Transformations and Fates of Terrigenous Dissolved Organic Matter in River-Influenced Ocean Margins

Cedric Gael Fichot
University of South Carolina

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TRANSFORMATIONS AND FATES OF TERRIGENOUS DISSOLVED ORGANIC MATTER IN RIVER-INFLUENCED OCEAN MARGINS

by

Cédric G. Fichot

Bachelor of Science
Florida Institute of Technology, 2000

Master of Science
Dalhousie University, 2004

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University of South Carolina

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Accepted by:

Ronald H. Benner, Major Professor

Robert C. Thunell, Committee Member

John L. Ferry, Committee Member

Alexander Yankovsky, Committee Member

Simon Bélanger, Committee Member

Lacy Ford, Vice Provost and Dean of Graduate Studies
DEDICATION

This dissertation is dedicated to my beloved wife Erin, my daughter Emmeline and her soon-to-be-born brother or sister, and my parents Annick and Daniel.
ACKNOWLEDGEMENTS

I am grateful to Steven E. Lohrenz, Wei-Jun Cai, and Kjell Gundersen for providing berths on the GulfCarbon cruises, and to Leanne Powers and the crews of the R/V Cape Hatteras and the R/V Hugh Sharp for their assistance with sample collection onboard. I also express my gratitude to Karl Kaiser for his general assistance in the laboratory, Yuan Shen for amino acid analyses, Wei-Jun Cai’s group (University of Georgia) for pH measurements, and Steven E. Lohrenz’s group (University of Southern Mississippi) for sharing nitrate and nitrite data, William L. Miller for access to the diffuse attenuation data and the Optronics spectroradiometer, Elise Kennedy and Dandan Duan for assistance with dark incubation experiment data, and Ebenezer Nyadjro for facilitating access to the WHOI evaporation data. Finally, I thank the National Science Foundation for funding this work.
ABSTRACT

Rivers contribute about 0.25 Pg of terrigenous dissolved organic carbon (tDOC) to the ocean each year. The fate and transformations of this material have important ramifications for the metabolic state of the ocean, air-sea CO₂ exchange, and the global carbon cycle. Stable isotopic compositions and terrestrial biomarkers suggest tDOC must be efficiently mineralized in ocean margins. Nonetheless, the extent of tDOC mineralization in these environments remains unknown, as no quantitative estimate is available. The complex interplay of biogeochemical and physical processes in these systems compounded by the limited practicality of chemical proxies (organic biomarkers, isotopic compositions) make the quantification of tDOC mineralization in these dynamic systems particularly challenging. In this dissertation, new optical proxies were developed (Chapters 1 and 2) and facilitated the first quantitative assessment of tDOC mineralization in a dynamic river-influenced ocean margin (Chapter 3) and the monitoring of continental runoff distributions in the coastal ocean using remote sensing (Chapter 4).

The optical properties of chromophoric dissolved organic matter (CDOM) were used as optical proxies for dissolved organic carbon concentration ([DOC]) and %tDOC. In both proxies, the CDOM spectral slope coefficient ($S_{275-295}$) was exploited for its informative properties on the chemical nature and composition of dissolved organic matter. In the first proxy, a strong relationship between $S_{275-295}$ and the ratio of CDOM absorption to [DOC] facilitated accurate retrieval (+/- 4%) of [DOC] from CDOM. In the
second proxy, the existence of a strong relationship between $S_{275-295}$ and the DOC-normalized lignin yield facilitated the estimation of the %tDOC from $S_{275-295}$. Using the proxies, the tDOC concentration can be retrieved solely from CDOM absorption coefficients ($\lambda = 275-295$ nm) in river-influenced ocean margins.

The practicality of optical proxies facilitated the calculation of tDOC mineralization rates on the Louisiana shelf. Seasonal tDOC mass balances for the shelf revealed that between 26% (winter) and 71% (summer) of the mixed layer tDOC is mineralized during its residence on the shelf. Independent approaches further indicated biomineralization accounts for 60% of the tDOC mineralization whereas photomineralization contributes only 8%. The remaining 32% was attributed to the coupled photo-biomineralization. On an annual basis, our results indicated ~40% of the tDOC discharged by the Mississippi and Atchafalaya rivers to the Louisiana shelf (~1 Tg tDOC) is mineralized within 2 to 3 months. This extensive mineralization on the shelf is direct evidence ocean margins act as efficient filters of tDOC between the land and ocean.

Finally, the amenability of $S_{275-295}$ to ocean color remote sensing was demonstrated, and facilitates the real-time, synoptic monitoring of tDOC and freshwater runoff in coastal waters. Implementation of this approach provided the first pan-Arctic distributions of tDOC and continental runoff in surface polar waters, and will help understand the manifestations of climate change in this remote region.
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<th>Definition</th>
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<tbody>
<tr>
<td>AO</td>
<td>Arctic Oscillation</td>
</tr>
<tr>
<td>AQY</td>
<td>Apparent Quantum Yield</td>
</tr>
<tr>
<td>AR</td>
<td>Atchafalaya River</td>
</tr>
<tr>
<td>CAA</td>
<td>Canadian Arctic Archipelago</td>
</tr>
<tr>
<td>CDOM</td>
<td>Chromophoric Dissolved Organic Matter</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon Dioxide</td>
</tr>
<tr>
<td>CuO</td>
<td>Cupric Oxide</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved Organic Carbon</td>
</tr>
<tr>
<td>DOM</td>
<td>Dissolved Organic Matter</td>
</tr>
<tr>
<td>DU</td>
<td>Dobson Unit</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Precision Liquid Chromatography</td>
</tr>
<tr>
<td>M-ARS</td>
<td>Mississippi-Atchafalaya River System</td>
</tr>
<tr>
<td>MLR</td>
<td>Multiple Linear Regression</td>
</tr>
<tr>
<td>MR</td>
<td>Mississippi River</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular Weight</td>
</tr>
<tr>
<td>NADW</td>
<td>North Atlantic Deep Water</td>
</tr>
<tr>
<td>NAO</td>
<td>North Atlantic Oscillation</td>
</tr>
<tr>
<td>NGoM</td>
<td>Northern Gulf of Mexico</td>
</tr>
<tr>
<td>PAL</td>
<td>p-hydroxybenzaldehyde</td>
</tr>
<tr>
<td>PAD</td>
<td>p-hydroxybenzoic acid</td>
</tr>
</tbody>
</table>
PON .............................................................................................................. p-hydroxyacetophenone
SAL ........................................................................................................... Syringylaldehyde
SAD .......................................................................................................... Syringic Acid
SON .......................................................................................................... Acetosyringone
SSC .......................................................................................................... Spectral Slope Coefficient
TDAA ..................................................................................................... Total Dissolved Amino Acids
TDLP ....................................................................................................... Total Dissolved Lignin Phenols
TDLP-C ................................................................................................. Carbon-normalized Total Dissolved Lignin Phenols
tDOC ....................................................................................................... Terrigenous Dissolved Organic Carbon
tDOM ....................................................................................................... Terrigenous Dissolved Organic Matter
UV .............................................................................................................. Ultraviolet
VAL .............................................................................................................. Vanillin
VAD ........................................................................................................... Vanillic Acid
VON .......................................................................................................... Acetovanillone
CHAPTER 1

A NOVEL METHOD TO ESTIMATE DOC CONCENTRATIONS FROM CDOM ABSORPTION COEFFICIENTS IN COASTAL WATERS⁵

1.1 INTRODUCTION

Conventional methods for the analysis of Dissolved Organic Carbon (DOC) are restricted to measurements of discrete samples and are limited to providing synoptic coverage on relatively small spatial scales. The estimation of DOC concentrations, [DOC], through measurement of the optical properties of dissolved organic matter (DOM) (absorption and fluorescence) therefore represents a compelling alternative. Under optimal conditions and with proper instrumentation, the optical properties of DOM can be rapidly and continuously acquired in situ [Vodacek et al., 1997; Hitchcock et al., 2004].

The relationship between [DOC] and DOM absorption (Chromophoric Dissolved Organic Matter, CDOM) has been investigated in a variety of coastal systems [Ferrari et al., 1996; Del Vecchio and Blough, 2004a; Guéguen et al., 2005]. Although strong positive correlations have been observed between CDOM absorption coefficients, \( a_g(\lambda) \), and [DOC], the relationship varies among geographical regions and seasons [Blough and Del Vecchio, 2002]. For example, the ratio of \( a_g(\lambda) \) to [DOC] varies seasonally by more than 25-fold in the Middle Atlantic Bight alone [Del Vecchio and Blough, 2004a]. Such

variability in this ratio sets a limit on our capability to predict [DOC] from simple linear relationships between DOC and CDOM. The spectral characteristics of $a_g(\lambda)$ are representative of the types of chromophores present in DOM [Del Vecchio and Blough, 2004b]. A single exponential fit (Eq. (1.1)) is typically used to describe the spectral dependency of $a_g(\lambda)$:

$$a_g(\lambda) = a_g(\lambda_0) \cdot \exp(-S(\lambda - \lambda_0))$$

(1.1)

where $\lambda_0 < \lambda$ and $S$ is the spectral slope coefficient in the $\lambda_0$ to $\lambda$ nm spectral range. Several studies have related the spectral characteristics of DOM absorption to the chemical and structural nature of DOM such as molecular weight and aromaticity [Chin et al., 1994; Helms et al., 2008]. Other studies utilized molar absorptivity or carbon-specific UV absorbance as indicators of the molecular weight and aromatic content of organic matter isolates [Chin et al., 1994; Weishaar et al., 2003]. A linkage between the spectral characteristics of $a_g(\lambda)$ and the ratio $a_g(\lambda)$:[DOC] is therefore possible. If such a connection exists for DOM in the marine environment it could be exploited to improve predictions of [DOC] from measurements of $a_g(\lambda)$.

In this study, we explore the relationship between $S$ and the ratio $a_g(\lambda)$:[DOC] in surface waters of the Northern Gulf of Mexico (NGoM), with the intent of testing this hypothesis. Following recommendations by Helms et al. [2008] on the use of $S$ in the 275–295 nm spectral range, a strong relationship between $S_{275–295}$ and $a_g(\lambda)$:[DOC] was discovered. This connection is exploited in a method to accurately estimate [DOC] from simple in situ measurements of $a_g(275)$ and $a_g(295)$ in coastal areas. Its applicability in other marine systems is discussed.
1.2 METHODS
Surface water from the NGoM was collected and filtered for DOC analysis and CDOM absorbance measurements. A total of 222 stations \((n = 222)\) were sampled during five research cruises (January, April, July, October/November 2009 and March 2010) as part of the GulfCarbon project. About 50 stations were sampled per cruise (Fig. 1.1a) with the exception of January 2009 when 24 stations were sampled. Representing a salinity range of 0-37, these samples include most water types typically encountered in river-dominated ocean margins. DOC analysis was done by High Temperature Combustion (HTC) and CDOM absorbance, \(A(\lambda)\), was measured using a dual-beam spectrophotometer.

Absorbances were converted to absorption coefficients, \(a_g(\lambda)\), and spectral slope coefficients, \(S\), were calculated using linear fits of log-linearized \(a_g(\lambda)\). The carbon-specific absorption coefficients of DOM were calculated as the ratio of \(a_g(\lambda)\) to DOC concentration and are denoted here as \(a^*_{g}(\lambda)\), with units of \(m^{-1} \mu M^{-1}\). The value of \(a^*_{g}(\lambda)\) at \(\lambda = 355\) nm was calculated for consistency with previous studies [Vodacek et al., 1997; Del Vecchio and Blough, 2004a]. Detailed sampling and methods are provided in Appendix A.

Surface water from the Beaufort Sea was sampled in August 2009 as part of the Malina project. A total of 33 stations \(n = 33)\) were sampled across a salinity gradient of 0 to 30 and [DOC] and absorbance were measured as described above.

1.3 DYNAMICS OF DOC AND CDOM IN THE NORTHERN GULF OF MEXICO
The measured range of DOC concentrations, ([DOC]: 63–611 \(\mu M\)) spanned an order of magnitude over the salinity range of 0 to 37. The strong relationship between salinity and
[DOC] \( (r^2 = 0.83) \) indicates that DOM dynamics in surface waters were, to a first degree, dominated by terrigenous inputs (inset of Fig. 1.2a). Within this general view, however, a significant seasonality and deviation from linear mixing at salinity extremes was apparent (Fig. 1.2a). A poor correlation observed between [DOC] and salinity at salinities less than 20 \( (r^2 = 0.18) \) indicated the presence of multiple riverine sources with varying DOM properties. This observation is in agreement with earlier studies demonstrating varying mixing behavior of DOC as it transits from estuaries to the Gulf of Mexico \([Guo et al., 1998]\).

The NGOM is a river-dominated system in terms of DOM optical properties \([Chen and Gardner, 2004; Conmy et al., 2004; D'Sa and DiMarco, 2009]\). A strong, linear relationship \( (r^2 = 0.90) \) was observed in the present study between [DOC] and the CDOM absorption coefficient, \( a_g(355) \) (inset of Fig. 1.2b). However, this strong relationship is misleading for the purpose of retrieving [DOC] from \( a_g(355) \). The ratio \( a_g(355):[DOC]=a^*_{g}(355) \), varies by a factor of 55, from a minimum value of \( 5.3 \times 10^{-4} \text{ m}^{-1} \mu\text{M}^{-1} \) in the most oligotrophic sample to a value of \( 2.9 \times 10^{-2} \text{ m}^{-1} \mu\text{M}^{-1} \) in freshwater. The trend, range and values of \( a^*_{g}(355) \) observed in this study are in general agreement with those observed by \( Del Vecchio and Blough [2004a] \) in the Middle Atlantic Bight. Some of this variability can be attributed to the conservative mixing of river water and seawater along the salinity gradient and can be accounted for in a linear relationship of the form

\[
[\text{DOC}] = a + b \cdot a_g(355),
\]

where \( a \) and \( b \) are regression coefficients. However, a magnified view of the relationship between [DOC] and \( a_g(355) \) (Fig. 1.2b) also shows a strong seasonality and some non-linearity which can result from: 1) the presence of multiple riverine sources with different \( a^*_{g}(355) \); 2) the decoupling between the autochtonous...
sources and sinks of DOC with those of CDOM; and 3) photobleaching, known to decrease $a^*_g(355)$ [Del Vecchio and Blough, 2004a]. This variability cannot be constrained in the simple linear model and although seasonal linear models can be derived, their implementation is always difficult.

Numerous studies have investigated the dynamics of the spectral slope coefficient in aquatic environments and have concluded that it is of limited utility as a biogeochemical indicator [Blough and Del Vecchio, 2002]. However, the spectral range used among investigators has been inconsistent, generally broad (e.g., 290-700 nm) and restricted to the UV-A and visible domains. Helms et al. [2008] recently suggested the use of $S_{275-295}$ (UV-B domain, narrow range) as an indicator of photochemical alterations and DOM molecular weight and source in the marine environment. In light of their results, a remarkable finding of the present study is a strong relationship between $S_{275-295}$ and $a^*_g(355)$ (Fig. 1.2c), which is best approximated by an exponential equation of the form: $a^*_g(355) = \exp(\alpha - \beta \cdot S_{275-295}) + \exp(\gamma - \delta \cdot S_{275-295})$, where $\alpha$, $\beta$, $\gamma$ and $\delta$ are regression coefficients. This relationship is remarkable because a strong connection does not exist between $a^*_g(355)$ and other spectral slope coefficients such as $S_{300-350}$, $S_{300-400}$ or $S_{350-400}$ in this data set (inset of Fig. 1.2c), thereby highlighting the unique potential of the 275-295 nm spectral range to retain information about DOM composition and the ratio of $a_g(\lambda)$ to [DOC]. The strong link between $S_{275-295}$ and $a^*_g(355)$ is indicative that the dynamics of these two DOM properties are regulated by the same processes. Although gaining a full understanding of the dynamics responsible for this relationship is beyond the scope of this manuscript, it can be inferred from a few recent studies that the
processes responsible for the variabilities in $S_{275-295}$ and $a^*_g(355)$ are of the same nature [Del Vecchio and Blough, 2004a; Helms et al., 2008; Ortega-Retuerta et al., 2009].

A unique and important aspect of $S_{275-295}$ not mentioned by Helms et al. [2008] is the unique position of the 275-295 nm spectral region on the outside edge of the natural solar spectrum (Fig. 1.1b). Even under optimal conditions, very few photons of $\lambda < 295$ nm are present in the natural environment. According to the work of Del Vecchio and Blough [2002] on the photobleaching of $a_g(\lambda)$ using monochromatic irradiations, the decrease in $a_g(\lambda)$ upon absorption of photons of wavelength $\lambda_{ex}$ is maximum at or near $\lambda = \lambda_{ex}$ and decreases exponentially towards other wavelengths. It is therefore expected that any natural photon absorbed would always lead to a greater change in $a_g(295)$ than in $a_g(275)$, and consequently, to an increase in $S_{275-295}$. In contrast, other spectral regions used for the determination of $S$ tend to overlap with the photochemically active part of the natural solar spectrum (typically 300-400 nm). A well-behaved response of $S$ to photobleaching is therefore unlikely for spectral regions other than 275-295 nm. This phenomenon can contribute to the erratic behavior of $S$ typically observed in the marine environment.

An important implication of the relationship between $S_{275-295}$ and $a^*_g(\lambda)$ in this system is the novel capability to constrain the variability in the ratio $a_g(\lambda):[\text{DOC}]$ using information contained in the spectral shape of $a_g(\lambda)$. Because $a_g(\lambda):[\text{DOC}]$ can vary by a large factor, exploiting this information can considerably improve the accuracy of $[\text{DOC}]$ retrieved from $a_g(\lambda)$. 

19
1.4 ESTIMATING DOC FROM CDOM

DOC concentrations can be retrieved from the combination of \( a_g(\lambda) \) and a non-linear fit of \( a^*(\lambda) \) versus \( S_{275-295} \). However, we found through extensive testing that the most accurate [DOC] were obtained by performing multiple linear regressions (MLR) of log-linearized [DOC] against log-linearized \( a_g(275) \) and \( a_g(295) \), as described in Eq. (1.2):

\[
\ln[\text{DOC}] = \alpha + \beta \cdot \ln[a_g(275)] + \gamma \cdot \ln[a_g(295)]
\]  

(1.2)

where \( \alpha, \beta, \) and \( \gamma \) are regression coefficients.

This method exploits all the useful information contained in \( S_{275-295} \) while being simpler, more direct and accurate. The best wavelengths for prediction of [DOC] were \( \lambda = 275, 295 \) nm. The use of additional variables in the MLR (e.g., \( a_g(\lambda) \) at \( \lambda = 275, 295 \) nm, salinity, chlorophyll-a fluorescence) did not improve the predictive capability of the model. A MLR against \( \ln[a_g(275)] \) and \( \ln[a_g(295)] \) therefore represents an optimal model.

In order to relieve the constraint of using a single MLR for a broad range of [DOC] (63-611 µM), the data were separated into two subsets and a specific MLR was done on each subset. The data were divided based on the cutoff value \( a_g(275) = 3.5 \) m\(^{-1}\), which corresponds to the median value in these data. The regression coefficients are provided in Table 1.1 and the performance of the model is evaluated in Fig. 1.3.

The performance of the model (Fig. 1.3b) was compared to that of a single regression of \( \ln[\text{DOC}] \) versus \( \ln[a_g(355)] \) model (Fig. 1.3a). A large seasonal bias and poor accuracy at low and high DOC concentrations resulted from the use of the single regression, even after log-linearization of [DOC] and \( a_g(355) \). An even larger bias and lower accuracy was observed if these values were not log-linearized before regression. The new approach demonstrates that the use of two carefully chosen wavelengths and
their use in MLR can considerably improve the accuracy of estimated DOC concentrations. Overall, [DOC] estimated using this approach were within ±4.2% of the measured [DOC]. For comparison, the percent error associated with replicates of [DOC] measurements was typically ±1%. A sensitivity analysis of the model also revealed that about half of the ±4.2% error could be attributed to errors in the reproducibility of the absorbance measurements. The distribution of points around the 1-to-1 line indicated that the percent error associated with the [DOC] retrieved using this approach was consistent over the entire [DOC] range (Fig. 1.3b). The error associated with the estimate is typically ±2.4 µM for a measured [DOC] value of 60 µM, and ±12 µM for a measured [DOC] value of 300 µM.

1.5 APPLICABILITY OF THE APPROACH

The results presented in the previous section are valid in the NGoM, for which the model was parameterized. Application of these parameters to other marine systems can therefore lead to unpredictable results. In order to test the applicability of the approach to a different coastal system, we applied it to independent data (n = 33) acquired in August 2009 in the Beaufort Sea, in a region influenced by the Mackenzie river outflow. Our results indicate that applying the approach to this region using the NGoM parameters results in decreased accuracy (±18% of measured [DOC]) and biases in the derived [DOC]. However, excellent accuracy (±4.7%) and a consistent percent error over the full range of measured [DOC] (66–458 µM) is obtained after the model was re-parameterized using local data (Fig. 1.3c and Fig. 1.4). The regression coefficients derived for the Beaufort Sea are given in Table 1.1.
Although the approach may be applied to other coastal environments, differences in DOM sources and regulatory processes make the re-parameterization of the model using local data necessary to achieve high performance. Suitable data have already been collected in other coastal systems such as the Middle Atlantic Bight [Del Vecchio and Blough, 2004a; Mannino et al., 2008] and are therefore readily available for parameterizing the model. For other marine systems where both the range in DOM properties and the chemical composition of DOM is less influenced by terrigenous inputs (e.g., Sargasso Sea), the validity of the approach itself remains to be assessed.

Besides its simplicity of implementation, this method presents a number of advantages that make it suitable for high-resolution and long-term in situ monitoring of [DOC] in coastal environments. First, absorbance measurements at only two wavelengths are required, which can be acquired at a fast rate while storing minimal amounts of data. Second, the values of $a_g(275)$ and $a_g(295)$ are high in most environments thereby making the approach less sensitive to limitations in the precision of the instrument. Third, the relationship between [DOC] and $a_g(275)$ or $a_g(295)$ should remain minimally affected by changes in inorganic ion concentrations (e.g., nitrate, nitrite, bromide and bisulfide) [Johnson and Coletti, 2002]. Finally, if the model is parameterized using representative data, the approach should be applicable to a given region for all seasons using a single parameterization.
Figure 1.1 (a) Station locations in the Northern Gulf of Mexico. (b) CDOM absorption coefficient spectra, $a_g(\lambda)$, and corresponding spectral slope coefficient, $S_{275-295}$, for three contrasting water samples. The y-axis for $a_g(\lambda)$ is a log scale. $S_{275-295}$ is typically low in river water and increases in coastal and oligotrophic waters. A modeled, downward plane irradiance spectrum just above the sea surface, $E_d(0^+,\lambda)$, is overlaid and illustrates the absence of photons at wavelengths $\lambda < 295$ nm. $E_d(0^+,\lambda)$ was modeled for June 21st, 12:00 p.m., at latitude 28°N, with 300 DU of ozone, and a clear sky. These conditions correspond to the maximal incident irradiance expected in the Northern Gulf of Mexico.
Figure 1.2 Relationships between different DOM properties in the Northern Gulf of Mexico: (a) [DOC] vs. salinity; (b) $a_g(355)$ vs. [DOC]; (c) $a_g^*(355) = a_g(355)\cdot[DOC]$ vs. $S_{275-295}$. In Fig. 1.2a and 1.2b, the inset plots present linear regressions for the entire range of the data whereas the main plots magnify the 50-300 μM [DOC] range. In Fig. 1.2c, the inset plot shows the lack of relationship between $S_{350-400}$ and $a_g^*(355)$. 
Figure 1.3 (a) [DOC] estimated using a single linear regression of ln[DOC] against ln[$a_g(355)$] in the Northern Gulf of Mexico; (b) [DOC] estimated using the new approach in the Northern Gulf of Mexico. (c) [DOC] estimated using the new approach in the Beaufort Sea, after re-parameterization of the model using local data (see Fig. 1.4 in for station locations). In all plots, “Estimated DOC” indicates concentrations estimated from $a_g(\lambda)$. 
Figure 1.4 Station locations in the Beaufort Sea (Western Arctic Ocean), in a region influenced by the Mackenzie River outflow. The new approach presented in the manuscript performed well in this region after re-parameterization of the model using local data (see Fig. 1.3c in the manuscript).
Table 1.1 Parameters $\alpha$, $\beta$ and $\gamma$ derived from the multiple linear regressions of $\ln[\text{DOC}]$ against $\ln[a_g(275)]$ and $\ln[a_g(295)]$ for the Northern Gulf of Mexico and the Beaufort Sea.

