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Robert G. M. Spencer

Aron Stubbins
Old Dominion University

Peter J. Hernes

Kenneth Mopper
Old Dominion University, kmopper@odu.edu

Anthony K. Aufdenkampe

See next page for additional authors

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Authors

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Photochemical degradation of dissolved organic matter and dissolved lignin phenols from the Congo River

Robert G. M. Spencer,^{1,2} Aron Stubbins,³ Peter J. Hernes,² Andy Baker,⁴ Kenneth Mopper,³ Anthony K. Aufdenkampe,⁵ Rachael Y. Dyda,² Vincent L. Mwamba,⁶ Arthur M. Mangangu,⁶ Jose N. Wabakanghanzi,⁶ and Johan Six¹

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[1] Photochemical degradation of Congo River dissolved organic matter (DOM) was investigated to examine the fate of terrigenous DOM derived from tropical ecosystems. Tropical riverine DOM receives greater exposure to solar radiation, particularly in large river plumes discharging directly into the open ocean. Initial Congo River DOM exhibited dissolved organic carbon (DOC) concentration and compositional characteristics typical of organic rich blackwater systems. During a 57 day irradiation experiment, Congo River DOM was shown to be highly photoreactive with a decrease in DOC, chromophoric DOM (CDOM), lignin phenol concentrations (Σ_8) and carbon-normalized yields (Λ_8), equivalent to losses of ~45, 85–95, >95 and >95% of initial values, respectively, and a +3.1 ‰ enrichment of the $\delta^{13}\text{C}$ -DOC signature. The loss of Λ_8 and enrichment of $\delta^{13}\text{C}$ -DOC during irradiation was strongly correlated ($r = 0.99$, $p < 0.01$) indicating tight coupling between these biomarkers. Furthermore, the loss of CDOM absorbance was correlated to the loss of Λ_8 (e.g., a_{355} versus Λ_8 ; $r = 0.98$, $p < 0.01$) and $\delta^{13}\text{C}$ -DOC (e.g., a_{355} versus $\delta^{13}\text{C}$; $r = 0.97$, $p < 0.01$), highlighting the potential of CDOM absorbance measurements for delineating the photochemical degradation of lignin and thus terrigenous DOM. It is apparent that these commonly used measurements for examination of terrigenous DOM in the oceans have a higher rate of photochemical decay than the bulk DOC pool. Further process-based studies are required to determine the selective removal rates of these biomarkers for advancement of our understanding of the fate of this material in the ocean.

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1. Introduction

[2] Global riverine export of terrigenous dissolved organic carbon (DOC) is approximately 0.25 Pg and thus represents a significant source of reduced carbon that can fuel biogeochemical cycling in coastal margins. Riverine dissolved organic matter (DOM) has historically been considered to be derived from highly degraded soil organic matter, thus its efficient removal in the marine environment presented a paradox [Hedges *et al.*, 1997]. However, microbial and photochemical degradation have both been shown to be

important processes for the efficient removal of terrigenous DOM from the oceans [Amon and Benner, 1996; Hernes and Benner, 2003] as well as sequential photochemical and microbial degradation whereby photoproducts stimulate bacterial growth [Mopper and Kieber, 2002]. To date little work has focused on the degradation processes of riverine DOM derived from tropical ecosystems in which DOM receives greater exposure to solar radiation and warmer temperatures [Benner, 2002]. Such work is of key importance to understanding the fate of terrigenous DOC in the oceans as three large tropical rivers (the Amazon, Congo and Orinoco) account for ~26–28% of global riverine DOC input to the oceans [Coyne *et al.*, 2005]. Furthermore, these three large rivers discharge directly to the open ocean and exhibit large river plumes that are ideal locations for photochemical degradation [Vodacek *et al.*, 1997; Del Vecchio and Subramaniam, 2004].

[3] In contrast to numerous studies on the Orinoco and particularly the Amazon Rivers, comparatively little is known about the biogeochemistry of the Congo River. Previous Congo studies have focused on deriving total suspended sediment, particulate organic carbon and DOC fluxes [Mariotti *et al.*, 1991; Coyne *et al.*, 2005] and

¹Department of Plant Sciences, University of California, Davis, California, USA.

²Department of Land, Air, and Water Resources, University of California, Davis, California, USA.

³Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, Virginia, USA.

⁴School of Geography, Earth, and Environmental Sciences, University of Birmingham, Birmingham, UK.

⁵Stroud Water Research Center, Avondale, Pennsylvania, USA.

⁶Department of Soil Physics and Hydrology, Congo Atomic Energy Commission, Kinshasa, Democratic Republic of Congo.



Figure 1. Map of the Congo River Basin. The black arrow indicates the location of the sampling site in this study.

estuarine dynamics [Eisma and Van Bennekom, 1978; Cadee, 1984; Pak *et al.*, 1984]. However, to date no biochemical composition or isotope data exists for Congo River DOM. The Congo River is the second largest river in the World both in terms of the size of its drainage Basin ($\sim 3.7 \times 10^6 \text{ km}^2$) and its water discharge ($\sim 45,000 \text{ m}^3 \text{ s}^{-1}$) [Coynel *et al.*, 2005; Runge, 2007]. It also drains the second largest area of rain forest in the World ($\sim 2 \times 10^6 \text{ km}^2$), much of which still exists in a pristine state and has among the highest carbon content per hectare of any rain forest [Koenig, 2008], as well as large tracts of savanna and grassland. Of particular relevance to carbon export via the Congo River is the largest area of swamp forest in the World which is found in the Cuvette Congolaise at the center of the Basin [Coynel *et al.*, 2005; Duveiller *et al.*, 2008]. The Congo River shows an exceptionally stable discharge due to a drainage Basin that straddles the equator and therefore receives high rainfall in at least one part of the catchment throughout the year. A bimodal hydrological cycle is observed with maximum flows in December and May and minimum flows in August and March [Coynel *et al.*, 2005]. The Congo River is estimated to export $\sim 12.4 \text{ Tg a}^{-1}$ of DOC and is thus the second largest exporter of DOC after the Amazon River. For comparison it exports an equivalent amount of DOC per year as the three largest Arctic rivers (Yenisey, Lena and Ob) combined [Coynel *et al.*, 2005; Raymond *et al.*, 2007].

[4] Terrigenous DOM in the oceans has often been investigated by examining the unique terrestrial signatures of lignin phenols [Meyers-Schulte and Hedges, 1986; Opsahl and Benner, 1997; Hernes and Benner, 2006], stable carbon isotopes [Druffel *et al.*, 1992; Benner *et al.*,

1997] and chromophoric DOM (CDOM) [Vodacek *et al.*, 1997; Coble, 2008]. Therefore, it is extremely important to understand the susceptibility of these parameters to removal and selective alteration [Benner, 2002]. This study presents the first biochemical composition and isotope data for Congo River DOM. In this study, we address the sensitivity of these measurements with respect to photochemical degradation and thus examine an important pathway for DOM removal and alteration in marine environments. In addition, this is the first abiotic study on whole waters to examine the photochemical reactivity of biomarkers in tropical riverine DOM. As such it examines the impact of this important removal mechanism for tropical riverine terrigenous DOM exposed to irradiation in extensive river plumes. Finally, we examine the potential relationships between the terrigenous DOM biomarkers to determine the potential for utilizing CDOM to track photochemical degradation of terrigenous DOM in future studies.

