

## Photodissolution of particulate organic matter from sediments

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### Abstract

Irradiation of particulate organic matter (POM) at light intensities found at the earth's surface should induce reduction in molecular weight, as found for dissolved organic matter, and hence result in transfer to the dissolved phase. We studied Mississippi River suspended sediments to test if photodissolution can induce losses of POM similar to those observed between delivery and burial in coastal sediments. Irradiation experiments in a solar simulator demonstrated dissolution of tens of percent of the POM after several days of exposure to strong sunlight. Neither water type nor iron oxyhydroxide removal had large effect on the reaction extent, but temperature may be a strong controlling parameter. Ultraviolet and visible wavelengths drive this reaction. A hyperbolic response of reaction extent to photon flux allows significant reaction to occur in highly turbid suspensions, despite significant light penetration into the suspensions of only millimeters to centimeters. Our data do not yet allow quantitation of this reaction's contribution to POM loss between the Mississippi River and its depocenter, but they do demonstrate its potential significance under nearshore resuspension regimes. More importantly, these results point to a heretofore ignored role for photodissolution of particulate organic matter at the earth's surface.

Over the past two decades, a burgeoning literature has developed around the interaction between sunlight and natural dissolved organic matter (reviewed in Osburn and Morris 2003; Zepp 2003). Dissolved organic materials contain many chromophores that absorb light especially well at ultraviolet (UV) and visible energy wavelengths; this absorption results in a cascade of processes including photolysis to lower molecular weight organic compounds, generation of organic and inorganic radicals, stimulation of autotrophic and heterotrophic biological processes, and photobleaching of the residual organic material (e.g., Geller 1985; Mopper et al. 1991; Miller and Moran 1997).

POM also absorbs light at wavelengths similar to those of dissolved organic matter (Kirk 1980) and should therefore be susceptible to similar reactions. This type of reaction, however, has received very little attention. The effect of UV light on soil litter decomposition has been addressed (e.g., Moorhead and Callaghan 1994); high-intensity UV radiation has been used to study soil organomineral interactions (Skjemstad et al. 1993); and a variety of model systems (e.g., added organics to natural particles or vice versa) have been studied for their impact on photolysis of adsorbed organic matter (e.g., Miller and Zepp 1979a; Pullin et al. 2004; Tietjen et al. 2005). Nevertheless, the direct examination of

natural levels of sunlight interacting with natural aquatic sediments is largely missing.

A major finding from irradiation experiments with dissolved organic matter is that high molecular weight materials are converted to lower molecular weight compounds (e.g., Geller 1985). The partitioning of organic compounds between dissolved and adsorbed states responds strongly to molecular weight (Gu et al. 1995), so that such photolysis should result in increased partitioning of particulate organic matter toward the dissolved phase. Indeed, Pullin et al. (2004) showed that photoirradiation can drive this change in phase partitioning for natural dissolved organic matter adsorption onto goethite.

If such a reaction were to be significant in the aquatic environments, it would affect organic carbon cycling by partitioning it toward the upper water column (e.g., via benthic-pelagic coupling). Reactions of this type in aquatic environments should be maximized in areas of frequent resuspension, such as muddy rivers or littoral zones. It should be especially favored in lower latitudes where sunlight is more intense. Aller (1998) hypothesized that photochemical processes would enhance mineralization of organic matter from repetitively resuspended, shallow deltaic muds. Low-latitude deltaic deposits are, in fact, areas of especially strong loss of riverine organic carbon before burial (Trefry et al. 1994; Keil et al. 1997), the causes of which are not well understood but thought to be related to their frequent resuspension (Aller 2004). As part of a project to examine causes of organic carbon (OC) loss from Mississippi River sediments, we therefore examined the possibility of this reaction using suspended particulate material from the lower Mississippi River.

In this paper we address photodissolution reactions using a laboratory approach. Our objective is simply to test if significant photodissolution of natural sedimentary organic

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### Acknowledgments

We thank M. Wells for samples and equipment loan; K. Grimsley (United States Geological Survey) for samples; Louisiana Marine Consortium Laboratory staff for use of their facilities; and M. Allison, T. Bianchi, B. McKee, G. Kineke, A. Zimmerman, R. Keil, and reviewers for comments and discussions. This work was supported by the National Science Foundation (Integrated Carbon Cycle Research and Research Experience for Undergraduates Programs). Contribution 396 from the Darling Marine Center.

matter is possible under solar conditions representative of the subtropics, as well as to examine the potential roles of various parameters likely to vary in the field. Its applicability to field situations awaits more detailed, ongoing work on optics of field suspensions.

## Methods and materials

Water and sediment samples were collected from the lower Mississippi and Atchafalaya Rivers at locations including St. Francisville (north of Baton Rouge), a shallow subtidal site outside of Grand Pass on the Mississippi Birdfoot Delta, and Morgan City on the Atchafalaya River. Water samples were collected from boat or shore using water sampling gear or buckets. Sediments were collected by grabs or multicorer. Most water samples were returned to Maine overnight. On one occasion we separated suspended particulates from river water by continuous flow centrifugation at the Louisiana Marine Consortium Laboratory in Cocodrie, Louisiana. On one other occasion we used a Membrex GX Vortex Flow Filtration system immediately after collection. Upon receipt of water samples at our laboratory in Maine, water samples were subjected to continuous flow centrifugation in either a Sharples Supercentrifuge or a Sorvall RC-5C with a continuous flow head. Suspended sediments removed from suspension were freeze-dried, and to improve subsampling precision many samples were sieved ( $63\ \mu\text{m}$ ) prior to use in experiments. Sediment-specific surface area of sediments was measured using nitrogen gas sorption interpreted via the Brunauer-Emmett-Teller equation, as described by Mayer (1994).