<table>
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<th>$\beta$</th>
<th>$\gamma$</th>
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CHAPTER 2
THE SPECTRAL SLOPE COEFFICIENT OF CHROMOPHORIC DISSOLVED ORGANIC MATTER ($S_{275-295}$) AS A TRACER OF TERRIGENOUS DISSOLVED ORGANIC CARBON IN A RIVER-INFLUENCED OCEAN MARGIN

2.1 INTRODUCTION
The key processes controlling carbon transformations in ocean margins remain poorly quantified, thereby limiting our understanding of how the coastal ocean affects the ocean carbon cycle and atmospheric CO$_2$. Ocean margins account for $< 10\%$ of the global ocean surface area but play a disproportionately large role in ocean primary production, carbon remineralization and carbon burial [Gattuso et al., 1998; Muller-Karger et al., 2005]. Yet, estimation of carbon budgets remains a formidable challenge in ocean margins because the complex interplay of biogeochemical and physical processes inherent to these systems results in spatially and temporally variable carbon fluxes. Major questions thus remain as to whether ocean margins are net heterotrophic or autotrophic systems [Smith and Hollibaugh, 1993; Gattuso et al., 1998] and as to why some ocean margins are net sources of CO$_2$ to the atmosphere whereas others are net sinks [Borges et al., 2005; Cai et al., 2006]. Such uncertainties in net carbon metabolism and air-sea CO$_2$ exchange have left ocean margins largely unaccounted for in global carbon budgets

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Rivers exert an important control on carbon dynamics in ocean margins by contributing \( \sim 0.25 \, \text{Pg C yr}^{-1} \) of terrigenous dissolved organic carbon (tDOC) to the coastal ocean \cite{Hedges1997}. The fate of tDOC in the ocean and its effects on the net carbon metabolism of ocean margins are strongly dependent on whether tDOC is remineralized on the continental shelf or is transported to the open ocean. Isotopic and biomarker measurements indicate that tDOC represents a very small fraction of the dissolved organic carbon (DOC) pool in the ocean \cite{Druffel1992, Hedges1997, Opsahl1997} thereby suggesting that major remineralization routes of tDOC exist in ocean margins. Although considerable progress has been made understanding the processes involved in the remineralization of tDOC \cite{Smith1993, Cauwet2002, Mopper2002}, the extreme heterogeneity of river-influenced ocean margins represents a major challenge for providing quantitative estimates of these processes. Quantification of tDOC remineralization in ocean margins is largely restrained by the practicality of current tDOC proxies that rely on complex chemical analyses of biomarkers (e.g., lignin) or isotopic composition (e.g., \( \delta^{13} \text{C} \)). Innovative proxies capable of providing high-resolution estimates of tDOC and assessing regional features are therefore critically needed to improve carbon budgets in the coastal ocean.

The spectral absorption coefficient of chromophoric dissolved organic matter (CDOM), denoted here as \( a_g(\lambda) \) where \( \lambda \) is the wavelength, possesses attributes of a practical tracer of tDOC in river-influenced ocean margins. Optical measurements of CDOM are amenable to high-resolution and long-term monitoring using ship-based systems, moorings and remote sensing \cite{Hoge1995, Chen2004} and can therefore provide the spatio-temporal coverage necessary for a better understanding
of the fate of tDOC in ocean margins. Furthermore, recent advances in the biogeochemistry of lignin have revealed that a strong linear relationship between $a_g(\lambda)$ and dissolved lignin exists in rivers [Spencer et al., 2008; Benner and Kaiser, 2011] and in river-influenced ocean margins [Hernes and Benner, 2003], which suggests that lignin is an important chromophore of dissolved organic matter (DOM) in these environments. Lignin is also exclusively biosynthesized by vascular plants on land, and is therefore a biomarker of terrigenous DOM [Hedges and Mann, 1979; Opsahl and Benner, 1997]. This combination of properties defines lignin as a strictly terrigenous chromophore and suggests it is possible to trace this terrigenous component of DOM using $a_g(\lambda)$ in river-influenced ocean margins.

The CDOM spectral slope coefficient (SSC) in the 275-295 nm spectral range ($S_{275-295}$) could be a robust indicator of the DOC-normalized yield of dissolved lignin (TDLP-C) in river-influenced ocean margins, a quantity that can be exploited to estimate the fraction of DOC of terrigenous origin [Opsahl and Benner, 1997]. Helms et al. [2008] demonstrated that $S_{275-295}$ is a reliable proxy of CDOM average molecular weight (MW) and also suggested that $S_{275-295}$ is a potential indicator of photobleaching and DOM source in the marine environment. It was later demonstrated that $S_{275-295}$ is also an excellent indicator of the DOC-normalized absorption coefficient of CDOM in the surface waters of two contrasting river-influenced ocean margins, a feature exploited to accurately retrieve DOC concentrations (DOC) from $a_g(\lambda)$ in these systems [Fichot and Benner, 2011]. In light of this finding, the strong connection between lignin and $a_g(\lambda)$ suggest $S_{275-295}$ could be useful as a tracer of TDLP-C in river-influenced ocean margins.
In this study, we specifically test this hypothesis and demonstrate that a strong relationship exists between $S_{275-295}$ and TDLP-C in surface waters of the Northern Gulf of Mexico (NGoM). We further explore the origin of this relationship and use it to establish a new tracer of tDOC that is applicable on synoptic scales in river-influenced ocean margins. This tracer was developed using in situ measurements of $a_{e}(\lambda)$, DOC and lignin concentration acquired on a seasonal basis along a full salinity gradient in the surface waters of the NGoM. The NGoM is one of the largest river-influenced ocean margins in North America and represents an ideal environment for the development of this new approach.

2.2 METHODS
Surface water samples were collected as part of the GulfCarbon project, during five research cruises in the NGoM in January, April, July, and October-November 2009 and March 2010 (Fig. 2.1 and Table 2.1). The NGoM is one of the largest river-influenced ocean margins in North America, with the Mississippi River (MR) and the Atchafalaya River (AR) draining 41% of the contiguous USA and accounting for about 80% of the total freshwater input to the NGoM [Rabalais et al., 2002]. A total of 222 samples were collected for DOC and CDOM analyses with 104 matching samples for lignin analysis. Samples were collected across a salinity range of 0-37 and are representative of the majority of water types typically encountered in river-influenced ocean margins, from riverine to oligotrophic marine waters. Most samples were collected under well-mixed conditions from Niskin bottles mounted on a rosette with a conductivity-temperature-depth (CTD) instrument. Samples were collected with a polypropylene bucket deployed
from the bow of the ship when a strong vertical salinity gradient was observed in river
plumes.

Samples were gravity filtered from Niskin bottles using precombusted GF/F
filters (0.7-µm pore size) and stored frozen (-20°C) immediately after collection in
precombusted borosilicate glass vials. DOC analysis was conducted within a month of
collection by high temperature combustion using a Shimadzu total organic carbon (TOC)
TOC-V analyzer equipped with an autosampler [Benner and Strom, 1993]. Blanks were
negligible and the coefficient of variation between injections of a given sample was
typically ±0.6%. Accuracy and consistency of measured DOC concentrations was
checked by analyzing a deep seawater reference standard (University of Miami) every
sixth sample.

Samples were gravity filtered from Niskin bottles using Whatman Polycap
Aqueous Solution (AS) cartridges (0.2-µm pore size), collected in precombusted
borosilicate glass vials and stored immediately at 4°C until analysis in the laboratory. For
most samples, the absorbance was measured from 250 to 800 nm using a Shimadzu
ultraviolet (UV)-visible UV-1601 dual-beam spectrophotometer and 10-cm cylindrical
quartz cells. For highly absorbing samples, 5-cm cylindrical quartz cells or 1-cm quartz
cuvettes were used. An exponential fit of the absorbance spectrum over an optimal
spectral range was used to derive an offset value that was subtracted from the absorbance
spectrum [Johannessen and Miller, 2001; Fichot and Benner, 2011]. Absorbance
corrected for offset was then converted to Napierian absorption coefficient, \( a_g(\lambda) \) (m\(^{-1}\)).
The dependence of \( a_g(\lambda) \) on \( \lambda \) is typically described using Eq. (2.1):

\[
a_g(\lambda) = a_g(\lambda_0) \cdot \exp\left(-S(\lambda - \lambda_0)\right)
\] (2.1)
where $\lambda_0 < \lambda$ and $S$ is the spectral slope coefficient in the $\lambda_0-\lambda$ nm spectral range. Spectral slope coefficients were estimated using a linear fit of the log-linearized $a_g(\lambda)$ spectrum over their respective spectral range and are reported here with units of nm$^{-1}$.

Measurements of DOC and $a_g(350)$ were used to calculate DOC-normalized absorption coefficients ($a_g(350)$:DOC), expressed here in units of L mol$^{-1}$ cm$^{-1}$.

Samples were gravity filtered from Niskin bottles using Whatman Polycap AS cartridges (0.2-$\mu$m pore size), collected in 10 L high-density polyethylene carboys and acidified to pH $\approx$ 2.5-3 with 5 mol L$^{-1}$ sulfuric acid. Acidified samples were extracted onboard using C-18 cartridges (Varian MegaBond Elut) at a flow rate of 50 mL min$^{-1}$ (Louchouarn et al. 2000), and cartridges were stored at 4°C until elution in 30 mL of high precision liquid chromatography (HPLC)-grade methanol and stored at -20°C. Lignin was analyzed using the CuO oxidation method of [Kaiser and Benner, 2012].

Concentrations of lignin phenols were measured as trimethylsilyl derivatives using an Agilent 7890 gas chromatograph equipped with a Varian DB5-MS capillary column and an Agilent 5975 mass selective detector. The concentrations of nine lignin phenols were measured in this study: $p$-hydroxybenzaldehyde (PAL), $p$-hydroxyacetophenone (PON), $p$-hydroxybenzoic acid (PAD), vanillin (VAL), acetovanillone (VON), vanillic acid (VAD), syringaldehyde (SAL), acetosyringone (SON), syringic acid (SAD). PAL and PAD can be potentially produced from non-lignin sources during CuO oxidation [Benner and Kaiser, 2011], but a strong linear relationship ($R^2 \approx 0.95$) between the sum of $p$-hydroxy phenols (PAL+PAD+PON) and the sum of vanillyl phenols (VAL+VAD+VON), and a strong linear relationship ($R^2 \approx 0.99$) between PAL or PAD and PON, which is derived from lignin, indicated that PAL and
PAD were derived from lignin. The sum of six vanillyl and syringyl lignin phenols (TDLP₆), and the sum of nine \( p \)-hydroxyl, vanillyl and syringyl lignin phenols (TDLP₉) are reported in units of nmol L\(^{-1} \). Corresponding DOC-normalized lignin yields (TDLP₆-C and TDLP₉-C) are reported in units of %DOC.

Surface water from Sta. E0 (riverine) and F5 (marine) were collected during the GC4 cruise (Fig. 2.1) and combined with different mix-ratios to simulate conservative mixing of riverine DOC into marine waters. The riverine (Salinity = 0, DOC = 600 \( \mu \)mol L\(^{-1} \)) and marine (Salinity = 36.6, DOC = 78 \( \mu \)mol L\(^{-1} \)) samples were mixed in the following proportions (E0/F5 % vol.): 100/0, 50/50, 10/90, 2.5/97.5, 1.25/98.75, and 0/100, corresponding to salinities of 0, 18.3, 32.9, 35.8, 36.1 and 36.6, respectively. The TDLP₉-C values were calculated using mixing ratios and DOC and lignin phenol concentrations measured in the E0 and F5 samples. Theoretical \( a_g(\lambda) \) spectra were calculated in the same manner and 'theoretical' values of \( S_{275-295} \) were derived. The \( a_g(\lambda) \) spectra were also measured for each mixture and 'measured' values of \( S_{275-295} \) were calculated.

Samples for photobleaching experiments were gravity filtered from Niskin bottles using Whatman Polycap AS cartridges (0.2-\( \mu \)m pore size), collected in cleaned (450°C for 4 h) 500 mL Kimax glass bottles and stored immediately at 4°C. Prior to each experiment, samples were re-filtered through a 0.2-\( \mu \)m nylon membrane filter before dispensing into 5-cm pathlength quartz cells (Spectrocell CM-3050-T). Quadruplicates of each sample were irradiated under controlled illumination conditions and constant temperature (22.5°C) using an Atlas Suntest XPS+ solar simulator (Xenon lamp, 750 W) and a setup similar to the one used by Johannessen and Miller [2001]. Long-pass, 295-
nm cutoff filters (Schott N-WG295) were used to prevent unnatural radiation from reaching the samples. Irradiations lasted 48 h for most samples, and 72 or 96 h for a few samples. Changes in $a_g(\lambda) (\lambda = 250-800 \text{ nm})$ and $S_{275-295}$ were monitored every 24 h, regardless of total irradiation time. A total of 75 samples were processed during the five cruises. Duplicate experiments were conducted for six of the 75 samples.

Changes in TDLP$_9$-C during irradiation were measured using five samples collected during the GC5 cruise. About 250 mL of sample was divided and dispensed into eight quartz cells before irradiation using the same setup as in the photobeaching experiments (48 h irradiations). After irradiation, the eight subsamples were consolidated into one sample and analyzed for $a_g(\lambda) (\lambda = 250-800 \text{ nm})$, DOC and lignin, and TDLP$_9$-C and $S_{275-295}$ were calculated. About 250 mL of the original sample was also used in the same analyses in order to provide initial values.

During the GC5 cruise, surface waters from stations A1 and C1 (Fig. 2.1) were gravity filtered from Niskin bottles using precombusted GF/F filters (0.7-µm pore size) and used onboard in microbial degradation experiments. For both stations, 2 L of filtered water was divided into two treatments: unamended or amended with ~ 22 µmol (DOC) L$^{-1}$ of plankton DOM obtained from a diatom bloom [Davis and Benner, 2007]. For each treatment, triplicates dispensed in cleaned (450°C for 4 h), 125 mL Kimax glass bottles were immediately frozen at -20°C (initial time point) and matching triplicates were incubated onboard in the dark, at ambient seawater temperatures (10-20°C) and under oxic conditions. Incubation times were 12 days for sample A1 and 10 days for sample C1. Samples were frozen at -20°C after incubation. Triplicates were analyzed for DOC and total dissolved amino acids (TDAA) analyses. The TDAA concentrations were
measured as o-phthalaldehyde derivatives using an Agilent 1100 HPLC system with a fluorescence detector [Shen et al., 2012]. The rest of each sample was filtered through a 0.2-µm nylon membrane filter and analyzed for CDOM. The triplicates from each treatment and time point were combined prior to filtration and analyzed for CDOM as one sample.

2.3 RESULTS
The relationships between DOM properties and salinity indicated a dominant influence of terrigenous inputs from the MR and AR on DOM dynamics (Fig. 2.2). Values of DOC, TDLP<sub>9</sub>, TDLP<sub>9</sub>-C, <i>a</i><sub>g</sub>(350), and <i>a</i><sub>g</sub>(350):DOC were highest in the MR and AR, where they ranged from 232-611 µmol L<sup>-1</sup>, 71-491 nmol L<sup>-1</sup>, 0.22-0.68 %DOC, 3.96-17.52 m<sup>-1</sup> and 153-292 L mol<sup>-1</sup> cm<sup>-1</sup>, respectively. These DOM properties decreased from riverine to oligotrophic marine waters where they reached minimum values of 63 µmol L<sup>-1</sup> (DOC), 1 nmol L<sup>-1</sup> (TDLP<sub>9</sub>), 0.01 %DOC (TDLP<sub>9</sub>-C), 0.046 m<sup>-1</sup> (<i>a</i><sub>g</sub>(350)) and 5.8 L mol<sup>-1</sup> cm<sup>-1</sup> (<i>a</i><sub>g</sub>(350):DOC). Coefficients of determination (<i>R</i><sup>2</sup>) associated with seasonal linear regressions of DOM properties on salinity further indicated that 82-94%, 67-90%, 54-92%, 83-94% and 75-93% of the variability in DOC, TDLP<sub>9</sub>, TDLP<sub>9</sub>-C, <i>a</i><sub>g</sub>(350) and <i>a</i><sub>g</sub>(350):DOC, respectively, were related to changes in salinity.

The relationships between DOM properties and salinity also revealed distinct and seasonally variable riverine DOM sources (Fig. 2.2). Variability in riverine source was evident from seasonal changes and scatter in the relationships between DOC, TDLP<sub>9</sub>, TDLP<sub>9</sub>-C, <i>a</i><sub>g</sub>(350), <i>a</i><sub>g</sub>(350):DOC and salinities < 25. This observation is supported by large differences in these properties between the MR and the AR. The DOC, TDLP<sub>9</sub>,
TDLP$_9$-C, $a_g$(350), and $a_g$(350):DOC in the MR averaged (± SD) $296±54$ µmol L$^{-1}$, $135±52$ nmol L$^{-1}$, $0.37±0.10$ %DOC, $5.54±1.63$ m$^{-1}$ and $185±30$ L mol$^{-1}$ cm$^{-1}$, respectively, and are lower than in the AR where they averaged $438±106$ µmol L$^{-1}$, $266±147$ nmol L$^{-1}$, $0.48±0.18$ %DOC, $10.43±4.19$ m$^{-1}$ and $233±40$ L mol$^{-1}$ cm$^{-1}$, respectively. Paired $t$-tests further indicated that DOC, $a_g$(350), TDLP$_9$ and $a_g$(350):DOC were significantly higher ($p < 0.05$) in the AR than in the MR, but were inconclusive for TDLP$_9$-C ($p = 0.10$).

The spectral slope coefficient $S_{275-295}$ exhibited a non-linear dependence with salinity, in stark contrast to the lack of dependence exhibited by $S_{350-400}$ (Fig. 2.2F). The $S_{275-295}$ increased exponentially from a minimum value of 0.0135 nm$^{-1}$ in rivers to a maximum value of 0.0482 nm$^{-1}$ in oligotrophic marine waters. Comparatively, the range of $S_{275-295}$ values in the AR and MR (0.0135-0.0169 nm$^{-1}$) was minimal. Furthermore, $S_{275-295}$ averaged 0.0156 nm$^{-1}$ in the MR and 0.0150 nm$^{-1}$ in the AR, and a paired $t$-test indicated these values were not significantly different ($p = 0.09$). The dependence of $S_{275-295}$ with salinity also exhibited low seasonal variability with the exception of the summer, when $S_{275-295}$ in the MR, AR, and ocean was noticeably higher. A careful examination of each $a_g(\lambda)$ spectrum demonstrated that the lack of coherent trend for $S_{350-400}$ is not attributable to sensitivity issues with the spectrophotometer. Note, however, that the $S_{350-400}$ of nine samples (out of 222) were not shown in Fig. 2.2F because the detection limit of the spectrophotometer was reached at $\lambda < 400$ nm for these samples.

A positive, linear relationship ($R^2 \approx 0.93$) was observed between TDLP$_9$ and $a_g$(350) (Fig. 2.3A). This relationship held for all seasons ($0.89 < R^2 < 0.99$), but a seasonality in the lignin contribution to CDOM is evident from seasonal differences in
the value of slope coefficient $b$ of equation $TDLP_9 = a + b \cdot a_g(350)$. Minimum and maximum contributions were observed in summer 2009 ($b = 14.8$) and spring 2010 ($b = 32.9$), respectively. This strong linear relationship also implies that $a_g(350)$ can be used as a reliable indicator of $TDLP_9$. A simple model based on Eq. (2.2) was developed,

$$[TDLP_9] = \alpha + \beta \cdot \ln[a_g(350)]$$ (2.2)

where the regression parameters $\alpha$ and $\beta$ are provided in Table 2.2. The linear regression utilized log-linearized values because both $a_g(350)$ and $TDLP_9$ varied by more than two orders of magnitude. An error analysis revealed that $TDLP_9$ is estimated from $a_g(350)$ within ±22% using this simple model.

A striking relationship between $S_{275-295}$ and $a_g(350):DOC$ demonstrated that $S_{275-295}$ is an excellent indicator of the DOC-normalized absorption coefficient in this environment (Fig. 2.3B). Low values of $S_{275-295}$ are indicative of high DOC-normalized absorption coefficients in rivers, whereas high values of $S_{275-295}$ correspond to low DOC-normalized absorption coefficients in marine waters. No seasonality was observed. A simple model based on Eq. (2.3) can be used to derive $a_g(350):DOC$ from $S_{275-295}$ in the NGoM,

$$a_g(350):DOC = \exp(\alpha + \beta \cdot S_{275-295}) + \exp(\gamma + \delta \cdot S_{275-295})$$ (2.3)

where the regression coefficients $\alpha$, $\beta$, $\gamma$, and $\delta$ are provided in Table 2.2. An error analysis indicated $a_g(350):DOC$ is retrieved from $S_{275-295}$ within ±8%.

Finally, a non-linear relationship between $S_{275-295}$ and $TDLP_9$-C was observed (Fig. 2.4A). Low values of $S_{275-295}$ were indicative of high $TDLP_9$-C in rivers, whereas high values of $S_{275-295}$ corresponded to low $TDLP_9$-C in marine waters. No seasonality
was evident. The non-linear regression of TDLP$_9$-C on $S_{275-295}$ with Eq. (2.4) provided the best fit over the entire range of TDLP$_9$-C values (Fig. 2.4A),

$$TDLP_9 - C = \exp(\alpha + \beta \cdot S_{275-295}) + \exp(\gamma \cdot S_{275-295}) + \delta \cdot \exp(S_{275-295})$$

(2.4)

where $\alpha$, $\beta$, $\gamma$, and $\delta$ are the regression coefficients provided in Table 2.2. The non-linear regression was weighted with a 1:TDLP$_9$-C function for a balanced fit and a more representative model at low TDLP$_9$-C values. A comparison of measured and estimated TDLP$_9$-C demonstrated that the model estimated TDLP$_9$-C from $S_{275-295}$ within ±16% of measured TDLP$_9$-C values, consistently over the entire range of TDLP$_9$-C values (Fig. 2.4B). The error distribution was approximately normal and centered around zero with half of the estimates within ±10% error (boxplot in Fig. 2.4B). A strong linear relationship ($R^2 \approx 0.83$) between $S_{275-295}$ and TDLP$_9$-C was also observed for the AR and MR samples alone ($n = 10$).