2. Materials and Methods

2.1. Water Sample Collection and Processing

[5] The Congo River was sampled near Maluku ($04^{\circ}05'02''\text{S}$; $15^{\circ}31'36''\text{E}$) in January 2008 upstream from Kinshasa at a point just above where the river widens to form Pool Malebo (formerly Stanley Pool), which is a $\sim 35 \text{ km}$ long and $24\text{--}28 \text{ km}$ wide broadening of the river (Figure 1). No major tributaries enter the river in between the sampling site and where it discharges to the Atlantic Ocean [Eisma and Van Bennekom, 1978; Coynel *et al.*, 2005]. Thus DOM from this location is representative of

material exported into the Congo estuary and the Atlantic Ocean. The water sample (40 L) was collected from a boat in midchannel and pumped via a submersible pump from 6/10 of the total river depth at ~ 8 m in order to sample where organic matter concentrations are most representative of depth-integrated values [Aufdenkampe *et al.*, 2007]. Pumped water was subsequently filtered through precombusted (550°C) $0.3\ \mu\text{m}$ glass-fiber filters (ADVANTECH GF-75) and 5 L was shipped (<72 h; cold and in the dark) to Old Dominion University (Virginia, USA) for irradiation experiments. Within 24 h of arrival at Old Dominion University the water was further filtered (precleaned $0.1\ \mu\text{m}$ Whatman PolyCap) and transferred to quartzware for irradiation.

2.2. Dissolved Organic Carbon and Chromophoric Dissolved Organic Matter Analyses

[6] The concentration of DOC was measured using a high-temperature combustion instrument (Shimadzu TOC 5000) with four calibration standards bracketing the range of samples. All DOC data reported are the mean of three to five replicate injections, for which the coefficient of variance was less than 2%. Ultraviolet-visible absorbance spectra of CDOM were measured in duplicate on a diode array spectrophotometer (Agilent 8453) between 200 and 800 nm using a 3 mm quartz flow cell and ultrapure laboratory water (Milli-Q, Millipore) as a blank. The average value of duplicate absorbance measurements is used in this study and variation in duplicates at 300 nm was always less than $0.01\ \text{m}^{-1}$. Absorbance (A) data were converted to light absorption coefficients ($a\ \text{m}^{-1}$) following Hu *et al.* [2002]. Spectral slope (S) was calculated using a nonlinear fit of an exponential function to the absorption spectrum in the ranges of 275–295 and 350–400 nm using the equation:

$$a_g(\lambda) = a_g(\lambda_{\text{ref}})e^{-s(\lambda-\lambda_{\text{ref}})} \quad (1)$$

where $a_g(\lambda)$ is the absorption coefficient of CDOM at a specified wavelength, λ_{ref} is a reference wavelength and S is the slope fitting parameter. The spectral slope ratio (S_R) was calculated as the ratio of $S_{275-295}$ to $S_{350-400}$ [Helms *et al.*, 2008].

2.3. Lignin Phenol Analysis

[7] Lignin phenols were determined by alkaline CuO oxidation [Hedges and Ertel, 1982; Spencer *et al.*, 2008], followed by acidification and ethyl acetate extraction, which has a 70–90% recovery of both lignin phenols and internal standards [Goni and Montgomery, 2000]. Quantification of lignin phenols was carried out by GC-MS (Agilent 6890 gas chromatograph equipped with an Agilent 5973 mass selective detector and an Agilent J&W DB5-MS capillary column) using cinnamic acid as an internal standard and a five point calibration scheme [Hernes and Benner, 2002]. Eight lignin phenols were quantified in total for all samples and included three vanillyl phenols (vanillin, acetovanillone, vanillic acid), three syringyl phenols (syringaldehyde, acetosyringone, syringic acid), and two cinnamyl phenols (*p*-coumaric acid, ferulic acid). Blank concentrations of lignin phenols were low (40–50 ng) and thus blanks never exceeded 3% of the total lignin phenols in an extract. Replicate analyses of individual samples ($n = 3$) for lignin phenols yielded individual lignin phenol concentrations within $\leq 2\%$ and the mean is reported.

2.4. The $\delta^{13}\text{C}$ -DOC Analysis

[8] The $\delta^{13}\text{C}$ -DOC samples were analyzed at the University of California, Davis, stable isotope facility using an O.I. Analytical Model 1010 TOC Analyzer (OI Analytical, College Station, TX) interfaced to a PDZ Europa 20–20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK). Isotopic data is expressed with standard notation ($\delta^{13}\text{C}$) in parts per thousand (‰) relative to the Pee Dee Belemnite standard, where $\delta^{13}\text{C} = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000$, and R is the ratio of ^{13}C to ^{12}C . Replicate analyses of individual samples ($n = 3$) for $\delta^{13}\text{C}$ -DOC yielded $\delta^{13}\text{C}$ -DOC values with standard deviations of $\leq 0.2\ \text{‰}$ and the mean is reported.

2.5. Photodegradation Experiments

[9] Filtered ($0.1\ \mu\text{m}$) Congo River water was poisoned to prevent microbial regrowth by adding 1 mL of saturated mercuric chloride solution to 5 L of sample (effective concentration $\sim 14\ \text{mg L}^{-1}$). No differences were observed between DOC, CDOM, lignin and $\delta^{13}\text{C}$ -DOC measurements in poisoned versus unpoisoned initial sample, indicating that the addition of mercuric chloride did not cause any analytical interference. Previous control experiments have shown mercuric chloride has limited quantitative or qualitative impact upon CDOM photoreactivity [Helms *et al.*, 2008]. Owing to limited volumes of original sample shipped from the Democratic Republic of Congo, it was impossible to measure dark controls for the whole suite of analytes reported. However, reanalysis of aliquots of poisoned sample stored refrigerated for ~ 1 year show that CDOM has not altered over this time frame. Samples were irradiated for 57 days in $10 \times 500\ \text{ml}$ acid cleaned (1 M HCl), precombusted (550°C) quartz flasks with gas tight borosilicate stoppers [Stubbins *et al.*, 2008]. Flasks were placed upon a rotating Table (1 rpm) within a solar simulator containing 12 Q-Panel UV340 bulbs, which have spectral light similar to that of natural sunlight from the UV solar irradiance cut off at ~ 295 to 365 nm [Stubbins *et al.*, 2008], quantitatively the most important wavelength range for environmental photoreactions involving CDOM [Mopper and Kieber, 2002]. The light output from the solar simulator was measured using an International Light IL-1700 radiometer (equipped with a SUD240 sensor and a W#6931/300#14571 filter/diffuser), and was comparable to seasonally averaged noon sunlight intensity at the equator. In a previous study, Elizabeth River (Virginia, USA) water was irradiated for 5 h under both natural and simulated sunlight, and indicated that the solar simulator used here provided 127% of the CDOM photobleaching (integrated over 250 to 400 nm) occurring under winter midday sunlight at 36.89°N latitude and caused qualitatively similar shifts in CDOM light absorbance spectra to natural sunlight [Helms *et al.*, 2008]. Year-round solar irradiance at the mouth of the Congo is approximately three times higher than winter irradiance at 36.89°N . Therefore, the 57 days (1,368 h) the samples spent under the continuous solar simulator equate to approximately 38 days under 12 h of daylight (456 h) at the mouth of the Congo River. During the 57 day irradiation the flask stoppers were periodically removed to allow the sample headspace to equilibrate with laboratory air, preventing the samples from becoming anoxic due to dissolved oxygen consumption during the course of the irradiation. CDOM was chosen as

Table 1. Initial, Final, and Percent Remaining Post 57-Day Irradiation Experiment Values for Congo River CDOM, DOC, Lignin Phenol Concentration Σ_8 , Carbon-Normalized Yield Λ_8 , and $\delta^{13}\text{C}$ -DOC Values^a

	a_{254} (m^{-1})	a_{300} (m^{-1})	a_{355} (m^{-1})	a_{412} (m^{-1})	a_{443} (m^{-1})	DOC (mg L^{-1})	Σ_8 ($\mu\text{g L}^{-1}$)	Λ_8 (mg (100 mg OC) ⁻¹)	$\delta^{13}\text{C}$ -DOC (‰)
Initial (preirradiation)	153.07	92.09	45.30	18.87	11.97	10.70	76.5	0.72	-29.2
Final	7.32	4.75	3.73	1.84	1.68	5.81	1.6	0.03	-26.1
Percent remaining	4.78	5.16	8.23	9.75	14.07	54.28	2.1	3.88	-

^aPlus or minus standard deviation.

an indicator photoreactant as it is simple to measure and is known to correlate well with other measures of aromatic photoreactants. Flasks were sampled for CDOM periodically. Duplicate 500 mL flasks were collected when CDOM had reached ~80%, 60%, 30% and 5% of initial levels, providing a time series spanning the qualitative changes in DOM expected to occur during irradiation and data suitable for fitting decay curves over the entire photodegradation history of the DOM sample.