Irradiation experiments consisted of suspensions made from varying mixtures of different water types and sediments, which were then subjected to repeated periods of irradiation. Identical suspensions were kept as dark controls under the same stirring and temperature conditions. Irradiation experiments were carried out in a Suntest CPS+ or XLS+ (which were intercalibrated), which use a filtered xenon lamp to provide a close simulation of the solar spectrum. We used the maximum setting, which provides  $765\ \text{W cm}^{-2}$ —equivalent to subtropical sunlight at noon. Although early experiments were performed without temperature control resulting in suspensions that averaged  $35\text{--}40^\circ\text{C}$ , later experiments were carried out in a shallow-water bath that kept numerous samples at approximately room temperature.

Most experiments examining certain treatment effects (e.g., temperature, water composition) were performed with optically thin suspensions to expose all particles to the incident radiation. These optically thin experiments were done by placing suspensions in  $20 \times 2.4\ \text{cm}$  or  $10 \times 1.3\ \text{cm}$  (outer diameter) quartz tubes. The smaller tubes were closed with silicone stoppers, whereas the larger tubes were capped with Parafilm that in turn was protected by an Al foil covering. These tubes were agitated once per day by hand. Optically thicker suspensions (e.g., to test for effects of suspended sediment concentration) were irradiated in Pyrex beakers and stirred continuously using Variomag Poly multiple place stirrers. Each beaker was surrounded by blackened foil to isolate them optically from one another, but open

on top and covered with Saran wrap to eliminate evaporation. Because this wrapping reduced sharing of light among beakers, it can reduce net photochemical reaction relative to what might be expected from an areally more extensive water column in which lateral light scattering can allow scattered photons to do photochemical work without absorption by a black sink. We tested for such a reduction by comparing wrapped and unwrapped beakers and found only slight enhancement in unwrapped beakers (insufficient to affect interpretations reported here). The Saran wrap was tested for absorption and found to attenuate light negligibly throughout the wavelength range found to be important in the reaction (see following). All treatments were normally done in at least triplicate.

At the end of an irradiation treatment, suspended sediments were removed via syringe from irradiated or control experiments by filtration through a Whatman GF/F glass fiber filter. Particulate OC concentrations on filters rolled in tin foil were analyzed using a Perkin-Elmer 2400B Elemental Analyzer after fuming with HCl to remove carbonates (Mayer 1994). Filtrates were analyzed for dissolved OC using a Shimadzu 5000A TOC analyzer.

Numerous sample storage, pretreatment, and incubation conditions were varied to assess their impact on the photodissolution reactions. A sample of river water was run within 5 d of collection and again after freezing and thawing; the same was done for suspended sediment removed from a river suspension and then split into frozen and unfrozen aliquots to be reconstituted with the river water. We often found different levels of suspended particulate OC among these treatments, but the reaction extent (percent loss of carbon) remained similar among treatments. These tests gave us confidence that freeze-drying and storing samples frozen would not affect results. Water chemistry was varied in some experiments by using artificial seawater (Parsons et al. 1984) diluted to various salinities.

The effect of temperature was assessed using natural river water containing  $235\ \text{mg L}^{-1}$  suspended sediment. Optically thin samples in 100 mL quartz tubes were irradiated for 4 d at  $6\ \text{h d}^{-1}$  while held at ca.  $23^\circ\text{C}$  or  $35^\circ\text{C}$ . A duplicate of this experiment was performed while shielding the tubes with a thin film UV filter (Edmunds Scientific, G39-426) that removes wavelengths of  $<390\ \text{nm}$ .

The spectral sensitivity of these reactions was tested in beakers by covering 50 mL, 5 cm-deep suspensions of  $100\ \text{mg L}^{-1}$  (suspended sediment collected from springtime Atchafalaya River) with long-pass filters (315, 400, and 455 nm) or a band-pass filter ( $407 \pm 52\ \text{nm}$  at half-height; Edmunds Scientific, WG320, GG400, GG455, and BG12, respectively). Samples were irradiated for several days (33 h total) before filtration and measurement of particulate OC.

Reducible iron oxyhydroxides were extracted from sediment samples using the dithionite-citrate method of Loeppert and Inskeep (1996). Sediments with and without this treatment were then subjected to irradiation and control treatments using optically thin conditions.

Turbid waters scatter light intensely, so that scalar irradiance (light coming from all directions) is a more accurate measure of light available for photochemistry than is downward irradiance (Kirk 1983). To assess the depth attenuation

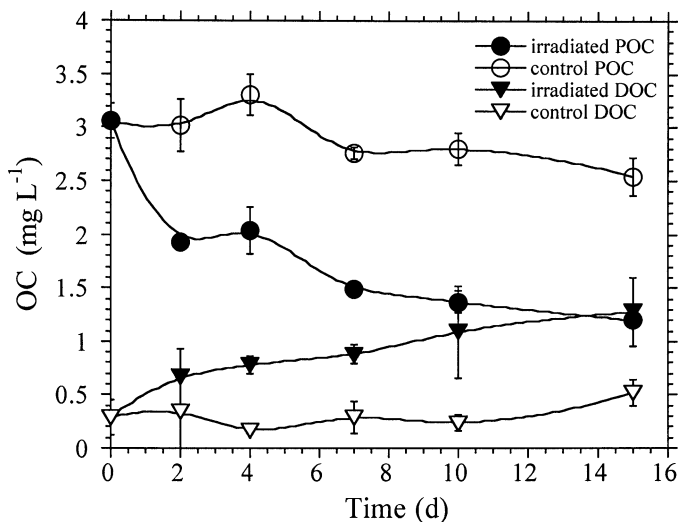


Fig. 1. Loss of particulate and appearance of dissolved organic carbon ( $\text{mg-OC L}^{-1}$ ) during incubation of Atchafalaya River suspended sediment under optically thin conditions in artificial seawater (salinity = 25). Irradiated samples received  $6 \text{ h d}^{-1}$  of  $765 \text{ W m}^{-2}$  sunlight, while control samples were kept in the dark. DOC measurements were made on the filtrates of the same samples that were measured for POC. Temperature was ca.  $35^\circ\text{C}$  during irradiation for treated and control samples. Error bars are standard deviations of triplicates.