Models based on the relationships between $a_g(350)$ and TDLP$_6$ (as in Eq. (2.2)), and between $S_{275-295}$ and TDLP$_6$-C (as in Eq. (2.4)) were also derived because the sum of six vanillyl and syringyl lignin phenols is commonly reported in the literature. Excellent linear relationships between TDLP$_6$ and TDLP$_9$ ($R^2 \approx 0.999$), and between TDLP$_6$-C and TDLP$_9$-C ($R^2 \approx 0.999$) justified the simple re-parameterization of Eq. (2.2) (TDLP$_6$) and Eq. (2.4) (TDLP$_6$-C) to derive the models. Their accuracy was slightly less than for TDLP$_9$ and TDLP$_9$-C, thereby supporting the primary use of TDLP$_9$ and TDLP$_9$-C in this study. Regression coefficients and error analyses are provided in Table 2.2. Note that the parameters and error analyses for all models (Table 2.2) are only adequate for the range of data collected in this study, and the reliability of the models cannot be guaranteed.
beyond the range of these variables: \(a_g(350)\) (0.046-17.52 m\(^{-1}\)), \(a_g(350)\) : DOC (6-292 L mol\(^{-1}\) cm\(^{-1}\)), and \(S_{275-295}\) (0.0135-0.0482 nm\(^{-1}\)).

The riverine DOM mixing experiment demonstrated that \(S_{275-295}\) is a conservative tracer of TDLP\(_7\) C during mixing (Fig. 2.5). Salinity and pH increased from 0 and 7.4 respectively in the riverine end member (E0), to 36.6 and 8.1 in the marine end member (F5), which is representative of the salinity and pH ranges typically observed in the NGoM. The \(S_{275-295}\) measured in the mixed solutions remained very close to the theoretical \(S_{275-295}\) values calculated from mixing ratios and end-member values. The \(S_{275-295}\) remains essentially unaffected by changes in the chemical environment of DOM (e.g., pH, ionic strength) during the mixing of river water in the ocean.

Photochemical experiments with 75 samples from the NGoM revealed that exposure of DOM to solar radiation consistently increased \(S_{275-295}\) (Fig. 2.6A). Regardless of season, origin of sample and irradiation time, \(a_g(\lambda)\) always decreased and \(S_{275-295}\) always increased during irradiation. The increasingly steeper lines with decreasing \(a_g(350)\) (Fig. 2.6A) further indicated the rate of change in \(S_{275-295}\) relative to that of \(a_g(350)\) is lowest in rivers and increases exponentially in the most oligotrophic marine waters (e.g., lowest \(a_g(350)\)). In contrast, the effects of photobleaching were highly unpredictable for \(S_{350-400}\) and other SSCs estimated in the UV-A and visible regions (e.g., \(S_{300-400}, S_{300-350}\)), varying greatly in direction and magnitude depending on sample origin or irradiation time, but without any clearly discernable pattern. A careful examination of the \(a_g(\lambda)\) spectra demonstrated that the unpredictable effects of photodegradation on \(S_{350-400}\) are not related to sensitivity issues with the spectrophotometer. This unpredictability is also evident in the data presented in Tables 2 and 3 of Helms et al. [2008]. The lignin
photodegradation experiments further revealed that increases in $S_{275-295}$ during irradiation were accompanied by decreases in TDLP$_9$-C in all five samples (Fig. 2.6B).

The DOM amendment and degradation experiments demonstrated that plankton CDOM production had moderate effects on $S_{275-295}$ (Table 2.3). The addition of $\sim 22$ µmol DOC L$^{-1}$ plankton DOM increased $S_{275-295}$ from 0.0168 to 0.0176 nm$^{-1}$ in sample A1 and from 0.0196 to 0.0204 nm$^{-1}$ in sample C1. This increase in $S_{275-295}$ is consistent with the measured $S_{275-295}$ (0.0259 nm$^{-1}$) in the plankton DOM inoculum. HPLC measurements further revealed that total hydrolyzable dissolved amino acids (TDAA) comprise $\sim 20\%$ of DOC in the plankton DOM inoculum. The plankton DOM addition resulted in a 260% and 290% increase in TDAA in samples A1 and C1, respectively. Proteins typically exhibit broad absorption bands centered at 280 nm. The large increase in TDAA resulting from the addition of protein-rich plankton DOM is consistent with the observed increase in $S_{275-295}$. This indicates the production of protein-rich plankton DOM can affect $S_{275-295}$.

The DOM amendment and degradation experiments further revealed that microbial degradation had minor effects on $S_{275-295}$ but might play an important role by balancing the effects of plankton DOM production (Table 2.3). Microbial degradation in the ‘no addition’ treatments resulted in a 1% decrease in $S_{275-295}$ after a 10-day incubation in sample C1, and a 2.4% decrease after a 12-day incubation in sample A1. The effects of microbial degradation were more substantial in the plankton DOM addition treatments with $S_{275-295}$ decreasing from 0.0176 to 0.0165 nm$^{-1}$ in sample A1 and from 0.0204 to 0.0189 nm$^{-1}$ in sample C1. This enhanced decrease in $S_{275-295}$ to below pre-addition values was also accompanied by a large decrease in DOC and TDAA to pre-addition levels, thereby revealing that most of the plankton DOC added to samples C1 and A1 was
remineralized within 10-12 days of incubation. The rapid removal of added DOM is consistent with plankton DOM being primarily composed of labile DOM such as proteins, and demonstrates that microbial degradation has the potential to rapidly neutralize the effects of plankton DOM additions on $S_{275-295}$.

The relationship between $S_{275-295}$ and TDLP$_9$-C can be used to develop the $S_{275-295}$ as a tracer of tDOC in the NGoM (Fig. 2.7). Lignin is a biomarker of terrigenous DOC, and TDLP$_9$-C can be used to estimate the fraction of terrigenous DOC (%tDOC) in the ocean [Meyers-Schulte and Hedges, 1986; Opsahl and Benner, 1997; Benner et al., 2005]. The %tDOC was calculated as in Eq. (2.5)

$$\%_{tDOC} = 100 \cdot \frac{TDLP_9 - C_{sample}}{TDLP_9 - C_{river}} \quad (2.5)$$

where TDLP$_9$-C$_{sample}$ and TDLP$_9$-C$_{river}$ are the percentages of DOC comprised by lignin in samples and rivers, respectively. Here, TDLP$_9$-C$_{sample}$ was estimated from $S_{275-295}$ using Eq. (2.4), and TDLP$_9$-C$_{river}$ was calculated as the average of all TDLP$_9$-C values measured in the MR and AR. The error associated with the retrieval of TDLP$_9$-C$_{sample}$ from $S_{275-295}$ and the uncertainty in TDLP$_9$-C$_{river}$ set limits on the accuracy of the tracer. It was demonstrated earlier that TDLP$_9$-C is retrieved from $S_{275-295}$ with an average error of ±16%. The uncertainty in TDLP$_9$-C$_{river}$, on the other hand, is related to the natural variability of TDLP$_9$-C in the MR and AR, where it averaged 0.38±0.10 %DOC (range: 0.22-0.49) and 0.48±0.2 %DOC (range: 0.24-0.68), respectively. Considering that tDOC and lignin in NGoM surface waters primarily originate from the MR and AR, TDLP$_9$-C$_{river}$ in surface waters of the NGoM is best represented by a normal distribution with mean 0.43 %DOC and standard deviation 0.15 %DOC, corresponding to the mean and standard deviation of all TDLP$_9$-C measurements made in the AR and MR ($n = 10$). An
uncertainty analysis based on the consideration of these two sources of error was performed and a 75% confidence interval of predicted %tDOC was calculated (Fig. 2.7). The approach can also be applied using TDLP$_6$-C$_{sample}$ and TDLP$_6$-C$_{rivers}$, where TDLP$_6$-C$_{river}$ in surface waters of the NGoM is best represented by a normal distribution with mean 0.35 %DOC and standard deviation 0.13 %DOC.

2.4 DISCUSSION

The applicability of the tDOC tracer presented in this manuscript relies on the existence of a strong relationship between $S_{275-295}$ and TDLP$_9$-C, which arises primarily from a combination of the following factors: 1) lignin is a chromophore unique to DOC of terrestrial origin, 2) photodegradation of CDOM consistently leads to an increase in $S_{275-295}$ and a decrease in TDLP$_9$-C, and 3) mixing and photobleaching are dominant processes regulating $S_{275-295}$ and TDLP$_9$-C in surface waters of river-influenced ocean margins.

Although spectral features of CDOM absorption have long been recognized as potentially informative in the characterization of DOM [Carder et al., 1989; Chin et al., 1994; Peuravuori and Pihlaja, 1997], variability in SSCs in the marine environment have proven difficult to interpret. The lack of clear trends in the ocean and the inconsistent spectral range and methodology used in the derivation of the SSC are primarily responsible for the lack of consensus on the use of this parameter in the marine environment [Blough and Del Vecchio, 2002]. The value of the SSC depends on the spectral range considered, thereby reflecting the inadequacy of the single exponential model (Eq. (2.1)) to capture the spectral nuances exhibited by $a_d(\lambda)$ [Twardowski et al., 2004]. A single exponential model only provides a reasonable description of the spectrum
over narrow spectral regions. These limitations led Helms et al. [2008] to propose the use of narrow SSCs as biogeochemical indicators. They demonstrated that $S_{275-295}$ and the dimensionless slope ratio $S_R$ ($S_{275-295}:S_{350-400}$) were strongly related to CDOM average molecular weight. They further revealed that $S_{275-295}$ and $S_R$ consistently increased upon irradiation and suggested they are potential indicators of photobleaching in the marine environment. An increase in $S_{275-295}$ upon irradiation of water samples from the Southern Ocean [Ortega-Retuerta et al., 2009] and the Congo River (first 12 days of irradiation) [Spencer et al., 2009] has been observed and is consistent with the data presented herein.

The present study also revealed that the response of $S_{275-295}$ to irradiation is unique among SSCs. The effects of irradiation were more pronounced for $S_{275-295}$ than for spectrally adjacent SSCs (e.g., $S_{254-275}$, $S_{295-320}$) and lead to unpredictable effects for SSCs with $\lambda > 320$ nm (e.g., $S_{350-400}$). In general, the net effects of photobleaching on SSCs are highly dependent on the spectral quality of irradiation [Tzortziou et al., 2007] and are therefore sensitive to spectral variations in incident solar irradiance, water column diffuse attenuation, and $a_g(\lambda)$ in the marine environment. In contrast to other SSCs, the response of $S_{275-295}$ to solar irradiation is unique because of the position of the 275-295 nm window on the outer edge of the incident solar spectrum. Few photons of wavelength $< 295$ nm are present in the environment, and under almost all natural aquatic conditions the rate of photon absorption by CDOM decreases sharply from 295 nm to 275 nm. Furthermore, the extensive work of [Del Vecchio and Blough, 2002; Del Vecchio and Blough, 2004b] on photobleaching indicates the fraction of initial $a_g(\lambda)$ lost upon absorption of photons $\geq 295$ nm is always greater at 295 nm than at 275 nm. Consequently, exposure of CDOM to solar radiation under natural conditions always results in a greater fractional decrease in
than in $a_g(275)$, thereby increasing $S_{275-295}$. This unique feature of $S_{275-295}$ makes it an excellent indicator of photobleaching and is critical for its application as a proxy of TDLP$_9$-C in river-influenced ocean margins.

The inflow of riverine inputs from the MR and AR and its physical mixing on the shelf represents a dominant mechanism regulating the dynamics of $S_{275-295}$ in the surface waters of the NGoM. The prominent role of riverine inputs on CDOM in the NGoM was revealed in previous studies [Chen and Gardner, 2004; D'Sa and DiMarco, 2009] and is confirmed here by the linearity of the seasonal trends in $a_g(350)$ and TDLP$_9$ with salinity. The observation that the exponential dependence of $S_{275-295}$ on salinity closely resembles a conservative SSC mixing curve [Stedmon and Markager, 2003] demonstrates the importance of mixing in the regulation of $S_{275-295}$ across the entire salinity gradient. The dynamics of $S_{275-295}$ are sensitive to variations in $S_{275-295}$ in the MR and AR, but the narrow range of $S_{275-295}$ values in the MR and AR (0.0135-0.0169 nm$^{-1}$) relative to that observed along the salinity gradient (0.0135-0.0482 nm$^{-1}$) indicates the natural variability of $S_{275-295}$ in the MR and AR represents a minor driver of the variability in the NGoM. These effects were most noticeable during the summer.

The large range of $S_{275-295}$ values along the salinity gradient indicates the influence of other regulatory processes. The riverine DOM mixing experiment revealed minimal effects of pH and ionic strength on $S_{275-295}$ and is in agreement with the findings of Blough et al. [1993] and Guo, W et al. [2007] in other river-influenced systems. A simple sensitivity analysis using measured nitrate and nitrite concentrations on 217 of the 222 samples used in this study and the published molar absorption coefficients of aqueous nitrate and nitrite [Gaffney et al., 1992; Riordan et al., 2005] demonstrated that
these inorganic species contribute minimally to the variability of $S_{275-295}$ in the NGOM. Biological processes also appeared to play a minor role in the regulation of $S_{275-295}$ because microbial degradation resulted in lower $S_{275-295}$ values, as was observed by [Helms et al., 2008] and [Ortega-Retuerta et al., 2009], and plankton-derived DOC and CDOM were rapidly consumed by microorganisms. Thus, neither biological processes nor changes in pH, ionic strength, nitrate or nitrite can account for the observed dynamics and trends in $S_{275-295}$.

This study demonstrated photobleaching is a major process regulating $S_{275-295}$ in surface waters. During transport from rivers to the outer shelf, CDOM mixes with waters of varying optical properties and is exposed to changing irradiation conditions. In light of the contrasting responses of $S_{275-295}$ and $S_{350-400}$ to solar exposure demonstrated in this study, the monotonic increase in $S_{275-295}$ with salinity and the corresponding lack of a coherent trend in $S_{350-400}$ are both consistent with the cumulative effects of photobleaching on CDOM. Furthermore, the observation that $S_{275-295}$ exhibits a greater range of values than other SSCs in the NGOM is also consistent with the prominent regulatory role of photobleaching and the greater sensitivity of $S_{275-295}$ to photobleaching relative to other SSCs. Higher $S_{275-295}$ values observed at salinities $>25$ during summer are consistent with the enhancement of photobleaching by high solar irradiance and shallow stratification of surface waters on the shelf. The strong relationship between $S_{275-295}$ and $a_g(350):DOC$ is consistent with evidence that photobleaching also decreases $a_g(\lambda):DOC$ very efficiently [Stubbins et al., 2010].

The large increase in $S_{275-295}$ along the salinity gradient is evidence that the suite of chromophores in riverine and marine CDOM is very different. A simple decrease in
the abundance of chromophores with increasing salinity would result in a decrease in $a_g(\lambda)$ but would leave $S_{275-295}$ unchanged, as a simple dilution of river water in milli-Q water can demonstrate. Chromophoric compounds can vary because they originate from different sources (terrigenous vs. marine), as revealed by the large difference in $S_{275-295}$ between rivers (0.0135-0.0169 nm$^{-1}$) and fresh plankton DOM (0.0259 nm$^{-1}$) observed in this study. Chromophores can also change as a result of photochemical or biological transformations in the water column. However, as previously discussed, photochemical degradation stands alone as a process capable of producing $S_{275-295}$ values $> 0.03$ nm$^{-1}$, thereby suggesting that CDOM is photochemically altered in surface waters of salinities $> 30$, regardless of origin (i.e., marine or terrigenous).

The results of this study are consistent with $S_{275-295}$ being closely related to CDOM molecular weight (MW) in the NGoM [Helms et al., 2008]. Biological processing, nitrate and nitrite concentrations, and CDOM alterations resulting from changes in pH and ionic strength have minimal effects on $S_{275-295}$. In contrast, the mixing of different chromophores and the cumulative effects of photobleaching appear largely responsible for the increasing trend in $S_{275-295}$ with salinity. Solar exposure is known to decrease CDOM MW [Mopper and Kieber, 2002]. Benner and Opsahl [2001] demonstrated the MW of DOC decreases across salinity gradients in the NGoM, and Helms et al. [2008] revealed that $S_{275-295}$ consistently increases with photochemically induced decreases in MW for a wide range of natural waters. Thus, the increase in $S_{275-295}$ with salinity observed in the NGoM is most likely representative of a decrease in CDOM MW along the salinity gradient. Consistent with this idea, continuous shifts from high MW to low MW CDOM along the freshwater-marine continuum were reported in the
lower Chesapeake Bay [Helms et al., 2008] and in the St.-Lawrence Estuary [Xie et al., 2012].

It appears $S_{275-295}$ is also related to lignin MW in the NGoM. Lignin is an aromatic heteropolymer and a known chromophore. Lignin concentrations covary strongly with $a_g(350)$ across the MR plume [Hernes and Benner, 2003] and in the Yukon River basin [Spencer et al., 2008]. Furthermore, the present study revealed that a strong relationship exists between $a_g(350)$ and lignin concentration throughout surface waters of the NGoM during all seasons, thereby indicating lignin in this environment is primarily regulated by the same dominant mechanisms as the rest of CDOM. Solar exposure of CDOM results in a simultaneous decrease in lignin concentration and $a_g(350)$ [Spencer et al., 2009; Benner and Kaiser, 2011] and therefore tends, like mixing, to preserve the relationship between lignin concentration and $a_g(350)$. Opsahl and Benner [1998] observed a shift in lignin MW from 90% high MW to 80% low MW upon 28 days of incubation in sunlight, and alteration of lignin composition further indicates solar exposure is responsible for the sharp decrease in lignin MW observed along the salinity gradient of the MR plume [Benner and Opsahl, 2001; Hernes and Benner, 2003]. These observations suggest $S_{275-295}$ is tightly linked to lignin MW. Consistent with this idea, recent work on the structural basis of CDOM optical properties suggests that intramolecular interactions between (partially oxidized) lignin aromatic moieties play an important role determining CDOM absorption properties [Del Vecchio and Blough, 2004b; Boyle et al., 2009].

The relationship observed between $S_{275-295}$ and TDLP9-C in surface waters of the NGoM arises primarily as a result of the concurrent effects of mixing and photodegradation on the lignin content of DOC and the MW distribution of lignin and
other chromophores (Fig. 2.8). This study revealed that several factors contribute to maintaining the relationship between $S_{275-295}$ and TDLP$_9$-C throughout the river to ocean continuum in the NGOM. First, $S_{275-295}$ and TDLP$_9$-C are strongly and linearly correlated in the MR and AR and exhibit little variability in these rivers relative to their range of variability in the marine environment. A strong relationship between comparable properties (lignin yield and slope ratio, $S_R$), was also observed in the upland catchments of the Congo River [Spencer et al., 2010]. Second, $S_{275-295}$ is a conservative tracer of TDLP$_9$-C during mixing of freshwater in the ocean. Third, photodegradation of CDOM consistently increases $S_{275-295}$ while decreasing TDLP$_9$-C, thereby indicating photodegradation results in the simultaneous decrease in CDOM and lignin MW and the removal of lignin from the DOC pool. Finally, microbial degradation shows little potential for altering TDLP$_9$-C on time scales of ocean margin dynamics [Opsahl and Benner, 1998; Heres and Benner, 2003]. The elevated production of marine DOC by planktonic organisms often observed at salinities of 20-30 [Benner and Opsahl, 2001] tends to disrupt this relationship and might be responsible for the increased scatter in data corresponding to these salinities.

The dual nature of lignin as a chromophore and a terrigenous component of DOC enables the use of $S_{275-295}$ as a tracer of the fraction of tDOC in a water sample, thereby providing new capabilities to trace tDOC on synoptic scales of significance to carbon cycling in ocean margins. It is important to note, however, that quantitative applications of this tracer assume preferential removal of lignin from tDOC by photochemical processes is balanced by preferential removal of other components of tDOC by microbial processes on times scales of ocean margin dynamics. Although further studies of the
relative kinetics of these processes in surface waters of river-influenced ocean margins is required to assess the extent to which this tracer is representative of bulk tDOC, the observation that photodegradation and biodegradation preferentially remove distinct components of riverine DOM on ocean-margin time scales provides support for this assumption [Benner and Kaiser, 2011]. Based on this assumption, Eqs. (2.4) and (2.5) can be used to estimate the %tDOC from optical measurements of $S_{275-295}$ in river-influenced ocean margins. In light of the recent work of [Fichot and Benner, 2011], this tracer provides new capabilities to estimate the concentration of tDOC and marine DOC from optical measurements of $a_g(\lambda)$ in the 275 to 295 nm range.

The application of this tracer is constrained to marine environments where a relationship between $S_{275-295}$ and TDLP$_9$-C exists. Until its range of applicability is better understood, the use of the tracer should be restricted to surface waters of river-influenced ocean margins where mixing and photobleaching are important processes regulating $S_{275-295}$ and the lignin content of DOC, and where lignin is an important chromophore in the CDOM pool. Because the extent to which photobleaching affects $S_{275-295}$ and TDLP$_9$-C relative to mixing is expected to vary among ocean margins, the parameters of Eq. (2.4) derived in the NGoM are not expected to apply to all river-influenced ocean margins. Preliminary results suggest that the tracer can be applied to the region of the Southeastern Beaufort Sea (Arctic Ocean) influenced by the Mackenzie River after re-parameterization of the relationship between $S_{275-295}$ and TDLP$_9$-C. Moreover, the value of TDLP$_9$-C$_{river}$ varies among river systems and seasons such that adequate knowledge of the variability in TDLP$_9$-C$_{river}$ is required for proper application of the tracer. Because of its practicality and general applicability to river-influenced regions of the ocean, this optical tracer of
tDOC represents an important new tool for improving coastal carbon budgets on scales of global significance.
Figure 2.1 Study area, sampling stations and major rivers to the Northern Gulf of Mexico. The Mississippi and Atchafalaya Rivers contribute about 80% of the freshwater input to this ocean margin. Detailed sampling information is provided in Table 2.1. The mixing experiment (Fig. 2.5) was done using surface water from Sta. E0 and F5, collected in November 2009. The DOM amendment and degradation experiments (Table 2.3) were conducted using surface water from Sta. A1 and C1, collected in March 2010.
Figure 2.2 Relationships between salinity and: (A) DOC, (B) TDLP₉, (C) TDLP₋₉-C, (D) $a_\varphi(350)$, (E) $a_\varphi(350)$:DOC, and (F) $S_{350-400}$ in the Northern Gulf of Mexico. (A-D) The inset plots provide enhanced views of the relationships at salinities > 25. (F) The inset demonstrates the lack of dependence of $S_{350-400}$ on salinity.
Figure 2.3 Relationship between (A) TDLP_{9} and \( a_{g}(350) \) and (B) \( a_{g}(350):DOC \) and \( S_{275-295} \). (A) The inset shows TDLP_{9} vs. \( a_{g}(350) \) on a log-log scale and the gray fitted line is defined by Eq. (2.2) and the corresponding coefficients (Table 2.2). (B) The gray fitted curve is defined by Eq. (2.3) and the corresponding coefficients are shown in Table 2.2.
Figure 2.4 (A) Relationship between TDLP$_{9}$-C and $S_{275-295}$ and non-linear regression curve of TDLP$_{9}$-C on $S_{275-295}$ (gray curve) defined by Eq. (2.4) and the corresponding coefficients (Table 2.2). (B) Plot of TDLP$_{9}$-C values estimated from $S_{275-295}$ against measured TDLP$_{9}$-C values. The inset boxplot represents the distribution of error (%) associated with estimated TDLP$_{9}$-C values relative to measured TDLP$_{9}$-C values: $M =$ median, $Q_1 =$ first quartile, $Q_3 =$ third quartile, and whiskers are set at ±1.5× the interquartile range. TDLP$_{9}$-C can be estimated from $S_{275-295}$ within ±16% in the NGom and the error is consistent over the entire range of TDLP$_{9}$-C values.
Figure 2.5 Riverine DOM mixing experiment used to assess the potential of measured $S_{275-295}$ to trace TDLP$_9$-C during a simple mixing event.
Figure 2.6 (A) Changes in $S_{275-295}$ and $a_g(350)$ as a result of photobleaching for 75 samples collected in the NGoM. Each individual line represents a different sample and each circle represents a time point. The inset provides an enhanced view for $a_g(350) \leq 2 \text{ m}^{-1}$. (B) Changes in TDLP$_9$-C and $S_{275-295}$ upon 48 h irradiation (solar simulator, 750 W) for five samples collected in March 2010 in the Mississippi River plume (open symbols) and in the Atchafalaya river plume (closed symbols). These five samples span a salinity range of 0 to 20.6.
Figure 2.7 $S_{275-295}$ as an indicator of %tDOC, the fraction of DOC of terrigenous origin. The values on the solid curve were calculated with Eq. (2.5), where TDLP$_9$-C was estimated from $S_{275-295}$ using Eq. (2.4) and the coefficients of Table 2.2, and the value TDLP$_9$-C$_{river} = 0.43$ %DOC. The dashed curves delineate the 75% confidence interval of predicted %tDOC calculated using an uncertainty analysis based on the known uncertainties in TDLP$_9$-C and TDLP$_9$-C$_{river}$. 