3. Results

3.1. Photodegradation of CDOM and DOC

[10] Congo River absorption coefficient (a) spectra exhibited approximately exponential decreases with increasing wavelength and showed loss across the spectrum upon irradiation (Table 1 and Figure 2a). Absorption coefficients between 254 and 443 nm were observed to decrease during the course of the 57 day irradiation by ~85–95% (Table 1 and Figure 2b). Concurrent DOC loss was equivalent to ~45%, from 10.70 to 5.81 mg L^{-1} (Table 1 and Figure 2b). The decrease in CDOM and DOC upon irradiation was described by a single, three-parameter exponential decay model ($C(t) = C_\infty + z_0 e^{-kt}$) (Table 2), where $C(t)$ = the modeled value at time (t); C_∞ = an adjustable parameter that represents the nonphotoreactive component (i.e., the component remaining at time equals infinity); z_0 = an adjustable parameter that represents the photoreactive component at time = 0; k = the rate of decay, t = the time (days) and e is the base of the natural logarithm. The exponential decay constant showed highest levels of CDOM photodegradation between 310 and 335 nm with the rate of decay (k) ranging from 0.0466 to 0.0957 d^{-1} between $a_{254} - a_{443}$, and the rate of decay for DOC was 0.0474 d^{-1} (Table 2).

[11] The spectral slope parameter (S) has been used in a wide range of studies to examine changes in DOM source and composition and typically a steeper S indicates low molecular weight material or decreasing aromaticity and a shallower S indicates DOM with a higher aromatic content and higher molecular weight [Blough and Del Vecchio, 2002; Obernosterer and Benner, 2004; Helms et al., 2008]. Helms et al. [2008] conducted a comprehensive study of S with varied aquatic systems and DOM sources and suggest calculating S over the ranges 275–295 nm and 350–400 nm, since the first derivative of natural-log spectra indicated the largest variations in these ranges. Helms et al. [2008] also show $S_{275-295}$ and S_R ($S_{275-295} : S_{350-400}$) to be correlated to DOM molecular weight and to generally increase upon irradiation, while $S_{350-400}$ generally decreases. Upon irradiation of Congo River water, $S_{350-400}$ decreased from 0.01521 nm^{-1} to 0.00720 nm^{-1} over 57 days of irradiation (Figure 3a). $S_{275-295}$ increased initially from 0.01234 nm^{-1} to 0.01619 nm^{-1} upon day 12 of irradiation. At some time point

between day 12 and day 57 of irradiation $S_{275-295}$ subsequently declined after the initial increase to 0.00996 nm^{-1} . At the start of the irradiation, S_R was 0.811 and increased rapidly over the first 12 days of the experiment to 1.359 and then gradually increased to 1.378 by day 57 (Figure 3b).

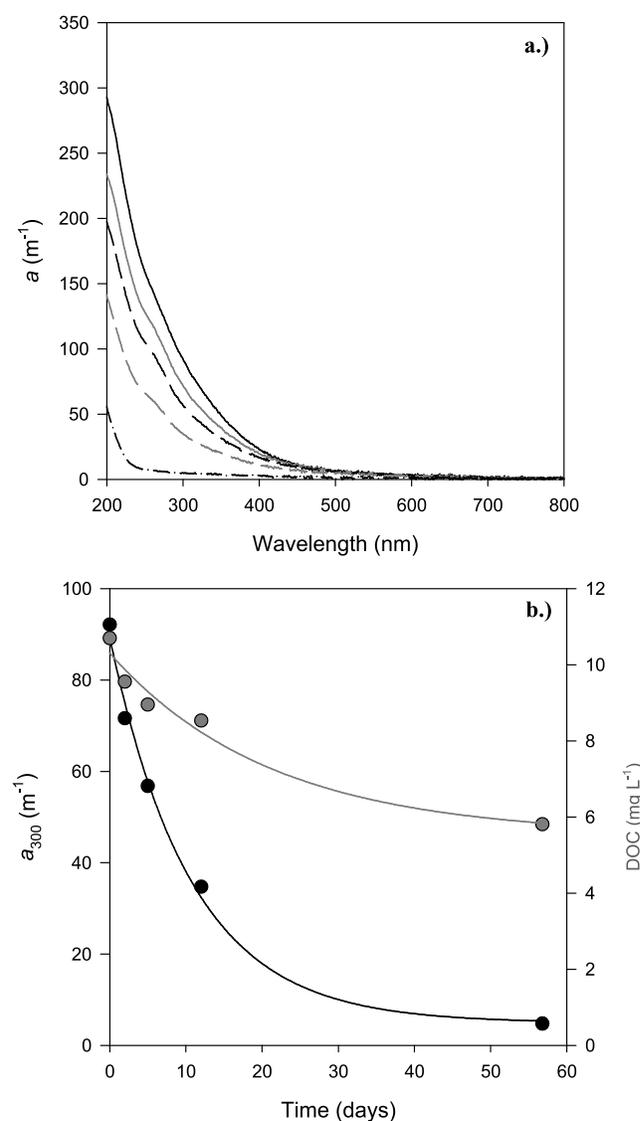


Figure 2. (a) Loss of CDOM absorbance with irradiation; t_0 , black solid line; t_2 , gray solid line; t_5 , black dashed line; t_{12} , gray dashed line; t_{57} , black dash-dot line. (b) Loss of CDOM absorbance (a_{300} , black circles, black line) and DOC (gray circles, gray line) during the course of the 57-day irradiation experiment.

Table 2. Three-Parameter Exponential Decay Model With Rate of Decay k for Congo River CDOM, DOC, Lignin Phenol Concentration Σ_8 , Carbon-Normalized Yield Λ_8 , and $\delta^{13}\text{C}$ -DOC Values for the 57-Day Irradiation Experiment

	a_{254}	a_{300}	a_{355}	a_{412}	a_{443}	DOC	Σ_8	Λ_8	$\delta^{13}\text{C}$ -DOC
C_∞	6.22	4.93	3.68	1.46	0.89	5.52	1.99	0.03	-25.99
z_0	143.26	84.45	40.24	17.39	11.01	4.79	73.90	0.70	-3.47
k (d^{-1})	0.0791	0.0936	0.0865	0.0679	0.0466	0.0474	0.156	0.127	0.107
r	0.998	0.997	0.997	1.000	0.998	0.982	1.000	1.000	0.990
p	<0.01	<0.01	<0.01	<0.01	<0.01	<0.05	<0.01	<0.01	<0.05

3.2. Photodegradation of Dissolved Lignin Phenols

[12] Lignin concentrations (Σ_8) and carbon-normalized yields (Λ_8) in this manuscript utilize the sum of three vanillyl phenols, three syringyl phenols and two cinnamyl

