Bioavailability of organic matter photodissolved from coastal sediments

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ABSTRACT: Photodissolution converts particulate organic matter to dissolved organic matter, which may affect its availability to heterotrophic organisms. We examined the ability of planktonic microbes to utilize photodissolved organic matter (PDOM) obtained from irradiating coastal sediments and a preparation of algal membranes. About half of the organic carbon that was photodissolved from algal particulate detritus was subsequently available to microbes over 2 wk of incubation in the dark, while that from the sediments appeared to be less bioavailable, the extent of utilization being 16 to 29%. Losses in total organic carbon during microbial incubation appeared as dissolved inorganic carbon, substantiating our inference of microbial usage. Accumulation of bacterial biomass was small relative to respiratory loss, which may be due to low growth efficiency by bacteria, or possibly grazing. Photoammonification converted some of the particulate nitrogen into inorganic ammonium; in the subsequent microbial processing of PDOM from sediments, this ammonium was reincorporated into organic matter. Thus, photodissolution shifts particulate organic matter to physical and chemical forms less available to metazoans and more available to osmotrophic microbes. This bioavailability, on a time scale of weeks, indicates that PDOM produced in nearshore resuspension zones can add fuel to planktonic microbial regeneration processes while the water remains on the shelf, but that major fractions of the PDOM are likely to be exported offshore.

KEY WORDS: Photodissolution · Bioavailability · Bacteria · Dissolved organic matter · Resuspended sediments · Photoammonification

INTRODUCTION

Sunlight can cause up to tens of percent of particulate organic matter (POM) to dissolve from sediments (Kieber et al. 2006, Mayer et al. 2006, Riggsbee et al. 2008) and from phytoplankton debris (Mayer et al. 2009a), a process termed photodissolution. This dissolution, or desorption, is much greater than occurs in the absence of light under similar resuspension conditions. Relatively fresh organic material is photodissolved from sediments, as indicated by high ^{14}C contents of POM lost from sediments upon irradiation (Mayer et al. 2009b). The subsequent fate of this photodissolved organic matter (PDOM), however, has

received little attention. While the bioavailability of irradiation products of pre-existing dissolved organic matter (DOM) has been extensively studied (e.g. Kieber et al. 1989, Miller & Moran 1997), that of PDOM has not.

The bioavailability of nutritional and contaminant organic materials in particulate form often increases upon their conversion to the dissolved form (Guerin & Boyd 1992, Keil et al. 1994). This phase conversion should especially benefit osmotrophic microbial communities because metazoans with enclosed digestive organs compete effectively for particulate food (Mayer et al. 2001). It follows, for reasons of both phase change and liberation of fresher organic mat-

ter, that POM released to the water column via photodissolution may be bioavailable to planktonic bacteria. Such availability could then affect the many biogeochemical processes associated with organic matter remineralization—e.g., carbon and nutrient cycling.

Deltaic sediments are potentially important sources of PDOM owing to the long residence time of fine-grained sediments in a shallow environment susceptible to frequent resuspension (Aller 1998). In this study we examined the potential for planktonic microbes to utilize PDOM that might be produced during sediment resuspension in the shallow deltaic environments of the Louisiana coastal zone. We also tested for PDOM formed from phytoplankton detritus—which might occur in any photic zone but is rich in the sediment delivered to the Louisiana coastal zone (Duan & Bianchi 2006). We used an experimental approach, inoculating solutions of PDOM and measuring the effects on bacterial numbers, organic and inorganic carbon, and various forms of nitrogen. We focused on a time scale of weeks, which represents the residence times of water masses in coastal waters, or in upper mixed layers, in order to test whether microbial loops on the shelf are stimulated by PDOM or whether the PDOM is largely exported offshore.

MATERIALS AND METHODS

Particle sources

We collected sediments from 3 sites in the Louisiana coastal region in order to answer our questions in the context of coastal sediment resuspension. One sample (FWB) was collected in the littoral region near Freshwater Bayou, about 85 km west of the mouth of the Atchafalaya River on 17 April 2003 (Estapa & Mayer 2010); its organic carbon concentration (2%) was dominated by terrestrial organic matter (Mayer et al. 2007). Two other sediments were collected near the Bird Foot delta of the Mississippi River. A nearshore sediment (P2S5) was collected at a water depth of 2 to 3 m a few kilometers outside the mouth of Baptiste Collette Bayou on 8 July 2004 (29° 25.008′ N, 89° 7.023′ W) shortly after a flood event of the Mississippi River. We used the 3 to 5 cm depth interval of the core which contained 2% organic carbon that was presumed to be dominantly terrigenous. An offshore sediment (MC-2) was collected east of the Birdfoot Delta (29° 01.268′ N, 88° 50.571′ W) at a depth of 200 m on 5 May 2004, and

we used the 2 to 3 cm depth interval whose 1.6% organic carbon concentration was 61% terrigenous (Mayer et al. 2007). These muds were collected by box corer or multicorer from a ship, freeze-dried, and stored frozen.