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Figure 2.8 Conceptual illustration of the relationship between $S_{275-295}$ and TDLP$_9$-C. The value of $S_{275-295}$ is closely linked to the average molecular weight (MW) of CDOM and lignin. On the continental shelf and slope of the NGoM, mixing and photodegradation are major processes controlling the lignin content of DOC and the MW distribution of lignin and other chromophores in surface waters. These processes shape the relationship between $S_{275-295}$ and TDLP$_9$-C along the river to ocean waters continuum.
Table 2.1 GulfCarbon 2009-2010 sampling information. $n$ is the number of samples collected for DOC and CDOM analyses whereas $n_{\text{lignin}}$ is the number of corresponding samples collected for lignin analyses. Ranges and median values of salinity and temperature are for all collected samples ($n$).

<table>
<thead>
<tr>
<th>Research cruise</th>
<th>Season</th>
<th>Sampling dates</th>
<th>Number of samples</th>
<th>Salinity</th>
<th>Temperature ($^\circ$C)</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$n$ ($n_{\text{lignin}}$)</td>
<td>min –max -median</td>
<td>min –max -median</td>
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<td>2009</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GC1</td>
<td>winter</td>
<td>09 Jan - 18 Jan</td>
<td>24 (18)</td>
<td>0 - 36.45 - 32.32</td>
<td>8.0 - 22.9 - 18.4</td>
</tr>
<tr>
<td>GC2</td>
<td>spring</td>
<td>20 Apr – 30 Apr</td>
<td>50 (23)</td>
<td>0 - 36.95 - 34.20</td>
<td>15.1 - 24.6 - 22.7</td>
</tr>
<tr>
<td>GC3</td>
<td>summer</td>
<td>19 Jul - 29 Jul</td>
<td>51 (21)</td>
<td>0 - 36.77 - 32.32</td>
<td>27.5 - 30.8 - 29.7</td>
</tr>
<tr>
<td>GC4</td>
<td>fall</td>
<td>29 Oct - 07 Nov</td>
<td>47 (22)</td>
<td>0 - 36.63 - 32.70</td>
<td>16.7 - 27.4 - 23.7</td>
</tr>
<tr>
<td>2010</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GC5</td>
<td>winter to spring</td>
<td>11 Mar – 20 Mar</td>
<td>50 (20)</td>
<td>0 - 36.48 - 28.32</td>
<td>10.6 - 20.3 - 17.0</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>222 (104)</td>
<td>0 - 36.95 - 32.16</td>
<td>8.0 - 30.8 - 22.7</td>
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</table>
Table 2.2 Coefficients and uncertainties associated with models developed for the retrieval of TDLP$_9$ or TDLP$_6$ from $a_g(350)$ (Eq. (2.2)), and for the estimation of $a_g(350)$:DOC and TDLP$_9$-C or TDLP$_6$-C from $S_{275-295}$ (Eqs. (2.3) and (2.4), respectively).

<table>
<thead>
<tr>
<th>Model</th>
<th>Output</th>
<th>Input</th>
<th>Coefficients</th>
<th>Uncertainty in estimates</th>
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<tbody>
<tr>
<td>Eq. (2.2)</td>
<td>TDLP$_9$</td>
<td>$a_g(350)$</td>
<td>$\alpha$ 2.966 $\beta$ 1.088 $\gamma$ - $\delta$ -</td>
<td>+/- 22%</td>
</tr>
<tr>
<td>Eq. (2.2)</td>
<td>TDLP$_6$</td>
<td>$a_g(350)$</td>
<td>$\alpha$ 2.525 $\beta$ 1.263 $\gamma$ - $\delta$ -</td>
<td>+/- 25%</td>
</tr>
<tr>
<td>Eq. (2.3)</td>
<td>$a_g(350)$:DOC</td>
<td>$S_{275-295}$</td>
<td>$\alpha$ 5.679 $\beta$ 81.229 $\gamma$ 8.459 $\delta$ 241.052</td>
<td>+/- 8%</td>
</tr>
<tr>
<td>Eq. (2.4)</td>
<td>TDLP$_9$-C</td>
<td>$S_{275-295}$</td>
<td>$\alpha$ 3.172 $\beta$ -267.566 $\gamma$ 0.228 $\delta$ -0.953</td>
<td>+/- 16%</td>
</tr>
<tr>
<td>Eq. (2.4)</td>
<td>TDLP$_6$-C</td>
<td>$S_{275-295}$</td>
<td>$\alpha$ 3.100 $\beta$ -273.952 $\gamma$ 0.387 $\delta$ -0.969</td>
<td>+/- 20%</td>
</tr>
</tbody>
</table>
Table 2.3 Results from DOM amendment and microbial degradation experiments. Incubation time was 12 days for Sta. A1 and 10 days for Sta. C1.

<table>
<thead>
<tr>
<th></th>
<th>Unamended</th>
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<th>Plankton DOM addition</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>(t = 0)</td>
<td>(t = \text{final})</td>
<td>(t = 0)</td>
<td>(t = \text{final})</td>
</tr>
<tr>
<td><strong>Station A1: Off Mobile Bay, Alabama (salinity = 23.3)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOC ((\mu)mol L(^{-1}))</td>
<td>168.0 ± 1.1</td>
<td>157.8 ± 0.8</td>
<td>190.8 ± 0.6</td>
<td>159.6 ± 1.1</td>
</tr>
<tr>
<td>TDAA (nmol L(^{-1}))</td>
<td>897.0 ± 11.4</td>
<td>643.3 ± 14.1</td>
<td>2331.0 ± 18.0</td>
<td>948.6 ± 11.5</td>
</tr>
<tr>
<td>(a_g(350)) (m(^{-1}))</td>
<td>2.35</td>
<td>2.36</td>
<td>2.55</td>
<td>2.34</td>
</tr>
<tr>
<td>(S_{275-295}) (nm(^{-1}))</td>
<td>0.0168</td>
<td>0.0164</td>
<td>0.0176</td>
<td>0.0165</td>
</tr>
<tr>
<td><strong>Station C1: Off Terrebonne Bay, Louisiana (salinity = 27.8)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOC ((\mu)mol L(^{-1}))</td>
<td>133.6 ± 0.7</td>
<td>132.1 ± 1.1</td>
<td>157.5 ± 0.5</td>
<td>130.0 ± 1.1</td>
</tr>
<tr>
<td>TDAA (nmol L(^{-1}))</td>
<td>730.9 ± 34.9</td>
<td>670.3 ± 35.5</td>
<td>2141.7 ± 49.6</td>
<td>858.9 ± 11.1</td>
</tr>
<tr>
<td>(a_g(350)) (m(^{-1}))</td>
<td>1.25</td>
<td>1.19</td>
<td>1.42</td>
<td>1.35</td>
</tr>
<tr>
<td>(S_{275-295}) (nm(^{-1}))</td>
<td>0.0196</td>
<td>0.0194</td>
<td>0.0204</td>
<td>0.0189</td>
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</tbody>
</table>
CHAPTER 3
TRANSFORMATIONS AND FATES OF TERRIGENOUS DISSOVED ORGANIC CARBON
IN A RIVER-INFLUENCED OCEAN MARGIN

3.1 INTRODUCTION
The fate of the 0.25-Pg of terrigenous dissolved organic carbon (tDOC) delivered each year to the ocean by rivers has important ramifications for the global organic carbon cycle but remains enigmatic [Hedges et al., 1997; Cauwet, 2002; Benner, 2004]. On the one hand, evidence suggests major rivers carry organic matter that is mostly soil-derived, diagenetically altered and relatively resistant to microbial decomposition [Hedges et al., 1994]. On the other hand, stable isotopic composition (δ¹³C) and terrestrial biomarkers indicate tDOC comprises a very small fraction of the dissolved organic carbon (DOC) in the open ocean [Meyers-Schulte and Hedges, 1986; Opsahl and Benner, 1997], thereby suggesting tDOC is efficiently mineralized in ocean margins [Hedges et al., 1997]. Although evidence has shown tDOC experiences substantial alterations over relatively short timescales in ocean margins [Benner and Opsahl, 2001; Cauwet, 2002; Hernes and Benner, 2003], the actual extent of its removal in these environments remains poorly known as no quantitative estimate of mineralization is available.

The extent of tDOC mineralization in ocean margins has important ramifications for their metabolic state and can influence their role in CO₂ exchange with the atmosphere [Smith and Hollibaugh, 1993; Gattuso et al., 1998; Cai, 2011]. Despite
considerable progress made in the past decade understanding the controls of CO₂ fluxes in ocean margins [Borges, 2005; Cai et al., 2006], it remains unclear whether river-influenced ocean margins are net producers or consumers of organic matter or are net sources or sinks of atmospheric CO₂. Extensive tDOC mineralization in ocean margins can contribute significantly to the net heterotrophy of these systems, whereas export of a substantial fraction of the tDOC off the margin can fuel heterotrophy in the open ocean and shift the metabolic balance there [Duarte et al., 2013; Ducklow and Doney, 2013]. The variable nature of carbon metabolism and air-sea CO₂ fluxes in river-influenced ocean margins highlights the need for a fundamental understanding of the key processes controlling carbon transformations in these systems.

The highly dynamic nature of river-influenced ocean margins makes the quantification of tDOC mineralization in these environments particularly challenging. A complex interplay of temporally and spatially variable environmental factors (e.g., temperature, solar radiation, nutrients) affects the rates of tDOC mineralization by biological and photochemical processes [Cauwet, 2002; Mopper and Kieber, 2002], and mesoscale shelf circulation can impact the residence time of tDOC in the ocean margin by favoring alongshore transport or promoting rapid cross-shelf export to the open ocean [Cho et al., 1998; Ohlmann and Niiler, 2005; Schiller et al., 2011]. Furthermore, the bioavailability of tDOC can vary substantially with river hydrograph and floodplain interaction [Benner et al., 1995; Holmes et al., 2008; Shen et al., 2012]. The inherent complexity of these systems is compounded by the practicality of current tDOC proxies that rely on complex analyses of organic biomarkers and isotopic compositions.
This study uses a new optical proxy for tDOC [Fichot and Benner, 2012; Fichot et al., 2013] and a mass balance approach to provide the first seasonal estimates of tDOC mineralization in a river-influenced ocean margin. The mass balance is determined for a section of the Louisiana shelf that receives the bulk of the discharge from the Mississippi River (MR) and the Atchafalaya River (AR). The Mississippi-Atchafalaya River System (M-ARS) is the largest river system in North America and contributes an average of 2.7 Tg tDOC to the Northern Gulf of Mexico (NGoM) each year [Shen et al., 2012]. The optical proxy is based on the lignin biomarker, and its practicality of measurement provides the spatial and temporal coverage required for the determination of seasonal tDOC mass balances in this heterogeneous and dynamic environment. Independent approaches are used to assess the relative contributions by biomineralization and photomineralization to the removal of tDOC in this river-influenced ocean margin.

3.2 METHODS

Field measurements were conducted as part of the GulfCarbon project. Conductivity-Temperature-Depth (CTD) casts and surface water samples were collected along a grid of 42 or 43 stations, during four research cruises in the NGoM in April, July, and October-November 2009 and March 2010 (Fig. 3.1 and Table 3.1). The total set of 169 samples and CTD profiles spanned a salinity range of 0 to ~37 and was representative of the majority of water types typically encountered in river-influenced ocean margins (riverine to oligotrophic marine). Salinity profiles were derived from the CTD casts. The mixed layer depth at each sampled station was derived from the salinity profiles and confirmed using CDOM fluorescence profiles acquired using a WetLabs ECO triplet in situ.
fluorometer. Surface water samples were collected and analyzed for DOC and CDOM. Briefly, samples for DOC were gravity filtered (0.7-µm) onboard from Niskin bottles, stored frozen (-20°C) in clean glass bottles (450°C for 4h), and analyzed in the home laboratory using high temperature combustion [Benner and Strom, 1993]. Samples for CDOM absorption coefficient spectra, $a_g(\lambda)$, were gravity filtered (0.2-µm) onboard from Niskin bottles, stored at 4°C in clean glass vials (450°C for 4h), and analyzed in the home laboratory using a dual-beam UV-visible spectrophotometer [Fichot and Benner, 2011]. The CDOM spectral slope coefficient, $S_{275-295}$, was estimated using a linear fit of the log-linearized $a_g(\lambda)$ spectrum between 275 and 295 nm. A total of 38 samples were also collected in clean glass bottles (450°C for 4h) for the determination of photomineralization apparent quantum yields in the laboratory. The samples were collected in contrasting water types using the procedure used for CDOM samples. Finally, a total of 75 diffuse attenuation coefficient spectra, $K_d(\lambda)$, were derived for surface waters from profiles of multispectral ($\lambda = 305-555$ nm) downwelling irradiance acquired in contrasting waters types using a Satlantic MicroPRO equipped with a surface reference [Fichot et al., 2008]. Additional details about field sampling and measurements are provided in Appendix A.

The shelf study area was defined to provide realistic interpolations between sampled stations and to encompass a region where the Mississippi River (MR) and Atchafalaya River (AR) represent the dominant input of tDOC (Fig. 3.1). The shelf was therefore delineated to the East and West by the 89.40°W and 93.66°W meridians, respectively. The Northern and Southern limits of the shelf study area were constrained by the 3-m and 200-m isobaths, respectively, using the 3-arc-second bathymetry from the
National Geophysical Data Center U.S. Coastal Relief Model.

As in Dinnel and Wiseman [1986] and Etter et al. [2004], 53% of the MR discharge and 100% of the AR discharge was assumed to flow into the shelf study area. Water discharge from the U.S. Army Corps of Engineers (USACE) and DOC concentrations from the USGS National Stream Quality Accounting Network (NASQAN) were used to calculate freshwater and DOC fluxes from the MR and AR between January 1, 2009 and June 30, 2010. A linear interpolation was used to estimate daily DOC concentrations between measurements [Shen et al., 2012]. Daily tDOC fluxes in the rivers were calculated as the product of the daily DOC concentration and daily water discharge. Transit time of river water between the gauging stations and the mouths of the MR and AR is on the order of 5 to 7 days [Shen et al., 2012]. Thus, a time lag of 6 days was applied to the MR and AR discharge data in order to match these data to the shelf processes investigated.

The vertical distribution of freshwater on the shelf was calculated for each season from the measured salinity profiles. Briefly, a nearest-neighbor interpolation was applied to the measured salinities across the shelf study area at 0.25-m depth increments between the surface and the 200-m isobath. The shelf area at each depth increment was constrained using the high-resolution bathymetry. Salinity was used to calculate the freshwater fraction, $f$, of any volume of water on the shelf as in Dinnel and Wiseman [1986]

$$f = (S_m - S) / S_m$$  \hspace{1cm} (3.1)

where $S$ is the salinity of any shelf water volume, and $S_m$ is the reference salinity corresponding to the marine end-member. For each season, $S_m$ was chosen as the mean of
the four highest surface salinities (Spring: 36.61; Summer: 36.69; Fall: 36.59; Winter: 36.48). Freshwater fractions and water volumes were used to calculate the vertical distribution of freshwater on the shelf. Note that Antarctic Intermediate Water (AAIW) impinging on the bottom of the shelf represents an external source of freshwater and was corrected for in the calculations (see Appendix A).

The calculation of tDOC mineralization rates for the shelf requires estimates of the time spent by the newly discharged tDOC in shelf surface waters. Newly discharged river water is expected to remain above the pycnocline during its transit on the shelf. The filling time for the freshwater volume found above the base of the pycnocline should therefore provide a reasonable estimate of the time spent by tDOC in shelf surface waters. Here, we specifically define the freshwater filling time, $T_{\text{filling}}$, as the time required to accumulate the freshwater volume $V_{FW}$ found above the base of the pycnocline. Considering that small rivers are minor contributors of freshwater to the shelf [Dinnel and Wiseman, 1986], filling time was calculated for each season by reverse-time integration of the daily balance between the M-ARS freshwater discharge, $Q(t)$, and the precipitation and evaporation rates over the shelf study area, $P(t)$ and $E(t)$, respectively. The filling time was calculated as shown in Eq. (3.2)

$$\int_{t-T_{\text{filling}}}^{t} [Q(t) + P(t) - E(t)] \, dt = V_{FW}$$

(3.2)

where $t$ is the day when $V_{FW}$ was determined, chosen here as the mid-point of each field sampling period. The freshwater volume $V_{FW}$ was calculated by integrating the vertical freshwater distribution from the surface to the base of the pycnocline, taken here as the depth where the rate of change of freshwater with depth decreases sharply. Daily
freshwater discharge from the M-ARS (53% MR + 100% AR) was derived as described above. Precipitation rates \( P(t) \) were estimated from pentad global gridded precipitation data from the Climate Prediction Center Merged Analysis of Precipitation. Evaporation rates \( E(t) \) were derived from the Woods Hole Objectively Analyzed air-sea fluxes data sets. Both data sets were linearly interpolated in space and time to provide daily rates over the shelf study area. Details about the source of the data is provided in Appendix A.

A mass balance approach was used to calculate the amount of tDOC mineralized (\( \text{tDOC}_{\text{mineralized}} \)) in the shelf mixed layer (Fig. 3.2). The mixed layer is the vertically homogenous surface layer from which field measurements were collected, and for which a reliable mass balance could be established. The mixed layer depth averaged ~13 m over the shelf and was shallower than the base of the pycnocline (~20-m). We assume the filling time for the mixed layer is the same as that for freshwater above the base of the pycnocline calculated as in Eq. (3.2). For each season, \( \text{tDOC}_{\text{mineralized}} \) was computed as in Eq. (3.3)

\[
\text{tDOC}_{\text{mineralized}} = \text{tDOC}_\text{conservative} - \text{tDOC}_\text{measured} \tag{3.3}
\]

where conservative tDOC (\( \text{tDOC}_\text{conservative} \)) is the amount of tDOC expected in the mixed layer assuming conservative behavior of tDOC, and measured tDOC (\( \text{tDOC}_\text{measured} \)) is the amount of tDOC present in the mixed layer. The field measurements of salinity, mixed layer depth, DOC concentration, and spectral slope coefficient (\( S_{275-295} \)) were used to derive \( \text{tDOC}_\text{conservative} \) and \( \text{tDOC}_\text{measured} \). These field measurements are representative of the mixed layer and were interpolated over the shelf using the Matlab ordinary-kriging functions of W. Schwanghart.
The interpolated $S_{275-295}$ and DOC concentration grids facilitated the calculation of tDOC$_{\text{measured}}$. Briefly, the tDOC concentration of any volume of water in the shelf mixed layer was calculated as the product of DOC concentration and the fraction of tDOC (%tDOC). The %tDOC was derived from $S_{275-295}$ [Fichot and Benner, 2012] (see Appendix A for details). The tDOC$_{\text{measured}}$ was computed as in Eq. (3.4) as the shelf-integrated product of the tDOC concentration and the volume of the mixed layer at any location $(x,y)$ on the shelf,

$$
tDOC_{\text{measured}} = \int_{\text{Shelf}} \int (tDOC)(x,y) \cdot V_{ML}(x,y) dx dy \quad (3.4)
$$

where $V_{ML}(x,y)$ is the mixed layer (ML) volume given by the mixed layer depth and surface area of the water parcel.

The interpolated grids of salinity and mixed layer depth facilitated the calculation of tDOC$_{\text{conservative}}$. Freshwater fractions derived from salinity (using Eq. (3.1)) and mixed layer depths facilitated the calculation of the total freshwater volume in the shelf mixed layer ($V_{FW}^{ML}$). The freshwater discharge and tDOC flux from the M-ARS integrated over the freshwater filling time facilitated the calculation of a discharge-weighted average tDOC concentration, ($tDOC_{M-ARS}$) that is representative of the freshwater volume present in the shelf mixed layer. Conservative tDOC was then estimated as

$$
tDOC_{\text{conservative}} = V_{FW}^{ML} \cdot \overline{[tDOC]_{M-ARS}} + (V_{ML}^{ML} - V_{FW}^{ML}) \cdot \overline{[tDOC]_{\text{marine}}} \quad (3.5)
$$

where $V_{ML}$ is the total volume of water in the mixed layer, and $\overline{[tDOC]_{\text{marine}}}$ is the tDOC concentration of the marine end-member, calculated here as the average tDOC concentration of the four samples with highest salinities during each sampling period.
Finally, the total tDOC mineralization rate for each season was calculated by dividing tDOC\textsubscript{mineralized} by its respective freshwater filling time, used here as an approximation of the time spent by tDOC in the shelf mixed layer.

Estimation of the photomineralization of tDOC requires knowledge of the amount of photons (\(\lambda = 290-490\) nm) absorbed annually by CDOM in the shelf mixed layer, defined here as \(\Xi\textsuperscript{ML}(\lambda)\). The \(\Xi\textsuperscript{ML}(\lambda)\) was estimated as

\[
\Xi\textsuperscript{ML}(\lambda) = E\textsubscript{od}(0^{-},\lambda) \cdot \overline{F}(\lambda)
\]  

(3.6)

where \(E\textsubscript{od}(0^{-},\lambda)\) is the spectral scalar downward irradiance incident just below the sea surface and integrated over the year in the study area, and \(\overline{F}(\lambda)\) is the average, spectrally-resolved fraction of incident irradiance absorbed by CDOM in the shelf mixed layer. The monthly, cloud-corrected irradiance climatology computed by [Fichot and Miller 2010] facilitated the derivation of \(E\textsubscript{od}(0^{-},\lambda)\) for the study area. The average function \(\overline{F}(\lambda)\) for the shelf mixed layer was determined from 75 sets of concurrent \textit{in situ} measurements of mixed layer depth, and spectral CDOM absorption and diffuse attenuation coefficient collected during the present study (see section 2.1). A function \(F(\lambda)\) (\(\lambda = 290-490\) nm) was calculated for each set of \textit{in situ} data using Eq. (3.7)

\[
F(\lambda) = \frac{a\textsubscript{g}(\lambda)}{K\textsubscript{d}(\lambda)} \cdot (1 - \exp(-K\textsubscript{d}(\lambda) \cdot z\textsubscript{MLD}))
\]  

(3.7)

where \(a\textsubscript{g}(\lambda)\) is the spectral CDOM absorption coefficient, \(K\textsubscript{d}(\lambda)\) is the spectral diffuse attenuation coefficient, and \(z\textsubscript{MLD}\) is the mixed layer depth. The average of the 75 functions \(F(\lambda)\) yielded the function \(\overline{F}(\lambda)\) used to calculate \(\Xi\textsuperscript{ML}(\lambda)\) in Eq. (3.6). The derivation of Eq. (3.7) is shown in Appendix A.
The amount of tDOC photomineralized in the shelf mixed layer over the course of one year, \( \Psi_{PM}^{ML} \), was calculated as

\[
\Psi_{PM}^{ML} = \bar{\phi}_{PM} \cdot \bar{B} \cdot \int_{290}^{490} \Xi_{Exp}(\lambda) d\lambda
\]

where \( \bar{\phi}_{PM} \) is the broadband (non-spectral) apparent quantum yield (AQY) for tDOC photomineralization, and \( \bar{B} \) is a correction factor (see below). Here, \( \bar{\phi}_{PM} \) is an average of 38 broadband AQYs determined during this study for distinct samples collected along the salinity gradient. Briefly, the AQYs were determined in the home laboratory by conducting a full-spectrum irradiation of each sample (quadruplicates) using a solar simulator and controlled illumination conditions. Irradiations lasted 48 h for most samples (72 h for a few samples), and long-pass 295-nm cutoff filters were used to prevent unnatural radiation from reaching the samples. The AQY was determined as

\[
\bar{\phi}_{PM} = \frac{[\text{DOC}]_{\text{final}} - [\text{DOC}]_{\text{initial}}}{\int_{290}^{490} \Xi_{Exp}(\lambda) d\lambda}
\]

where \([\text{DOC}]_{\text{initial}}\) and \([\text{DOC}]_{\text{final}}\) are the mean DOC concentrations of quadruplicate samples at the beginning and end of the experiments, respectively, and \( \Xi_{Exp}(\lambda) \) is the total amount of photons absorbed by CDOM over the course of irradiation (mol photons L\(^{-1}\)). Here, \( \Xi_{Exp}(\lambda) \) is integrated over the \( \lambda = 290-490 \) nm spectral range. This approach makes the fundamental assumption that only tDOC is removed from the DOC pool upon irradiation. As a result of spectral differences in illumination between the solar simulator and the mixed layer, a bias in \( \Psi_{PM}^{ML} \) can result from the use of broadband AQYs determined using a solar simulator. Here, the factor \( \bar{B} = 0.706 \) was calculated and used.
as in Eq. (3.8) to correct for this bias. Further details about the photochemical experiments and approaches used to calculate $\Xi^{\text{Exp}}(\lambda)$ and $\overline{B}$ are provided in Appendix A.