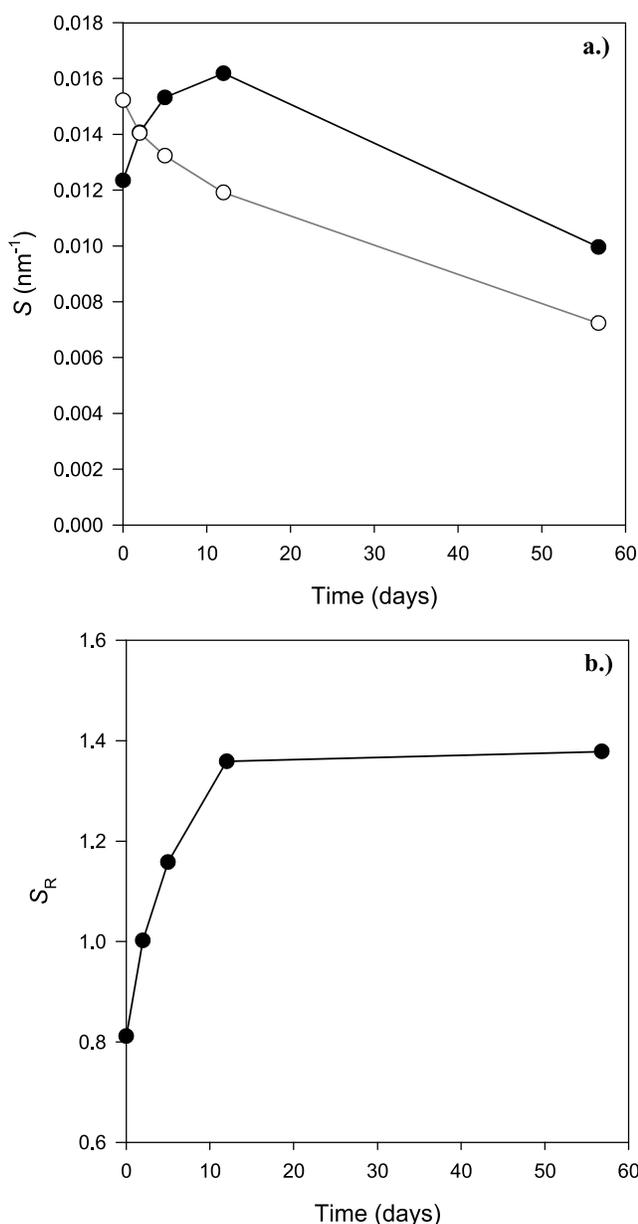


Figure 3. (a) Change in $S_{275-295}$ (solid circles, black line) and $S_{350-400}$ (open circles, black line) during the course of the 57-day irradiation experiment. (b) Change in S_R ($S_{275-295}$: $S_{350-400}$) during the course of the 57-day irradiation experiment.

phenols. Initial Σ_8 for Congo River water was $76.5 \mu\text{g L}^{-1}$, which declined during the 57 days of irradiation to $1.6 \mu\text{g L}^{-1}$ (Tables 1 and 3 and Figure 4a). The relative contribution of vascular plant-derived material to organic matter pools can be assessed by the Λ_8 of lignin ($\text{mg (100 mg OC)}^{-1}$). In the nonirradiated sample, Λ_8 was $0.72 \text{ mg (100 mg OC)}^{-1}$ and declined to $0.03 \text{ mg (100 mg OC)}^{-1}$ by day 57 of the irradiation experiment (Tables 1 and 3 and Figure 4b). Thus, both Σ_8 and Λ_8 showed a greater than 95% decrease during the 57 days of irradiation with the greatest decrease during the initial 12 days. Similar to CDOM and DOC, the decrease in Σ_8 and Λ_8 upon irradiation was described by a single, three-parameter exponential decay model (Table 2). The rate of decay for Σ_8 and Λ_8 was 0.156 and 0.127 d^{-1} , respectively (Table 2). Within the vanillyl and syringyl phenol families the acid precursors showed the slowest rates of decay and in the syringyl family the ketone and aldehyde precursors showed similar rates of decay (intact monomers in lignin polyphenols are actually propylphenols, and the CuO oxidation cleaves one or two carbons from the propyl sidechain). However, vanillin precursors were more resistant to photodegradation than acetovanillone precursors, which were observed to be the most photochemically reactive individual phenols.

[13] Cinnamyl:vanillyl (C:V) and syringyl:vanillyl phenol (S:V) ratios in the nonirradiated Congo River sample were 0.15 and 0.68, respectively (Table 3 and Figure 5a). During the 57 day irradiation C:V showed no significant change and was 0.14 at the final time point, whereas S:V showed no change during the first 12 days of the irradiation but increased dramatically to 1.16 by the end of the irradiation (Table 3 and Figure 5a). The ratios of vanillic acid to vanillin (Ad:Al_v) and syringic acid to syringaldehyde (Ad:Al_s) within the initial Congo River sample were 1.38 and 1.11, respectively (Table 3 and Figures 5b and 5c). Both (Ad:Al_v) and (Ad:Al_s) showed large increases during the

Table 3. Lignin Phenol Parameter and $\delta^{13}\text{C}$ -DOC Values During the Course of the 57-Day Irradiation Experiment^a

Time (days)	DOC (mg L^{-1})	Σ_8 ($\mu\text{g L}^{-1}$)	Λ_8 ($\text{mg (100 mg OC)}^{-1}$)	Λ_8 (mg (100 mg OC) ⁻¹)		$\delta^{13}\text{C}$ -DOC (%)		
				C:V	S:V	(Ad:Al) _v	(Ad:Al) _s	
0	10.70	76.5	0.72	0.15	0.68	1.38	1.11	-29.2
2	9.56	55.2	0.58	0.12	0.69	1.97	1.29	-29.0
5	8.95	35.9	0.40	0.12	0.66	3.28	1.94	-28.1
12	8.53	14.2	0.17	0.14	0.66	3.30	2.76	-26.7
57	5.81	1.6	0.03	0.14	1.16	3.48	2.78	-26.1

^aParameters: Σ_8 , lignin phenol concentration; Λ_8 , carbon-normalized yield; C:V, cinnamyl:vanillyl phenol ratios; S:V, syringyl:vanillyl phenol ratios; (Ad:Al_v), vanillic acid:vanillin ratios; (Ad:Al_s), syringic acid:syringaldehyde ratios.

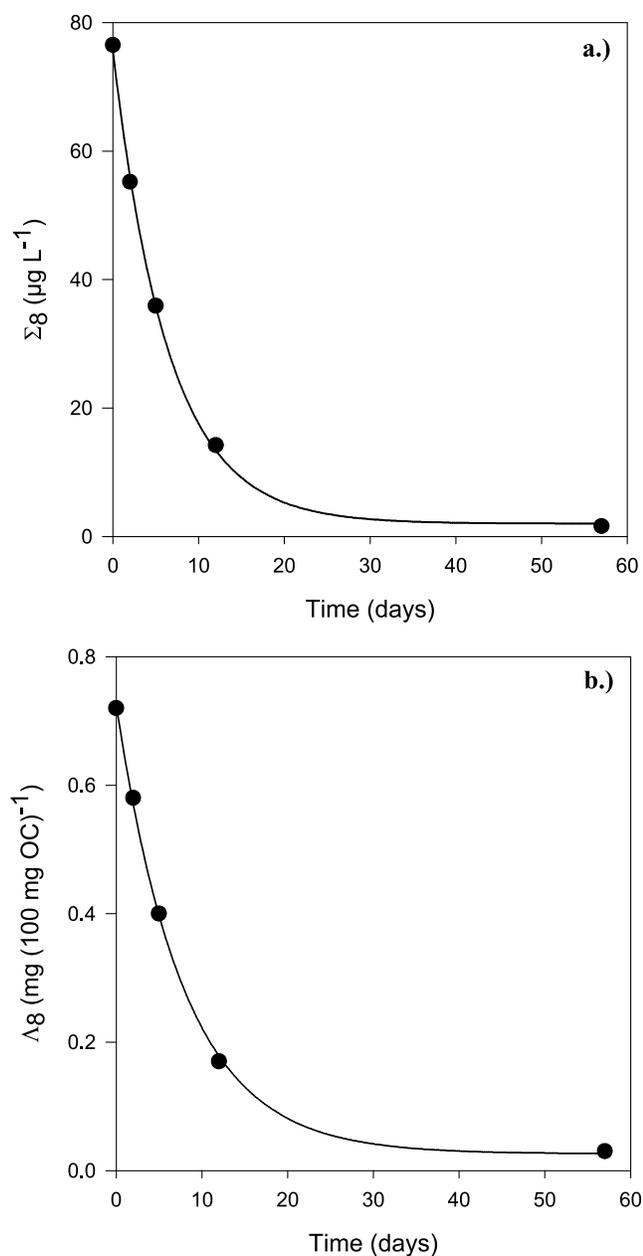


Figure 4. Change during the course of the 57-day irradiation experiment of (a) lignin phenol concentration (Σ_8) and (b) lignin phenol carbon-normalized yield (Λ_8).

first 12 days of the irradiation (i.e., to 3.30 and 2.76, respectively) and subsequently gradually increased (i.e., to 3.48 and 2.78) by the end of the 57 day irradiation (Table 3 and Figures 5b and 5c). $(\text{Ad:Al})_v$ and $(\text{Ad:Al})_s$ values increased with decreasing Σ_8 , highlighting the greater photodegradation of the vanillyl and syringyl aldehyde precursors (Figure 5d).