of scalar irradiance in our muddy suspensions, we employed chemical actinometers placed at various depths in laboratory suspensions of Mississippi River particulates. Nitrate and nitrite actinometers (Jankowski et al. 1999, 2000) provided detection at the UVA-UVB boundary and in the middle UVA range, with response bandwidths of 311–333 nm (mean = 322 nm) and 330–380 nm (mean = 355 nm), respectively. The actinometer solutions were contained in  $10 \times 1.2 \text{ cm}$  (o.d.) quartz tubes. These tubes were placed horizontally, offset to avoid shading, in continuously stirred suspensions and centered at depths ranging from 0.5 to 6.5 cm. The suspensions ranged from 36 to  $450 \text{ mg L}^{-1}$  of suspended sediment that had been refrigerated for 5 months. The experiments were run for varying periods of time, which preliminary kinetics experiments showed to be sufficient to develop enough signal without saturating the actinometer.

## Results

Exposure of an optically thin suspension of suspended particulates from the Atchafalaya River in the solar simulator resulted in a loss of 64% of the OC from the particulate phase over a 15 d period of  $6 \text{ h d}^{-1}$  irradiation (Fig. 1). The bulk of the 15-d reaction extent occurred by 7 d, and thus we used 7–9 d periods for many ensuing experiments. The dark control in this experiment showed only a 16% loss from the particulate phase, indicating a strong impact of irradiation. This loss of organic carbon from the solid phase largely appeared in the solution phase, and so we term this process *photodissolution*.

The photodissolution extent of the experiment in Fig. 1, calculated as the difference between the irradiated treatment

and nonirradiated control, was at the upper end of the range of dissolution extents found in numerous experiments with different sediment samples (Table 1). One reason for this high extent was the  $35\text{--}40^\circ\text{C}$  temperatures reached in the tubes; subsequent experiments showed that maintenance at room temperature ( $23^\circ\text{C}$ ) lowered reaction extents by roughly one third. Photodissolution extents as small as a few percent were found in experiments with shorter irradiation times, different sediments, and other conditions (discussed following). In general, photodissolution extents of several tens of percent were found for most riverine sediments after several days of irradiation at  $6 \text{ h d}^{-1}$ .

Suspended sediments had OC concentrations of  $10.5\text{--}48.4 \text{ mg OC g}^{-1}$ , although most samples had values of roughly  $20 \text{ mg OC g}^{-1}$  (Table 1). Correcting for grain size variations by dividing by specific surface area values, the resultant organic matter loadings ranged from 0.41 to  $1.3 \text{ mg OC m}^{-2}$ . A seasonal sampling of riverine suspended particulate matter (SPM) at St. Francisville was subjected to the same irradiation conditions to test for inherent susceptibility of different source materials to photodissolution. These samples showed a lesser variability in initial OC concentrations from 18.1 to  $30.7 \text{ mg OC g}^{-1}$ . They exhibited remarkably similar photodissolution extents of 21–24% after 2 d of  $10 \text{ h d}^{-1}$  irradiation, indicating minimal change in the inherent susceptibility of SPM to photodissolution on a seasonal basis. A sample of subtidal sediment recently deposited by the river during a flood stage, but collected just offshore of the Mississippi Delta, showed a similar reaction extent as river samples that were irradiated for the same time period.

A sample of mud from the exposed subaerial bank of the Mississippi River at St. Francisville gave an OC:surface area (OC:SFA) value of  $0.31 \text{ mg OC m}^{-2}$ . On the other hand, a sample of subaqueous mud collected from the deeper and unlit part of the channel in the Atchafalaya River gave a higher OC:SFA ratio of 0.46, typical of suspended sediment values.

During irradiation, about half of the OC lost from the particulate phase typically appeared in the dissolved phase, indicating that the reaction was largely the hypothesized photodissolution. The carbon that did not appear in the dissolved organic carbon (DOC) fraction was presumably lost to wall adsorption or oxidation by some combination of metabolism (Kieber et al. 1989; Moran and Zepp 1997) and/or photochemical oxidation (Miller and Zepp 1995; Andrews et al. 2000). These carbon losses, which made up 6–33% of initial particulate organic carbon (POC), were much greater than ones found in the dark controls.

We tested a potential role for iron oxyhydroxides in affecting reaction extent by subjecting samples before and after dithionite extraction to irradiation. Although dithionite extraction removed some OC from the particulates (to be reported in a separate paper), the extent of photodissolution of the remaining POC was similar to that found with the unextracted control sediment. This result indicates not only that reducible iron oxyhydroxides are unimportant to the photodissolution reaction, but also that OC held in these iron phases has similar photoreactivity as OC in other particulate forms.

The importance of the solution phase to the photodisso-

Table 1. List of experiments testing for POC loss after irradiation.

