 1** Mean (and standard deviation) POC and PON concentrations for photolysis experiments, and C and N compositions of sediment used in photolysis experiments

|  |  | PON (mg l$^{-1}$) | POC (mg l$^{-1}$) | C/N | Org. C% | N% |
|---|---|---|---|---|---|---|
| Bradley Cr. | Raw | 2.6 (0.1) | 33.2 (1.1) | 15.0 (0.3) | 8.5 (0.4) | 0.7 (0.02) |
| Bradley Cr. | Autoclaved | 2.0 (0.1) | 28.0 (1.3) | 16.0 (0.2) | 8.7 (0.2) | 0.6 (0.01) |
| Cont. Shelf | Site 1 | 0.5 (0.05) | 8.9 (1.2) | 22.2 (0.4) | 2.3 (0.3) | 0.1 (0.01) |
| Cont. Shelf | Site 2 | 0.6 (0.04) | 9.5 (0.3) | 19.9 (4.2) | 4.3 (0.1) | 0.3 (0.02) |

For creek sediments $n = 4$, for continental shelf sediments $n = 2$

**Table 2** Mean rates of nutrient release from Bradley Creek sediments, normalized for total suspended solids

|  |  | DON (μmol g$^{-1}$ h$^{-1}$) | NO$_x^-$ (μmol g$^{-1}$ h$^{-1}$) | NH$_4^+$ (μmol g$^{-1}$ h$^{-1}$) | PO$_4^{3-}$ (μmol g$^{-1}$ h$^{-1}$) | TDN (μmol g$^{-1}$ h$^{-1}$) |
|---|---|---|---|---|---|---|
| Dark | Raw | 1.2 (0.4) |  | −0.68 (0.12) |  |  |
| Light | Raw | 2.0 (0.4) | −0.12 (0.05) | 0.34 (0.13) | 0.09 (0.005) | 2.2 (0.5) |
| Dark | Autoclaved |  |  |  | 0.08 (0.01) |  |
| Light | Autoclaved | 3.4 (0.6) |  | 6.7 (0.7) | 0.14 (0.02) | 10 (1.0) |

Only statistically significant rates ($p < 0.05$) are shown, values in parentheses are standard error

For unfiltered creek water exposed to light, NH$_4^+$ decreased ($p = 0.002$) while TDN ($p = 0.001$) increased, primarily as a result of an increase in DON ($p = 0.01$). Because ambient particles likely included some phytoplankton, these effects may result from biological processes such as photosynthesis; however, photolysis of organic matter associated with ambient particles may have also contributed to the increase in TDN.

The effect of irradiation of resuspended sediments on nutrient concentrations was evaluated by comparing changes in nutrient concentrations as a function of irradiation time between irradiated flasks and dark controls (Figs. 3 and 4). Release rates (μmol g$^{-1}$ h$^{-1}$) of these dissolved constituents are summarized in Table 2 (only statistically significant rates are shown). Concentrations of TDN increased significantly (36%) in light-exposed suspended raw sediment whereas changes in dark controls were not significant (Table 2). As the initial time point was taken after addition of sediment, initial concentrations include contributions from sediment porewater (Kieber et al. 2006). For inorganic nutrients, NH$_4^+$ increased (relative to initial values) by 33%, NO$_x^-$ decreased by 5%, and PO$_4^{3-}$ increased by 44% over the 6 h irradiation (Figs. 3a and 4a). Because 6 h of simulated sunlight approximates the light exposure for one mid-summer day, the estimated daily rates (for summer) of photolytic nutrient release are 13.2 and 0.54 μmol g$^{-1}$ day$^{-1}$ for TDN and PO$_4^{3-}$, respectively.