We also used phytoplanktonic particulate debris to assess the bioavailability of PDOM derived from a clearly labile starting material. We isolated the membrane-plus-wall fractions of a green flagellate—*Tetraselmis* sp. (strain 429; Reed Mariculture)—by bursting the cells using ultrasonication in an ice bath and centrifuging to remove the soluble, cytoplasmic, supernatant material. The precipitate was washed with deionized water and centrifuged several times. Only the particulate fraction was used, thereby specifically excluding the soluble cytoplasmic material that is released when the algae burst.

Irradiation and biodegradation experiments

Using these starting materials, we tested for the role of irradiation time in controlling the bioavailability of PDOM, the loss of PDOM, the production of mineralization products from various substrates, and the relative bioavailability of PDOM and DOM released from sediment in the dark. PDOM was always produced using simulated sunlight, using a Suntest XLS+; this instrument, with a solar filter, delivers a simulated solar spectrum with a total energy level of 760 W m^{-2}, which is equivalent to a mid-day subtropical sun.

To compare the bioavailability of PDOM from sediments and from algal particulate detritus, the P2S5 and MC-2 sediments and *Tetraselmis* detritus were irradiated for 68 h. Suspensions of 100 mg l^{-1} (*Tetraselmis* particulates) and 1000 mg l^{-1} (sediment samples) were made in artificial seawater that had all major salts except inorganic carbon (Na, K, Ca, Mg, Sr, Cl, Br, SO$_4$, BO$_3$, prepared according to the Aquil salts recipe of Price et al. 1988/89) and was spiked with a mixed trace element stock to provide final concentrations of 56 nmol l^{-1} Fe, 5 nmol l^{-1} Cu and Mo, 10 nmol l^{-1} Co, 19 nmol l^{-1} Zn, 77 nmol l^{-1} Mn and 1 μmol l^{-1} F. Suspensions were placed in 200 ml glass beakers to a depth of approximately 2.5 cm, covered with quartz lids, and irradiated from above. They were continually stirred with glass stir bars over a multiplace stirring plate during irradiation, and kept at 20 to 22°C by immersing the beakers in a bath in which cooling water circulated via a pump from an external isothermal bath. Evaporative losses were replaced by adding deionized water. At the end

of the irradiation, the suspensions were analyzed for total organic carbon and nitrogen, ammonium, and nitrite-plus-nitrate (see 'Analyses' below).

Residence times of water on the Louisiana shelf are weeks to months (Dinnel & Wiseman 1986) and are probably shortest in the colder months (Walker et al. 2005) when frequent resuspension by the passage of a cold front would enhance photodissolution. The filtrates from these irradiated suspensions were therefore immediately subjected to biodegradation for up to 60 d. Aliquots of 30 to 50 ml of filtrate from irradiations were spiked with monobasic potassium phosphate (to 10 µmol P l^{-1}), inoculated with 100 µl of surface seawater freshly collected from the shore of the Darling Marine Center in the Damariscotta estuary (Maine, USA), prefiltered through a Millipore polycarbonate membrane filter (8 µm), and placed into premuffled 125 ml glass flasks covered with black foil. The 8 µm pore size was chosen to allow a variety of bacteria to pass through the filter, despite the possible contamination by small grazers. These flasks were incubated on a slow rotary shaker in a light-tight box at 20 to 22°C. Evaporative losses were replaced with deionized water. Replicate flasks were sacrificed at 0, 3, 14 and 60 d, and subsampled by pipet while stirring. The sample at the t = 0 time point contained only dissolved organic carbon (DOC) because it had been filtered prior to incubation, but samples at the later time points contained a mixture of DOC and any new particulates (e.g. bacterial cells) that had formed during the biodegradation. Losses in total organic carbon (TOC) were considered to be respiratory losses (see 2 paragraphs below and 'Results'). For each time point, aliquots were analyzed for TOC, total nitrogen, dissolved inorganic nitrogen as ammonium, nitrate and nitrite, and bacterial numbers and sizes. We did not routinely measure pH in these experiments; in those that we did monitor, the initial pH (7 to 8) generally remained steady after irradiation, and either remained steady or decreased by no more than 0.5 pH unit after biodegradation.