Sampling date	Sampling location*	Time (h)†	TOC° (OC:SFA)‡	%POC loss (dark control)§	Temperature (°C)	Notes
30 Oct 01	St. Fran	18	48.4 (1.3)	37 (11)	35–40	Untreated river water
30 Oct 01	St. Fran	18	48.4 (1.3)	11–18 (2–5)	35–40	Effect of salinity (0, 5, 25)
31 Oct 01	Atchaf (SED)	54	19.3 (0.46)	55–59 (3–4)	35–40	Effect of salinity (0, 30.5)
31 Oct 01	Atchaf (SED)	24	19.3 (0.46)	23–31 (–16)	35–40	Effect of Mylar film
30 Oct 01	St. Fran (SED)	54	9.5 (0.31)	38–40 (–2.5–9)	35–40	
10 Apr 02	St. Fran	54	23.5 (n.d.)	55–61 (–8–3)	35–40	Fresh vs. freeze-dried sediment
10 Apr 02	St. Fran	54	23.5 (n.d.)	30–32 (–1–10)	35–40	Fresh vs. freeze-dried sediment
10 Apr 02	St. Fran	27	23.5 (n.d.)	35–39	35–40	Effect of salinity (0, 15)
10 Apr 02	St. Fran	X	23.5 (n.d.)	10–70 (3)	35–40	X = 0.0167, 0.167, 1.33, 6.0 h d <sup>-1</sup> , for 9 d (F4)
25 Feb 03	St. Fran	24	10.5 (0.43)	39–58 (8–23)	35–40	Refrigeration vs. freezing vs. freeze-drying
25 Feb 03	St. Fran	24	10.5 (0.43)	53–58 (11–23)	35–40	FeOx removal
25 Feb 03	St. Fran	90	10.5 (0.43)	60–73 (8–15)	35–40	Effect of salinity (0, 25) (F1)
25 Feb 03	St. Fran	24	10.5 (0.43)	5–42 (2–5)	23, 35	Effects of temperature, UV film
15 Apr 03	Morgan City	33	19.0 (0.41)	31 (no control)	15	Spectral dependence (F2)
15 Apr 03	Morgan City	42	19.0 (0.41)	17–36 (0–18)	15	Varying turbidity
15 Apr 03	Morgan City	42	19.0 (0.41)	23–28 (0–11)	15	Varying turbidity
7 Jul 04	St. Fran	60	29.6 (0.65)	29 (–5)	15	
7 Jul 04	St. Fran	30	29.6 (0.65)	15–20 (2–5)	15	Varying turbidity (F5)
8 Jul 04	MissD (SED)	90	20.9 (0.61)	40–41 (2–6)	23	Effect of salinity (0, 30.5)
7 Jul 04	St. Fran	20	29.6 (0.65)	22.9 (n.d.)	23	Seasonal comparison
25 Oct 04	St. Fran	20	18.4 (0.52)	22.5 (–1.7)	23	Seasonal comparison
15 Dec 04	St. Fran	20	30.7 (0.95)	23.7 (0.2)	23	Seasonal comparison
14 Mar 05	St. Fran	20	25.1 (0.72)	21.1 (–4.7)	23	Seasonal comparison
9 Apr 05	St. Fran	20	18.1 (0.58)	22.4 (–2.2)	23	Seasonal comparison
8 May 05	St. Fran	20	21.1 (0.53)	22.2 (–1.4)	23	Seasonal comparison

\* St. Fran, St. Francisville; Atchaf, Atchafalaya River; MissD, Mississippi Delta by Grand Pass. All sediments are suspended sediments from river except SED, which is deposited river sediment.

† total elapsed hours of irradiation.

‡ TOC°, initial total organic carbon (mg OC g<sup>-1</sup>); OC:SFA, initial organic carbon: specific surface area (mg OC m<sup>-2</sup>).

§ Range of %POC loss includes all treatments listed under Notes; the number in parentheses gives %POC loss in dark controls (occasional negative value indicate gain in POC due to either contamination or microbial uptake of DOC).

|| Experiments had treatment differences besides those parameters listed, so comparisons among them should be made with care. F(number) refers to Figure number that shows data from this experiment.

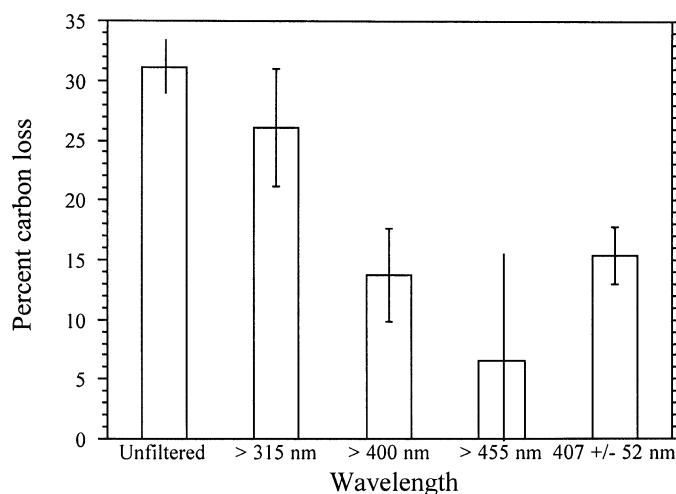


Fig. 2. Percent organic carbon loss under varying spectra from springtime Atchafalaya River suspended sediments (100 mg L<sup>-1</sup>) in artificial seawater (salinity = 30.5) after 33 h irradiation. Unfiltered treatment was full 765 W m<sup>-2</sup> sunlight; the >315, >400, and >455 nm treatments are long-pass filters; and the 407 ± 52 nm is a band-pass filter. Experiment was run at temperature = 15°C. Error bars with ticks are standard deviations of triplicates, whereas bars without ticks are ranges of duplicates.

lution reaction was tested in several ways, all using optically thin suspensions in quartz tubes. Experiments run in Mississippi River water that was either fresh, frozen/thawed, or refrigerated for 4 d or 1 month all showed similar losses of POC after 4 d of irradiation. Little difference was seen between irradiation losses of POC using distilled water versus Mississippi River water, implying that the dissolved materials in natural river water are not important to the photodissolution reaction. The effect of salinity was measured by running experiments in distilled water versus artificial seawater at varying salinities; little to no impact of salinity on POC or TOC loss was found. Similarly, Sandvik et al. (2000) found little effect of salinity on photochemical production of singlet oxygen from dissolved organic matter in waters from the Mississippi Delta region.

Photodissolution showed a broad spectral sensitivity. Long-pass filters showed that UV wavelengths could account for about half of the total reaction extent, and visible wavelengths were capable of inducing the other half (Fig. 2). Our use of long-pass filters provides little resolution of action spectra for these reactions, but clearly much of the reaction can occur in the absence of all UV wavelengths. This spectral response is qualitatively similar to ones found for photolysis of dissolved organic matter (e.g., Miller et al. 2002).