3.3. Photodegradation of $\delta^{13}\text{C}$ of DOC

[14] The $\delta^{13}\text{C}$ value of initial Congo River DOC was $-29.2 \pm 0.1 \text{ ‰}$ (Tables 1 and 3). During the course of the irradiation the signature of the DOC sample became progressively enriched in ^{13}C relative to the initial DOC

(Table 3 and Figure 6a). The enrichment in $\delta^{13}\text{C}$ was described by a single, three-parameter exponential decay model with a rate of decay of 0.107 d^{-1} (Table 2) and after 57 days of irradiation the $\delta^{13}\text{C}$ value was $-26.1 \pm 0.2 \text{ ‰}$ (Tables 1 and 3 and Figure 6a). This highlights the selective photodegradation of DOM moieties depleted in ^{13}C . A strong correlation was observed between Λ_8 and $\delta^{13}\text{C}$ during the course of the irradiation experiment (Figure 6b; $r = 0.99$, $p < 0.01$).

4. Discussion

4.1. Congo River DOM

[15] The approximate exponential decrease in Congo River CDOM spectra with increasing wavelength (Figure 2a), has been observed in other natural waters [Blough and Del Vecchio, 2002; Twardowski et al., 2004; Helms et al., 2008]. The Congo River exhibits DOC concentration and compositional characteristics typical of organic rich blackwater rivers, with absorption coefficients at 300 (a_{300}) and 355 nm (a_{355}) of 92.09 and 45.30 m^{-1} , respectively (Table 1) [Battin, 1998; Spencer et al., 2007; Helms et al., 2008]. The high DOC concentration (10.70 mg L^{-1}) also demonstrates the organic-rich nature of Congo River water and is comparable to previous studies of Congo DOC concentrations [Cadee, 1984; Coynel et al., 2005] and blackwater tributaries of the Amazon and Orinoco rivers [Hedges et al., 1994; Amon and Benner, 1996; Battin, 1998]. Spectral slope and slope ratio values ($S_{275-295} = 0.01234 \text{ nm}^{-1}$, $S_{350-400} = 0.01521 \text{ nm}^{-1}$ and $S_R = 0.811$), are also highly comparable to values in other organic rich systems [Helms et al., 2008; Spencer et al., 2009], suggesting that comparable sources and processing are involved in all these systems.

[16] The dissolved lignin phenol concentration for the Congo River ($\Sigma_8 = 76.5 \text{ } \mu\text{g L}^{-1}$; Tables 1 and 3) exceeds most previous rivers studied, indicating significant vascular plant sources for Congo River DOM. Typical dissolved lignin phenol concentrations in temperate rivers such as the Mississippi have been shown to range from 14 to 42 $\mu\text{g L}^{-1}$ [Benner and Opsahl, 2001] and near the mouth of the Amazon River to be 38 $\mu\text{g L}^{-1}$ [Hedges et al., 2000]. However, lignin phenols isolated from blackwater tributaries of the Amazon using XAD-8 resins had riverine concentrations ranging from 53 to 72 $\mu\text{g L}^{-1}$ [Ertel et al., 1986] much closer to Σ_8 values observed for the Congo River in our study. The high Σ_8 observed in the Congo River water is comparable to values observed in high-latitude northern rivers at the height of the spring flush (up to 73.5 $\mu\text{g L}^{-1}$) concurrent with intense leaching of surface vegetation and organic rich soil layers [Spencer et al., 2008]. The carbon-normalized yield of 0.72 ($\text{mg (100 mg OC)}^{-1}$) for Congo River DOM (Tables 1 and 3) is also high in comparison to other rivers, further highlighting the high vascular plant inputs to the system. For example, Λ_8 for a diverse range of river sources (glacial and groundwater dominated to blackwaters) and water discharges ranged from 0.05 – 0.49 ($\text{mg (100 mg OC)}^{-1}$) in the Yukon River Basin [Spencer et al., 2008], while values in the Sacramento-San Joaquin River Delta for Λ_8 had a median of 0.36 ($\text{mg (100 mg OC)}^{-1}$) across a wide range of habitats and land use types [Eckard et al., 2007].

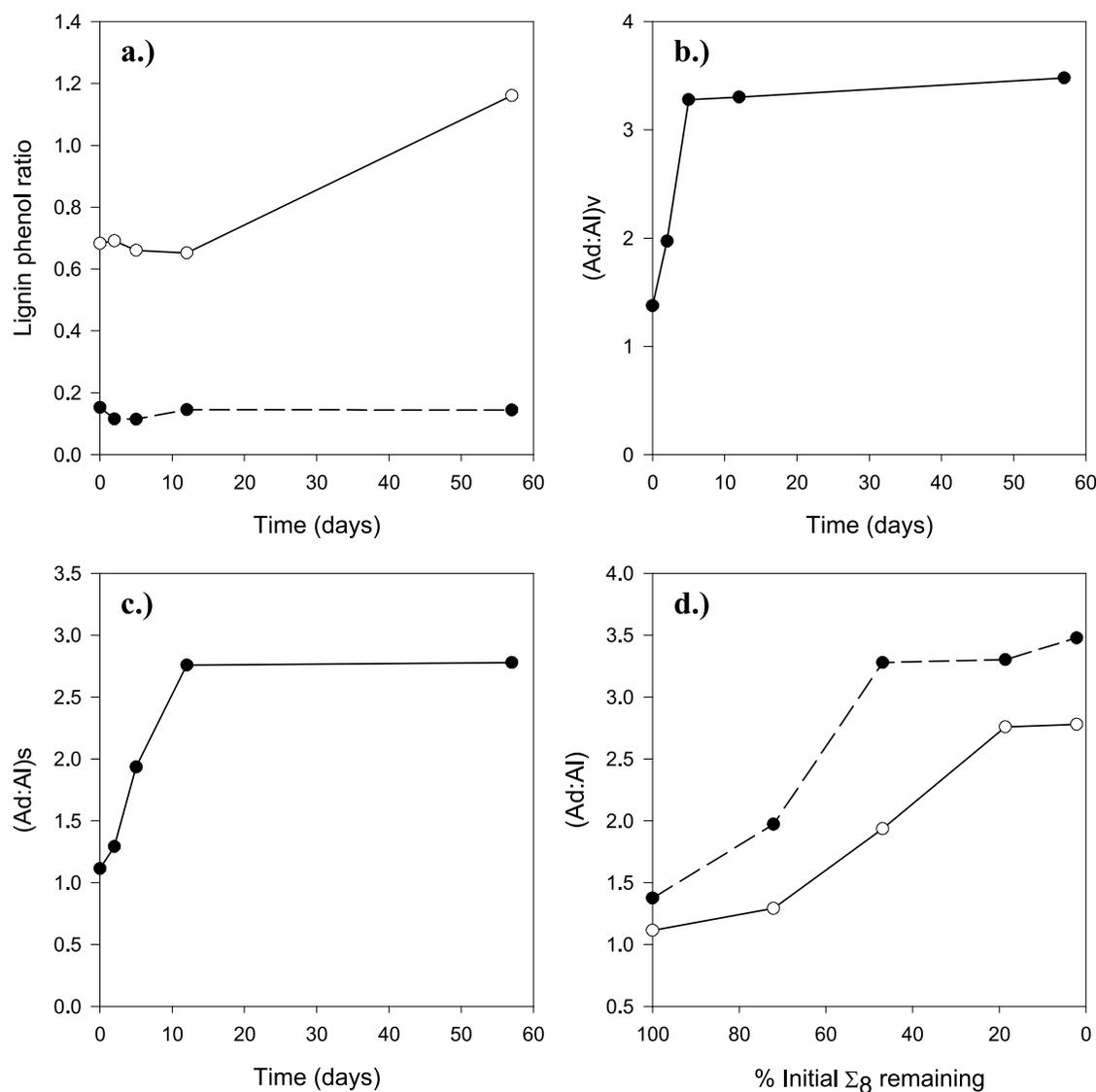


Figure 5. Change in Congo River diagnostic lignin parameters during the course of the 57-day irradiation experiment: (a) cinnamyl:vanillyl (C:V, solid circles, black dashed line) and syringyl:vanillyl (S:V, open circles, black line); (b) vanillic acid:vanillin ratios (Ad:Al)_v; (c) syringic acid:syringaldehyde ratios (Ad:Al)_s; and (d) (Ad:Al)_v (solid circles, black dashed line) and (Ad:Al)_s (open circles, black line) versus percent initial lignin phenol concentration (Σ_8) remaining.