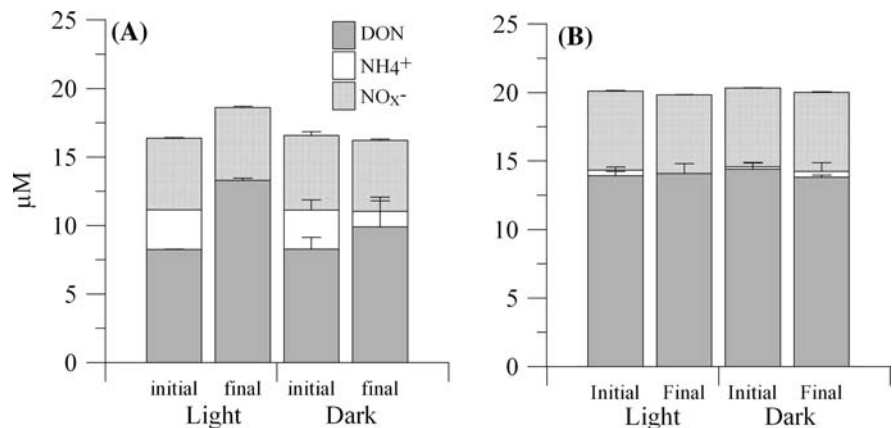**Fig. 1** Initial and final DON, NH$_4^+$, and NO$_x^-$ concentrations from incubations with no sediment additions: unfiltered (**a**) and 0.2 μm-filtered (**b**) Bradley Creek water. *Error bars* represent +1 standard deviation of duplicate treatments

**Fig. 2** Initial and final $PO_4^{3-}$ concentrations from incubations with no sediment additions: unfiltered (**a**) and 0.2 μm-filtered (**b**) Bradley Creek water. *Error bars* represent +1 standard deviation of duplicate treatments
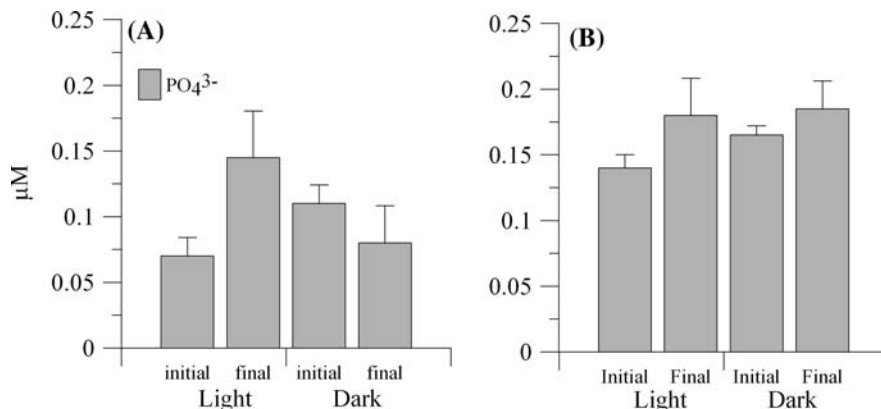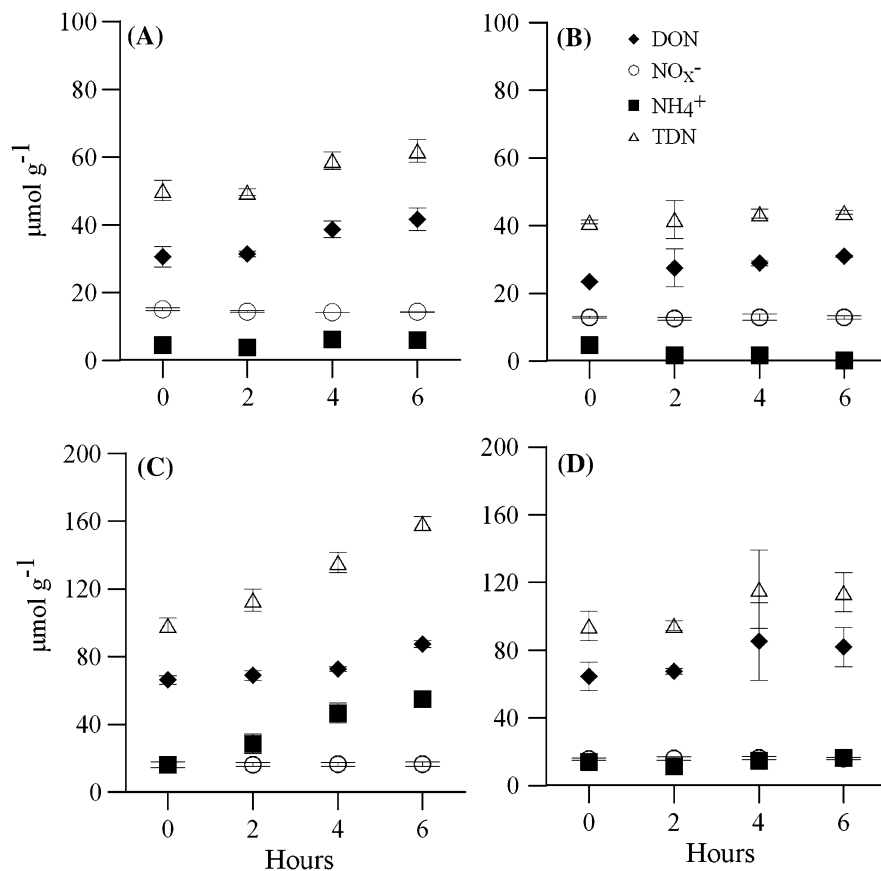


