

**Photochemical changes in chemical markers of sedimentary organic matter
source and age**

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Abstract

Several chemical markers of organic matter source and age are shown to be susceptible to light-induced alteration. To test for the photochemical lability of markers previously employed for sediments from the Louisiana coastal zone, we subjected sediments under resuspension conditions to simulated sunlight, and monitored changes in C:N and Br:OC ratios, $\delta^{13}\text{C}$, $\Delta^{14}\text{C}$, and lignin composition. Markers of terrigenous origin (high C:N, lignin) decreased and $\delta^{13}\text{C}$ became enriched in sediments containing primarily terrigenous organic matter, while a marker of marine organic matter (Br:OC) decreased in samples containing significant contributions from this source. Preferential loss of ^{14}C from all sediments indicated enhanced photochemical lability of organic matter of relatively recent origin, consistent with the changes in chemical markers. Most, but not all, experimental alterations are consistent with field distributions of these markers. Relatively small experimental changes in the markers in combination with confounding processes in the environment, however, prevent these parallel trends from providing any more than a consistency test for the importance of photochemical reactions in this region.

Keywords: photochemical; organic matter; isotopes; lignin; bromine; sediments; USA, Mississippi

1. Introduction

A burgeoning literature over the past two decades indicates that dissolved organic matter exposed to sunlight undergoes a variety of optical, chemical and biological changes (cf. Osburn and Morris, 2003). Among these changes are alterations of chemical attributes that indicate the history and source of the organic matter. For example, light degrades dissolved lignin, not only reducing its overall concentration but also producing identifiable degradation products, and altering ratios of compounds used to detect plant sources (Opsahl and Benner 1998; Hernes and Benner, 2003).

Fewer studies have addressed the photochemistry of organic matter associated with particulates. Contaminants associated with sediments and soils can be photodegraded (Miller and Zepp, 1979; Balmer et al., 2000). Natural levels of sunlight have been shown to photodissolve sedimentary organic matter, a reaction that possibly leads to significant losses from the particulate phase in coastal zone (Mayer et al., 2006; Kieber et al., 2006). Whether photochemistry acts to alter compounds on the solid or dissolve them away, there will be net change in the composition of the remaining particulate material. Because as much as several tens of percent of particulate organic matter may be subject to photo-dissolution, and photochemical alteration of the remaining organic matter remains possible, this process has the potential to radically alter the composition of the residuum.

Sources of organic matter to the sediments of the Louisiana coastal zone have been studied for many years. Different chemical indicators have given varying estimates of sources and consequently affected our understanding of the

redistribution of organic matter types (e.g., Hedges and Parker, 1976; Goñi et al., 1998; Bianchi et al., 2002; Gordon and Goñi, 2004; Bianchi et al., 2006; Mayer et al., 2007; Mead and Goñi, 2008; Waterson and Canuel, 2008). Sediment delivered by the Mississippi River commonly deposits quickly nearshore, and spends months in these shallows before burial or removal to deeper and more permanent depocenters (Allison et al., 2000). During this period of resuspension in the shallows, photochemical alteration of these particulates is likely (Aller, 1998; Mayer et al., 2006). Thus, the possibility that irradiation may affect some of these chemical source indicators in sediments needs to be addressed.

In this study, we employ experiments to examine the impact of intense irradiation on some chemical indicators used in the Louisiana coastal zone. Our purposes are to determine (1) how irradiation affects various chemical markers, and (2) to test for consistency between observed experimental changes and data from field sites.

2. Methods and Materials

Three sediment samples were selected to represent a range of riverine to marine end-members found in this region. Material delivered by the Mississippi River was represented by suspended sediment collected from surface waters in July, 2004 in the lower part of the Bird's Foot delta at Venice, LA ("Venice"). We mixed ca. 200 L of muddy river water with ca. 40 L of clear seawater (collected the prior day from the mid-water column to the east of the Bird's Foot delta), to promote flocculation of the river mud. After overnight settling onboard ship, the clear

supernatant was decanted, and the remaining concentrate returned to the lab for clarification by centrifugation. A second sample represented nearshore suspended sediment containing a small contribution of marine organic matter, collected from the coastal muddy plume of the Atchafalaya River. This sample was collected using a small boat within 100m of shore, in a water depth of 1-2m, at a site 400m west of the shipping channel at Freshwater Bayou (“FWB”) in April, 2003. The highly turbid sample was allowed to settle, the clear supernatant decanted and the remaining concentrate centrifuged to collect the sediment. Last, near-surface mud (1-3 cm) from the mid-shelf region represents sediment that has had a longer opportunity to lose terrigenous organic matter and gain marine organic matter. We used a sample collected west of the Bird’s Foot delta (28.93°N, 90.07°W, depth = 72 m) in May, 2005 (“P4S8” – Mayer et al., 2007). All sediments were freeze-dried for storage and, upon thawing, sieved at 63 μm prior to use in experiments.