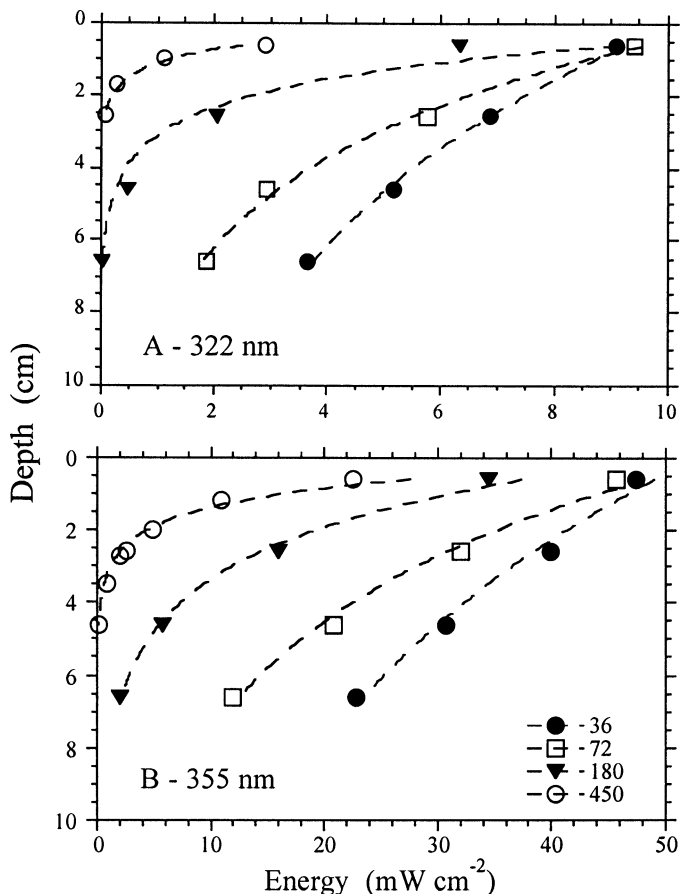


Fig. 3. Attenuation of scalar irradiance in suspensions of varying suspended sediment concentration at 322 ( $\pm 11$ ) and 355 ( $\pm 25$ ) nm (nitrate and nitrite actinometers, respectively). Numbers in symbol legend refer to suspended sediment concentration ( $\text{mg L}^{-1}$ ). Lines represent exponential best fits.

A separate experiment using plastic film to remove wavelengths of  $<390$  nm showed reduction of about one third of photodissolution at  $35^\circ\text{C}$ , but interestingly it reduced photodissolution by more than 80% at  $23^\circ\text{C}$ . This possible strong temperature dependence of photodissolution induced by lower energy wavelengths was not pursued, but it warrants further work.

Based on this spectral sensitivity, we determined the depth penetration of UV wavelengths into suspensions of sediment varying in concentration. Use of nitrate and nitrite actinometers (for spectral bands of  $322 \pm 11$  nm and  $355 \pm 25$  nm, respectively) provided scalar irradiance values assuming that the cylindrical actinometers capture light similarly to a small sphere. For our restricted purpose of assessing depth attenuation relationships, this assumption seems reasonable. Scalar irradiance captured by the actinometers attenuated exponentially with water depth (Fig. 3a,b), with e-folding depths ranging from several centimeters at  $36 \text{ mg L}^{-1}$  to several millimeters at  $450 \text{ mg L}^{-1}$  for each of these wavelengths. These results are similar to those found by Miller and Zepp (1979a) for various river sediments. The lower wavelength (322 nm) underwent greater relative attenuation with increasing suspended sediment concentration, consis-

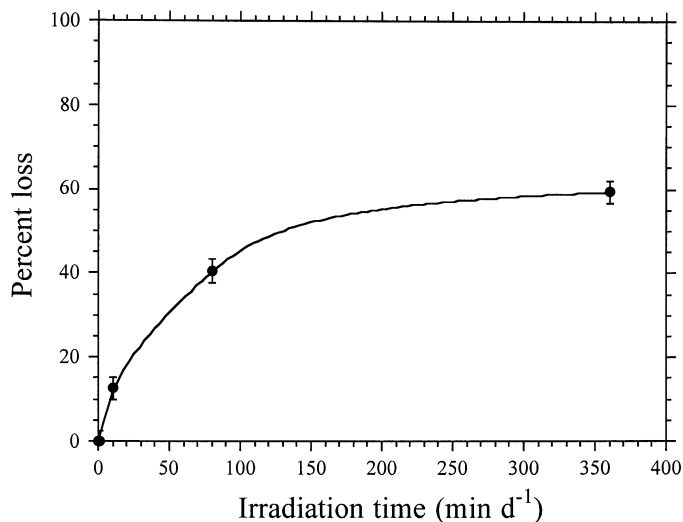


Fig. 4. Percent organic carbon loss from Mississippi River suspended particulates in distilled water after 9 d under varying minutes per day of full  $765 \text{ W m}^{-2}$  irradiation. The control incubation lost only 3% of its particulate organic carbon. Error bars are standard deviations of triplicates.

tent with increasing absorption of light by the sediment particles at lower wavelengths (Kirk 1980). A separate experiment using the same sediment but after a much shorter storage time since collection resulted in about a factor of two greater penetration of light into the suspensions, implying that attenuation likely varies with factors such as degree of particle aggregation.

This small penetration of light into muddy suspensions led to experiments to determine the irradiance requirements for photodissolution. We explored both duration of irradiation and suspended sediment concentration as separate ways to vary the photon flux to particles. Varying the daily dosage of light to optically thin suspensions resulted in hyperbolic behavior of photodissolution extent (Fig. 4), with most of the reaction extent that was caused by  $360 \text{ min d}^{-1}$  irradiation also achievable with  $80 \text{ min d}^{-1}$  irradiation.