**Fig. 3** DON, dissolved $NO_x^-$, dissolved $NH_4^+$, and TDN concentrations in experiments with raw Bradley Creek sediment in light (**a**) and dark (**b**) treatments, and autoclaved Bradley Creek sediment in light (**c**) and dark (**d**) treatments. *Error bars* represent ±1 standard deviation of duplicate treatments



In order to validate sedimentary organic matter (SOM) photolysis as a viable mechanism for nutrient release, a photolysis study was also performed with sterilized components (autoclaved sediments and 0.2 μm filtered creek water, Figs. 3 and 4). The autoclaved creek sediments released DON, $NH_4^+$, and $PO_4^{3-}$ when exposed to light at similar or higher release rates relative to raw sediments (Table 2).

Autoclaved sediments produced a relatively larger proportion of TDN as $NH_4^+$ compared to raw sediments (Fig. 3c), and $PO_4^{3-}$ was released in the dark controls for autoclaved sediments and not for raw sediments (Fig. 4). These differences from the results of raw sediment irradiations indicate that autoclaving likely altered the SOM, despite the similarity in bulk organic matter characteristics

**Fig. 4** Dissolved $PO_4^{3-}$ concentrations in experiments with raw Bradley Creek sediment in light (**a**) and dark (**b**) treatments, and autoclaved Bradley Creek sediment in light (**c**) and dark (**d**) treatments. *Error bars* represent ±1 standard deviation of duplicate treatments
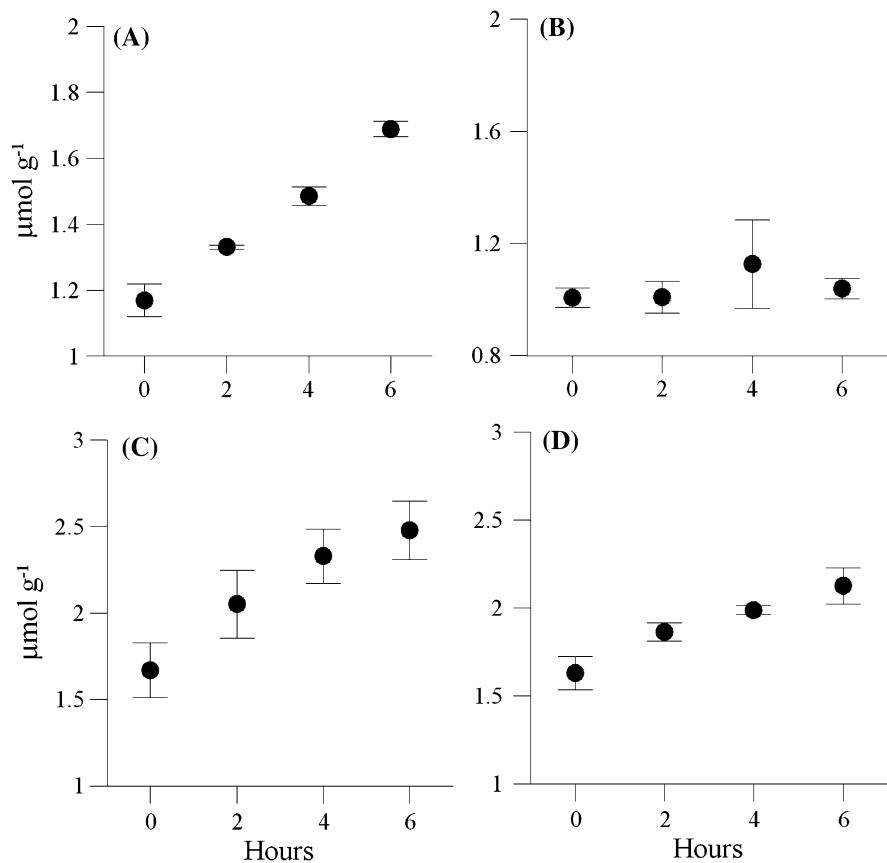


(Table 1). Nevertheless, differences between light and dark treatments of autoclaved sediments demonstrate that SOM photolysis in a sterile system can produce dissolved nutrients and organic matter at rates similar to or higher than those observed in experiments with raw sediments.