[17] Carbon-normalized yields based solely on the ubiquitous vanillyl phenol (V) have been suggested as an appropriate end-member to estimate the vascular plant component of DOM within rivers as they eliminate some of the uncertainty derived from the considerable variation in sources and reactivity of the syringyl and cinnamyl phenols [Hernes *et al.*, 2007]. In this study the carbon-normalized vanillyl yield ($V = 0.39 \text{ (mg (100 mg OC)}^{-1})$) exceeded the combined sum of the carbon-normalized syringyl and cinnamyl yields ($S = 0.27 \text{ (mg (100 mg OC)}^{-1})$; $C = 0.06 \text{ (mg (100 mg OC)}^{-1})$) as has been observed in previous studies [Lobbés *et al.*, 2000; Aufdenkampe *et al.*, 2007; Spencer *et al.*, 2008]. The Congo River V of $0.39 \text{ (mg (100 mg OC)}^{-1})$ is higher than that observed in high-latitude northern rivers [Spencer *et al.*, 2008] and autochthonous dominated rivers such as the San Joaquin [Eckard *et al.*, 2007] and is within the range reported for Amazonian

rivers [Hedges *et al.*, 2000; Aufdenkampe *et al.*, 2007]. Utilizing a mean leachate/sorption end-member from a diverse range of angiosperm and gymnosperm sources with a V yield of $1.53 \text{ (mg (100 mg OC)}^{-1})$ [Hernes *et al.*, 2007], it is estimated that the vascular plant component of DOC in the Congo River is 25%. In reality the vascular plant component could be substantially higher if representative leachates of DOM sources found within the catchment yield significantly lower carbon-normalized yields [Spencer *et al.*, 2008]. Depleted $\delta^{13}\text{C}$ values of DOC ($-29.2 \pm 0.1 \text{ ‰}$) in the Congo River (Tables 1 and 3) suggest that the vascular plant component may indeed be underestimated by a generic V end-member value. The stable carbon isotopic composition ($\delta^{13}\text{C}$) of terrigenous DOC derived from C3 plants, which dominate the Congo River Basin [Mariotti *et al.*, 1991], has been shown to be depleted in relation to marine DOC. For example, terrigenous and marine $\delta^{13}\text{C}$ -DOC

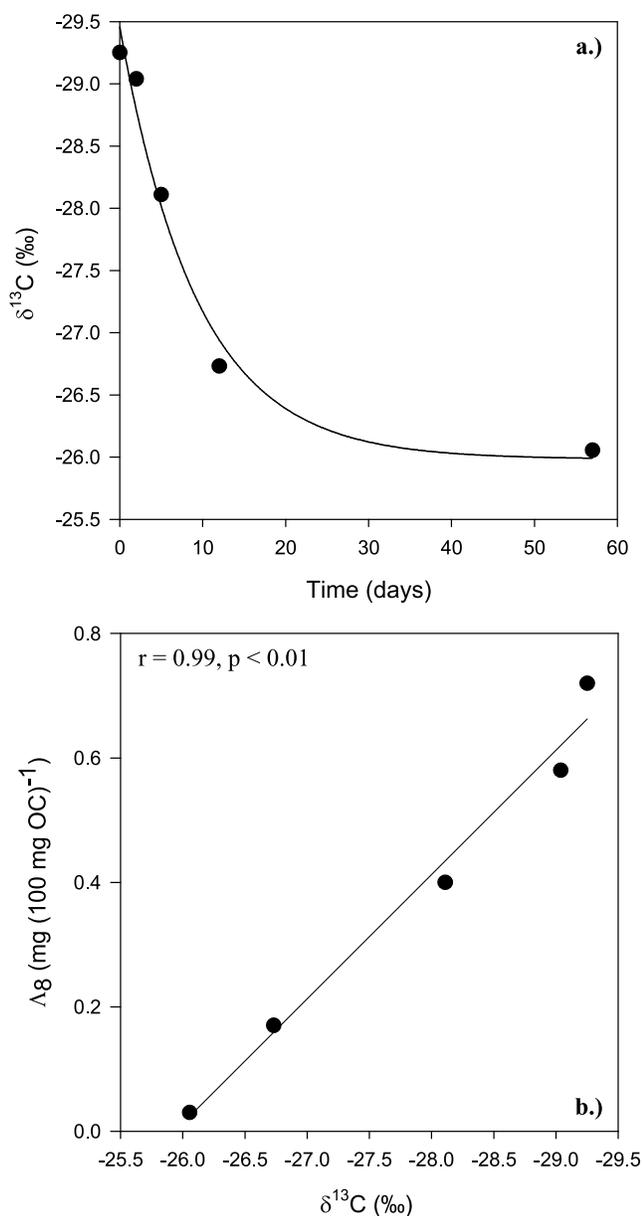


Figure 6. (a) Change during the course of the 57-day irradiation experiment of $\delta^{13}\text{C}$ -DOC. (b) Correlation between lignin phenol carbon-normalized yields (Δ_8) and $\delta^{13}\text{C}$ -DOC during the course of the 57-day irradiation experiment.

values typically range from ~ -30 to -25 ‰ and ~ -23 to -18 ‰, respectively, and thus $\delta^{13}\text{C}$ ratios have been used as a tracer for terrigenous DOC in the ocean [Hedges *et al.*, 1997; Bauer, 2002; Benner *et al.*, 2005]. The $\delta^{13}\text{C}$ value for Congo River DOC in this study is highly comparable to $\delta^{13}\text{C}$ -DOC values from near the mouth of the Amazon River ranging from -29.2 to -29.6 ‰ [Hedges *et al.*, 1994, 2000; Aufdenkampe *et al.*, 2007].

[18] Syringyl (S) and cinnamyl phenols (C) are uniquely present in angiosperms and nonwoody tissues, respectively, and thus ratios of S and C to the ubiquitous vanillyl phenols (V) can be used to distinguish between angiosperm and

gymnosperm sources (S:V) and between nonwoody and woody tissues (C:V) [Hedges and Mann, 1979]. Ratios of C:V and S:V in the Congo River sample (0.15 and 0.68, respectively; Table 3), indicate a combination of traditionally defined angiosperm nonwoody tissues and gymnosperm woody sources [Hedges and Mann, 1979] in the absence of degradative alteration or phase change partitioning [Hernes *et al.*, 2007]. Previous studies have used (Ad:Al)_v and (Ad:Al)_s to assess the degradation state of organic matter as higher relative CuO oxidation yields have been linked to increased degradation in time series [Opsahl and Benner, 1995; Hernes and Benner, 2003]. However, leaching and sorption can also lead to significant fractionation of lignin phenols, including the elevation of (Ad:Al)_v and (Ad:Al)_s [Hernes *et al.*, 2007]. (Ad:Al)_v and (Ad:Al)_s ratios from the Congo River sample (1.38 and 1.11, respectively; Table 3) are comparable to those observed in the Amazon [Hedges *et al.*, 2000], Mississippi [Hernes and Benner, 2003] and high-latitude northern rivers [Lobbis *et al.*, 2000; Spencer *et al.*, 2008] and are not necessarily a result of significant degradation.