To test for bromine loss in sediments that contain primarily marine organic matter, we also performed experiments on two sediment samples collected in the Gulf of Maine. We used the 2-3 cm depth interval from cores collected in August, 2004 - one from 234 m depth in Wilkinson Basin and the other from 162 m depth in Jeffreys Basin. These samples were also freeze-dried and stored frozen until the experiments.

Our experimental design tested for the impact of irradiation, such as might occur in the Louisiana nearshore zone, on chemical markers (Mayer et al., 2006). Accordingly, we conducted irradiation experiments in a Suntest XLS+, which provides an intensity (765 W cm^{-2}) and spectrum of UV and visible wavelengths

similar to that of a mid-day, sub-tropical sun. To provide sufficient sediment for chemical analyses, we made up 500 mg L⁻¹ suspensions in artificial seawater (Br-free). This sediment concentration is high, but within the range of surficial concentrations observed in the field during resuspension events (Kineke et al., 2006). Suspensions were made up in replicate glass beakers, covered with UV-transparent, quartz cover plates, and placed under the lamp in a multiple-place stirring plate in a water bath maintained at 20 to 22°. These beakers were irradiated from above. The Gulf of Mexico samples were irradiated and stirred continuously for 70 h. The Gulf of Maine samples were irradiated and stirred for 68h in a 970 mg L⁻¹ suspension. Continuous irradiation was chosen to maximize the role of light and minimize the role of microbial processing during the experimental period. Dark controls, consisting of similar suspensions incubated at the same temperature and shaded by black foil, tested for non-photochemical changes in composition. Upon termination of the irradiation, suspensions were clarified immediately by centrifugation for 20 min. at 12,000 rpm. Dark controls were clarified and stored by the same procedure. Sediment was then freeze-dried and split for the various analyses.

Particulate organic carbon and total nitrogen concentrations were analyzed after vapor-phase acidification (concentrated HCl) on a Perkin-Elmer 2400B Elemental Analyzer, with an analytical coefficient of variation of <5%. Dissolved organic carbon concentrations in the supernatants were analyzed using the non-purgeable organic carbon method on a Shimadzu TOC-V CPH analyzer. Carbon isotopes (¹⁴C and ¹³C) in the particulates were measured by accelerator mass

spectrometry at the Woods Hole NOSAMS facility, using procedures published at <http://www.nosams.who.edu/clients/data.html>. Only singlicates were analyzed for changes in the carbon isotope composition of sediments upon irradiation. Analysis for bromine was performed by instrumental neutron activation analysis by Activation Labs (Ancaster, Ontario), with an analytical coefficient of variation of 2%.

For lignin analysis, sediment sub-samples were first washed in distilled water to remove sea-salt. Samples were analyzed for lignin-phenols using the cupric oxide method of Hedges and Ertel (1982), as modified by Goni and Hedges (1992). Samples were weighed to include 3 to 5 mg of organic carbon and transferred to stainless steel reaction vessels. Samples were digested with CuO in 2N NaOH in the absence of O₂ at 150°C for 3 hours. Reaction products were extracted with diethyl ether, dried, and converted to trimethylsilyl derivatives with trimethylsilane (TMS) using Bis-(trimethylsilyl)-trifluoroacetamide (BSTFA). Lignin oxidation products were analyzed with a Varian model CP 3800/2000 Gas Chromatograph/Mass Spectrometric Detector (GC-MS).