This low requirement for irradiation suggests that particles in optically thick suspensions, which would normally attenuate scalar irradiance quickly (Fig. 3), could achieve significant photodissolution. We therefore experimented with suspensions varying from  $80$  to  $800 \text{ mg L}^{-1}$  in 5-cm-deep water columns under  $765 \text{ W cm}^{-2}$  irradiation. If the actinometry data (Fig. 3) represent the scalar irradiance field as experienced by individual particles, then the integrated areas of these plots are proportional to the irradiance available for photochemical work for the average particle being actively mixed throughout the depth range. This integration showed that individual particles in the  $800 \text{ mg L}^{-1}$  suspension would receive only 15% of the irradiance of those in the  $80 \text{ mg L}^{-1}$  suspension. The photodissolution extents after 5 d were, nevertheless, only slightly decreased in the  $800 \text{ mg L}^{-1}$  suspension relative to the  $80 \text{ mg L}^{-1}$  one (Fig. 5). Although it is possible that the small difference in reaction extents at 5 d were due to exhaustion of the fraction of organic matter susceptible to photodissolution, this possibility is inconsis-

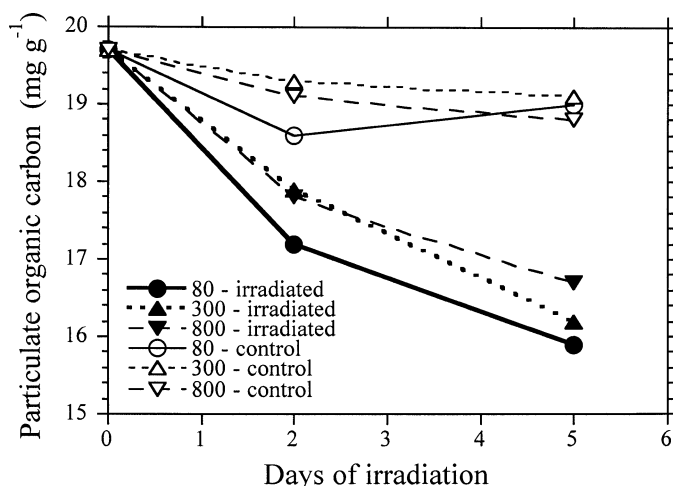


Fig. 5. Particulate organic carbon concentrations ( $\text{mg g}^{-1}$ ) of sediments in 5 cm deep suspensions with 80, 300, and 800  $\text{mg L}^{-1}$  of Mississippi River sediment. Experiment was run at 23°C under 765  $\text{W m}^{-2}$  irradiation for 6  $\text{h d}^{-1}$ ; controls were held at the same temperature. Error bars not shown for clarity. Coefficient of variation was always <5% and almost always <3%.

tent with the similarly small difference in reaction extents at 2 d, at which time the substrate was certainly not exhausted.

The controls in this experiment included stirred and unstirred suspensions kept dark to test for the effect of resuspension alone in effecting loss of particulate OC. These controls showed little to no stimulation of POC loss resulting from resuspension. As the thickness of the sediment was no more than a couple of millimeters in the richest, unstirred suspension, this experiment does not provide a test of the effect of sediment fluidization hypothesized by Aller (1998), which might be manifest in sediment deposits of greater thickness.

## Discussion

The photodissolution of organic matter from sediments is not surprising given the many reports of photolysis of colloidal and dissolved forms of natural organic matter from many environments. Particulate organic matter clearly contains materials with similar chromophoric properties as those found in dissolved organic matter, with respect to strong absorbance in the UV and visible range (e.g., Kirk 1980; Ertel and Hedges 1983), and transfer of some of the absorbed energy into reactions that lead to dissolution would be expected. What is perhaps surprising is the large fraction of particulate organic matter that is susceptible to this form of phase change under natural levels of irradiation.

We found photodissolution of up to two thirds of the particulate OC in some experiments under optimal conditions of irradiation, time, and temperature. These photodissolution losses are similar to the total OC loss that appears in the transition from the river to its depocenter (Keil et al. 1997). For example, in the experiment above (Fig. 1), the initial OC:SFA ratio was 0.43  $\text{mg OC m}^{-2}$ . After the loss of 64% of its OC, the OC:SFA ratio fell to 0.15  $\text{mg OC m}^{-2}$ , a

value consistent with those on the shelf off of the Mississippi River (Mayer 1994).

Our experimental conditions likely do not, however, pertain to the majority of particulates delivered to the Mississippi depocenter, and so we cannot predict the extent of this reaction under field conditions from the data so far. This determination will require further study of the absorbance characteristics of particulate organic matter, its exposure to photon flux under varying field conditions, and the role of secondary photochemical reactions. It seems unlikely that photodissolution will cause significant loss of particulate organic matter during riverine transport, assuming optical depths of millimeters to centimeters combined with water column depths of meters to tens of meters and river flow times of 1–2 d between our river collection site and the ocean.

A scenario that seems more feasible, however, is the deposition of riverine particulates in shallow deltaic environments followed by months of frequent resuspension events. In the Mississippi Delta region, as in many other deltas, most riverine particulates deposit quickly from the nearshore deltaic plume (Wright and Nittrouer 1995; Allison et al. 2000; Corbett et al. 2004), shifting to deeper depocenters after months of repeated resuspension events. This continual resuspension and exposure of deposited particulates to sunlight provides an opportunity for progressive and cumulative photodissolution. Certainly the sediment we collected from one of these shallow sites (MissD) remained as susceptible to photodissolution as the riverine SPM (Table 1). Whether there is sufficient opportunity to cause photodissolution extents of tens of percent remains to be answered. In addition, some riverine sediments are transferred quickly to deeper benthic environments and would have little chance for the solar exposure hypothesized here. Other shallow-water environments may host this photodissolution reaction, including mudflats, river banks, and shallow littoral zones of lakes.