## Continental shelf

TSS concentrations for the two continental shelf sediment suspensions were $390 \pm 350$, and $220 \pm 20$ mg $l^{-1}$, respectively. In situ TSS in the ambient water column was 15 mg $l^{-1} \pm 13$ mg $l^{-1}$. The continental shelf sediment was less organic-rich and had higher C/N ratios compared to sediments from the tidal creek site (Table 1). After 1 day of exposure to natural sunlight, the light-exposed suspensions with continental shelf sediment and unfiltered seawater had significantly higher $NH_4^+$ ($p = 0.004$), $PO_4^{3-}$ ($p = 0.003$), as well as TDN ($p = 0.022$) concentrations compared to dark controls

(Fig. 5). For the first experiment, differences between nutrient concentrations in light and dark treatments with sediment yielded apparent photochemical fluxes (normalized to sediment dry weight) of $0.09 \pm 0.30$, $0.12 \pm 0.07$, and $4.7 \pm 5.9$ μmol $g^{-1}$ $h^{-1}$ for $NH_4^+$, $PO_4^{3-}$, and TDN, respectively. For the second experiment, these apparent fluxes were $1.8 \pm 0.5$, $0.09 \pm 0.01$, and $2.6 \pm 1.3$ μmol $g^{-1}$ $h^{-1}$ for $NH_4^+$, $PO_4^{3-}$, respectively.

## Discussion

Sediment samples in our incubation experiments were obtained from very different depositional environments. Bradley Creek sediments were taken from a brackish intertidal zone, which is vulnerable to erosion (Mwamba and Torres 2002), whereas the continental shelf represents a primarily depositional environment for riverine material. These sites therefore represent theoretical endpoints in the mobilization and transport of resuspended sediment. The

**Fig. 5** DON, $NO_x^-$, and $NH_4^+$ in sunlight photolysis experiments and dark controls with continental shelf sediments from Site 1 (**a**) and Site 2 (**b**). Treatments represent 0.2 μm-filtered water with no added sediment, unfiltered water with no added sediment, and unfiltered water with added sediment. *Error bars* represent +1 standard deviation of duplicate treatments (for unfiltered water and unfiltered water + sediment) or for duplicate analyses from one tube (filtered water)
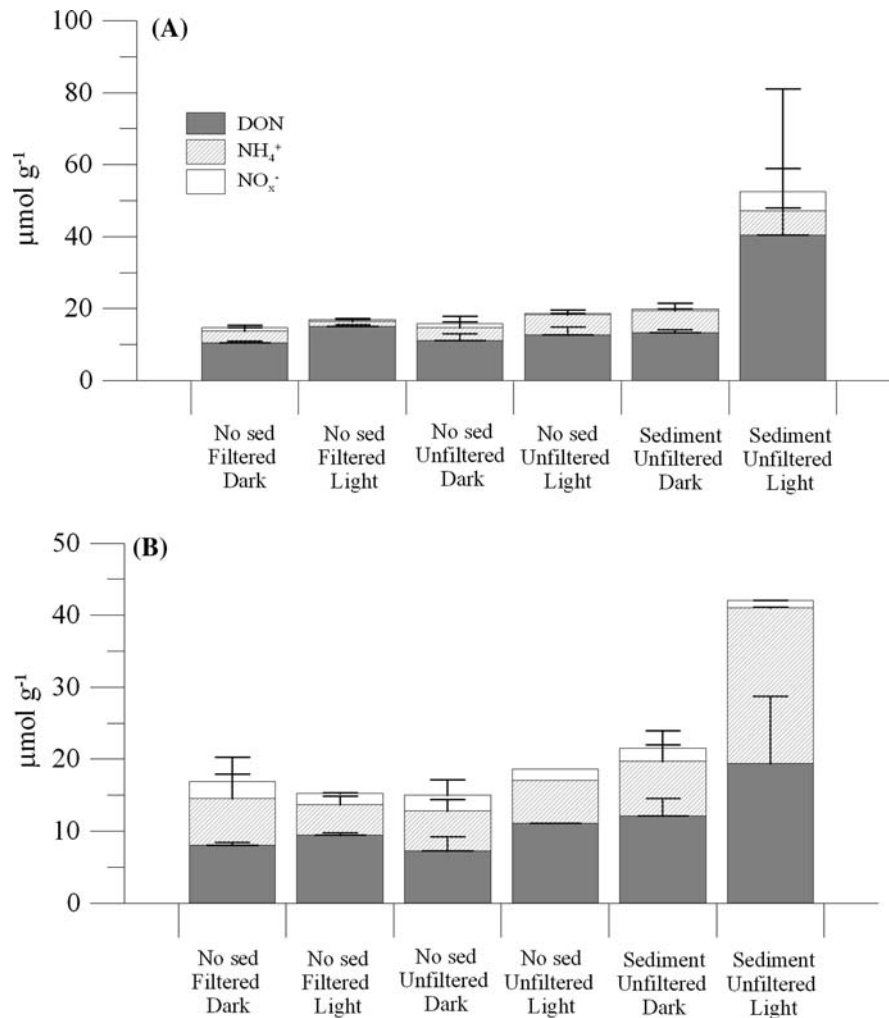