Experiments were conducted to investigate the microbial degradation of lignin in water samples collected from a river and four marine environments along the South Carolina coast (salinity range: 23.1-35.1). Large-volumes (20 L) of unfiltered water were collected and incubated in the dark at room temperature (~22°C). Subsamples (4 L) were collected after about 10 d, 30 d and 90 d of incubation. Water samples were filtered (0.2-$\mu$m), extracted on a Megabond Elut C-18 cartridge, and analyzed for dissolved lignin phenols using the cupric oxide oxidation method and gas chromatography with mass spectrometry [Kaiser and Benner, 2012]. The sum of $p$-hydroxyl, vanillyl and syringyl phenols (TDLP$_9$) was determined [Fichot and Benner, 2012], and an exponential decay constant ($k$) was derived for lignin (TDLP$_9$) biomineralization in each experiment.

3.3 RESULTS

Freshwater represented 3.3-4.6% of the total volume of water present on the shelf (Table 3.2). Total freshwater volumes on the shelf increased from 96.9 to 135.5 km$^3$ between spring and winter during the 2009-2010 study period. The vertical distribution of freshwater decreased rapidly with depth and was remarkably similar among seasons, with the exception of winter when a large volume of freshwater was confined to the surface layer (Fig. 3.3a). The base of the shelf pycnocline was observed at 20 m in spring, 21 m in summer, 20 m in fall, and 19 m in winter. The volume of freshwater present above the base of the pycnocline ($V_{\text{FW}}$) was estimated to be 81.1 km$^3$, 88.8 km$^3$, and 96.7 km$^3$ in
spring, summer, and fall, respectively. A larger freshwater volume (125.9 km$^3$) was observed during the winter, corresponding to 93% of the total freshwater volume present on the shelf.

Reverse-time integrations based on the freshwater volumes on the shelf yielded filling times of approximately two to three months depending on the season (Fig. 3.3b and Table 3.2). Filling times were estimated to be 53 d, 51 d, 96 d and 68 d for the spring, summer, fall and winter, respectively, and were notably longer during fall as a result of low river discharge, typical for the M-ARS during the late summer/early fall. River discharge from the M-ARS ranged three-fold and was the dominant process regulating freshwater supply to the shelf. Net precipitation played a minor role, affecting the shelf freshwater volumes by only a few percent. Evaporation exceeded precipitation in all seasons but the spring, and therefore represented a freshwater sink over the shelf. Freshwater filling times should represent a reasonable estimate of the average time spent by tDOC in the shelf surface waters, because newly discharged freshwater is expected to reside above the base of the pycnocline.

Measurements of mixed layer depth and salinity revealed that ~50% of the total freshwater present on the shelf was in the mixed layer (Table 3.3). The volume of the mixed layer ranged from 562 to 1285 km$^3$, representing between 19% and 43% of the total volume of the shelf. An increase in the volume of the mixed layer was always associated with a decrease in the freshwater content of the mixed layer (range: 5-10%), consistent with enhanced vertical mixing. As a result, the freshwater volume of the mixed layer only varied from 50.5 to 66.6 km$^3$ and corresponded to 41 to 58% of the total freshwater present on the shelf. Calculations using the measurements of in situ optical
properties and mixed layer depth further revealed >90% of the incident UV-visible irradiance ($\lambda = 290$-$490$ nm) was attenuated within the mixed layer. Together, these observations indicate that, on average, half of the tDOC discharged by the M-ARS resides in the mixed layer and is exposed to photochemically active solar radiation while on the shelf.

The interpolated field measurements of mixed layer depth, salinity, DOC concentration and CDOM spectral slope coefficient ($S_{275-295}$) were used to calculate the mass balance of tDOC in the shelf mixed layer (Fig. 3.4). The tDOC mass balance also required the calculation of average tDOC concentrations representative of the riverine and marine end-members (Table 3.4). Discharge-weighted average tDOC concentrations ($[t\text{DOC}]_{M-ARS}$) representative of river water delivered by the M-ARS during each filling time period exhibited important seasonal variability. The $[t\text{DOC}]_{M-ARS}$ ranged from a minimum of 315 $\mu$mol L$^{-1}$ in winter to a maximum of 400 $\mu$mol L$^{-1}$ in summer. In contrast, average tDOC concentrations of the marine-end-member ($[t\text{DOC}]_{marine}$) were two orders of magnitude lower than in the rivers and ranged from 2.3 to 3.5 $\mu$mol L$^{-1}$.

Estimates of the conservative tDOC reservoir in the shelf mixed layer ($t\text{DOC}_{\text{conservative}}$) varied seasonally from 0.241 to 0.320 Tg tDOC (Table 3.5). These estimates are based on the freshwater volume in the mixed layer and assume conservative behavior of the tDOC delivered by the M-ARS. Seasonal differences in $t\text{DOC}_{\text{conservative}}$ were driven by variations in $[t\text{DOC}]_{M-ARS}$ and the mixed layer freshwater volume. Seasonal variations in $[t\text{DOC}]_{\text{marine}}$ had a minimal effect on the computations. In contrast, the measured tDOC reservoir in the shelf mixed layer ($t\text{DOC}_{\text{measured}}$) ranged from 0.075 to
0.221 Tg tDOC and was therefore consistently lower and more variable than the estimates of the conservative tDOC reservoir.

The difference between the conservative and measured tDOC reservoirs represents the tDOC deficit that can be attributed to mineralization processes. The amount of tDOC mineralized in the shelf mixed layer ranged three-fold from 0.063 Tg tDOC in winter to 0.182 Tg tDOC in summer, with intermediate estimates of ~0.1 Tg C in the spring and fall (Table 3.5). These estimates correspond to the mineralization of 26-71% of the tDOC discharged by the M-ARS to the shelf mixed layer (Fig. 3.5). The rate of mineralization of tDOC can be estimated by dividing the amount of tDOC mineralized by the freshwater filling time. Estimated tDOC mineralization rates ranged from a minimum of 0.028 Tg tDOC 30d$^{-1}$ in winter to a maximum of 0.108 Tg tDOC 30d$^{-1}$ in summer. Using the four seasonal rates, the total amount of tDOC mineralized in a year was estimated at 0.681 Tg tDOC for the shelf mixed layer.

The amount of tDOC photomineralized in the shelf mixed layer is directly dependent on the amount of photons absorbed by CDOM in the mixed layer, $\Xi_{ML}(\lambda)$ (mol photons m$^{-2}$ nm$^{-1}$), calculated here as the product of the downward scalar irradiance incident just below the ocean surface, $E_{od}(0^\circ,\lambda)$, and the fraction of irradiance absorbed by CDOM in the mixed layer, $\overline{F}(\lambda)$ (Fig. 3.6). Spectrally, $E_{od}(0^\circ,\lambda)$ increased with increasing wavelength (Fig. 3.6a). The daily, spectrally integrated irradiance $E_{od}(0^\circ,t)$ increased 2.5-fold between December and May (inset in Fig. 3.6a). The maximum was observed in May and not in June or July because of the greater cloud coverage typically observed during summer in the Northern Gulf of Mexico. In contrast to the incident irradiance, a sharp decrease in $\overline{F}(\lambda)$ with increasing wavelength was observed. The
spectral dependence of $E_{od}(0, \lambda)$ is primarily the result of two factors: 1) the greater diffuse attenuation of irradiance in the ultraviolet (UV) relative to the visible region, and 2) the greater contribution of CDOM to the total absorption coefficient in the UV relative to the visible region. Because $E_{od}(0, \lambda)$ and $\bar{F}(\lambda)$ exhibited opposite trends with wavelength, the value of $\Xi_{ML}(\lambda)$ in the UV-A ($\lambda = 320\text{-}400$ nm) was somewhat comparable to that in the visible ($\lambda = 400\text{-}490$ nm). In the photochemically efficient UV-B region ($\lambda = 290\text{-}320$ nm), $\Xi_{ML}(\lambda)$ was substantially lower than in the UV-A and decreased exponentially with decreasing wavelength.

The magnitude of photomineralization is also directly dependent on the apparent quantum yield of tDOC photomineralization. The 38 apparent quantum yields for photomineralization ($\phi_{PM}$) determined in this study exhibited high variability, ranging from 10 to $124 \mu$mol tDOC mol photons$^{-1}$ (Fig. 3.7). The variability was minimal at low salinities (<15) and maximal at high salinities (>25), but remained difficult to constrain as no relationship between $\phi_{PM}$ and either salinity, DOC concentration, CDOM absorption coefficient or $S_{275\text{-}295}$ was observed. However, the average of the 38 apparent quantum yields, $\bar{\phi}_{PM} = 56 \mu$mol tDOC mol photons$^{-1}$, was fairly representative for both low and high salinity samples.

Comparisons of the amounts of photons absorbed by CDOM in the mixed layer and in irradiated samples indicated a 48-h exposure in the solar simulator (750 W) was equivalent to ~4 months of solar exposure in the shelf mixed layer. This large discrepancy between exposure in the solar simulator and in the shelf mixed layer must be taken into account before experimental results are applied to natural waters. The 48-h irradiation used to determine the apparent quantum yields in this study were
representative of the solar exposure experienced by tDOC during its time spent on the shelf (51-96 days). Calculations using the average apparent quantum yield $\bar{\phi}_{pm}$ revealed that 0.054 Tg tDOC is photomineralized in a year in the shelf mixed layer.

Lignin biodegradation experiments conducted in this study yielded exponential decay constants for the microbial mineralization of lignin (sum of $p$-hydroxy, vanillyl and syringyl phenols: TDLP$_9$) that ranged from $k = 0.0023$ d$^{-1}$ to 0.0071 d$^{-1}$ (Table 3.6). Similar decay constants using the sum of vanillyl and syringyl phenols (TDLP$_6$) were derived and ranged from $k = 0.0029$ d$^{-1}$ to 0.0068 d$^{-1}$. These decay constants (using TDLP$_6$) are comparable to the value of 0.0032 d$^{-1}$ derived from a 28-day dark incubation of Mississippi River water [Opsahl and Benner, 1998], but were significantly lower than the constant derived from a 10-day incubation of Mississippi River plume water ($k = 0.0254$ d$^{-1}$) and higher than the constant derived from a 1.7-year incubation of Mississippi River water ($k = 0.0012$ d$^{-1}$), respectively [Hernes and Benner, 2003]. The four experiments with coastal seawater presented herein (using TDLP$_9$) yielded an average decay constant $\bar{k} = 0.0049$ d$^{-1}$ with a standard error of 0.0010 d$^{-1}$. This decay constant is therefore representative of lignin biomineralization during a 90-day period at ~22°C, which is similar to the annual average surface water temperature observed in the Northern Gulf of Mexico.

Assuming lignin biomineralization rates are representative for bulk tDOC, the average decay constant for lignin indicated 0.076 Tg tDOC (+/- 0.013 Tg tDOC) is biomineralized in the mixed layer during the average 67-day freshwater filling time in the study region. On an annual basis, biomineralization removes 0.415 Tg tDOC from the shelf mixed layer.
A comparison of photochemical and biological processes revealed microbial degradation was the dominant process mineralizing tDOC in the shelf mixed layer (Fig. 3.8). Biomineralization accounted for ~60% of the total annual tDOC mineralization (0.681 Tg tDOC), which was determined independently using a mass balance approach. In contrast, the estimated photomineralization of 0.054 Tg tDOC represented only 8% of the total tDOC mineralization. Considering the shelf mixed layer is exposed to solar radiation, the remaining 32% could be attributable to the coupled photo-biomineralization of tDOC. Although ultimately mediated by microorganisms, the coupled photo-biomineralization of tDOC involves photochemical alterations of tDOC that release dissolved organic compounds of enhanced bioavailability.

3.4 DISCUSSION

The Mississippi-Atchafalaya River System (M-ARS) is the largest in North America, draining 41% of the contiguous United States and supplying over 80% of the total freshwater input to the Gulf of Mexico. Between 1996 and 2010, the M-ARS discharged an annual average of 660 km³ of freshwater and 2.70 Tg of tDOC to the northern Gulf of Mexico [Shen et al., 2012]. On average, ~53% of the MR discharge flows westward of the delta [Dinnel and Wiseman, 1986; Zhang et al., 2012], so the average freshwater discharge and tDOC flux to the study area on the Louisiana shelf were 444 km³ yr⁻¹ and 1.88 Tg tDOC yr⁻¹. The freshwater discharge and tDOC flux during the year of this study (March 2009-2010) were higher than average, amounting to 595 km³ (34% higher) and 2.63 Tg tDOC (39% higher). The AR contributed 45% of the freshwater and 55% of the tDOC. The higher tDOC concentrations in the AR relative to
the MR (432 $\mu$mol L$^{-1}$ versus 306 $\mu$mol L$^{-1}$) are due to interactions of the AR with its highly productive floodplain (e.g., bayous, cypress swamps, marshes) [Shen et al., 2012].

The M-ARS dominates freshwater and tDOC inputs to the Louisiana shelf. Other rivers in the region are very minor contributors of freshwater [Dinnel and Wiseman, 1986; Etter et al., 2004] and, presumably, of tDOC. During March 2009-2010, net evaporation removed 17 km$^3$ of freshwater over the shelf (86 km$^3$ precipitation, 104 km$^3$ of evaporation), a small amount relative to the 444 km$^3$ discharged. Inputs of tDOC through precipitation should be minimal based on an average DOC concentration of 64 $\mu$mol L$^{-1}$ in rainwater over coastal and marine areas [Willey et al., 2000]. Assuming all rainwater DOC is terrigenous, the 86 km$^3$ of precipitation over the shelf that year would contribute a maximum of 0.066 Tg tDOC, corresponding to 2.5% of the M-ARS input. Louisiana’s coastal marshes could be important sources of tDOC to surrounding bays [Bianchi et al., 2009], but contributions to the shelf study area are likely to be relatively minor due to rapid remineralization in bay waters (Mike Dagg, personal communication).

The large freshwater discharge from the M-ARS has a major influence on the hydrography of the Louisiana shelf. The shelf study region contained an average of 114 km$^3$ of freshwater (ranging 97-135 km$^3$), accounting for ~4% of the total water volume. Dinnel and Wiseman [1986] reported freshwater volumes on the Louisiana and Texas shelf were minimal in winter and maximal during summer as a result of the spring freshet. In the present study, the maximal freshwater volume (135 km$^3$) was observed in mid-March 2010, due to very high river discharge during early 2010 [Shen et al., 2012]. Our results indicated ~85% of the freshwater was located above the base of the
pycnocline in the upper 20 m of the water column and ~50% resided in the mixed layer (average depth 13 m). This freshwater distribution indicates ~2.25 Tg of the tDOC discharged by the M-ARS during March 2009-2010 resided in the top 20-m of the water column, and that 1.3 Tg of it resided in the mixed layer.

The freshwater volumes present on the shelf were equivalent to 17-23% of the annual freshwater discharge adjusted for net evaporation over the shelf, indicating freshwater in the shelf study region is replaced every 72 days on average. While this average value is representative for the shelf on a annual basis, more representative estimates for surface waters and the mixed layer were obtained for each sampling period by deriving filling times (51-96 d) for the freshwater volume above the base of the pycnocline. These timescales are therefore representative of the time tDOC resides in surface waters of the shelf study region.

The mass balance revealed that the removal and presumed mineralization of tDOC in the mixed layer is both extensive and seasonally variable. The annual mineralization of 0.681 Tg tDOC indicates that on average about half of the 1.3 Tg tDOC that should be present in the mixed layer is mineralized during its 2-to-3 months in the shelf study region (Fig. 3.9). To the extent of our knowledge, this mass balance represents the first such assessment of tDOC mineralization on a continental shelf, and provided estimates that are consistent with shelves and margins acting as major sinks of tDOC transported in continental runoff [Hedges et al., 1997]. The observation that tDOC mineralization rates increased four-fold between winter and summer (0.028 to 0.108 Tg tDOC 30d\(^{-1}\)) is consistent with elevated rates of photochemical and biological processes during summer due to greater solar exposure and elevated temperatures.
Bioassay experiments indicated microbial degradation is the dominant mineralization mechanism for tDOC in the shelf mixed layer. The annual biomineralization of 0.415 Tg tDOC accounts for about 60% of the total tDOC mineralization estimated by mass balance (Fig. 3.9). This rate is a representative average for the year because the annual average temperature in the shelf mixed layer and the bioassay experiment temperatures (~22°C) were similar. Average temperatures in the shelf mixed layer ranged from ~17°C in winter to ~30°C in summer. Assuming a temperature coefficient ($Q_{10}$) of 2 [Raymond and Bauer, 2000], biomineralization rates could vary ~2.5-fold between winter and summer, explaining some of the observed seasonal variability in total mineralization rate.

Photomineralization of tDOC played a less significant role in the mineralization of tDOC than previously thought in this environment [Miller and Zepp, 1995]. The annual photomineralization determined in this study (0.054 Tg tDOC) corresponded to only 8% of the total mineralization in the shelf mixed layer. Direct photochemical processes were therefore responsible for the mineralization of 4% of the tDOC in the mixed layer, and 2% of the total tDOC discharged by the M-ARS to the shelf study region (Fig. 3.9). The rate provided in this study represents an upper estimate because of the assumption that only tDOC is lost during photomineralization. This assumption, however, is supported by multiple observations that exposure of plankton-derived DOM to intense solar radiation leads to negligible photomineralization [Ziegler and Benner, 2000; Obernosterer and Benner, 2004].

The surprisingly low magnitude of photomineralization in the shelf mixed layer stems from relatively low apparent quantum yields. Overall, the broadband AQYs for
photomineralization determined in this study (range: 10-124 µmol DOC (mol photons)$^{-1}$) were of comparable magnitude to AQYs for dissolved inorganic carbon photoproduction determined by Bélanger et al. [2006] for Arctic coastal waters (range: ~10-35 µmol DOC (mol photons)$^{-1}$) and by White et al. [2010] for Delaware Bay waters (range: ~23-145 µmol DOC (mol photons)$^{-1}$), Johannessen and Miller [2001] for inshore water (~48 µmol DOC (mol photons)$^{-1}$), but was lower than the coastal AQY determined by Johannessen and Miller [2001] (~260 µmol DOC (mol photons)$^{-1}$). Minor losses of DOC (a few %) were observed in the samples after 48-h irradiations in the solar simulator despite large numbers of photons absorbed by CDOM (~0.02 to 0.4 mol photons L$^{-1}$ over λ = 290-490 nm). For a given irradiation time, the amount of photons absorbed by CDOM (per unit volume) is typically orders of magnitude greater in a solar simulator than it is in the shelf mixed layer. Our calculations revealed that a 48-h irradiation in the solar simulator is equivalent to an average of ~4 months natural irradiation in the shelf mixed layer. The mineralization of ~4% of tDOC over 2 to 3 months in the shelf mixed layer is consistent with this observation.

The coupling between photochemical and biological processes appears to represent a more important mechanism in tDOC mineralization than photomineralization. In addition to direct photomineralization, exposure of DOM to solar radiation has been shown to produce low molecular weight DOM, including a variety of carbonyl compounds that are rapidly utilized by microbes [Kieber et al., 1989; Miller and Moran, 1997]. Photochemical alterations of terrigenous DOM and deep-water DOM have been shown to enhance biomineralization and bacterial growth, whereas solar exposure of plankton DOM and surface DOM has been shown to have no or opposite effects [Benner
and Biddanda, 1998; Tranvik and Bertilsson, 2001; Obernosterer and Benner, 2004]. In this study, the independent assessments of total mineralization, biomineralization and photomineralization indicate the photochemical enhancement of biomineralization, referred to here as photo-biomineralization, could account for as much as 32% of the total tDOC mineralization rate in the shelf mixed layer. The 2.5-fold increase in incident irradiance between winter and summer can explain some of the enhanced tDOC mineralization observed during the summer.

The mixed layer is the part of the water column where most of the photochemistry occurs, particularly in coastal waters [Zafiriou et al., 2008; Fichot and Miller, 2010]. The in situ optical properties and mixed layer depths acquired during this study revealed that 90% (\(\lambda = 490\) nm) to 100% (\(\lambda = 290\) nm) of the incident photochemically active irradiance is attenuated within the mixed layer. Photochemical processes below the mixed layer can therefore be considered negligible. About 35% of the freshwater and tDOC in the shelf study region resides below the mixed layer and above the base of the pycnocline. The calculated filling times for freshwater above the pycnocline are representative for this water mass as well as the mixed layer. Application of the tDOC biomineralization decay constant yielded an annual tDOC mineralization of 0.29 Tg tDOC in this water mass.

The remaining freshwater on the shelf lies below the pycnocline and accounts for 15% of the total freshwater. The residence time of freshwater is poorly known in these deeper waters, and lower temperatures and the presence of hypoxic and anoxic areas make it very difficult to calculate a reasonable tDOC mineralization rate for this water mass. Ignoring this part of the shelf, photochemical and biological processes mineralized
~1 Tg tDOC during the year from March 2009-2010. The tDOC flux from the M-ARS was 1.88 Tg tDOC to the study area during this period, indicating ~53% was rapidly degraded to carbon dioxide in shelf waters receiving the discharge from this large river system.

The estimates of tDOC mineralization presented in this study provide direct evidence that ocean margins act as major “filters” of terrigenous DOC between the land and the open ocean. The observation that ~40% of the M-ARS tDOC is mineralized within 2 to 3 months on the Louisiana shelf is indeed consistent with past evidence that little tDOC exists in the open ocean and that ocean margins must act as major sinks of tDOC [Hedges et al., 1997; Opsahl and Benner, 1997]. The mesoscale circulation on the northern Gulf of Mexico shelf indicates that a large fraction of the M-ARS tDOC is exported westward from the Louisiana shelf to the Texas shelf, where it resides for an additional several months [Dinnel and Wiseman, 1986; Etter et al., 2004; Ohlmann and Niiler, 2005]. The mineralization of M-ARS tDOC in the NGoM ocean margin is therefore likely much higher than the 40% estimated for the Louisiana shelf alone.