Quantification was based upon internal standards; new response factors were generated with each batch by using a mixed standard of the target compounds. The average coefficient of variation, based upon duplicates, for the sum of lignin-phenols is less than 8% while that for individual compounds ranged from 1 to 19%. Eight lignin phenols, *p*-hydroxycinnamic acid, vanillin, acetovanillone, syringaldehyde, vanillic acid, acetosyringone, syringic acid and ferulic acid, were quantified and used as molecular indicators for source and

diagenetic state of vascular plant tissue. Lambda-8 (Λ_8) is defined as the total weight in mg of the sum of vanillyl (vanillin, acetovanillone, vanillic acid), syringyl (syringaldehyde, acetosyringone, syringic acid), and cinnamyl (*p*-hydroxycinnamic and ferulic acid) phenols, normalized to 100 mg of sediment organic carbon (Hedges and Parker, 1976). Total cinnamyl/vanillyl (C/V) and syringyl/vanillyl (S/V) phenols are used as indicators of plant source while acid:aldehyde ratios of vanillic acid to vanillin ((Ad/Al)_v) and syringic acid to syringaldehyde ((Ad/Al)_s) were used as indices of lignin decay (Hedges et al., 1988).

All data reported in this paper, with the exception of carbon isotope compositions, agree reasonably well with data from other experiments that we conducted; those data are not presented here.

3. Results and Discussion

3.1 Carbon and nitrogen

Under the conditions of 70 h irradiation in a 500 mg L⁻¹ suspension, the Gulf of Mexico samples lost 27 - 37% of their particulate organic carbon (Table 1). Almost all of this loss appeared in the dissolved organic carbon pool – 99%, 93%, and 95% in the Venice, FWB, and P4S8 samples, respectively - as found in previous work (Mayer et al., 2006). The small remainders were likely photo-remineralized to dissolved inorganic carbon (Estapa, unpub. data). Particulate

organic carbon concentrations in the dark controls remained essentially unchanged. Somewhat lower percentages of total nitrogen were lost from the particulates.

The C:N ratio of the remaining sediment thus declined by about one integer unit for each sediment. The organic matter lost from the particulates, calculated from changes in solid phase composition, had a much higher C:N than that of the bulk particulate organic matter in the non-irradiated sediments. The highest values (13, 15) of this lost material were in the samples dominated by terrigenous organic matter. Because this photodissolved material was partially remineralized, these C:N values of material lost from particulates do not necessarily correspond exactly to the C:N values of photodissolved organic matter.

3.2 *Bromine:carbon ratios*

Most Br in Louisiana coastal sediments derives from the ocean and is presumably associated with marine-derived organic matter (Mayer et al., 2007). The Br:OC ratios of the initial sediments prior to irradiation indicate that marine organic matter made up 15% and 33% of the total organic matter of samples FWB and P4S8, respectively. These values differ slightly from those reported in Mayer et al. (2007), due to sub-sampling and sample pretreatment. The content of Br decreased by about 3/4 during irradiation - i.e. to a much greater extent than that of total organic matter (Table 1). The concentrations of Br remaining in the sediments after irradiation were as low as typical riverine suspended sediments (Mayer et al., 2007), implying that most marine-derived Br was lost. The high Br:OC ratios of the

missing organic matter (3.7, 5.8), calculated from mass balance, were consistent with a dominantly marine component in the photodissolved organic material.

Sediments from the Louisiana coastal zone rarely are dominated by marine organic matter, so we also tested sediments from the Gulf of Maine which typically contain very little terrestrial organic matter (Mayer et al., 1988). These two samples – from Wilkinson Basin and Jeffreys Basin - lost 27% and 26% of their TOC, and 82% and 86% of their Br contents, respectively. Their Br:OC ratios decreased from 6.2 to 1.5 mg-Br gOC⁻¹ and 7.8 to 1.5 mg-Br gOC⁻¹, respectively, thereby also assuming largely terrestrial values upon irradiation. Because the remaining organic matter must remain largely marine-derived, we infer that the Br loss represents greater loss of the tracer than of the organic matter it traces. In other words, irradiation can cause selective loss of Br-containing compounds from marine organic matter.

This high fractional loss of Br is consistent with the generally high photochemical lability of organobromine compounds. Many brominated organic contaminants – e.g., polybrominated flame retardants – are very susceptible to photochemical degradation (Ahn et al., 2006).