sediment–water mixtures contained TSS concentrations that were approximately 20–30 times ambient particulate concentrations, but were conservative with respect to expected concentrations in disturbed environments. For example, moderate to high winds can increase TSS up to two orders of magnitude in coastal environments (Leonard et al. 1995; Walker 2001; Sheremet et al. 2005). Therefore, our nutrient flux estimates should be environmentally relevant for perturbed systems. Exposure of resuspended sediments to light occurs for a limited amount of time due to particle settling. However, because measurable changes in nutrients occurred after only a few hours exposure to light, it is probable that particles with settling rates of <0.002 cm s$^{-1}$ are likely to remain in irradiated surface waters long enough for photochemical changes to occur. This settling rate encompasses

particle sizes ranging from fine silt (2–5 μm) to clay (<2 μm; Jackson 1973). Therefore, even brief resuspension events from which sediment rapidly resettles (e.g., boat wakes, bioturbation) may produce measurable nutrient increases, particularly in fine-grained, organic-rich sediments.

Our results demonstrate that resuspended sediments exposed to light release dissolved inorganic and organic nutrients, but the mechanism of release is still unclear. Nutrient release occurred in a sterile system (with autoclaved sediment and filtered water) at similar or higher rates than raw sediment, suggesting that SOM photolysis is a viable explanation for our experimental results. However, any "kill" treatment necessarily alters organic matter to some extent (Tuominen et al. 1994); therefore, fluxes from autoclaved and raw sediment cannot be directly

compared to estimate contributions from biological processes. Nevertheless, biologically-mediated processes that might increase TDN (e.g., $N_2$ fixation) would not be expected to increase $PO_4^{3-}$ as well. Furthermore, assimilation of inorganic nutrients by autotrophs should decrease, rather than increase nutrient concentrations in the light. Therefore, we interpret the increases in dissolved nutrients in our experiments as the result of predominantly photochemical processes. Photolytic release of $NH_4^+$ and $PO_4^{3-}$ has not, to our knowledge, been previously reported. Riggsbee et al. (2008) found increases in DON, but no increase in DIN or soluble reactive phosphorous upon exposure of similar sediment concentrations to 6 h of simulated sunlight. However, differences in our results are likely caused by sediment characteristics, as the previous study examined inland, freshwater sediments, whereas our study focused on estuarine and marine sediments.

Some small but significant trends in our data suggest that biological processes decreased rates of inorganic nutrient release from irradiated sediments. Ammonium concentrations for raw tidal creek sediments decreased in the dark control ($-0.68$ μmol $g^{-1}$ $h^{-1}$) and $NO_x^-$ decreased in the light treatment ($-0.12$ μmol $g^{-1}$ $h^{-1}$). These changes appear to be driven predominately by biological processes because decreases did not occur in analogous autoclaved sediments (Fig. 3). Although decreases in $NH_4^+$ could be caused by nitrification, assimilation is more likely because no significant increases in $NO_x^-$ were detected. Part of the assimilated DIN may have been released as DON, which increased in the both the light and dark for raw sediment (Fig. 3a, b). The increase in $NH_4^+$ in the light for raw tidal creek sediments should therefore be viewed as a minimum value because it likely represents a balance between biological assimilation and photochemical production. The gross photochemical flux of $NH_4^+$ (calculated as the difference between light and dark treatments) is approximately $1.0 \pm 0.1$ μmol $g^{-1}$ $h^{-1}$.