A separate set of aliquots of the P2S5 PDOM filtrate were subjected to a single-time-point biodegradation experiment to test for the effects of various phosphate concentrations. Three aliquots were spiked as described in the paragraph above to give phosphate concentrations of 0, 2 and 10 µmol l^{-1}, and the trace metal micronutrients were identical to those listed in the paragraph above except that Fe was spiked to 10 nmol l^{-1}. These solutions were then inoculated and incubated as in the paragraph above, and sampled at 14 d only.

A subsample of the P2S5 sediment was also subjected to a separate irradiation and biodegradation experiment to assess whether losses of TOC during the biodegradation step indeed represented respiratory production of inorganic carbon. A 1000 mg l^{-1} sediment suspension in artificial seawater was irradiated for 48 h and then filtered through a Whatman GFF filter. The filtrate was inoculated with 100 µl of freshly collected seawater that had been prefiltered through a Millipore polycarbonate membrane filter (8 µm). A subsample was taken for dissolved inorganic carbon analysis. Duplicates of the filtrate for each incubation time point were then placed into 125 ml Erlenmeyer flasks that were sealed with silicone stoppers, covered in muffled aluminum foil, and sealed with Parafilm to hold them in place. The headspace for each flask was sampled using a stainless steel syringe for inorganic carbon analysis at the beginning of the incubation; the headspace volume was determined using separate experiments calibrating fill level of the flask to headspace volume, which then allowed us to calculate a mass of carbon. The solutions were then incubated in the dark for up to 13 d. At each time point, flasks were sacrificed for analyses of TOC, total nitrogen, inorganic carbon (headspace, and in solution), and bacterial numbers and sizes.

We tested for the role of irradiation time in controlling bioavailability using the FWB sediment. Suspensions of 1 g l^{-1} in artificial seawater (but with bicarbonate included) were irradiated for 0, 8 and 48 h, the PDOM filtered and then inoculated as in the previous paragraph. After 13 d of dark incubation, the inoculated samples were analyzed for TOC and nitrogen. In a related experiment, suspensions of the same sediment were subjected to 0 and 48 h of either irradiation or dark; in this case, the PDOM from the irradiated treatment and the dark control, that had each been incubated for 48 h, were submitted to a biodegradation experiment, as in the previous paragraph.

Analyses

Particulate organic carbon (POC) and particulate nitrogen on filters were analyzed on a Perkin-Elmer 2400B Elemental Analyzer, after gas-phase acidification with concentrated HCl to remove mineral carbonate. Filtrates and bacterial suspensions were analyzed for organic carbon or total nitrogen using a Shimadzu TOC-V CPH analyzer with a TNM-1 total nitrogen detector. For samples that had been incu-

bated for biodegradation, the carbon, consisting of DOC plus any ingrown POC, is reported as TOC. Concentrations of dissolved inorganic carbon (DIC) were measured on the Shimadzu analyzer by sparging without the combustion step. Gas-phase inorganic carbon was sampled from the headspace of stoppered incubation flasks with a gas chromatograph needle and syringe and injected into the manual injection port of the Shimadzu analyzer. Dissolved ammonium concentrations were determined on a Lachat QuikChem FIA+ analyzer, using the alkaline, phenol–hypochlorite spectrophotometric method as described in the instrument manual (method #31-107-06-1-B). The sum of nitrite and nitrate concentrations was measured spectrophotometrically on the Lachat analyzer using cadmium reduction of nitrate to nitrite, followed by spectrophotometric determination of the diazo dye formed with sulfanilamide (method #31-107-04-1-C). Some total dissolved nitrogen measurements were performed on the Lachat instrument, using the same nitrate-plus-nitrite method following oxidation by a heated alkaline persulfate-UV digestion using the Lachat preparation module (method #31-107-04-3-A). Organic nitrogen was calculated as total nitrogen minus inorganic nitrogen forms.