Nevertheless, the presence of tDOC in the deep ocean is evidence that some tDOC escapes mineralization in ocean margins [Meyers-Schulte and Hedges, 1986; Opsahl and Benner, 1997; Opsahl et al., 1999]. As evidenced by the strong seasonality in tDOC mineralization observed in this study, the efficiency of ocean margins as tDOC filters between land and ocean can vary substantially. The extent of mineralization in ocean margins depends on factors such as shelf dimensions, mesoscale shelf circulation, riverine inputs, water temperature and solar exposure, which regulate the residence time and mineralization rate of tDOC. In the case of the northern Gulf of Mexico, the rapid
export of Mississippi River plume water off the Louisiana shelf is known to occur regularly [Wiseman and Dinnel, 1988; Schiller et al., 2011; Zhang et al., 2012] and represents a potentially important export mechanism of M-ARS tDOC to the open Gulf. In the Arctic Ocean, large riverine inputs and slow mineralization rate due to low temperatures and solar exposure leads to the export of ~1.7 Tg tDOC to the North Atlantic, an equivalent of 25-33% of the annual tDOC discharged by Arctic rivers [Benner et al., 2005].

The extensive mineralization in ocean margins has important ramifications for the fate and cycling of tDOC in the global ocean. Measurements of the lignin biomarker in the open ocean and ocean interior have suggested tDOC cycles on timescales of 21-132 years in the ocean [Opsahl and Benner, 1997], which is much more rapid than the 4000-6000-yr turnover time of bulk DOC [Williams and Druffel, 1987]. The mineralization of a large fraction of tDOC over short timescales in ocean margins implies that the actual residence time of tDOC in the open ocean can be significantly longer than 21-132 years. A global tDOC mineralization of ~50% in ocean margins would double the residence time to 42-262 years. A mineralization of 90% would increase it ten-fold to 210-1320 years, and thereby suggest 10% of the tDOC discharged by rivers cycles in the open ocean on timescales similar to the mixing time of the ocean. Longer timescales for tDOC mineralization in the open ocean than in ocean margins is consistent with the export of more refractory tDOC components off ocean margins. The export of tDOC to the ocean interior represents a mechanism by which carbon dioxide fixed on land is sequestered in the deep ocean for centuries to millennia [Benner et al., 2005].
Finally, the mineralization of tDOC has important implications for the metabolic state and CO₂ exchange in ocean margins. The northern Gulf of Mexico ocean margin has been shown to act either as a net source or a net sink of CO₂ to the atmosphere. Air-sea CO₂ fluxes reported in the Mississippi River plume area ranged from -1 mmol CO₂ m⁻² d⁻¹ in summer (net sink of atmospheric CO₂) to >1 mmol CO₂ m⁻² d⁻¹ in spring, and ~5 mmol CO₂ m⁻² d⁻¹ in fall (net sources of atmospheric CO₂) [Lohrenz et al., 2010]. By comparison, the seasonal tDOC mineralization rate estimated for the shelf mixed layer (0.028 to 0.108 Tg tDOC 30d⁻¹) correspond to CO₂ production rates that range from 1.1 mmol CO₂ m⁻² d⁻¹ in winter to 4.7 mmol CO₂ m⁻² d⁻¹ in summer. Atmospheric CO₂, water temperature, primary production and community respiration represent the important factors regulating CO₂ fluxes in coastal waters [Cai, 2011]. Nevertheless, these comparable ranges suggest the seasonal variations in tDOC mineralization are sufficiently large to affect the role of this river-influenced ocean margin in CO₂ exchange with the atmosphere.
Figure 3.1 Study area, sampling stations, and geographical limits of the shelf study area in the Northern Gulf of Mexico. The study area is delineated by the 3-m and 200-m isobaths (North-South limits), and the 89.40°W and 93.66°W meridians (East-West limits). The study area covers a surface area $A_{\text{shelf}} = 62,068 \text{ km}^2$ and represents a total volume of water $V_{\text{shelf}} = 2945 \text{ km}^3$. The contours represent isobaths in the study area. Isobaths are set at 10-m increments, with the exception of the first isobath that is set at 3 m. On average, 100% of the Atchafalaya River discharge and 53% of the Mississippi River discharge flows into this region of the shelf [Dinnel and Wiseman, 1986]. The Mississippi-Atchafalaya River System largely dominates riverine inputs to the shelf study area.
Figure 3.2 Simplified flowchart describing the approach used to calculate the mass balance of tDOC and the corresponding tDOC mineralization rates in the shelf mixed layer.
Figure 3.3 (a) Vertical freshwater distribution on the shelf, calculated for each season from salinity profiles acquired in the field using a CTD. The inset plots display the same data using a log-scale for depth (y-axis) to highlight the base of the “pycnocline”, where the rate of change in freshwater with depth decreases sharply. (b) Illustration of the reverse-time integration used to derive the seasonal freshwater filling times. Here, freshwater filling time is defined specifically as the time required by the Mississippi-Atchafalaya River System (M-ARS) to accumulate the freshwater volume present on the shelf above the base of the pycnocline, considering the effects of precipitation and evaporation over the shelf. Here, $Q(t)$ refers to the freshwater discharge from the M-ARS (gray line, right y-axis), which includes 100% of the Atchafalaya River discharge and 53% of the Mississippi River discharge [Dinnel and Wiseman, 1986]. $P(t)$ and $E(t)$ refer to the precipitation rate and evaporation rate over the shelf, respectively. The difference between $Q(t)$ (gray line) and $Q(t)+P(t)-E(t)$ (black line) illustrates the net effect of precipitation and evaporation.
Figure 3.4 Surface grids of (a) salinity, (b) mixed layer depth, (c) DOC concentration, and (d) CDOM spectral slope coefficient, $S_{275-295}$. The interpolation of the discrete field measurements using ordinary kriging provided realistic grids for the shelf. The data shown here are for the Spring cruise but equivalent data were derived for the four seasons. These data represent the basic properties used to calculate the tDOC mass balance in the shelf mixed layer.
Figure 3.5 Seasonal and annual mass balance of tDOC in the shelf mixed layer (2009-2010). The full pie corresponds to the conservative tDOC, that is the total amount of tDOC expected in the shelf mixed layer considering the volume of freshwater and assuming conservative behavior of the tDOC discharged by the M-ARS. For each season, the estimated value for conservative tDOC is provided above the pie chart. The measured tDOC is the amount of tDOC actually present in the shelf mixed layer. The mineralization of tDOC explains the discrepancy between conservative tDOC and measured tDOC.

Spring: 0.273 Tg tDOC
- tDOC mineralized: 38%
- Measured tDOC: 62%

Summer: 0.257 Tg tDOC
- tDOC mineralized: 71%
- Measured tDOC: 29%

Fall: 0.320 Tg tDOC
- tDOC mineralized: 31%
- Measured tDOC: 69%

Winter: 0.241 Tg tDOC
- tDOC mineralized: 26%
- Measured tDOC: 74%
Figure 3.6 (a) Annual downward scalar irradiance spectrum, $E_{od}(0', \lambda)$, incident just below the sea surface. The spectrum is an average for the study area and includes a correction for the effects of clouds. The inset illustrates the seasonal variability of the incident irradiance spectrally integrated over the $\lambda = 290$-$490$ nm range. (b) Function $\bar{F}(\lambda)$ (black line) representing the fraction of incident $E_{od}(0', \lambda)$ that, on average, is absorbed by CDOM in the shelf mixed layer. The function $\bar{F}(\lambda)$ was calculated as the average of 75 functions $F(\lambda)$ derived from field measurements of mixed layer depth, and spectral CDOM absorption and diffuse attenuation coefficients. The gray shaded area outlines the standard deviation associated with $\bar{F}(\lambda)$. (c) The amount of photons absorbed annually by CDOM in the shelf mixed layer, calculated as the product of $E_{od}(0', \lambda)$ and $\bar{F}(\lambda)$. 

Figure 3.7 Broadband apparent quantum yields for tDOC photomineralization plotted against salinity. A total of 38 apparent quantum yields were determined in the laboratory using samples collected during this study in various water types along the salinity gradient. The apparent quantum yields were determined using full-spectrum irradiations (under a 295-nm cut-off filter), and are therefore broadband averages. The apparent quantum yields are provided in units of $\mu$mol(DOC) mol(photons)$^{-1}$. The dashed line represents the average value of 45 $\mu$mol(DOC) mol(photons)$^{-1}$ used in the calculation of the amount of tDOC photomineralized in a year.
Figure 3.8 Relative contributions of photomineralization and biomineralization to the total mineralization of tDOC in the shelf mixed layer. The mass balance used to calculate the annual total mineralization (0.681 Tg tDOC) was independent from the approaches used to calculate the photomineralization (0.054 Tg tDOC) and biomineralization (0.415 Tg tDOC). The photo-biomineralization rate was obtained by difference.
Figure 3.9 Conceptual representation of tDOC mineralization on the Louisiana shelf. About 50% and 85% of the total freshwater present on the shelf is located in the mixed layer (yellow surface layer) and above the base of the pycnocline (~20 m), respectively. About 50% of the tDOC that transits in the mixed layer is mineralized within 2 to 3 months, with photomineralization accounting for 4%, biomineralization accounting for 30%, and photo-biomineralization potentially accounting for the remaining 16%. More than 90% of the incident photochemically active radiation ($\lambda = 290\text{-}490$ nm) is attenuated in the shelf mixed layer, such that photochemical processes are only significant in this part of the water column. Biomineralization is therefore expected to be the only mineralization process at work below the mixed layer. Our calculations suggest that out of the 2.6 Tg tDOC delivered by the M-ARS to the shelf study area between March 2009 and March 2010, a minimum of 1 Tg tDOC was mineralized on the shelf. About 0.7 Tg tDOC of this 1 Tg was mineralized in the mixed layer.
### Table 3.1 General information during four cruises to the study region (see sampling stations in Fig. 3.1).

<table>
<thead>
<tr>
<th>Season</th>
<th>Sampling dates</th>
<th>Number of samples</th>
<th>Salinity</th>
<th>Temperature (°C)</th>
<th>[DOC] (µmol L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$n$</td>
<td>Min - max / median</td>
<td>Min - max / median</td>
<td>Min - max / median</td>
</tr>
<tr>
<td>Spring</td>
<td>20 Apr – 30 Apr 2009</td>
<td>42</td>
<td>0 - 36.95 / 33.19</td>
<td>15.1 - 23.4 / 22.6</td>
<td>74.9 - 401.6 / 111.2</td>
</tr>
<tr>
<td>Summer</td>
<td>19 Jul – 29 Jul 2009</td>
<td>43</td>
<td>0 - 36.77 / 32.02</td>
<td>28.5 - 30.8 / 29.8</td>
<td>79.0 - 343.1 / 132.4</td>
</tr>
<tr>
<td>Fall</td>
<td>29 Oct – 07 Nov 2009</td>
<td>41</td>
<td>0 - 36.63 / 32.92</td>
<td>16.7 - 27.4 / 23.7</td>
<td>77.8 - 599.3 / 113.4</td>
</tr>
<tr>
<td>Winter</td>
<td>11 Mar – 20 Mar 2010</td>
<td>43</td>
<td>0 - 36.48 / 28.06</td>
<td>10.6 - 20.3 / 16.9</td>
<td>63.2 - 358.9 / 140.5</td>
</tr>
</tbody>
</table>
Table 3.2 Seasonal freshwater volumes and filling times ($T_{\text{filling}}$) in the study region. $Q$ refers to freshwater discharge from the Mississippi-Atchafalaya River system, and $P-E$ refers to the net freshwater volume added or removed by precipitation and evaporation over the shelf. $T_{\text{filling}}$ is the freshwater filling time.

<table>
<thead>
<tr>
<th>Season</th>
<th>Total freshwater volume on the shelf (km$^3$)</th>
<th>Freshwater volume present above the base of the shelf pycnocline (km$^3$)</th>
<th>$Q$ (km$^3$)</th>
<th>$P-E$ (km$^3$)</th>
<th>$T_{\text{filling}}$ (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>96.9</td>
<td>81.0</td>
<td>78.8</td>
<td>2.2</td>
<td>53</td>
</tr>
<tr>
<td>Summer</td>
<td>107.8</td>
<td>88.8</td>
<td>93.5</td>
<td>-4.7</td>
<td>51</td>
</tr>
<tr>
<td>Fall</td>
<td>116.7</td>
<td>96.7</td>
<td>100.2</td>
<td>-3.5</td>
<td>96</td>
</tr>
<tr>
<td>Winter</td>
<td>135.5</td>
<td>125.9</td>
<td>130.0</td>
<td>-4.1</td>
<td>68</td>
</tr>
</tbody>
</table>
Table 3.3 Total and freshwater volumes of the shelf mixed layer, and fractions of the total shelf freshwater present in the mixed layer.

<table>
<thead>
<tr>
<th>Season</th>
<th>Volume of the shelf mixed layer (km$^3$)</th>
<th>Freshwater volume of the shelf mixed layer (km$^3$)</th>
<th>Fraction of the total shelf freshwater present in the mixed layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>920</td>
<td>56.1</td>
<td>58%</td>
</tr>
<tr>
<td>Summer</td>
<td>586</td>
<td>50.5</td>
<td>47%</td>
</tr>
<tr>
<td>Fall</td>
<td>1285</td>
<td>66.6</td>
<td>57%</td>
</tr>
<tr>
<td>Winter</td>
<td>562</td>
<td>58.1</td>
<td>41%</td>
</tr>
</tbody>
</table>
Table 3.4 Seasonal average tDOC concentrations for the riverine ([tDOC]$_{M-ARS}$) and marine ([tDOC]$_{marine}$) end-members used in the calculation of conservative tDOC. The [tDOC]$_{M-ARS}$ represents the weighted averages of the discharge from the Mississippi-Atchafalaya River system (M-ARS).

<table>
<thead>
<tr>
<th>Season</th>
<th>[tDOC]$_{M-ARS}$ ($\mu$mol L$^{-1}$)</th>
<th>[tDOC]$_{marine}$ ($\mu$mol L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>369</td>
<td>2.3</td>
</tr>
<tr>
<td>Summer</td>
<td>400</td>
<td>2.3</td>
</tr>
<tr>
<td>Fall</td>
<td>345</td>
<td>3.1</td>
</tr>
<tr>
<td>Winter</td>
<td>315</td>
<td>3.5</td>
</tr>
</tbody>
</table>
Table 3.5 Seasonal mass balances of tDOC in the shelf mixed layer. The total amount of tDOC mineralized in the shelf mixed layer (tDOC\(_{\text{mineralized}}\)) is the difference between tDOC\(_{\text{conservative}}\) and tDOC\(_{\text{measured}}\).

<table>
<thead>
<tr>
<th>Season</th>
<th>Conservative tDOC(_{\text{conservative}}) (Tg C)</th>
<th>Measured tDOC(_{\text{measured}}) (Tg C)</th>
<th>tDOC(_{\text{mineralized}}) (Tg C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>0.273</td>
<td>0.170</td>
<td>0.103</td>
</tr>
<tr>
<td>Summer</td>
<td>0.257</td>
<td>0.075</td>
<td>0.182</td>
</tr>
<tr>
<td>Fall</td>
<td>0.320</td>
<td>0.221</td>
<td>0.099</td>
</tr>
<tr>
<td>Winter</td>
<td>0.241</td>
<td>0.178</td>
<td>0.063</td>
</tr>
</tbody>
</table>
Table 3.6 Exponential decay constants for the microbial degradation of dissolved lignin-derived phenols (sum of \( p \)-hydroxy, vanillyl and syringyl phenols; nmol L\(^{-1}\)).

<table>
<thead>
<tr>
<th>Location</th>
<th>Salinity</th>
<th>Incubation time (d)</th>
<th>Decay constant ( k ) (d(^{-1}))</th>
<th>Number of time points (n)</th>
<th>( R^2 )</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mississippi River</td>
<td>0</td>
<td>28</td>
<td>0.0032</td>
<td>5</td>
<td>0.20</td>
<td>Opsahl and Benner, 1998</td>
</tr>
<tr>
<td>Mississippi River</td>
<td>0</td>
<td>620</td>
<td>0.0012</td>
<td>2</td>
<td>n/a</td>
<td>Hernes and Benner, 2003</td>
</tr>
<tr>
<td>Mississippi River Plume</td>
<td>8.5</td>
<td>10</td>
<td>0.0238</td>
<td>2</td>
<td>n/a</td>
<td>Hernes and Benner, 2003</td>
</tr>
<tr>
<td>Broad River, SC</td>
<td>0</td>
<td>94</td>
<td>0.0059</td>
<td>4</td>
<td>0.95</td>
<td>This study</td>
</tr>
<tr>
<td>Coastal water, SC (Ashley Estuary)</td>
<td>23.1</td>
<td>90</td>
<td>0.0071</td>
<td>4</td>
<td>0.99</td>
<td>This study</td>
</tr>
<tr>
<td>Coastal water, SC (near Isle of Palms)</td>
<td>33.9</td>
<td>88</td>
<td>0.0050</td>
<td>4</td>
<td>0.98</td>
<td>This study</td>
</tr>
<tr>
<td>Coastal water, SC (near Hunting Island)</td>
<td>34.6</td>
<td>91</td>
<td>0.0050</td>
<td>3</td>
<td>0.94</td>
<td>This study</td>
</tr>
<tr>
<td>Coastal water, SC (near Winyah Bay)</td>
<td>35.1</td>
<td>90</td>
<td>0.0023</td>
<td>3</td>
<td>0.84</td>
<td>This study</td>
</tr>
</tbody>
</table>
CHAPTER 4
PAN-ARCTIC DISTRIBUTIONS OF CONTINENTAL RUNOFF IN THE ARCTIC OCEAN*

4.1 INTRODUCTION
Continental runoff influences surface ocean processes throughout the Arctic. Rivers discharge about 3,300 km$^3$ yr$^{-1}$ of buoyant freshwater to the Arctic Ocean [Rachold et al., 2004] where it sustains a halocline that isolates the upper 200-m layer from a warmer, saltier Atlantic layer [Aagaard and Carmack, 1989]. This upper layer represents only 0.1% of the global ocean volume but receives 11% of global riverine discharge from a circumpolar drainage basin that encompasses over 10% of the world’s land surface area. Riverine input is evident throughout the Arctic from low salinities and high concentrations of terrigenous dissolved organic matter (tDOM) in polar surface waters [Opsahl et al., 1999; Benner et al., 2005]. Arctic rivers discharge onto the world’s largest continental shelves that surround and cover more than half of the Arctic Ocean area [Jakobsson et al., 2004]. These river-influenced ocean margins are dominant features of the Arctic and important regions of sea-ice production, biological productivity, carbon sequestration and processes that drive biogeochemical cycles on a basin-wide scale.

The impact of rivers on the freshwater content and biogeochemistry of the Arctic Ocean is strongly influenced by the residence time of riverine inputs and their pathway

to the North Atlantic Ocean. The average residence time of Arctic shelf water ranges from months to years depending on shelf region [Schlosser et al., 1994; MacDonald et al., 2004]. Variations in atmospheric forcing can affect residence time by dramatically altering continental runoff routing and distribution in the Arctic Ocean [MacDonald et al., 2004; Bauch et al., 2009]. Climate-driven changes in runoff distribution have been linked to large inter-annual and decadal variations in the freshwater content of the Arctic Ocean, and these fluctuations have important ramifications for North Atlantic meridional overturning circulation [Morison et al., 2012]. Furthermore, changes in runoff routing through the Arctic Ocean can regulate the extent to which Arctic tDOM is incorporated into North Atlantic Deep Water (NADW) and distributed in the global ocean [Benner et al., 2005]. Despite their global significance, continental runoff routing and distribution in the Arctic remain poorly understood and difficult to predict in this remote and under-sampled region of the global ocean. Here, a new optical proxy for tDOM implemented using remote sensing of ocean color facilitates the synoptic and retrospective monitoring of continental runoff in the Arctic Ocean, and provides a novel approach to assess climate-driven changes in the Arctic.

4.2 METHODS

Surface water samples and data \((n = 106)\) used to establish the relationship between \(S_{275-295}\) and TDLP\(_9\)-C (Fig. 4.1a) were acquired during several field expeditions to the Arctic Ocean between 2005 and 2010, including the Amundsen Gulf, Gulf of Ob, and the Beaufort, Chukchi, Laptev and East Siberian Seas (Fig. B.1, Appendix B). Samples for DOC and CDOM were filtered onboard and analyzed in the home laboratory using high
temperature combustion [Benner and Strom, 1993] and a dual-beam UV-visible spectrophotometer [Fichot and Benner, 2011; 2012], respectively. Samples for dissolved lignin (1-10 L) were extracted onboard [Louchouarn et al., 2000] and analyzed using the cupric oxide oxidation method and gas chromatography with mass spectrometry [Kaiser and Benner, 2012]. DOC-normalized yields of nine lignin phenols (TDLP9-C) were calculated [Fichot and Benner, 2012], and the non-linear regression of TDLP9-C on S275–295 utilized the exponential function shown in Eq. (4.1),

\[ \text{TDLP}_9 - C = \exp(\alpha + \beta \cdot S_{275-295}) \cdot \exp(\gamma \cdot S_{275-295}) + \delta \cdot \exp(S_{275-295}) \] (4.1)

where \( \alpha = 2.7428, \beta = -245.5899, \gamma = 1.6669, \) and \( \delta = -0.9932 \) are the derived regression coefficients.

The in situ measurements of ocean color \( (n = 236) \) and concurrent CDOM samples used in the \( S_{275-295} \) algorithm development (Fig. 4.1b) were collected during the Malina and ICESCAPE field expeditions (Appendix B, Fig. B.2). Multispectral remote-sensing reflectances, \( R_{rs}(\lambda) \), were derived for 5 wavelengths \( (\lambda = 443, 488, 531, 555 \) and \( 667 \) nm) from profiles made with a Biospherical Compact-Optical Profiling System (C-OPS) [Hooker et al., 2012], and the corresponding CDOM samples were collected and analyzed according to NASA standard protocols [Pegau et al., 2002]. “Measured” \( S_{275-295} \) were calculated from CDOM absorption coefficient spectra, and regressed on \( R_{rs}(\lambda) \) using the multiple linear regression described in Eq. (4.2),

\[ \ln[S_{275-295}] = \alpha + \beta \cdot \ln[R_{rs}(443)] + \gamma \cdot \ln[R_{rs}(488)] \]
\[ + \delta \cdot \ln[R_{rs}(531)] + \epsilon \cdot \ln[R_{rs}(555)] + \zeta \cdot \ln[R_{rs}(667)] \] (4.2)

where \( \alpha = -3.4567, \beta = 0.4299, \gamma = 0.0924, \delta = -1.2649, \epsilon = 0.8885, \) and \( \zeta = -0.1025 \) are the derived regression coefficients. This data set covers a broad range of water types found in river-influenced ocean margins, including high-CDOM and sediment-laden
coastal environments, productive waters at intermediate salinities and oligotrophic waters at higher salinities. The inclusion of data from the Chukchi Sea in summer (ICESCAPE) further demonstrates that the algorithm performs very well in areas where tDOM is relatively low and biogenic particles are abundant and variable. Similar accuracy of $S_{275-295}$ retrievals was obtained using data collected seasonally in the northern Gulf of Mexico in various water types ranging from riverine to oligotrophic, thereby indicating that the approach used in the algorithm is robust.