Increases in nutrients measured in experiments with continental shelf sediments also represent net differences between photochemical production and biological processes such as assimilation, as they were performed with unfiltered water as well as raw sediment. However, changes in nutrient concentrations that occurred during irradiations with unfiltered

creek water (Figs. 1 and 2) and unfiltered seawater (Figs. 5 and 6) show relatively small differences from experiments with filtered water. This suggests that nutrient fluxes from ambient particles (whether biological or photochemical) are small compared to fluxes in the presence of sediments. Nevertheless, the gross photochemical release of nutrients from continental shelf sediments may be higher than the measured increases, due to assimilation of nutrients by phytoplankton.

## Implications

Coastal zones receive nutrient inputs from a variety of sources, including groundwater, rivers, rainwater, and diffusive benthic fluxes. Sediment resuspension is by nature episodic, and so comparison of long-term nutrient fluxes is difficult. Another uncertainty is the changes in light field associated with sediment resuspension, and the role of turbidity in vertical transport of sediment into and out of the photic zone. An earlier study by Mayer et al. (2006) demonstrated that photodegradation rates of SOM decreased with increasing sediment concentrations in 5-cm deep suspension (also the approximate depth of suspensions in the current study). The elevated TSS concentrations used in our study may have caused particle shading, resulting in an underestimation of potential photochemical fluxes occurring at the surface of the water or under conditions of lower TSS. Despite these caveats, our results should provide a reasonable estimate of the integrated photochemical flux in the top 5 cm of a turbulent water body.

Based on our experiments, TSS concentrations of 100 mg $l^{-1}$ would generate nutrient release of approximately 1.32 μmol $l^{-1}$ $day^{-1}$ TDN and 0.05 μmol $l^{-1}$ $day^{-1}$ $PO_4^{3-}$ in the top 5 cm of Bradley Creek and 2.1 μmol $l^{-1}$ $day^{-1}$ TDN and 0.07 μmol $l^{-1}$ $day^{-1}$ $PO_4^{3-}$ in the top 5 cm of the continental shelf. This corresponds to areal fluxes for TDN and $PO_4^{3-}$ (respectively) of 66 μmol $m^{-2}$ $day^{-1}$ and 2.7 μmol $m^{-2}$ $day^{-1}$ for Bradley Creek and 100 and 3.4 μmol $m^{-2}$ $day^{-1}$ for the continental shelf. Atmospheric wet deposition is probably the most relevant comparison for these fluxes, as rain events are also an episodic source that deliver nutrients to surface waters. In Wilmington, NC, rainwater has a volume-weighted average TDN concentration of 22 μM (Kieber et al. 2005); therefore, an average rain event