Samples from biodegradation experiments for bacterial analysis were preserved by adding Lugol's iodine solution (Fluka 62650) to PDOM samples in a 1:25 ratio in glass scintillation vials and stored at 5 to 6°C in the dark. For counting and sizing bacteria, preserved samples were added to Hoeffer box wells, and 25 µl of 12 mmol l^{-1} sodium thiosulfate solution were added to each well for each millliliter of pre-

served sample to remove the color of the iodine. After 5 min, 6 µl of a 7 mmol l^{-1} solution of 4′,6-diamidino-2-phenylindole (DAPI) was added to the well for each milliliter of sample, and filtered onto black polycarbonate filters (0.2 µm). The filters were mounted on microscope slides with a drop of immersion oil and then covered with a second drop of oil and a cover slip. Slides were stored at –16°C in the dark for up to 2.5 yr; tests showed no change in the numbers or size of bacteria during storage. Bacteria were counted with a Zeiss epifluorescence microscope using a 125× oil immersion lens. Photographs of the cells were captured with a KX-85 digital camera (Apogee Instruments) using CRI Microcolor Imaging software. Cell images were processed and measured using Image Tool (University of Texas Health Science Center). Cells were categorized as either cylindrical rods or spherical cocci, their volumes were individually calculated by image analysis, and dry weights were determined using the size-dependent allometric relationship of Loferer-Krössbacher et al. (1998); finally, the carbon content was calculated assuming a C:dry weight ratio of 0.5.

RESULTS

Phytoplankton particulate detritus and sediments each photodissolved strongly under simulated sunlight after 68 h, with organic matter losses from the particulate phase of about a third in each case (Table 1). The majority of this photodissolution appeared as PDOM, producing hundreds of µmol l^{-1} of DOC and tens of µmol l^{-1} of dissolved organic

Table 1. Particulate and dissolved compositional data for irradiation experiments with *Tetraselmis* membranes, offshore sediment (MC-2) and nearshore sediment (P2S5). All concentrations are means of triplicates and are given as µmol l^{-1} (µM); C:N values are molar ratios. POC = particulate organic carbon; PN = particulate nitrogen; C:N$_P$ = C:N of particulates; DOC = dissolved organic carbon; DON = dissolved organic nitrogen; C:N$_D$ = C:N of dissolved organic matter; NH$_4$ = dissolved ammonium; NO$_x$ = nitrite plus nitrate. All tabulated values used 10 µmol P l^{-1}. Numbers in parentheses after data values are one standard deviation

Irradiation	POC (µM)	PN (µM)	C:N$_P$	DOC (µM)	DON (µM)	C:N$_D$	NH$_4$ (µM)	NO$_x$ (µM)
Tetraselmis								
Before	3298 (226)	408 (36)	8.1	227 (9)	4.8 (1)	47	4.4 (0.3)	0.8 (0.02)
After 68 h	2309 (187)	302 (25)	7.6	933 (39)	61 (8)	15.3	13.4 (1)	1 (0.08)
MC-2								
Before	1449 (34)	132 (11)	11.0	35 (8)	3.9 (0.4)	9.0	1.1 (0.2)	0.6 (0.03)
After 68 h	860 (18)	87.9 (6)	9.8	304 (4)	24 (0.7)	12.7	3.7 (0.1)	0.8 (0.23)
P2S5								
Before	1646 (29)	137 (9)	12.0	45 (6)	3 (1.5)	15	2.1 (0.3)	0.9 (0.05)
After 68 h	1104 (127)	107 (12)	10.3	338 (37)	25 (1.5)	13.5	4.8 (0.1)	1 (0.003)

nitrogen from the suspensions. The amount of DOC that appeared was less than the amount of POC lost, presumably due to photo-oxidation of part of the organic matter to CO_2 (Estapa & Mayer 2010). The C:N ratios of the particulate organic matter decreased in each case, and the PDOM (corrected for DOM present before the irradiation) had C:N ratios ranging from 12.7 to 13.6 (mol/mol). Ammonium also appeared in each suspension; this photoammonification accounted for 11 to 14% of total nitrogen photodissolution. Photoammonification has been observed previously upon irradiation of POM (Southwell et al. 2010) and DOM (Bushaw et al. 1996, Vähätalo & Zepp 2005). Very small increases in nitrite-plus-nitrate were found, accounting for on the order of 1% of total nitrogen photodissolution.

After inoculation, PDOM solutions showed significant losses of TOC of up to 47, 22 and 29% for *Tetraselmis* particulate detritus, the nearshore sediment (P2S5) and the offshore sediment (MC-2), respectively, on a time scale of days to weeks (Table 2). The bulk of the losses in TOC occurred by 14 d. The 60 d time course experiment using the nearshore sediment (P2S5) showed a significant loss of total nitrogen (up to 40%) over time. Because we checked carefully for gravitational settling of particulates at all stages of the sampling process, and believe that we measured all possibly important nitrogenous materials in the fluid phase, we interpret this loss as

probably due to biofilm formation on the walls of the incubation flasks. The results of this 60 d time course experiment were therefore excluded from our interpretation of the data.