3.3 *Carbon isotopes*

The initial ¹⁴C abundance for the riverine suspended sediment sample (Table 1) was slightly higher than found for a range of Atchafalaya River suspended sediments by Gordon and Goñi (2003), and that of the P4S8 sample was consistent with previous reports of sediment ¹⁴C abundances in the shelf region (Goñi et al.,

1998; Gordon and Goñi, 2004). After irradiation, the ^{14}C in the particulate phase declined for all three sediments, with the Fraction Modern parameter decreasing by 7-12%. Although no analyses were performed on the dark control treatments, the small changes in particulate organic carbon in the dark controls make it unlikely that such large changes could have occurred in the absence of irradiation. Mass balance calculations show that the carbon lost from the solid phase upon irradiation (i.e. photodissolved) had $\Delta^{14}\text{C}$ values of 97, 36, and -205 per mil, for the riverine suspended material (Venice), coastal suspended material (FWB), and shelf bottom sediment (P4S8) samples, respectively. Thus, relatively fresh material was especially susceptible to photodissolution. Along the river-to-shelf transition represented by these three samples, the material lost from the particulates became progressively older. The organic carbon lost from the riverine end-member and coastal water suspended sediments was dominated in each case by bomb test-influenced, radiocarbon signatures, indicating very fresh material. Consistent with this finding, we have found in separate irradiation experiments that fresh algal detritus is indeed quite susceptible to light-induced dissolution under the same conditions as the experiments reported here (unpub. data).

The shelf sediment (P4S8), on the other hand, lost material with a $\Delta^{14}\text{C}$ value of -205 per mil, significantly lower than would be expected from modern planktonic composition (Goñi et al., 1998). Thus, older particulate organic matter was also susceptible to photodissolution.

Small changes were observed in the $\delta^{13}\text{C}$ values of these sediments upon irradiation (Table 1). The riverine suspended sediment became slightly heavier,

with mass balance indicating loss of material with $\delta^{13}\text{C}$ of -25.1 per mil that suggested terrestrial organic matter of C_3 origin. Opsahl and Zepp (2001) also found preferential loss of isotopically light carbon from the dissolved organic matter of river water upon irradiation, but found a much greater increase in $\delta^{13}\text{C}$ of the residual pool than observed here. The FWB sample also became slightly heavier, but lost material of intermediate isotopic composition and the shelf-deposited sediment became slightly lighter. Given the uncertainty of assigning source information from $\delta^{13}\text{C}$ values for organic matter mixtures from this region (Goñi et al., 1998), it is impossible to infer the nature of the lost material in these latter two samples.

3.4 *Lignins*

Lignins were more susceptible to loss upon irradiation than was total organic carbon (Table 2). The Λ_8 parameter, representing the sum of lignin monomer concentrations normalized to total organic carbon, began with values in keeping with previous reports (e.g., Bianchi et al., 2002; Gordon and Goñi, 2004). Upon irradiation, Λ_8 decreased strongly. The two samples dominated by terrigenous organic matter – Venice and FWB – had higher initial Λ_8 , which decreased by 56 to 77% upon irradiation. In the shelf sediment (P4S8), with older organic matter and a lower initial Λ_8 value, the loss was only 40% upon irradiation, though this smaller loss may be due to the lesser photochemical reaction in this experiment compared to the same sediment used for the other parameters (i.e. compare irradiation-induced

losses of organic carbon in Table 1 vs. Table 2). These strong lignin losses were consistent with photochemical loss of lignin from dissolved organic matter from this region (Opsahl and Benner 1998; Hernes and Benner, 2003), as well as the photo-lability of lignin in other organic matrices - e.g., grassland litter (Henry et al., 2008). Further, this high loss of lignins agreed with the decreases in C:N ratio described above, because ligniferous plant detritus generally has higher C:N ratios.

The composition of the lignins changed less than did their total concentrations. The initial S/V and C/V values for these samples resembled riverine and marine samples previously reported for this area (e.g., Bianchi et al., 2002, Gordon and Goñi, 2004). The nearshore suspended particulate material (FWB) was the most enriched in non-woody, angiosperm-derived organic matter (based on its high C/V), in keeping with its known transport to distal depocenters in this region (Bianchi et al., 1997). Both S/V and C/V decreased in the two samples richest in recent riverine organic matter (Venice and FWB), with little to no change in the most offshore sample (P4S8). Opsahl and Benner (1998) also found decreases in S/V, though they found increases in C/V, upon irradiation of dissolved organic matter. These drops in S/V and C/V suggest preferential loss of angiosperm lignins, especially those derived from non-woody plants.