**Fig. 6** Dissolved $PO_4^{3-}$ in sunlight photolysis experiments and dark controls with continental shelf sediments from Site 1 (**a**) and Site 2 (**b**). Treatments represent 0.2 μm-filtered water with no added sediment, unfiltered water with no added sediment, and unfiltered water with added sediment. *Error bars* represent +1 standard deviation of duplicate treatments (for unfiltered water and unfiltered water + sediment) or for duplicate analyses from one tube (filtered water)
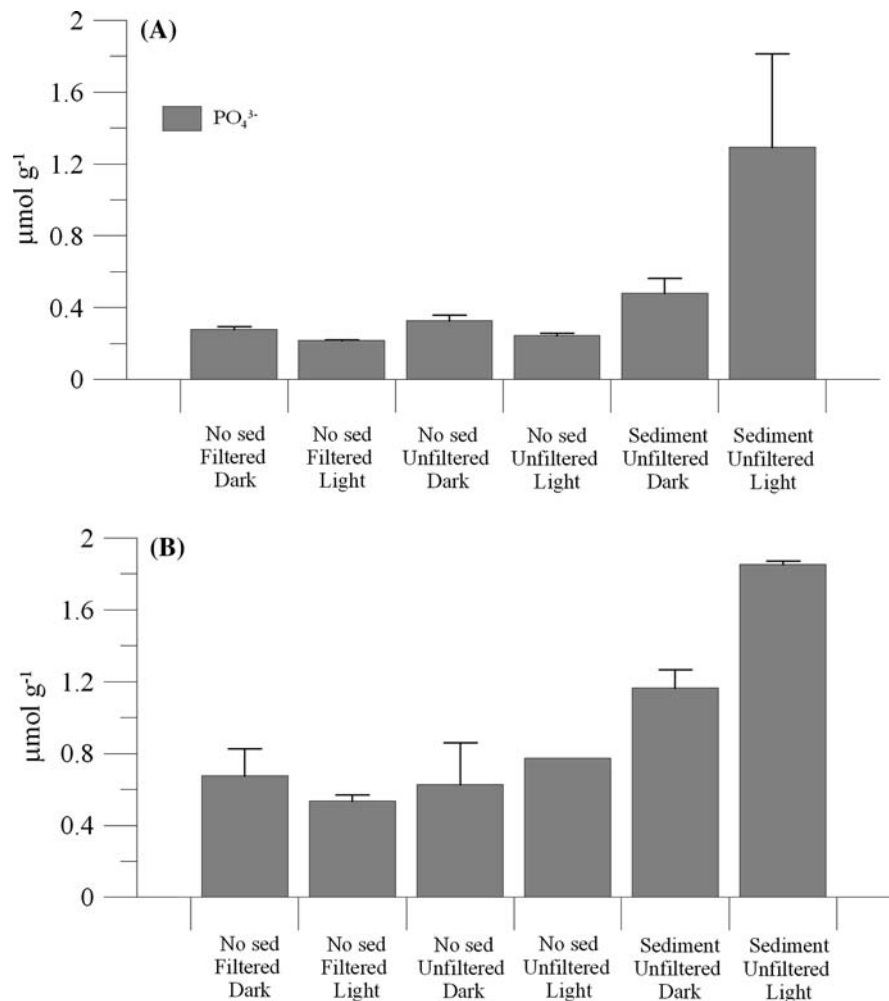
of 16 mm (Kieber, unpub. data) would deposit approximately 350 μmol m$^{-2}$ of dissolved N. This suggests that sediment photolysis N fluxes are probably small in comparison, though they may be relatively more important in areas that receive less rainfall. However, $PO_4^{3-}$ concentrations in rainwater are typically low, and Wilmington, NC has a minimum N:P of 54 (Willey and Kiefer 1993), whereas the N: P ratio of nutrients released by sediment photolysis was approximately 24 - 29. Therefore, sediment photolysis may be a proportionally larger source of $PO_4^{3-}$ compared to TDN.

Experiments with tidal creek sediments were performed in a relatively controlled laboratory setting, with filtered water and constant light levels from a solar simulator. In contrast, experiments with continental shelf sediments were performed in the field with unfiltered water and natural light. Despite the different sediments used and the differences in experimental conditions, the exhibited fluxes of organic and inorganic nutrients from sediments of the same order of magnitude. This suggests that the nutrient release rates measured in the laboratory experiments are environmentally relevant and that irradiation of resuspended sediments likely increases dissolved nutrient concentrations in situ. The fate of these dissolved nutrients is unknown. Primary productivity is generally N-limited in Bradley Creek and in other nearby tidal creeks (Posey et al. 2002; Mallin et al. 2004) as well as in adjacent continental shelf waters (Paerl et al. 1999). Therefore, increases in inorganic nutrients upon photolysis of resuspended sediments would likely increase local water column primary productivity. However, some photochemically released nutrients may be exported downstream, especially organic forms that are less available to primary producers. Transport and

continued photolytic remineralization of this DON (Bushaw et al. 1996; Wang et al. 2000) could affect nutrient availability far downstream from the original resuspension event. Therefore, photolysis of resuspended sediments represents a potentially significant source of dissolved N and P for coastal regions. To our knowledge, little is yet known about this process, including environmental controls on rates or effects from organic matter source material. Given the abundance of shallow coastal environments that are nutrient-limited, photolytic production of nutrients from sediment could constitute an important control on nearshore primary productivity.

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