In the 14 d experiment with nearshore (P2S5) sediment, we tested for the effect of different phosphate concentrations on the biodegradation of PDOM. We found losses of TOC of 23, 18 and 16% at 0, 2 and 10 µmol P l^{-1}, respectively (Table 2). This apparent inverse relationship between phosphate concentration and the loss of TOC is not strong, and is not statistically significant given coefficients of variation of 14% after error propagation.

Photoproduced ammonium showed different fates during the biodegradation time courses, depending on the source of the PDOM (Table 2). The PDOM from the irradiation of *Tetraselmis* particulate detritus underwent further net ammonification under microbial decay, increasing to Day 14 and then remaining unchanged at Day 60. In the offshore (MC-2) sediment sample, ammonium initially increased slightly by Day 3, but then fell strongly thereafter by Day 60. A strong decrease in ammonium was found with PDOM from the nearshore sediment between Days 0 and 14. Independently of ammonium production or consumption, we observed consistent lowering of the C:N ratios of organic matter accompanying decreases in TOC.

Bacterial cell numbers increased during the incubation, by at least an order of magnitude, to values of

Table 2. Particulate and dissolved compositional data for biodegradation experiments with *Tetraselmis* membranes, offshore sediment (MC-2), and nearshore sediment (P2S5) (see Table 1). All concentrations are means of triplicates and are given as µmol l^{-1} (µM); C:N values are molar ratios. TOC = dissolved plus particulate organic carbon; TON = dissolved plus particulate organic nitrogen; C:N_T = C:N of dissolved plus particulate organic matter; NH_4 = dissolved ammonium; NO_x = nitrite plus nitrate; Bact-C = carbon contained in bacterial cells. Numbers in parentheses after data values are one standard deviation. Parenthetical expressions at P2S5 14 d are concentrations of phosphate spikes; all other tabulated values used 10 µmol P l^{-1}

Biodegradation (d)	TOC (µM)	TON (µM)	C:N_T	NH_4 (µM)	NO_x (µM)	Bact-C (µM)
Tetraselmis						
0	933 (39)	61 (8)	15.4	13.4 (1)	1 (0.08)	0.8 (1.1)
3	736 (26)	50 (11)	14.6	18 (1.8)	0.9 (0.28)	14.7 (0.5)
14	503 (13)	36 (7)	14.1	26 (4.2)	1.3 (0.17)	23.6 (0.7)
60	494 (23)	39 (11)	12.6	26 (4.5)	0.4 (0.39)	14.8 (7.9)
MC-2						
0	304 (4)	24 (0.7)	12.7	3.7 (0.1)	0.8 (0.23)	0.09 (0.1)
3	265 (12)	21 (3)	12.7	4.7 (0.3)	1.0 (n.a.)	1.3 (0.2)
14	243 (7)	23 (3)	10.4	4.1 (0.9)	1.2 (0.08)	3.0 (0.7)
60	216 (13)	27 (1)	8.1	1.5 (0.5)	1.3 (0.15)	2.0 (0.7)
P2S5						
0	338 (37)	25 (1.5)	13.7	4.8 (0.1)	1 (0.003)	0.3 (0.04)
14 (P = 10)	284 (9)	29 (2)	9.9	1.3 (0.3)	1 (0.06)	7.0 (1.5)
14 (P = 2)	278 (11)	29 (1)	9.8	1.3 (0.1)	1 (0.13)	8.5 (0.9)
14 (P = 0)	262 (9)	28 (2)	9.4	1.1 (0.3)	1 (0.11)	4.5 (0.9)

up to 1×10^7 cells ml^{-1} for the *Tetraselmis* particulate detritus, 4×10^6 cells ml^{-1} for the nearshore (P2S5) sediment and 1.7×10^6 cells ml^{-1} for the offshore (MC-2) sediment. Grazing may have reduced bacterial production, as inocula were filtered at 8 μm, although no grazers were observed on the slides. Aggregation of cells was observed by Day 60, leading to greater variance in the counts. The carbon content of these cells, calculated from measured cell sizes, reached values of up to 24 μmol l^{-1} (Table 2). These bacterial carbon values are small compared to both TOC standing stocks and the TOC lost from the suspensions during the incubations.