Oxidation of lignins increases acid:aldehyde (Ad/Al) ratios, especially for the vanillyl phenols (Opsahl and Benner, 1995). The only significant change in the composition of the remaining particulate lignin in our experiments was an increase in the acid:aldehyde ratio for the vanillyl lignins ((Ad/Al)_v). This increase was qualitatively similar to increases in (Ad/Al)_v of dissolved lignin found by Opsahl

and Benner (1998) and Hernes and Benner (2003). Quantitatively, however, the $(\text{Ad}/\text{Al})_v$ increases in our particulate phases were much smaller than the two-fold and greater increases reported for dissolved organic matter. In P4S8, the increase was greater for the dark control than the irradiated sample. These smaller increases for particulate than for dissolved organic matter may have been due to simple surface area:volume considerations; Bonini et al. (2002) found lignin photo-degradation to proceed most quickly on outer surfaces of lignin polymers. Changes in the $(\text{Ad}/\text{Al})_s$ ratio, on the other hand, were small and inconsistent.

Thus, irradiation caused significant loss of identifiable lignin phenols from the particulate phase, but less fractionation or alteration during this loss. The small changes in alteration indicators (e.g., Ad/Al ratios) suggested that loss was due to dissolution rather than modification in place, though it was possible that irradiation altered the lignins to chemical structures that we did not detect. Transfer of lignins to the dissolved phase would be consistent with the apparent desorption of lignin during early estuarine mixing observed by Hernes and Benner (2003).

3.5 Implications for use of chemical markers

Most of the changes observed in this study, including the elemental and isotopic alterations, must derive from mass loss from the particulate phase. Only in the case of lignin might the observed changes in the residual phase have been due to alteration left in place; in other words, ligniferous organic matter might have remained on the particles in a form outside of our analytical window.

Irradiation caused marine (Br) and terrestrial (lignin) OM source indicators to be preferentially lost from the samples in which they were significantly present. The decrease in Λ_8 in the riverine sample, containing only terrigenous organic matter, implied that lignin is a poor quantitative indicator of terrigenous origin, if sediments are substantially affected by irradiation. Likewise, our finding that Br:OC ratio in irradiated Gulf of Maine sediments (containing only marine-derived organic matter) decreased as strongly as the Louisiana sediments (with mixed provenance) showed that irradiation can obviate the use of this marker as well. Because ^{14}C was also preferentially lost from all samples upon irradiation, we infer that these source indicators represented younger material. Of course, any other oxidative attack (e.g., microbial decay) on sediments that removes chemical markers more rapidly than total organic matter will lead to the same problem.

Light-induced alteration affects other chemical markers of organic matter source or lability in addition to the ones examined here. Compounds with demonstrated sensitivity to photochemical degradation include a variety of lipids and pigments (Nelson, 1993; Rontani, 2001). Similarly, photodegradation resulted in significant alteration of the abundance and composition of amino acids in high molecular weight dissolved organic matter (<0.2 μm and > 1kD) from the Pearl River (USA) (Shiller et al., 2006).

The term photodissolution implies simply a transfer from the solid to the liquid phase, and may involve any of several types of mechanisms in the transfer. As one example, it may represent a light-enhanced desorption that resulted from photochemical alteration of molecular properties that affect adhesion of organic

molecules to a surface. In this context, our ^{14}C results were consistent with those of Butman et al. (2007), who found non-photochemical desorption of soil organic matter into seawater to release relatively young organic matter. It is possible that photodissolution resulted significantly from secondary oxidation reactions caused by formation of reactive oxygen species (ROS) during irradiation. Lignin photo-degradation, for example, is thought to result extensively from such secondary reactions (reviewed in Lanzalunga and Bietti, 2000). In this context, our ^{14}C results agreed with the results of Eusterhues et al. (2005) and Zimmermann et al. (2007), who found non-photochemical oxidation, using reagents such as hydrogen peroxide, to release relatively young organic matter from soils.

The observed experimental changes are at least consistent with the possibility that photochemistry affects these source indicators in the Mississippi coastal region. We have previously hypothesized (Mayer et al., 2006) that photo-dissolution is most likely to occur in the shallow coastal regions where Mississippi River sediment quickly settles upon arrival (Wright and Nittrouer, 1995) and thence undergoes months of resuspension before removal from the shallows (Allison et al., 2000). The light exposure accumulating during this extended period of resuspension would be expected to alter the various chemical markers as per the experiments reported here.