MODIS Aqua data were accessed from the NASA ocean color website (http://oceancolor.gsfc.nasa.gov/). Monthly NAO and AO indices were acquired from the NOAA Earth System Research Laboratory website (http://www.esrl.noaa.gov/psd/data/climateindices). The Mackenzie River discharge data were obtained from the Environment Canada Water Office website (http://www.wateroffice.ec.gc.ca). Eurasian river discharge was obtained from the ArcticRIMS website (http://rims.unh.edu/data.shtml).

4.3 RESULTS

Dissolved lignin is well established as a biomarker of tDOM in oceanic waters [Meyers-Schulte and Hedges, 1986; Opsahl and Benner, 1997] and has been successfully applied as a tracer of riverine inputs in the Arctic Ocean [Opsahl et al., 1999; Benner et al., 2005]. However, its use relies on the collection of seawater samples and land-based laboratory analyses that prevent synoptic applications. Lignin is also an important chromophore in tDOM, a property that facilitates detection using optical properties. Here, we demonstrate that the spectral slope coefficient of chromophoric dissolved organic
matter (CDOM) between 275 and 295 nm ($S_{275-295}$) is a practical and reliable optical proxy for dissolved lignin and tDOM across various river-influenced ocean margins of the Arctic Ocean [*Fichot and Benner*, 2011; 2012] (Fig. 4.1a). An increase in $S_{275-295}$ is indicative of a decrease in the tDOM content of surface waters. Under the assumption that $S_{275-295}$ behaves conservatively, an increase in $S_{275-295}$ corresponds to a diminishing influence of continental runoff. Biological degradation has little effect on $S_{275-295}$ [Helms *et al.*, 2008; *Fichot and Benner*, 2012] and photodegradation of tDOM in polar surface waters is not extensive [Benner *et al.*, 2005; Bélanger *et al.*, 2006], thereby warranting the assumption and the use of $S_{275-295}$ as a tracer of tDOM and freshwater runoff in river-influenced ocean margins of the Arctic.

The practicality of the $S_{275-295}$ proxy resides in its amenability to remote sensing. The development of an empirical algorithm reveals that $S_{275-295}$ can be estimated from ocean color with excellent and consistent accuracy (within ± 4%) over the broad range of water types and $S_{275-295}$ values observed in the Arctic Ocean (Fig. 4.1b). The strong connection between $S_{275-295}$ and ocean color in river-influenced ocean margins exists because the optical property $S_{275-295}$ is an excellent tracer of tDOM [*Fichot and Benner*, 2012] and the gradients of ocean color in river-influenced ocean margins are primarily driven by the constituents of continental runoff. The $S_{275-295}$ algorithm thus facilitates the synoptic and real-time monitoring of tDOM and freshwater runoff in the Arctic using ocean-color remote sensing.

Implementation of the $S_{275-295}$ algorithm using MODIS *Aqua* ocean color provides the first pan-Arctic view of average tDOM distributions in river-influenced ocean margins during August 2002-2009 (Fig. 4.1c). The influence of the three largest Arctic
rivers on tDOM distributions is evident along the entire Siberian margin. One of the most 
striking features is the overwhelming amount of tDOM in the Laptev and East Siberian 
Seas, indicating a large portion of Eurasian river tDOM and runoff is routed alongshore 
in an eastward direction. This observation is supported by measurements of high *in situ* 
concentrations of dissolved organic carbon of terrigenous origin in the East Siberian Sea 
in August 2008 [Alling et al., 2010], and is consistent with shelf water residence times of 
several years in this region [Schlosser et al., 1994; MacDonald et al., 2004]. Low $S_{275-295}$ 
values along the Alaskan coast in the Chukchi Sea depict the transport of Yukon River 
tDOM to the Arctic Ocean in the Alaska Coastal Current and indicate notable tDOM 
contributions by smaller Alaskan rivers (e.g., Noatak and Kobuk Rivers). Most of the 
runoff and tDOM from the Mackenzie River enters the Beaufort Sea and appears to be 
entrained in the gyre circulation of the southern Canada Basin. A relatively small fraction 
of the discharge from the Mackenzie River was routed to the Labrador Sea via the 
Canadian Arctic Archipelago (CAA).

Assessment of inter-annual variability in tDOM distribution revealed a change in 
the routing of Mackenzie River discharge over the last decade (Fig. 4.2; and Appendix B 
Figs. B.3 and B.4). The Mackenzie River outflow progressed from an alongshore, 
eastward path to the CAA in 2002 (Fig. 4.2a) to a cross-shelf, northwestward path to the 
Canada Basin since 2006 (Fig. 4.2b). This routing switch has important implications for 
the fate of North American runoff and tDOM. Routing through the CAA favors the 
export of North American tDOM to the Labrador Sea [Walker et al., 2009]. Although the 
magnitude of this export remains unknown, deep ocean convection in the Labrador Sea 
can sequester tDOM in North Atlantic Deep Water for centuries [Benner et al., 2005]. In
contrast, routing to the Canada Basin contributes to longer-term storage of runoff and processing of tDOM within the Beaufort Gyre and Arctic Ocean [Benner et al., 2005; Bélanger et al., 2006]. This decadal shift to greater export of Mackenzie River runoff to the Canada Basin during 2006-2011 could contribute to less North American tDOM being sequestered in the deep ocean.

The routing of Mackenzie River outflow since 2006 coincides with observations of a rapid accumulation of freshwater in the Canada Basin. Freshening began in the 1990s and accelerated in the late 2000s [McPhee et al., 2009; Proshutinsky et al., 2009; Yamamoto-Kawai et al., 2009; Rabe et al., 2011]. The realization that a large accumulation of freshwater in the Canada Basin could impact global ocean circulation stimulated research to identify the freshwater sources and climatic forcing responsible for observed changes in salinity. Pacific water, ice-melt, precipitation and river runoff are distinct sources of freshwater to the Canada Basin. The relative contributions of these freshwater sources to the freshening are typically estimated using tracers (e.g. δ¹⁸O, alkalinity, salinity) or are indirectly calculated using complex models [Macdonald et al., 2002; Schlosser et al., 2002; Serreze et al., 2006; Yamamoto-Kawai et al., 2008; Yamamoto-Kawai et al., 2009; Morison et al., 2012]. The lignin-based $S_{275-295}$ proxy presented here substantiates the riverine origin of freshwater and provides a direct means to distinguish continental runoff from other freshwater sources using remote sensing.

The acceleration of the Beaufort Gyre due to the strengthening of the Beaufort High [Giles et al., 2012] and routing of Eurasian river runoff to the Canada Basin driven by the Arctic Oscillation [Morison et al., 2012] are complementary and currently leading explanations for the freshening of the Basin [Mauritzen, 2012]. The remotely sensed
runoff distributions presented in this study (Fig. 4.2, and Appendix B Figs. B.3 and B.4) further suggest the recurrent influx of Mackenzie River runoff to the Canada Basin in the late 2000s was also a significant source of freshwater to the Basin and contributed to the freshening. The temporal sequence of the Mackenzie River discharge in 2008 provides unambiguous evidence that the spring freshet was directly and rapidly injected into the Canada Basin during June and July (Fig. 4.3). In situ measurements of salinity, $\delta^{18}O$, and alkalinity from an independent study [Yamamoto-Kawai et al., 2009] corroborate that Mackenzie River runoff was a minor source of freshwater to the Canada Basin in the early 2000s but increased in the southern part of the Basin in 2007.

The contribution of North American runoff to the Canada Basin freshwater budget appears to be shifting in response to climatic forcing. A freshwater budget based on data from 2003-2004 estimated about 40% of North American runoff enters the Canada Basin [Yamamoto-Kawai et al., 2008]. The mean freshwater residence time in the Basin is about 10 years [Yamamoto-Kawai et al., 2008], so this estimate is representative of the decade leading up to 2004. Although significant freshwater contributions from the Mackenzie River to the Basin were observed during that decade [Macdonald et al., 1999], this estimate does not integrate the increasing contributions from North American runoff since 2006. The detailed progression of the 2008 Mackenzie River outflow indicated up to 155 km$^3$ of Mackenzie freshwater was released into the Canada Basin in June and July alone (Fig. 4.3), indicating more than half of the discharge from the Mackenzie has been entering the Canada Basin since 2006. Increasing contributions of North American runoff to the Canada Basin are consistent with enhanced Ekman
pumping resulting from the wind-driven spin-up of the Beaufort Gyre [Giles et al., 2012] and therefore appear to result from recent trends in climate variability.

Discharge from major Arctic rivers has increased over the past decades in response to climate variability [Peterson et al., 2002; McClelland et al., 2006; Shiklomanov and Lammers, 2009]. Climatic forcing of river discharge is evident between 2002 and 2009 from the strong correspondence between the North Atlantic Oscillation (NAO) or Arctic Oscillation (AO) wintertime indices and the river discharge anomaly of Eurasian rivers (Fig. 4.4a). Manifestations of inter-annual discharge fluctuations in the Arctic Ocean are best illustrated in the Kara Sea, which receives inputs from the Ob and Yenisei rivers. The Kara Sea is a semi-enclosed margin that is largely ice-free during summer, which facilitates inter-annual comparisons of remotely sensed variables. Inter-annual comparisons revealed consistency between discharge from the Ob and Yenisei rivers and the average $S_{275-295}$ value for the Kara-Sea sector (Fig. 4.4b). The correspondence between discharge and tDOM in the Kara Sea is particularly striking when comparing 2002 and 2005, which are representative of high and low discharge years between 2002 and 2009 (Fig. 4.4c). This demonstrates climate-driven changes in the tDOM inventory of the surface Arctic Ocean are traceable using this approach.

4.4 DISCUSSION

The $S_{275-295}$ proxy and algorithm presented in this study facilitate the real-time and synoptic monitoring of tDOM and freshwater runoff in surface polar waters. The foundation of the $S_{275-295}$ proxy on the lignin biomarker is fundamental to the approach. The “terrigenous” attribute of lignin substantiates the riverine origin of dissolved organic
matter and freshwater. Its “chromophoric” property, on the other hand, facilitates implementation with remote sensing. Although the Arctic remains one of the most challenging environments for remote sensing, it is also a region where remote sensing has much to offer given the logistical restrictions and high costs of field surveys, particularly on the Siberian shelves. The applicability of the approach will improve as the extent and duration of sea-ice cover decrease, allowing for greater spatial and temporal coverage.

New capabilities to monitor surface tDOM distributions will prove valuable for understanding future climate-driven changes in the biogeochemistry of the Arctic. Permafrost thawing and precipitation in drainage basins of Arctic rivers are projected to intensify with escalating atmospheric temperatures and thereby enhance the mobilization of soil organic matter to the Arctic Ocean [Frey and Smith, 2003; Benner et al., 2004; Frey and Smith, 2005; Guo et al., 2007; Amon et al., 2012]. The fate of this material and its effects on biogeochemical cycles will depend on its routing and residence time in polar surface waters [Benner et al., 2005]. Furthermore, processing of organic matter in surface waters is influenced by factors that are currently being altered by climate change (e.g., ice cover, water temperature). Multiyear records of remotely sensed tDOM distributions provide direct evidence of how the routing, inventory, storage and residence time of tDOM in surface polar waters change in response to climatic forcing. Such applications will thus provide crucial information for understanding the fate of immobilized soil organic matter and its impacts on biogeochemical cycles in this rapidly changing Arctic environment.

Finally, remote sensing of continental runoff provides useful insights about the sources of freshwater in the Arctic Ocean. Ice melt, precipitation and runoff are all
increasing under the current climatic trends [Serreze et al., 2000; McClelland et al., 2006], and are altering the freshwater budget of the Arctic Ocean. Remotely sensed runoff distributions provide direct evidence of continental runoff contributions to specific regions of the surface Arctic Ocean, and will thereby help understand the mechanisms responsible for future changes in the Arctic freshwater budget. It is important to remember, however, that the uncoupling of river water from its tDOM component during the winter freeze-thaw cycle [Amon, 2004] hampers the use of this approach to assess year-to-year changes in freshwater runoff storage. Future applications will also likely include studying the influence of continental runoff on biological processes, such as primary production, in polar surface waters.
Figure 4.1 The CDOM spectral slope coefficient, $S_{275-295}$, as a tracer of riverine inputs in the Arctic Ocean. (a) The relationship between $S_{275-295}$ and dissolved lignin carbon yield (TDLP$_{9-C}$) across various Arctic river-influenced ocean margins. (b) A performance evaluation of the $S_{275-295}$ algorithm. On average, $S_{275-295}$ can be estimated from ocean color within 4% of $S_{275-295}$ values measured in situ. (c) Implementation of the algorithm using MODIS Aqua ocean color providing a pan-Arctic view of an August climatology (2002-2009) of $S_{275-295}$. Increasing $S_{275-295}$ values are indicative of a decreasing fraction of tDOM. The four largest Arctic rivers are labeled and ranked in order of decreasing discharge: Yenisei (1), Lena (2), Ob (3), and Mackenzie (4). River-influenced margins of the Arctic are labeled: Gulf of Ob (GO), Kara Sea (KS), Laptev Sea (LS), East Siberian Sea (ESS), Chukchi Sea (CS), Beaufort Sea (BS) and Amundsen Gulf (AG). The contour lines represent the 2000-m isobath.
Figure 4.2 Inter-annual changes in the routing of Mackenzie River runoff. (a) The Mackenzie River outflow in 2002, showing eastward transport of North American runoff to the Canadian Arctic Archipelago. (b) The Mackenzie River outflow in 2008, showing northwestward transport of North American runoff to the Canada Basin. A progressive switch from eastward to northwestward routing occurred between 2002 and 2011 (Figures B.3 and B.4) and coincides with the rapid freshening of the Canada Basin. The $S_{275-295}$ algorithm was implemented using 4-km resolution, yearly-binned, MODIS Aqua ocean color. The Mackenzie River is labeled (4). The contour line represents the 2000-m isobath and outlines the Canada Basin.
Figure 4.3 Temporal sequence of the Mackenzie River freshet release into the Canada Basin during June and July 2008. The $S_{275–295}$ algorithm was implemented using 4-km resolution, 8-day-binned, MODIS Aqua ocean color acquired between June 1 and August 3. The discharge value ($\text{km}^3$) displayed on each panel indicates the cumulative Mackenzie River discharge released between May 1 (start of the freshet) and the end of each 8-day period. The contour line represents the 2000-m isobath and delineates the Canada Basin. The Mackenzie River is labeled (4).
Figure 4.4 Climatic forcing of major Eurasian riverine inputs.  (a) The North Atlantic Oscillation (NAO) and Arctic Oscillation (AO) wintertime indices (DJFM: Dec-Jan-Feb-Mar) in relation to the combined discharge anomaly of the Yenisei, Lena and Ob rivers between 2002 and 2009. High NAO and AO indices are typically associated with higher precipitation over Northern Eurasia. River discharge is calculated as the cumulative discharge from May 1 to August 30, and the anomaly is relative to the 2002-2009 average.  (b) Average $S_{275-295}$ values for surface waters of the Kara Sea in relation to the combined discharge of the Yenisei and Ob rivers between 2002 and 2009. The $S_{275-295}$ values for the Kara Sea were calculated as the average value in the region displayed in panel (c). River discharge is calculated as the cumulative discharge from May 1 to August 30.  (c) Distributions of riverine inputs during high (2002) and low (2005) discharge years. The years correspond to low and high average $S_{275-295}$ values observed in the Kara Sea between 2002 and 2009. The $S_{275-295}$ algorithm was implemented using MODIS Aqua ocean color data averaged from May to October. The Yenisei and Ob rivers are labeled (1) and (3), respectively.
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APPENDIX A
SUPPLEMENTARY METHODS

A.1 DETAILED FIELD SAMPLING AND MEASUREMENTS

Samples for DOC were gravity filtered from Niskin bottles using precombusted GF/F filters (0.7-µm pore size) and stored frozen (-20°C) immediately after collection in precombusted borosilicate glass vials. DOC analysis was conducted within a month of collection by high temperature combustion using a Shimadzu total organic carbon (TOC) TOC-V analyzer equipped with an autosampler [Benner and Strom, 1993]. Blanks were negligible and the coefficient of variation between injections of a given sample was typically ±0.6%. Accuracy and consistency of measured DOC concentrations was checked by analyzing a deep seawater reference standard (University of Miami) every sixth sample.

Samples for CDOM were gravity filtered from Niskin bottles using Whatman Polycap Aqueous Solution (AS) cartridges (0.2-µm pore size), collected in precombusted borosilicate glass vials and stored immediately at 4°C until analysis in the laboratory. For most samples, the absorbance was measured from 250 to 800 nm using a Shimadzu ultraviolet (UV)-visible UV-1601 dual-beam spectrophotometer and 10-cm cylindrical quartz cells. For highly absorbing samples, 5-cm cylindrical quartz cells or 1-cm quartz cuvettes were used. An exponential fit of the absorbance spectrum over an optimal spectral range was used to derive an offset value that was subtracted from the absorbance spectrum [Johannessen and Miller, 2001; Fichot and Benner, 2011]. Absorbance
corrected for offset was then converted to Napierian absorption coefficient, $a_g(\lambda)$ (m$^{-1}$).

The dependence of $a_g(\lambda)$ on $\lambda$ is typically described as

$$a_g(\lambda) = a_g(\lambda_0) \exp(-S(\lambda - \lambda_0))$$  \hspace{1cm} (A.1)

where $\lambda_0 < \lambda$ and $S$ is the spectral slope coefficient in the $\lambda_0$-$\lambda$ nm spectral range. The spectral slope coefficient, $S_{275-295}$, was estimated using a linear fit of the log-linearized $a_g(\lambda)$ spectrum over the 275 to 295 spectral range, and is reported here with units of nm$^{-1}$.

Samples for photomineralization experiments were gravity filtered from Niskin bottles using Whatman Polycap AS cartridges (0.2-$\mu$m pore size), collected in cleaned (450°C for 4 h) 500-mL Kimax glass bottles and stored immediately at 4°C until analysis. Prior to each experiment, samples were re-filtered through a 0.2-$\mu$m Whatman nylon membrane filter.

During this study, a total of 75 diffuse attenuation coefficient spectra, $K_d(\lambda)$ (where $\lambda$ = 305, 325, 340, 380, 412, 443, 490, and 555 nm), were derived from optical casts acquired in various waters types and during different seasons. Profiles of multispectral downwelling irradiance, $E_d(\lambda,z)$ where $z$ is the depth were obtained using a Satlantic MicroPRO equipped with a surface reference that also measured above-surface downwelling irradiance, $E_d(\lambda,0^+)$ [Fichot et al., 2008]. At each sampled station, synchronous measurements of $E_d(\lambda,z)$ and $E_d(\lambda,0^+)$ were acquired from multiple optical casts (3 or 4 in oligotrophic waters and up to 20 in coastal waters). The data were binned together and were used to calculate profiles of optical depth, $z(\lambda,z)$, as

$$\zeta(\lambda,z) = -\ln\left(\frac{E_d(\lambda,z)}{E_d(\lambda,0^-)}\right)$$  \hspace{1cm} (A.2)
where $E_d(\lambda, 0^-) = E_d(\lambda, 0^+)/1.04$ [Austin, 1974]. For a finite depth interval $\Delta z = z_2 - z_1$ (where $z_2 > z_1$) of homogenous water column, the diffuse attenuation coefficient over that depth interval, $K_d(\lambda, \Delta z)$, can be expressed as

$$K_d(\lambda, \Delta z) = -\frac{\ln\left(E_d(\lambda, z_2)/E_d(\lambda, z_1)\right)}{\Delta z}. \quad (A.3)$$

Thus, for any homogenous water column extending from the surface (e.g., the mixed layer), the diffuse attenuation coefficient can be estimated as

$$K_d(\lambda) = \frac{\zeta(\lambda, z)}{\Delta z}. \quad (A.4)$$

For each wavelength ($\lambda = 305, 325, 340, 380, 412, 443, 490,$ and $555$ nm), a robust regression of $\zeta(\lambda, z)$ against $z$ was performed for the layer that stretched from just below the surface to whichever one of the following depth was reached first: mixed layer depth, second optical depth (depth $z$ where $\zeta(\lambda, z) = 2$), or the depth where the detection limit of the instrument is reached. The slope of the robust regression provided a reliable estimate of $K_d(\lambda)$. Note that in order to preserve the quasi-inherent property of $K_d(\lambda)$, the irradiance measurements used to derive were always done when solar zenith angles were inferior to $\sim 45^\circ$.

A.2 DATA SOURCE

The 3-arc-second bathymetry used to delineate the shelf study area and facilitate the calculation of volumes on the shelf was obtained from the National Geophysical Data Center U.S. Coastal Relief Model (http://www.ngdc.noaa.gov/mgg/coastal/crm.html). Daily discharges for the MR and AR were monitored at Tarbert Landing (Mississippi)
and Simmesport (Louisiana), respectively, and are available from the USACE website (http://www.mvn.usace.army.mil/eng/edhd/wcontrol/discharge.asp).

DOC concentrations from the MR and AR were collected roughly every two weeks near Melville (Louisiana) and St. Francisville (Louisiana), respectively, and are available from the NASQAN website (http://water.usgs.gov/nasqan/). Precipitation rates were estimated from pentad global gridded precipitation data (2.5° by 2.5° spatial resolution) from the Climate Prediction Center Merged Analysis of Precipitation (CMAP) website (http://www.cpc.ncep.noaa.gov/products/global_precip/html/wpage.cmap.html). Evaporation rates were derived from the Woods Hole Objectively Analyzed air-sea fluxes data sets (http://oaflux.whoi.edu).

A.3 DETAILED OF CALCULATIONS USED IN THE tDOC MASS BALANCE

Two-dimensional gridding of the surface discrete field measurements (salinity, DOC, mixed layer depth and $S_{275-295}$) was achieved by ordinary kriging using the “ordinary kriging”, “variogram” and “variogramfit” functions developed for Matlab by Wolfgang Schwanghart. Within the kriging procedure, the best fits of the experimental variograms were obtained by using either an exponential function (for DOC and $S_{275-295}$), or a spherical function (for salinity, and mixed layer depth).

The influence of Antarctic Intermediate Water (AAIW) was evident offshore wherever salinity profiles with sub-surface maxima ($S \approx 36.5$) gradually decreased to the specific AAIW salinity of 34.9 at depths $> 500$ m. AAIW-influenced water masses impinging on the bottom of the outer shelf represented an external source of freshwater to
the shelf, and was corrected for by setting the salinity of waters found below the sub-
surface salinity maximum to 36.5 (the sub-surface salinity maximum).