The experiment using PDOM from the nearshore sediment (P2S5) — to compare the loss of TOC with inorganic carbon gain — found that they were equivalent, with 63 ± 29 μmol l^{-1} (mean ±1 SD) of TOC lost and 62 ± 16 μmol l^{-1} of inorganic carbon (DIC plus headspace CO_2) produced over the 13 d incubation (Fig. 1). This agreement provides confidence that the TOC losses reported in the other experiments reported here do represent primarily remineralization of organic matter. The 24% loss of TOC over 13 d in this experiment corroborates that found in these other experiments. Bacterial growth produced communities of up to 5.7×10^6 cells ml^{-1} by Day 13. Converted into carbon, this cellular net production reached 10 μmol l^{-1} over the 13 d — a result similar to that with the other experiment with this sediment (Table 2).
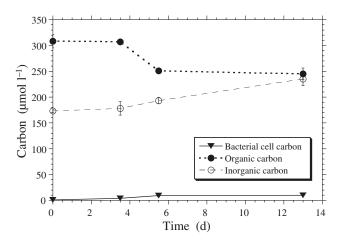

Fig. 1. Total organic carbon lost, total inorganic carbon gained, and bacterial cellular carbon accumulating during biodegradation of photodissolved organic matter (PDOM) from irradiated nearshore sediment (P2S5). Inorganic carbon is the sum of dissolved inorganic carbon (DIC) and headspace CO_2, normalized to the volume of liquid. Organic carbon is from direct measurement. Bacterial cellular carbon was calculated from cell numbers and sizes. Error bars are ±1 SD
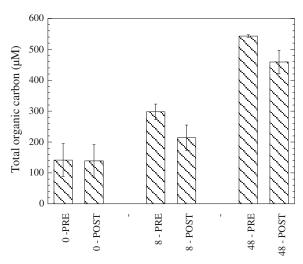

Fig. 2. Effect of irradiation time on biodegradability of photodissolved organic matter (PDOM) from the Freshwater Bayou (FWB) sediment. Bars represent total organic carbon (TOC) after irradiation for 0, 8 or 48 h, either before (PRE) or after (POST) inoculation and biodegradation for 13 d. Error bars are ±1 SD

Only miniscule changes in nitrite-plus-nitrate were observed in both the irradiation and biodegradation experiments. Changes were observed in both directions, with none >0.6 μmol l^{-1}.

The 68 h irradiation used in these experiments is probably longer than the kind of irradiation experienced by sediments in the field. To test whether the extent of biodegradation was affected strongly by this long irradiation, we subjected 1 of the nearshore sediments (FWB) to 0, 8 and 48 h of irradiation and incubated the resultant filtered PDOM from each. The DOC yields were 142, 298 and 543 μM, respectively (Fig. 2). The loss in TOC from the t = 0 treatment was 2 (±75)%, while the 8 h PDOM lost 28 (±22)%, and the 48 h PDOM lost 15 (±8)% (Fig. 2). While there may be a reduction in bioavailability between the 8 and 48 h irradiation times, the high variance prevents any significant differences being inferred. Further, both microbial biodegredation extents are similar to those of PDOM from the 68 h irradiation found for the other sediments. The incident irradiance given to these suspensions is approximately equivalent to that received at mid-day at the latitude of Louisiana. Assuming 6 h d^{-1} of this irradiance, these experiments received light doses that are roughly equivalent to those received in the field during a range of 1 to 11 d. The actual irradiance received per particle will depend on many factors — e.g. depth of water column, presence of competing light absorbers — and are beyond the scope of this paper. Nevertheless, for this range of irradiation

times, there was no discernible effect of irradiation time on bioavailability; in all cases there was significant, but not major, biodegradation of PDOM over a period of 2 wk.

As a variation on this experiment, we compared bioavailability of dissolved organic matter from the same FWB sediment incubated for 48 h with and without irradiation. The PDOM concentration in the 48 h dark control (96 ± 10 µM) was equivalent to the amount released at time = 0 (78 ± 23 µM), while the concentration increased to 376 ± 55 µM after 48 h of irradiation. This release of PDOM was lower than that recorded in the other experiment with this sediment, and may be related to slightly different pH and/or stirring conditions between the 2 experiments. The organic carbon in the 48 h dark control showed small biodegradation of 6 (±21)%, while the sample irradiated for 48 h showed a greater loss of 24 (±38)%, corroborating results from the experiment (Fig. 2). Again, large propagated variance prevents differentiating between bioavailability of DOM among treatments, although, in all cases, PDOM from irradiated treatments showed greater biodegradability than did DOM dissolved under dark conditions. For these non-irradiated treatments, our results corroborate those of Butman et al. (2007) who found that soil organic matter, desorbed into seawater, biodegraded by tens of percent. Samples irradiated for 8 and 48 h in this experiment yielded biodegradation results similar to those of the 68 h irradiation of other sediments.