Organic carbon, nitrogen, and lignin concentrations in the Louisiana margin drop significantly and quickly upon entry into this nearshore zone (e.g., Gordon and Goñi, 2004), with magnitudes that are consistent with our photochemical experiments. However, both hydrodynamic sorting and other, non-photochemical

oxidation of organic-rich particles such as biological remineralization (Bianchi et al., 2002; Trefry et al., 1994) are also consistent with these decreases. The C:N ratio of the residual particulate organic matter decreased during our experiments, consistent with a similar drop in the river to shelf transition (Gordon and Goñi, 2004). The lignin S/V ratios decreased slightly in our experiments, consistent with similar river-shelf changes found by Bianchi et al. (2002) and Gordon and Goñi (2003). On the other hand, the C/V ratios also decreased in the Venice and FWB samples, but did not show decreases in field samples (Bianchi et al., 2002; Gordon and Goñi, 2003). Lack of change in (Ad/Al)_s ratios in our experiments was consistent with the lack of change in the field (Goñi et al., 1998; Bianchi et al., 2002; Gordon and Goñi 2003, 2004). Although the (Ad/Al)_v ratio increased in a consistent though small fashion in our experiments, there is little evidence for an increase in this parameter in the transition from river to shelf sediments (Goñi et al., 1998; Bianchi et al., 2002; Gordon and Goñi, 2003, 2004). ¹⁴C concentrations also decreased from river to slope (Gordon and Goñi, 2004), though not as strongly as found here, and are also consistent with our experimental data though subject to the same caveats about winnowing and other oxidative processes. $\delta^{13}\text{C}$ values increase (i.e. become isotopically heavier) from river to shelf (Hedges and Parker, 1976), with fairly rapid increases from the river to shallow nearshore sediments (Goñi et al., 1998; Bianchi et al., 2002; Gordon and Goñi, 2004). These increases are generally considered to be due to incorporation of marine-derived organic matter or perhaps winnowing of isotopically light C₃ detritus and residual enrichment of isotopically heavy, terrigenous C₄ detritus, but they are also consistent with our

experimental results on the riverine sample. Field Br:OC ratios (Mayer et al., 2007) are low in riverine suspended sediments due to lack of marine organic matter, are higher but still low in near-coastal regions subject to resuspension and hence irradiation, and highest in the offshore sample, where marine organic matter inputs would raise Br concentrations but irradiation no longer has an influence. The intense loss of Br upon irradiation, as well as loss of organic matter with relatively high $\delta^{13}\text{C}$ from the offshore sample, implies photochemical loss of marine-derived organic matter, though the results from the Gulf of Maine samples indicate that the drop in Br:OC ratio is even greater than that of marine organic matter. Use of a comprehensive set of provenance indicators by Gordon and Goñi (2003) showed that accumulation of marine organic matter at shallow stations was considerably lower than would be expected from $\delta^{13}\text{C}$ values alone. Thus, field distributions of Br:OC ratios were consistent with photochemical inhibition of accumulation of marine organic matter or its Br:OC tracer in the shallow coastal zone. Nevertheless, this pattern could also be explained by less accumulation of marine-derived organic matter in this zone due to restricted primary production or faster sedimentation rates.

Thus, the field data provided a picture consistent with photochemical influence on compositions, but not strongly indicative of it. Except for the losses in total organic matter, Λ_8 , and Br, most of the experimental and field changes were fairly small. The small losses in lignin compositions implied physically rather than chemically selective mechanisms of loss, such as winnowing or non-selective dissolution. Non-photochemical processes (microbial attack, winnowing) could

produce similar trends in many parameters. The nearshore incineration zone, where irradiation is hypothesized to play a role (Aller, 1998; Mayer et al, 2006), is one of intense oxidation. Better tests for the specific participation of photochemical reactions in this oxidative milieu will have to come from parameters that are unique to photochemical alteration; possible candidates include lipid alteration products (Rontani, 2001; Marchand et al., 2005) and perhaps photobleaching of particulate organic matter.

As with any photochemical process, the importance of these reactions in the field is likely to be light-limited. We are currently assessing light penetration into various zones along the Louisiana coast and its absorption by the reactive particulates in these zones.

This work was instigated by questions on the Louisiana coast, but many other environments will be susceptible to the reactions demonstrated here. For example, low-latitude mudflats are strong candidates for intense reaction zones. Photo-sensitive chemical markers should be used with care in such environments.