4.2. Photodegradation of Congo River CDOM and DOC

[19] Riverine DOM has been shown to be susceptible to photochemical degradation resulting in a loss of CDOM and DOC [Vodacek *et al.*, 1997; Moran *et al.*, 2000]. Congo River CDOM and DOC showed extensive losses during the 57 days of irradiation (Figure 2 and Tables 1 and 2). Photochemical loss of DOC was slower than CDOM photobleaching as highlighted in Figure 2b and this is consistent with previous studies [Moran *et al.*, 2000; Vahatalo and Wetzel, 2004]. Furthermore, the CDOM and DOC data from the irradiation were best described by a single, three-parameter exponential decay model (Figure 2b and Table 2). These results suggest the existence of a residual pool of nonphotoreactive CDOM and DOC with a low CDOM:DOC ratio. Such a model for photochemical decay of terrigenous DOC is intuitive given that as photodegradation progresses the amount of solar radiation required to produce a corresponding relative loss of DOC increases [Moran *et al.*, 2000]. Further evidence for a nonphotoreactive pool for DOM comes from the lack of photoreactivity of equatorial Pacific Ocean (400 m) CDOM [Opsahl and Benner, 1998] and nonphotoreactive terrigenous DOC [Obernosterer and Benner, 2004]. The highest levels of photochemical degradation of CDOM occurred between 310 and 335 nm which is comparable to the range of maximum photobleaching of CDOM observed by Opsahl and Benner [1998] (320–360 nm) and Moran *et al.* [2000] (centered at 350 nm). The CDOM absorbance in this region has also been shown to correlate with dissolved lignin phenol concentrations (i.e., terrigenous DOM) [Hernes and Benner, 2003; Spencer *et al.*, 2008], thus providing clear evidence of the potential of photochemistry for removing terrigenous DOM and especially its biochemical signature from the oceans.

[20] The spectral slope parameter has generally been shown to increase with photodegradation of terrigenous CDOM [Moran *et al.*, 2000; Obernosterer and Benner, 2004; Vahatalo and Wetzel, 2004], however, decreases have also been reported [Morris and Hargreaves, 1997; Gao and

Zepp, 1998]. Such inconsistency in the response of S to photodegradation has been attributed to the spectral quality of irradiation [Tzortziou *et al.*, 2007], and methodological differences in wavelength ranges used to derive the S parameter in various studies and also different fitting routines. When these methodological differences are accounted for, the response of terrigenous CDOM to irradiation appears to be consistent [Stedmon *et al.*, 2000; Twardowski *et al.*, 2004; Helms *et al.*, 2008]. In agreement with previous work [Helms *et al.*, 2008], $S_{275-295}$ and S_R were found to increase in this study, while $S_{350-400}$ decreased during the initial stages of photobleaching (Figures 3a and 3b). S_R continued to increase and $S_{350-400}$ to decrease during the full 57 days of irradiation (Figure 3b). However, after prolonged photodegradation we found $S_{275-295}$ to decrease (Figure 3a). Therefore it is suggested that $S_{350-400}$ or S_R could be better parameters for investigating long-term photodegradation or extensively photobleached waters.

[21] The initial increase and subsequent decrease in $S_{275-295}$ during irradiation occurred as the maximal region of primary photobleaching was 310–335 nm and so $S_{275-295}$ increased initially as this region bleached. However, as time progressed and wavelengths above 300 nm became more extensively photobleached due to greater overlap with the irradiance spectrum, the region of maximum photobleaching shifted toward shorter wavelengths (i.e., into the UV). Eventually all chromophores above 280 nm became extensively photobleached resulting in a shallower $S_{275-295}$ at the end of the irradiation. $S_{350-400}$, however, continued to decrease throughout the irradiation due to maximal photobleaching moving to shorter wavelengths where they have greater overlap with the irradiance spectrum.

[22] During the course of the irradiation a +3.1 ‰ enrichment of the $\delta^{13}\text{C}$ -DOC of Congo River DOM was observed (Tables 1 and 3 and Figure 6a), which was also best fitted to a single, three-parameter exponential decay model (Table 2). Such an enrichment in the residual $\delta^{13}\text{C}$ -DOC value after irradiation has been observed previously [Opsahl and Zepp, 2001; Osburn *et al.*, 2001] and has potential implications for utilizing $\delta^{13}\text{C}$ -DOC for delineating terrigenous carbon in marine systems. Specifically, enrichment of terrigenous $\delta^{13}\text{C}$ -DOC values due to photochemical degradation shifts the $\delta^{13}\text{C}$ -DOC signature toward typical marine values and thus complicates the use of $\delta^{13}\text{C}$ -DOC for tracking terrigenous DOC in the oceans. The $\delta^{13}\text{C}$ composition of oceanic DOC is essentially identical to marine sources [Druffel *et al.*, 1992; Benner *et al.*, 1997] and this has been interpreted as an indication of minimal terrigenous DOC in the oceans, particularly because isotopic data was assumed to be insensitive to chemical and biological alterations [Hedges *et al.*, 1997]. Although the $\delta^{13}\text{C}$ -DOC isotopic shift is not large enough to significantly change this interpretation for open ocean DOC, it is large enough to warrant future studies examining microbial and combined photochemical and microbial impacts on terrigenous $\delta^{13}\text{C}$ -DOC values for studies in coastal margins near riverine outflows.

4.3. Photodegradation of Congo River Dissolved Lignin Phenols

[23] The >95% loss in both Σ_8 and Λ_8 during the 57 days of irradiation (Table 1 and Figures 4a and 4b) highlights the

susceptibility of dissolved lignin to photochemical degradation. Previous studies have also shown lignin phenols to be highly photochemically reactive but similar to CDOM and DOC there appears to be a component of the dissolved lignin pool that is not susceptible to photochemical degradation [Opsahl and Benner, 1998; Hernes and Benner, 2003]. Studies of model lignin compounds indicate that monomers completely surrounded by other (degraded) monomers may be shielded from photochemical effects [McNally *et al.*, 2005]. The rate of decay of lignin phenols was also best described by a single, three-parameter exponential decay model (Table 2). The Σ_8 had a much higher rate of decay than the bulk DOC pool (Table 2) and thus indicates that the relative abundance of lignin in terrigenous DOM will decline during photodegradation at a rate not representative of the bulk DOM pool. After 57 days of irradiation the Λ_8 value of 0.03 (mg (100 mg OC)⁻¹) is comparable to Λ_6 (total of the six vanillyl and syringyl phenols) values of ~0.03 (mg (100 mg OC)⁻¹) at salinities ≥ 33.5 in the Mississippi River plume as measured on solid phase extraction samples, but is still higher than Atlantic Ocean Λ_6 values [Opsahl and Benner, 1997; Hernes and Benner, 2006]. However, this experiment was conducted under optimum conditions for photodegradation and does not take into account microbial degradation rates of lignin compared to bulk DOC, thus the combined effects on Λ_8 are not entirely clear [Opsahl and Benner, 1998; Hernes and Benner, 2003]. Although lignin is clearly highly susceptible to photochemical degradation, the extent to which this occurs in natural systems is dependent on the exposure time riverine DOM receives. The greatest exposure occurs toward high salinities in estuaries and river plumes where low-salinity river water spreads into a thin layer on the surface, sediment loads have settled out and no longer shield DOM with the same effectiveness and dilution with optically clearer waters results in less CDOM self-shading. Congo River freshwater has been shown to be confined to the upper 15 m for the first 200 km of the plume and low-salinity waters from the Congo plume are known to extend seven to eight hundred kilometers from the mouth [Eisma and Van Bennekom, 1978; Pak *et al.*, 1984]. The large surface plume of the Congo River in conjunction with its relatively low sediment load in comparison to other large rivers [Coynel *et al.*, 2005], as well as the significant photoreactivity observed in this study and its outflow position near the equator suggest photochemical degradation may be a significant pathway for the removal of Congo terrigenous DOM as it enters coastal waters.