DISCUSSION

This study shows that the DOM resulting from irradiation of sediments and algal detritus is partially bioavailable on a time scale of weeks. Together, the loss of TOC (catabolism) and the bacterial cell carbon measurements indicate that at least about half of the PDOM from the *Tetraselmis* particulate detritus was bioavailable. At 14 d there was a loss of 430 µmol l^{-1} organic carbon, which we interpret as remineralization, plus an increase of 23 µmol l^{-1} carbon in bacterial biomass, all relative to 933 µmol l^{-1} organic carbon in the PDOM at the beginning of the incubation.

Sedimentary PDOM showed consistently lower, although still significant, bioavailability. For the offshore sediment sample, at least 21% of the initial PDOM was bioavailable by 14 d, using the same logic as for algal detritus. For the nearshore (P2S5) sediment, at least 18% was bioavailable by 13 d. Bacterial numbers were not measured for the experi-

ments with the nearshore FWB sediment but, assuming that bacterial production was similarly low in proportion to the loss of TOC, <28% of its PDOM was bioavailable over 13 d.

These 3 sediments include 2 from the nearshore zone—one each from the widely separated Mississippi and Atchafalaya depositional regimes. They represent sediment most likely to be resuspended in water shallow enough to allow for photochemical action; these 2 sediments contain primarily terrestrial organic matter inherited from the river. The third sample (MC-2) derived from a deeper water site and represents an opportunity to examine the bioavailability of PDOM from sediment with a higher proportion (39%) of marine organic matter. Notwithstanding these different sources, the PDOM bioavailability was similar among the 3 sediment samples, and indeed similar to values reported for non-irradiated DOM in a range of aquatic systems (Sondergaard & Middelboe 1995). Thus, microbes can use significant, but not major, fractions of PDOM from sedimentary sources for catabolism plus biomass creation on a time scale of 2 wk.

It would be expected that fresh algal material would yield PDOM of higher bioavailability than that from sediments, and our findings corroborate this expectation. Nevertheless, the 2- to 3-fold difference seems smaller than is probably the case for the relative bioavailability of the original particulate substrates. This narrowed difference is perhaps due to preferential photodissolution of relatively young—and thus probably more bioavailable—organic matter (Mayer et al. 2009b). Wetz et al. (2008) found that about half of the DOC derived from phytoplankton, via non-photolytic processes, biodegraded over 3 d, while we observed only about 20% biodegradation at this time point (Table 2); as their methods and materials differed from those reported here, no direct comparison should be drawn, but over the longer time scale of 14 d our results reached the same extent of decay as was reported for their shorter experiments.

Our measurements may have missed production by non-bacterial organisms, such as protozoan grazers, or production of detrital organic carbon such as dead cells, dissolved metabolites or mucus secretions. These products would appear in the measured TOC pool and would thus not show up as either losses of TOC or increases in cellular bacterial-C. The lack of grazers observed during the bacterial counts, however, argues against a major role for grazing in our experiments. Nevertheless, our assessment of the extent of bioavailability is restricted to

catabolic production of inorganic carbon and net anabolic production of live bacterial biomass.

This omission of non-bacterial production also makes problematic an accurate inference of bacterial assimilation efficiencies from PDOM. Further, small losses of total nitrogen from the suspensions allow for cell production in biofilms of the order of the net cell production we measured in suspension. Nevertheless, apparent bacterial growth efficiencies—calculated as net bacterial cellular carbon increase divided by the sum of net bacterial cellular carbon increase and loss of TOC (Tranvik & Höfle 1987)—were 10, 5 and 3% over Days 3, 14 and 60, respectively, for the incubation of *Tetraselmis* particulate detritus. The MC-2 sediment yielded even lower values of 4 and 5% at Days 3 and 14, respectively. The P2S5 sediment experiment, assessing DIC production (Fig. 1), yielded 13% at Day 13; values for earlier days have large variances. If these values are approximately correct, then these bacterial growth efficiencies are generally similar, or lower, than is typical in such experiments with irradiated DOM (e.g. Pullin et al. 2004), which are, in turn, often lower than those on non-irradiated DOM (Farjalla et al. 2001, Smith & Benner 2005). Such low efficiencies might be due to photochemical production of highly oxygenated substrates, with low energy contents (Bertilsson & Tranvik 1998). Estapa & Mayer (2010) found that irradiation of marine particulates led to higher oxygen uptake, per mole of DIC produced, than has been reported for irradiation of DOM, consistent with significant production of these oxygenated compounds.