4. Conclusions

These experiments show that sunlight can indeed affect several chemical indicators of sedimentary organic matter source and age, in ways largely consistent both with results from other fields of study and with marker patterns observed in the field. In some cases the influence of sunlight was quite strong, while in others it was small compared to that described in other studies. Fresher organic materials will be lost most strongly upon irradiation, with concomitant impact on biomarkers of these

materials. Though field distributions of markers in the Louisiana coastal region generally agree with the results of laboratory experiments, the concordance provides no more than a consistency test for the impact of irradiation on sediments in this region.

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Table 1. Changes in organic carbon (mg g^{-1}), total nitrogen (mg g^{-1}), C:N ratio (wt/wt), Br content ($\mu\text{g g}^{-1}$) and Br:OC ratio (mg-Br gOC^{-1}), and carbon isotopes ($\delta^{13}\text{C}$ and ^{14}C as $\Delta^{14}\text{C}$ (per mil) or Fraction Modern (FM)) upon irradiation and dark control experiments. Samples include Mississippi River suspended sediment (Venice), coastal suspended sediment (FWB), and mid-shelf deposited sediment (P4S8). The %-loss data refer to the proportion of initial TOC, TN, or Br concentrations that were lost after irradiation, while the composition data (in italics: C:N, Br:OC, $\delta^{13}\text{C}$, ^{14}C (FM) and $\Delta^{14}\text{C}$) refer to properties of the material lost during irradiation.

		TOC	TN	C:N	Br	Br:OC	$\delta^{13}\text{C}$	^{14}C (FM)	$\Delta^{14}\text{C}$
Venice	Before Irradiation	18.7	2.0	9.4	n.d.	n.d.	-23.8	0.8261	-168
	After Irradiation	13.6	1.6	8.5	n.d.	n.d.	-23.3	0.7274	-267
	Dark Control	20.2	2.1	9.6	n.d.	n.d.	n.d.	n.d.	n.d.
%-loss or	<i>composition</i>	27	20	13			-25.1	1.09	97
FWB	Before Irradiation	20	2.3	8.7	29	1.5	-22.8	0.8790	-115
	After Irradiation	14	1.9	7.4	7	0.5	-22.5	0.8150	-179
	Dark Control	20	2.3	8.7	28	1.4	n.d.	n.d.	n.d.
%-loss or	<i>composition</i>	30	17	15	76	3.7	-23.5	1.03	36
P4S8	Before Irradiation	10.2	1.2	8.5	29	2.8	-22.3	0.7026	-292
	After Irradiation	6.4	0.8	7.8	7	1.1	-22.8	0.6513	-344
	Dark Control	11	1.2	9.2	29	2.6	n.d.	n.d.	n.d.
%-loss or	<i>composition</i>	37	32	10	76	5.8	-21.5	0.79	-205

Table 2. Lignin changes in irradiation experiments. Parameters include total organic carbon (TOC, mg g^{-1}); Λ_8 , which is the sum of vanillyl phenols (V: vanillin, acetovanillone, vanillic acid), syringic phenols (S: syringaldehyde, acetosyringone, syringic acid), and coumarinyl phenols (C: *p*-hydroxycinnamic and ferulic acids), all normalized to TOC (units of $\text{mg-lignins } 100 \text{ mg-TOC}^{-1}$); S/V and C/V ratios, and acid:aldehyde ratios of vanillyl ((Ad/Al)_v) and syringyl ((Ad/Al)_s) phenols.

Note that the sub-sampling and irradiations were conducted at a different time than for the other parameters investigated, and although most samples have similar TOC values as those in Table 1, the P4S8 sample showed considerably less TOC loss upon irradiation. The production of DOC in this experiment did agree with the previous experiment, leading to total carbon values after irradiation in excess of those prior to irradiation. We therefore suspect that this POC value is in error.

		TOC	Λ_8	S/V	C:V	(Ad/Al) _v	(Ad/Al) _s
Venice	Before Irradiation	18.7	1.39	1.06	0.17	0.41	0.32
	After Irradiation	13.6	0.32	0.88	0.10	0.49	0.27
	Dark Control	20.2	1.20	1.04	0.17	0.40	0.30
FWB	Before Irradiation	19.8	1.55	0.95	0.36	0.39	0.30
	After Irradiation	14.7	0.68	0.76	0.28	0.57	0.35
	Dark Control	21.1	1.65	1.00	0.39	0.42	0.31
P4S8	Before Irradiation	10.1	1.02	0.97	0.21	0.32	0.24
	After Irradiation	9.4	0.62	1.03	0.24	0.39	0.25
	Dark Control	11.2	1.11	0.94	0.24	0.52	0.34