We cannot specify the chemical mechanism of photodissolution from our data. Photolysis, in which a redox-driven photochemical reaction makes compounds with lower molecular weight, seems likely. However, there are other candidate mechanisms, such as changes in molecular conformation or functionality, that affect solubility. For example, the oxygen uptake that typically accompanies photolysis of dissolved organic matter (Andrews et al. 2000) would probably lead to more hydrophilic organic molecules that would partition toward the dissolved state. The low sensitivity of this reaction to either changing solution conditions or loss of iron oxyhydroxides suggests that the principal reactants are light and the particulate organic matter itself. The ability of the reaction to proceed under the reduced average light, but frequent brief exposure, that would occur in the well-stirred conditions of high suspended particulate concentrations (Fig. 5) suggests that secondary reactions are important in the kinetics or eventual extent of reaction. Such reactions can continue while irradiated particles or their photochemically reactive intermediates are mixed downward into unlit depths (Neale et al. 2003). The photochemical literature is rich in examples of photosensitized reactions in which secondary oxidants form upon the initial light absorption event and then cause further reactions.

Photochemical reactions of particulate organic matter may be as extensive as those of dissolved organic matter under certain conditions. If downwelling irradiance in turbid suspensions is absorbed largely by particulate organic matter—and by dissolved organic matter in nonturbid waters—then the penetration of light to organic matter would be similar in turbid and nonturbid systems if scaled to carbon-equivalent depths. The flux of photons to suspended particulate organic matter will depend on the competition for these photons by dissolved organic matter and the mineral component of sediments. Without knowledge of the specific absorbance characteristics of either of the sedimentary components (mineral and organic matter), it is difficult to make predictions for various field scenarios. We do not know the relative importance of the mineral versus organic components in light absorption for our samples, but the bleaching of particles upon organic matter oxidation (unpub. data) implies that the organic component is a strong contributor. Miller and Zepp (1979b) also found a weak, positive relationship between the specific attenuation coefficients of suspended particulates and their organic matter content, although they stressed that this relationship was inconclusive as to the contribution of organic matter to overall attenuation. Finally, the relative specific absorption of light by dissolved versus particulate organic matter is needed to assess competition between these two phases in waters containing significant concentrations of each.

Conversion of organic matter from particulate to dissolved form has a number of implications for its subsequent fate. In the case of riverine particulate organic matter arriving at the coast, the subsequent fate of the organic matter liberated by photodissolution will be in the water column rather than in the sediments. For example, it will become available for transport further into the ocean than would be the case in its particulate form. Remineralization of this material will affect water column, rather than sedimentary, ecosystems and diagenetic sequences.

It is unclear if our incomplete carbon budgets, defined as the lower POC plus DOC after irradiation relative to the initial POC before irradiation, represent oxidation or wall adsorption. If the former, then oxidation (presumably to carbon monoxide and dioxide) was presumably due to some combination of photochemical and metabolic reactions. These fates remain to be investigated. Dissolution of organic materials often enhances their bioavailability, and microbial respiration of products from photolysis of DOM is well established (e.g., Kieber et al. 1989). If significant mineralization occurred by either photochemical or biological pathways, then nitrogen accompanying the mineralized organic matter may become available for phytoplankton or bacterial uptake. This photochemical process may thus mobilize sedimentary nitrogen as a nutrient in coastal waters. Mayer et al. (1998) calculated that the magnitude of nitrogen release from particulates delivered by the Mississippi River to its depocenter could rival that of dissolved inorganic nitrogen delivery by river water, and this photochemical reaction has the potential to account for some of that release. The timing of nitrogen release would be delayed relative to the initial delivery of sediment to the coastal zone, providing a longer term source of nutrients.

Our experiments demonstrate that sedimentary organic matter is indeed susceptible to photodissolution by natural levels of sunlight to form dissolved organic matter—a reaction consistent with previous work on photolysis of dissolved organic matter. Our first-order examination of factors affecting this reaction finds light limitation and temperature to be the strongest controls on reaction extent. The potential extent of photodissolution of particulate organic matter resembles the total loss of OC observed for Mississippi River particulates after deposition on the shelf. Although further work is required to establish the contribution of this reaction to that loss, resuspension of deposited particulates seems to be the most likely process that will expose sufficient particles to sufficient photons.

## References

- ALLER, R. C. 1998. Mobile deltaic and continental shelf muds as fluidized bed reactors. *Mar. Chem.* **61**: 143–155.
- . 2004. Conceptual models of early diagenetic processes: The muddy seafloor as an unsteady, batch reactor. *J. Mar. Res.* **62**: 815–835.
- ALLISON, M. A., G. C. KINEKE, E. S. GORDON, AND M. A. GONI. 2000. Development and reworking of a seasonal flood deposit on the inner continental shelf off the Atchafalaya River. *Cont. Shelf Res.* **20**: 2267–2294.
- ANDREWS, S. S., S. CARON, AND O. C. ZAFIRIOU. 2000. Photochemical oxygen consumption in marine waters: A major sink for colored dissolved organic matter. *Limnol. Oceanogr.* **45**: 267–277.
- CORBETT, D. R., B. MCKEE, AND D. DUNCAN. 2004. An evaluation of mobile mud dynamics in the Mississippi River deltaic region. *Mar. Geol.* **209**: 91–112.
- ERTEL, J. R., AND J. I. HEDGES. 1983. Bulk chemical and spectroscopic properties of marine and terrestrial humic acids, melanoidins and catechol-base synthetic polymers, p. 143–163. *In* R. F. Christman and E. T. Gjessing [eds.], *Aquatic and terrestrial humic materials*. Ann Arbor Science.
- GELLER, A. 1985. Light-induced conversion of refractory, high molecular weight lake water constituents. *Schweiz. Z. Hydrol.* **47**: 21–26.
- GU, B., J. SCHMITT, Z. CHEN, L. LIANG, AND J. F. MCCARTHY. 1995. Adsorption and desorption of different organic matter fractions on iron oxide. *Geochim. Cosmochim. Acta* **59**: 219–229.
- JANKOWSKI, J. J., D. J. KIEBER, AND K. MOPPER. 1999. Nitrate and nitrite ultraviolet actinometers. *Photochem. Photobiol.* **70**: 319–328.
- , ———, ———, AND P. J. NEALE. 2000. Development and intercalibration of ultraviolet solar actinometers. *Photochem. Photobiol.* **71**: 431–440.
- KEIL, R. G., L. M. MAYER, P. D. QUAY, J. E. RICHEY, AND J. I. HEDGES. 1997. Loss of organic matter from riverine particles in deltas. *Geochim. Cosmochim. Acta* **61**: 1507–1511.
- KIEBER, D. J., J. MCDANIEL, AND K. MOPPER. 1989. Photochemical source of biological substrates in sea water: Implications for carbon cycling. *Nature* **341**: 637–639.
- KIRK, J. T. O. 1980. Spectral absorption properties of natural waters: Contribution of the soluble and particulate fractions to light absorption in some inland waters of South-eastern Australia. *Aust. J. Mar. Freshwater Res.* **31**: 287–296.
- . 1983. *Light and photosynthesis in aquatic systems*. Cambridge Univ. Press.
- LOEPPERT, R. H., AND W. P. INSKEEP. 1996. Iron, p. 639–664. *In* D.