Biodegradation of PDOM in the field might follow pathways different from those found in our experiments, which tested for availability to free-living microbes. Our experimental design isolated PDOM from both its particulate source and from other dissolved organic matter likely to be present in the field, preventing interaction with other water-column processes. PDOM in the field is probably pulsed into water masses on much shorter time scales and, hence, at lower concentrations than in our experiments. This PDOM would mix with pre-existing DOM, and each would probably be subject to further photochemical transformations that can either increase or decrease their bioavailability (Kieber et al. 1989, Miller & Moran 1997, Benner & Ziegler 2000, Tranvik & Bertilsson 2001, Pullin et al. 2004).

Simple phase shift of compounds from particulate to dissolved forms should shift availability from multicellular organisms to osmotrophic unicellular ones, but photochemical changes to molecular forms may enhance this shift in at least 2 ways. First, photochemical photoproduction of low-molecular-weight carbonyl compounds (Kieber et al. 1989, Zhou & Mopper 1997) creates substrates uniquely accessible by bacteria (Bertilsson & Tranvik 1998). Such compounds would elevate the C:N ratio of PDOM, and bacterial respiration of these substrates may be one explanation for the drop in C:N ratio over time (Table 2), although even non-irradiated DOM tends to drop its C:N ratio during bacterial incubation (Wetz et al. 2008). Second, photoammonification converted particulate nitrogen to a form that favors its use by microbes, and provides a particle-sourced analog to photoammonification from dissolved humic materials (Bushaw et al. 1996). PDOM with high C:N ratios (Table 1) might require this ammonium for the formation of microbial biomass, and mixtures of ammonium with dissolved organic matter with a varying C:N ratio thus lead to varying assimilation efficiencies (Goldman et al. 1987, Touratier et al. 1999). The ammonium uptake during the incubation of the sediment-derived PDOM (Table 2) may represent such bacterial assimilation of this compound. Of course, we do not know whether the ammonium and high-C:N PDOM came from molecules that were previously bioavailable, and hence cannot assess the net effect on bioavailability of the separate dissolution of these 2 materials.

Photodissolution in a coastal environment probably occurs during sediment resuspension, because various light absorbers in the water column shield the undisturbed bottom from irradiation. A photochemical shift in bioavailability from multicellular to unicellular consumers will be accompanied by a shift from sediment to water-column heterotrophs. Because the decay of sedimentary organic matter in deltaic environments, such as the Louisiana coastal zone, is usually dominated by sediment microbes (Alongi & Robertson 1995, Aller & Aller 2004), this vertical shift may be more significant than the phyletic one. The PDOM bioavailability of only a few tens of percent, on shelf mixing time scales, further implies that the eventual metabolism of the PDOM will more likely occur offshore rather than in the coastal region. Because photodissolution is enhanced by higher temperatures, as well as by higher light fluxes (Mayer et al. 2006), this shunting toward offshore, planktonic, microbial communities will be stronger in warmer and shallower ecosystems.

Phytoplankton production may also be enhanced by photoammonification (Southwell et al. 2010), as found for irradiation of dissolved organic matter (e.g. Vähätalo & Järvinen 2007). Such input of sedimen-

tary nitrogen into planktonic primary production would add to the benthic–pelagic flux that otherwise occurs during resuspension (Lawrence et al. 2004).

The lack of nitrification in our biodegradation experiments does not necessarily apply to field situations, because nitrifying bacteria are usually associated with suspended particles (Brion et al. 2000) that were eliminated from our pre-filtered biodegradation experiments. Nitrification may be more important in the typically muddy coastal waters of the Mississippi delta region.

In summary, significant—although not major—fractions of PDOM are susceptible to metabolism by microbial populations in coastal water columns, although the majority will probably persist as DOM to be exported offshore. Many aspects of PDOM bioavailability reflect previous findings from the irradiation of DOM, albeit with the large difference that they apply to organic material derived from solid phases. These microbial reactions will probably affect pathways and locations of both primary and secondary production. The net impacts on microbial production may well differ from those shown in our experiments, as these impacts will depend on factors such as pre-existing water-column communities, nutrients and suspended sediments.

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