[24] The diagnostic lignin phenol composition ratio of C:V showed no apparent change during irradiation (Table 3 and Figure 5a), indicating that cinnamyl phenols and vanillyl phenols overall show similar rates of photochemical degradation. However, in marine samples, trace concentrations of lignin-derived cinnamyl phenols are masked considerably by nonlignin sources, such as the conversion of the amino acid tyrosine in small percentages to *p*-coumaric acid during CuO oxidation [Hernes and Benner, 2002, 2003]. Thus, C:V values in marine samples are rather meaningless and photochemical changes to this parameter would have minimal impact for lignin interpretations in marine DOM. In contrast, S:V values increased considerably by day 57 of the irradiation experiment, demonstrating

that vanillyl phenols are more susceptible to photodegradation than syringyl phenols. This apparently contradicts findings with Mississippi River and estuarine waters that showed a decrease in S:V during photooxidation incubations [Opsahl and Benner, 1998; Hernes and Benner, 2003]. However, each of those incubations was terminated after ~80% of the initial lignin was degraded. In this study, all of the increase in S:V occurred after the incubation progressed beyond 80% (Figure 5a). This points toward a nonphotoreactive lignin component of <5% with a significantly elevated S:V signature that can easily be masked during early degradation, but becomes relatively more important as degradation progresses. Thus, elevated S:V values in Mississippi River plume waters at salinity 35.4 (1.27 versus ~0.8 at lower salinities) would suggest that photodegradation of lignin had largely run to completion [Hernes and Benner, 2003]. Likewise, the S:V value of 1.16 at the end of the irradiation of Congo River water was nearly double the starting value of 0.68, and also indicates nearly complete photodegradation.

[25] The lignin diagenetic indicators of (Ad:Al)_v and (Ad:Al)_s were both observed to increase during irradiation reflecting a greater degree of degradation (Table 3 and Figures 5b and 5c). The greater proportion of vanillic acid and syringic acid as the experiment proceeded could be an indication of inherently less photoreactivity in the precursors to these compounds. However, white-rot fungi have been shown to convert aldehyde precursors to acid precursors [Hedges et al., 1988]. Hence higher relative yields of vanillic acid and syringic acid could reflect such a conversion. In litter bag decomposition studies changes in Ad:Al only became obvious when <25% of the original material remained [Opsahl and Benner, 1995]. However, changes in Ad:Al due to photochemical degradation began upon irradiation and continued in conjunction with declining Σ_8 (Figure 5d). The (Ad:Al)_v value of 3.48 at the end of the irradiation is comparable to the increase seen in previous studies and toward the maximum values observed in marine samples [Opsahl and Benner, 1998; Hernes and Benner, 2003, 2006]. The (Ad:Al)_s value of 2.78 is also comparable to the increase seen in a previous study and the maximum values reported for marine samples [Hernes and Benner, 2003]. Both (Ad:Al)_v and (Ad:Al)_s in this irradiation study inversely track Σ_8 (Figure 5d), thus there may be potential to utilize these diagnostic parameters as indicators of the extent of degradative loss of riverine DOM in plume waters if end-member values can be clearly defined.

[26] Relationships between high carbon-normalized lignin phenols and depleted $\delta^{13}\text{C}$ -DOC have been previously used as evidence for the presence of terrigenous DOM within the oceans [Opsahl and Benner, 1997; Benner et al., 2005]. The correlation between Λ_8 and $\delta^{13}\text{C}$ during irradiation of Congo River DOM (Figure 6b) highlights the tight coupling between these biomarkers, is consistent with lignin phenols that are depleted in $\delta^{13}\text{C}$ relative to bulk DOC, and indicates that lignin phenols are biomarkers for other DOM moieties that are highly photochemically reactive [Opsahl and Zepp, 2001; Osburn et al., 2001]. Interestingly the loss of CDOM absorbance was also strongly correlated to loss of lignin phenols (e.g., a_{355} versus Λ_8 ; $r = 0.98$, $p < 0.01$) and $\delta^{13}\text{C}$ -DOC (e.g., a_{355} versus $\delta^{13}\text{C}$; $r = 0.97$, $p < 0.01$). Thus, CDOM absorbance measurements

may have potential for delineating the photochemical degradation of lignin and thus terrigenous DOM. Relationships between CDOM absorbance and lignin phenols in the Mississippi River plume have already been established [Hernes and Benner, 2003] and thus CDOM measurements that can be measured in situ and via satellite may also be developed as powerful tools for examining the fate of terrigenous DOM in coastal waters [Coble, 2008; Mannino et al., 2008].

4.4. Fate of Terrigenous DOM in the Ocean

[27] Conceptual models for riverine DOM sources have historically focused on aged and degraded soil organic matter pools, due in part to the apparent degraded molecular signature for lignin [Ertel et al., 1986] and amino acids [Hedges et al., 1994]. However, recent studies have drawn attention to the fact that in reality the degraded molecular signature likely results from the simple processes of leaching and sorption, and in fact, riverine DOM may be quite 'fresh' [Aufdenkampe et al., 2001; Hernes et al., 2007]. Recent work on Arctic rivers has also shown increased lability concurrent with the spring flush [Holmes et al., 2008] when such rivers have been shown to have an increased lignin carbon-normalized yield [Spencer et al., 2008]. Microbial degradation has also been shown to remove lignin phenols in river waters [Opsahl and Benner, 1998; Hernes and Benner, 2003]. Such evidence points to a terrigenous DOM pool that is more susceptible to microbial degradation than previously thought. Photochemical degradation also clearly removes terrigenous DOM from the oceans and is especially effective at eliminating and modifying parts of the DOM pool that are commonly used to track terrigenous inputs and dynamics, including CDOM, $\delta^{13}\text{C}$ -DOC and lignin phenols. Although a robust quantitative assessment of the fate and photochemical alteration of terrigenous DOM within the Congo River plume and the Atlantic Ocean is not possible with the available data, it is informative to note that a clear photochemically induced shift in the CDOM, lignin phenol and $\delta^{13}\text{C}$ -DOC signatures of Congo River DOM toward those of marine DOM was observed and that the majority of the photochemical alteration took place in the first 12 days of irradiation in the solar simulator. This equates to approximately 8–9 days of exposure in surface waters at the equator. As DOM residence times in the Congo plume and Atlantic Ocean are likely to exceed this relative exposure time by at least an order of magnitude, it is also likely that the CDOM, lignin phenol and $\delta^{13}\text{C}$ -DOC signatures of photochemically degraded riverine DOM reported here are qualitatively consistent with the signatures of photochemically degraded terrestrial DOM in the ocean. Thus it seems apparent that the combined processes of photochemical and microbial degradation are capable of removing and transforming terrigenous DOM such that identification of terrigenous DOM in marine systems is more challenging. Further process-based studies are required to examine the combined photochemical and microbial removal rates of biomarkers used to investigate the terrigenous DOM pool in the ocean and to assess how accurately these combined removal rates track the bulk terrigenous DOC pool. It would also be prudent to examine removal rates and mechanisms for other potential biomarkers of terrigenous DOM such as polynu-

clear aromatic hydrocarbons [Burns *et al.*, 2008] and if possible to examine comprehensive compositional and structural information through novel techniques such as Fourier transform ion cyclotron mass spectrometry to gain further insight into the fate of this material in the oceans.

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- A. K. Aufdenkampe, Stroud Water Research Center, 970 Spencer Road, Avondale, PA 19311, USA.
- A. Baker, School of Geography, Earth, and Environmental Sciences, University of Birmingham, Birmingham B15 8TT, UK.
- R. Y. Dyda and P. J. Hernes, Department of Land, Air, and Water Resources, University of California, One Shields Avenue, Davis, CA 95616, USA.
- A. M. Mangangu, V. L. Mwamba, and J. N. Wabakanhanzi, Department of Soil Physics and Hydrology, Congo Atomic Energy Commission, P.O. Box 868, Kinshasa XI, Democratic Republic of Congo.
- K. Mopper and A. Stubbins, Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529, USA.
- J. Six and R. G. M. Spencer, Department of Plant Sciences, University of California, One Shields Avenue, Davis, CA 95616, USA. (rgspencer@ucdavis.edu)