- L. Sparks [ed.], Methods of soil analysis. Part 3, chemical methods. Soil Sci. Soc. Am. Book Series.
- MAYER, L. M. 1994. Surface area control of organic carbon accumulation in continental shelf sediments. *Geochim. Cosmochim. Acta* **58**: 1271–1284.
- , R. G. KEIL, S. A. MACKO, S. B. JOYE, K. C. RUTTENBERG, AND R. C. ALLER. 1998. The importance of suspended particulates in riverine delivery of bioavailable nitrogen to coastal zones. *Biogeochem. Cycles* **12**: 573–579.
- MILLER, G. C., AND R. G. ZEPP. 1979a. Photoreactivity of aquatic pollutants sorbed on suspended sediments. *Env. Sci. Technol.* **13**: 860–863.
- AND ———. 1979b. Effects of suspended sediments on photolysis rates of dissolved pollutants. *Water Res.* **13**: 453–459.
- MILLER, W. L., AND M. A. MORAN. 1997. Interaction of photochemical and microbial processes in the degradation of refractory dissolved organic matter from a coastal marine environment. *Limnol. Oceanogr.* **42**: 1317–1324.
- , ———, W. M. SHELDON, R. G. ZEPP, AND S. OPSAHL. 2002. Determination of apparent quantum yield spectra for the formation of biologically labile photoproducts. *Limnol. Oceanogr.* **47**: 343–352.
- AND R. G. ZEPP. 1995. Photochemical production of dissolved carbon from terrestrial organic matter: Significance to the oceanic organic carbon cycle. *Geophys. Res. Lett.* **22**: 417–420.
- MOORHEAD, D. L., AND T. CALLAGHAN. 1994. Effects of increasing ultraviolet B radiation on decomposition and soil organic matter dynamics: A synthesis and modeling study. *Biol. Fertil. Soils* **18**: 19–26.
- MOPPER, K., X. ZHOU, R. J. KIEBER, D. J. KIEBER, R. J. SIKORSKI, AND R. D. JONES. 1991. Photochemical degradation of dissolved organic carbon and its impact on the oceanic carbon cycle. *Nature* **353**: 60–62.
- MORAN, M. A., AND R. G. ZEPP. 1997. Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. *Limnol. Oceanogr.* **42**: 1307–1316.
- NEALE, P. J., W. W. HELBLING, AND H. E. ZAGARESE. 2003. Modulation of UVR exposure and effects by vertical mixing and advection, p. 107–136. *In* E. W. Helbling and H. Zagarese [eds.], UV effects in aquatic organisms and ecosystems. Royal Soc. Chem.
- OSBURN, C. L., AND D. P. MORRIS. 2003. Photochemistry of chromophoric dissolved organic matter in natural waters, p. 185–217. *In* E. W. Helbling and H. Zagarese [eds.], UV effects in aquatic organisms and ecosystems. Royal Soc. Chem.
- PARSONS, T. R., Y. MAITA, AND C. M. LALLI. 1984. A manual of chemical and biological methods for seawater analysis. Pergamon.
- PULLIN, M. J., C. A. PROGRESS, AND P. A. MAURICE. 2004. Effects of photoirradiation on the adsorption of dissolved organic matter to goethite. *Geochim. Cosmochim. Acta* **68**: 3643–3656.
- SANDVIK, S. L. H., P. BILSKI, J. PAKULSKI, C. F. CHIGNELL, AND R. B. COFFIN. 2000. Photogeneration of singlet oxygen and free radicals in dissolved organic matter isolated from the Mississippi and Atchafalaya River plumes. *Mar. Chem.* **69**: 139–152.
- SKJEMSTAD, J. O., L. J. JANIK, M. J. HEAD, AND S. G. McCLURE. 1993. High energy ultraviolet photo-oxidation: A novel technique for studying physically protected organic matter in clay- and silt-sized aggregates. *J. Soil Sci.* **44**: 485–499.
- TIETJEN, T., A. V. VÄHÄTALO, AND R. G. WETZEL. 2005. Effects of clay mineral turbidity on dissolved organic carbon and bacterial production. *Aquatic Sci.* **67**: 51–60.
- TREFRY, J. H., S. METZ, T. A. NELSEN, R. P. TROCINE, AND B. J. EADIE. 1994. Transport of particulate organic carbon by the Mississippi River and its fate in the Gulf of Mexico. *Estuaries* **17**: 839–849.
- WRIGHT, L. D., AND C. A. NITTROUER. 1995. Dispersal of river sediments in coastal seas—6 contrasting cases. *Estuaries* **18**: 494–508.
- ZEPP, R. G. 2003. Solar UVR and aquatic carbon, nitrogen, sulfur and metals cycles, p. 137–183. *In* E. W. Helbling and H. Zagarese [eds.], UV effects in aquatic organisms and ecosystems. Royal Soc. Chem.

Received: 16 May 2005

Accepted: 26 October 2005

Amended: 2 November 2005