The DOC-normalized lignin yield in each sample, TDLP$_9$-C, was estimated from
the spectral slope coefficient, $S_{275-295}$, following the approach of *Fichot and Benner*
[2012]. Briefly, $S_{275-295}$ was used to derive TDLP$_9$-C using Eq. (A.5)

$$TDLP_9\cdot C = \exp(\alpha + \beta S_{275-295}) + \exp(\gamma S_{275-295}) + \delta \exp(S_{275-295}) \quad (A.5)$$

where $\alpha = 3.172$, $\beta = -267.566$, $\gamma = 0.228$, and $\delta = -0.953$ are the parameters provided in
*Fichot and Benner* [2012] for the Northern Gulf of Mexico. The fraction of tDOC, $f_{tDOC}$, was derived from TDLP$_9$-C using the approach of *Fichot and Benner* [2012], as shown in
Eq. (A.6)

$$f_{tDOC} = \frac{TDLP_9\cdot C}{TDLP_9\cdot C_{M-ARS}} \quad (A.6)$$

where TDLP$_9$-C$_{M-ARS}$ is a representative value of the DOC-normalized lignin yield in the
M-ARS. A representative value for TDLP$_9$-C$_{M-ARS}$ was calculated for each season
investigated (Table A.1). A strong linear relationship ($R^2 = 0.82$, $p = 0.0003$) exists in the
MR and AR between total dissolved lignin phenols, TDLP$_9$ (mol C units) and DOC
concentration (= tDOC in rivers) (Fig. A.1). This relationship facilitated the derivation of
daily TDLP$_9$ flux from the daily MR and AR tDOC fluxes. For each season, TDLP$_9$-C$_{M-ARS}$
was calculated as the ratio of the TDLP$_9$ flux (mol C units) to tDOC flux corresponding to the shelf freshwater filling time of that season.
A.4 DERIVATION OF $F(\lambda)$

The rate of photon absorption by CDOM at any given depth of a homogenous water column such as the mixed layer can be calculated exactly as in Eq. (A.7)

$$\Xi(\lambda, z) = E_o(\lambda, 0^-) \cdot e^{-K_o(\lambda)z} \cdot a_g(\lambda)$$  \hspace{1cm} (A.7)

where $E_o(\lambda, z)$ is the spectral scalar irradiance incident just below the surface, $K_o(\lambda)$ is the spectral diffuse attenuation coefficient of scalar irradiance, $a_g(\lambda)$ is the spectral CDOM absorption coefficient, $\lambda$ is the wavelength, and $z$ is the depth. In the vast majority of natural waters, it is very reasonable to assume that the downward scalar irradiance $E_{od}(\lambda, 0^-) \approx E_o(\lambda, 0^-)$ and the diffuse attenuation coefficient of downward irradiance $K_d(\lambda) \approx K_o(\lambda)$ [Fichot and Miller, 2010]. Under these assumptions, Eq. (A.7) can be rewritten as in Eq. (A.8)

$$\Xi(\lambda, z) = E_{od}(\lambda, 0^-) \cdot e^{-K_d(\lambda)z} \cdot a_g(\lambda)$$ \hspace{1cm} (A.8)

Integrating $\Xi(\lambda,z)$ between the surface and the mixed layer depth provides an estimate of the total rate of photons absorbed by CDOM in the mixed layer, $\Xi_{ML}(\lambda,z)$, which can be simplified to

$$\Xi_{ML}(\lambda) = \int_0^{MLD} \Xi(\lambda,z) \, dz = \int_0^{MLD} E_{od}(\lambda, 0^-) \cdot e^{-K_d(\lambda)z} \cdot a_g(\lambda) \, dz$$

$$= E_{od}(\lambda, 0^-) \int_0^{MLD} e^{-K_d(\lambda)z} \cdot a_g(\lambda) \, dz$$

$$= E_{od}(\lambda, 0^-) \cdot F(\lambda)$$  \hspace{1cm} (A.9)

where the function $F(\lambda)$ represents the fraction of incident irradiance $E_{od}(\lambda, 0^-)$ absorbed by CDOM in the mixed layer:
\[ F(\lambda) = \int_0^{\text{MLD}} e^{-K_d(\lambda)z} \cdot a_g(\lambda) \, dz \]  
(A.10)

Since the mixed layer can be assumed homogenous, \( a_g(\lambda) \) is considered independent of \( z \), and Eq. (A.10) can be simplified as

\[ F(\lambda) = a_g(\lambda) \int_0^{\text{MLD}} e^{-K_d(\lambda)z} \, dz \]  
(A.11)

Solving the integral yields Eq. (A.12)

\[ F(\lambda) = -\frac{a_g(\lambda)}{K_d(\lambda)} \left[ e^{-K_d(\lambda)z} \right]_0^{\text{MLD}} \]  
(A.12)

such that \( F(\lambda) \) in the homogenous mixed layer becomes strictly a function of \( a_g(\lambda), K_d(\lambda) \) and mixed layer depth, \( z_{\text{MLD}} \), as summarized in Eq. (A.13):

\[ F(\lambda) = \frac{a_g(\lambda)}{K_d(\lambda)} \left( 1 - e^{-K_d(\lambda)z_{\text{MLD}}} \right) \]  
(A.13)

### A.5 DETERMINATION OF APPARENT QUANTUM YIELDS FOR PHOTOMINERALIZATION

The photomineralization experiments were done in the home laboratory within a few weeks of collection. Prior to each experiment, samples were re-filtered through a 0.2-µm Whatman nylon membrane filter before dispensing into 5-cm pathlength quartz cells (Spectrocell CM-3050-T). A total of 38 samples were processed. Quadruplicates of each sample were irradiated under controlled illumination conditions and constant temperature (22.5°C) using an Atlas Suntest XPS+ solar simulator (Xenon lamp, 750 W) and a setup similar to the one used by Johannessen and Miller (2001). Long-pass, 295-nm cutoff filters (Schott N-WG295) prevented unnatural radiation from reaching the samples.
Quadruplicate DOC concentrations were measured before and after irradiation. The mean and standard error of the quadruplicate DOC concentrations was calculated for each sample and time point. Irradiations lasted 48 h for most samples, and 72 h for a few samples. Changes in $a_g(\lambda)$ ($\lambda = 250$-800 nm) were monitored every 24 h, regardless of total irradiation time. For each sample a broadband apparent quantum yield for tDOC photomineralization was derived from each photomineralization experiment as

$$\phi_{PM} = -\frac{[\text{DOC}]_{\text{final}} - [\text{DOC}]_{\text{initial}}}{\Xi_{290-490}^{\text{Exp}}}$$

(A.14)

where $[\text{DOC}]_{\text{final}}$ and $[\text{DOC}]_{\text{initial}}$ are the mean [DOC] of the quadruplicates at initial time and final time, respectively, and $\Xi_{290-490}^{\text{Exp}}$ is the total amount of photons absorbed by CDOM during irradiation, integrated over the 290-490 nm spectral range, and per unit L.

In the following, we provide a detailed explanation of how $\Xi_{290-490}^{\text{Exp}}$ was calculated. Figure A.2 provides a useful illustration for of the variables involved in those calculations.

The rate of photon absorbed by CDOM (mol(photons) m$^{-3}$ s$^{-1}$ nm$^{-1}$) at any given time ($t$) and at any vertical position in the quartz cell ($z$) can be calculated exactly as

$$\Xi_{290-490}^{\text{Exp}}(z,t,\lambda) = E_o(z,t,\lambda) \cdot a_g(z,t,\lambda)$$

(A.15)

where $E_o(z,t,\lambda)$ (mol(photons) m$^2$ s$^{-1}$ nm$^{-1}$) and $a_g(z,t,\lambda)$ (m$^{-1}$) are the spectral scalar irradiance and spectral CDOM absorption coefficient, respectively. The irradiation setup is designed such that the irradiance incident onto the solution of the quartz cell is overwhelmingly downwelling. It is also designed such that the average cosine of incident downwelling irradiance inside the cell can be assumed equal to 1. Under these conditions, it can be stated that $E_d(z,t,\lambda) = E_o(z,t,\lambda)$, where $E_d(z,t,\lambda)$ is the downwelling irradiance (mol(photons) m$^2$ s$^{-1}$ nm$^{-1}$).
Accordingly, Eq. (A.15) can be rewritten as

\[ \Xi^{\text{Exp}}(z, t, \lambda) = E_d(z, t, \lambda) \cdot a_g(t, \lambda) \]  

(A.16)

or,

\[ \Xi^{\text{Exp}}(z, t, \lambda) = E_d(0^-, t, \lambda) \cdot e^{-K_d(t, \lambda)z} \cdot a_g(\lambda) \]  

(A.17)

where \( E_d(0^-, t, \lambda) \) is the downwelling irradiance incident at the top of the solution (below the top quartz window) and \( K_d(t, \lambda) \) (m\(^{-1}\)) refers to the diffuse attenuation coefficient of downwelling irradiance in the solution. Under the assumption that the average cosine of downwelling irradiance inside the cell is equal to 1, it can be stated that

\[ K_d(t, \lambda) = a_i(\lambda, t) + b_{br}(\lambda, t) \]  

(A.18)

where \( a_i(\lambda, t) \) and \( b_{br}(\lambda, t) \) are the total absorption and total backscattering coefficients of the solution. Since the samples have been filtered through a 0.2-μm filter, the inherent optical properties of the solution are strictly driven by those of water and CDOM, and

\[ K_d(\lambda, t) = a_g(\lambda, t) + a_w(\lambda) + b_{bw}(\lambda) \]  

(A.19)

where \( a_g(\lambda, t) \) is the absorption coefficient of CDOM measured every 24 h over the course of irradiation, \( a_w(\lambda) \) is the spectral absorption coefficient of pure water provided by Wang [2008] (for \( \lambda = 290-400 \) nm) and Pope and Fry [1997] (for \( \lambda > 400 \) nm), and the \( b_{bw}(\lambda) \) is the backscattering coefficient of water from Morel [1974], interpolated to \( \lambda = 290 \) nm. The optical properties of water remain constant over the course of irradiation and are therefore independent of \( t \). As a result, Eq. (A.17) can be rewritten as

\[ \Xi^{\text{Exp}}(z, t, \lambda) = E_d(0^-, t, \lambda) \cdot e^{-[a_i(\lambda, t)+a_w(\lambda)+b_{bw}(\lambda)]z} \cdot a_g(\lambda, t) \]  

(A.20)

The average amount of photons absorbed by CDOM in the quartz cell during irradiation (mol(photons) L\(^{-1}\) nm\(^{-1}\)) considering self-shading (inner-filter effects) and CDOM
photobleaching, can be calculated by integrating Eq. (A.20) with depth and over time, dividing by the pathlength of the cell, and multiplying by 0.001 to convert units from \( \text{m}^{-3} \) to \( \text{L}^{-1} \).

\[
\Xi_{\text{Exp}}(\lambda) = 0.001 \cdot \frac{\int_{0}^{z_{\text{top}}} \int_{0}^{t_{\text{final}}} E_d(0^-, t, \lambda) \cdot e^{-\left(a_g(\lambda, t) + a_e(\lambda) + b_{\text{Tot}}(\lambda)\right)z} \cdot a_g(\lambda, t) \, dz \, dt}{\int_{0}^{z_{\text{top}}} \, dz}
\]  

(A.21)

Finally, the broadband absorption for the photochemically active spectral range is obtained by integrating \( \Xi_{\text{Exp}}(\lambda) \) spectrally between 290 and 490 nm

\[
\Xi_{\text{Exp}}^{290-490} = \int_{290}^{490} \Xi_{\text{Exp}}(\lambda) \, d\lambda
\]  

(A.22)

The optical properties of water are known and constant, and \( a_g(\lambda, t) \) was measured every 24 h during irradiation for every replicate of every sample. A reasonable value for \( E_d(0^-, t, \lambda) \) remains to be determined. Note that \( E_d(0^-, t, \lambda) \) is strictly dependent on the irradiance output by the solar simulator lamp and its dependence on \( t \) can be omitted as long as the solar simulator lamp remains stable. In the rest of this description, the dependence of \( E_d(0^-, t, \lambda) \) and other variables on the time \( t \) is therefore omitted. An Optronics Laboratories (OL) 756-2 High-Accuracy portable UV-VIS automated spectroradiometer (equipped with a OL 730-7Q-2.0 quartz fiber optic probe and a OL IS-270 2-inch integrating sphere) facilitated the calculation of \( E_d(0^-, \lambda) \). Figure A.3 provides a useful illustration of the approach and variables used to quantify \( E_d(0^-, \lambda) \).

The spectroradiometer was used to measure the incident downwelling irradiance, \( E_d^{\text{spectrorad}}(\lambda) \), under quartz cells filled up with Milli-Q. Knowing the spectral transmittance
$T(\lambda)$ of the quartz window, $E_d^{\text{spectrorad}}(\lambda)$ can be used to derive the downwelling irradiance at the bottom of the quartz cell

$$E_d(z_{\text{bottom}}, \lambda) = \frac{1}{T} \cdot E_d^{\text{spectrorad}}(\lambda)$$  \hspace{1cm} (A.23)

where in our case $T(\lambda) = T = 0.95$ (data from Spectrocell, Inc). On the other hand, $E_d(0^- , \lambda)$ can be expressed in terms of $E_d(z_{\text{bottom}}, \lambda)$ as

$$E_d(0^- , \lambda) = E_d(z_{\text{bottom}}, \lambda) \cdot e^{K_0(\lambda)z_{\text{bottom}}}$$ \hspace{1cm} (A.24)

where $z_{\text{bottom}}$ is equivalent to the pathlength of the quartz vessel (in this case $z_{\text{bottom}} = 0.05$ m). Considering that only pure water contributes to the attenuation within the quartz cell and that the average cosine of downwelling irradiance can be assumed equal to 1, it can be stated that $K_0(\lambda) = a_w(\lambda) + b_{bw}(\lambda)$, and Eq. (A.24) can be rewritten as

$$E_d(0^- , \lambda) = E_d(z_{\text{bottom}}, \lambda) \cdot e^{(a_w(\lambda) + b_{bw}(\lambda))z_{\text{bottom}}$$ \hspace{1cm} (A.25)

Combining Eq. (A.23) and (A.25) yields

$$E_d(0^- , \lambda) = \frac{1}{T} \cdot E_d^{\text{spectrorad}}(\lambda) \cdot e^{(a_w(\lambda) + b_{bw}(\lambda))z_{\text{bottom}}$$ \hspace{1cm} (A.26)

Measurements of $E_d(0^- , \lambda)$ using the spectroradiometer were carried out for 16 positions within the irradiation setup, and three times over the lifetime of each solar simulator Xenon lamp (~1500 h). The spectroradiometer was calibrated using a prior to each measurement and any newly installed Xenon lamp was conditioned by running the solar simulator for about 200 h before conducting any experiments and irradiance measurements. This conditioning assured the stability of the irradiance output.
A.6 DERIVATION OF CORRECTION FACTOR $B$

The sensitivity of the high temperature combustion method used for DOC analysis and the relatively small decrease in [DOC] upon irradiation did not allow the determination of spectral apparent quantum yields using a cut-off filter approach [Johannessen and Miller, 2001; Bélanger et al., 2006; White et al., 2010]. Instead, samples were exposed to a full spectrum (a 295-nm cut-off filter was used to prevent unnatural radiation from reaching the sample) and a broadband apparent quantum yield for the 290-490 nm spectral range was determined. However, the application of broadband AQYs can result in biases in calculated photochemical rates if the spectral dependence of $\Xi^{\text{Exp}}(\lambda)$ is different from that of $\Xi^{\text{ML}}(\lambda)$, where $\Xi^{\text{Exp}}(\lambda)$ and $\Xi^{\text{ML}}(\lambda)$ refer to the total amount of photons absorbed by CDOM in the mixed layer of the study area (in situ) and in the solution being irradiated in the solar simulator, respectively. For any AQY, the bias in photomineralization rates calculated using broadband AQYs can be quantified as in Eq. (A.27)

$$\beta = \frac{\bar{\phi}_{\text{PM}} \int_{290}^{490} \Xi^{\text{ML}}(\lambda) \, d\lambda}{\int_{290}^{490} \phi_{\text{PM}}(\lambda) \cdot \Xi^{\text{ML}}(\lambda) \, d\lambda}$$  (A.27)

where $\bar{\phi}_{\text{PM}}$ is any broadband AQY for photomineralization, and $\phi_{\text{PM}}(\lambda)$ is the unknown, spectrally-resolved version of that same AQY. Considering that broadband AQYs were determined using the illumination conditions of the solar simulator, $\bar{\phi}_{\text{PM}}$ and $\phi_{\text{PM}}(\lambda)$ can be related as in Eq. (A.28)

$$\bar{\phi}_{\text{PM}} = \frac{\int_{290}^{490} \phi_{\text{PM}}(\lambda) \cdot \Xi^{\text{Exp}}(\lambda) \, d\lambda}{\int_{290}^{490} \Xi^{\text{Exp}}(\lambda) \, d\lambda}$$  (A.28)
Combining Eq. (A.27) and (A.28) yields

\[
\beta = \frac{\int_{290}^{490} \phi_{PM}(\lambda) \cdot \Xi^{\text{Exp}}(\lambda) \, d\lambda \cdot \int_{290}^{490} \Xi^{\text{ML}}(\lambda) \, d\lambda}{\int_{290}^{490} \phi_{PM}(\lambda) \cdot \Xi^{\text{ML}}(\lambda) \, d\lambda \cdot \int_{290}^{490} \Xi^{\text{Exp}}(\lambda) \, d\lambda}
\]

(A.29)

The spectral dependences of \( \Xi^{\text{Exp}}(\lambda) \) and \( \Xi^{\text{ML}}(\lambda) \) can be derived by calculating

\[
\frac{\Xi^{\text{Exp}}(\lambda)}{\Xi^{\text{Exp}}} \text{ and } \frac{\Xi^{\text{ML}}(\lambda)}{\Xi^{\text{ML}}},
\]

respectively, where \( \Xi^{\text{Exp}} \) and \( \Xi^{\text{ML}} \) are averages over the \( \lambda = 290 \text{–} 490 \) nm spectral range. As spectral averages, \( \Xi^{\text{Exp}} \) and \( \Xi^{\text{ML}} \) are independent of \( \lambda \) and Eq. (A.29) can be rewritten in terms of these spectral dependences as in Eq. (A.30)

\[
\beta = \frac{\int_{290}^{490} \phi_{PM}(\lambda) \left( \frac{\Xi^{\text{Exp}}(\lambda)}{\Xi^{\text{Exp}}} \right) \, d\lambda \cdot \int_{290}^{490} \left( \frac{\Xi^{\text{ML}}(\lambda)}{\Xi^{\text{ML}}} \right) \, d\lambda}{\int_{290}^{490} \phi_{PM}(\lambda) \left( \frac{\Xi^{\text{ML}}(\lambda)}{\Xi^{\text{ML}}} \right) \, d\lambda \cdot \int_{290}^{490} \left( \frac{\Xi^{\text{Exp}}(\lambda)}{\Xi^{\text{Exp}}} \right) \, d\lambda}
\]

(A.30)

The magnitude of the bias therefore depends on two factors: (1) the differences between

\[
\frac{\Xi^{\text{Exp}}(\lambda)}{\Xi^{\text{Exp}}} \text{ and } \frac{\Xi^{\text{ML}}(\lambda)}{\Xi^{\text{ML}}},
\]

which can be calculated for each AQY determined, and (2) the spectral dependence of \( \phi_{PM}(\lambda) \), which is not known. In our situation,

\[
\frac{\Xi^{\text{Exp}}(\lambda)}{\Xi^{\text{Exp}}} \text{ and } \frac{\Xi^{\text{ML}}(\lambda)}{\Xi^{\text{ML}}}
\]

were significantly different, with the solar simulator spectrum being relatively enriched in UV-B and depleted in visible radiation relative to the in situ spectrum (Fig. A.4).

Considering that \( \phi_{PM}(\lambda) \) are decreasing exponential functions (e.g., similarly to the spectral dependencies of apparent quantum yields for DIC and CO photoproduction), the spectral differences shown in Fig. A.4 should lead to an overestimation of the calculated photomineralization rates when the broadband apparent quantum yields are
appiled with \textit{in situ} irradiances. To alleviate this problem, the factor \( B = 1 / \beta \) can be multiplied with the photomineralization rates calculated using broadband AQY \((\bar{\phi}_{\text{pm}})\) to yield more realistic photochemical rates that would be calculated using the spectrally resolved AQY \((\phi_{\text{pm}}(\lambda))\). Considering Eq. (A.30), the factor \( B \) can be calculated as

\[
B = \frac{\int_{290}^{490} \phi_{\text{pm}}(\lambda) \cdot \left( \frac{\Xi^{\text{ML}}(\lambda)}{\Xi^{\text{ML}}} \right) d\lambda \cdot \int_{290}^{490} \frac{d\lambda}{\left( \frac{\Xi^{\text{Exp}}(\lambda)}{\Xi^{\text{Exp}}} \right)} \cdot \int_{290}^{490} \frac{d\lambda}{\left( \frac{\Xi^{\text{ML}}(\lambda)}{\Xi^{\text{ML}}} \right)}}{\int_{290}^{490} \phi_{\text{pm}}(\lambda) \cdot \left( \frac{\Xi^{\text{Exp}}(\lambda)}{\Xi^{\text{Exp}}} \right) d\lambda \cdot \int_{290}^{490} \frac{d\lambda}{\left( \frac{\Xi^{\text{ML}}(\lambda)}{\Xi^{\text{ML}}} \right)}}
\]

(A.31)

Here, Eq. (A.31) can also be rewritten in terms of the spectral dependence of \( \phi_{\text{pm}}(\lambda) \) so that

\[
B = \frac{\int_{290}^{490} \left( \phi_{\text{pm}}(\lambda) / \bar{\phi}_{\text{pm}} \right) \cdot \left( \frac{\Xi^{\text{ML}}(\lambda)}{\Xi^{\text{ML}}} \right) d\lambda \cdot \int_{290}^{490} \frac{d\lambda}{\left( \frac{\Xi^{\text{Exp}}(\lambda)}{\Xi^{\text{Exp}}} \right)} \cdot \int_{290}^{490} \frac{d\lambda}{\left( \frac{\Xi^{\text{ML}}(\lambda)}{\Xi^{\text{ML}}} \right)}}{\int_{290}^{490} \left( \phi_{\text{pm}}(\lambda) / \bar{\phi}_{\text{pm}} \right) \cdot \left( \frac{\Xi^{\text{Exp}}(\lambda)}{\Xi^{\text{Exp}}} \right) d\lambda \cdot \int_{290}^{490} \frac{d\lambda}{\left( \frac{\Xi^{\text{ML}}(\lambda)}{\Xi^{\text{ML}}} \right)}}
\]

(A.32)

where \( \bar{\phi}_{\text{pm}} \) is the average of \( \phi_{\text{pm}}(\lambda) \) over the \( \lambda = 290 - 490 \) nm spectral range. A close approximation for \( B \) can be calculated using published, spectrally resolved AQY for the photoproduction of dissolved inorganic carbon (DIC), \( \phi_{\text{DIC}}(\lambda) \) \cite{Johannessen2001, Belanger2006, White2010}. Considering that most of the photomineralized tDOC is produced as DIC \cite{Miller1995, White2010}, the spectral dependence of \( \phi_{\text{DIC}}(\lambda) \) should closely resemble that of \( \phi_{\text{pm}}(\lambda) \). Under this assumption, the factor \( B \) can be closely approximated by computing

\[
B = \frac{\int_{290}^{490} \left( \phi_{\text{DIC}}(\lambda) / \bar{\phi}_{\text{DIC}} \right) \cdot \left( \frac{\Xi^{\text{ML}}(\lambda)}{\Xi^{\text{ML}}} \right) d\lambda \cdot \int_{290}^{490} \frac{d\lambda}{\left( \frac{\Xi^{\text{Exp}}(\lambda)}{\Xi^{\text{Exp}}} \right)} \cdot \int_{290}^{490} \frac{d\lambda}{\left( \frac{\Xi^{\text{ML}}(\lambda)}{\Xi^{\text{ML}}} \right)}}{\int_{290}^{490} \left( \phi_{\text{DIC}}(\lambda) / \bar{\phi}_{\text{DIC}} \right) \cdot \left( \frac{\Xi^{\text{Exp}}(\lambda)}{\Xi^{\text{Exp}}} \right) d\lambda \cdot \int_{290}^{490} \frac{d\lambda}{\left( \frac{\Xi^{\text{ML}}(\lambda)}{\Xi^{\text{ML}}} \right)}}
\]

(A.33)
where \( \bar{\phi}_{\text{DIC}} \) is the average of \( \phi_{\text{DIC}}(\lambda) \) over the \( \lambda = 290 - 490 \) nm spectral range. A total of 494 values for \( B \) were computed using a combination of 13 published \( \phi_{\text{DIC}}(\lambda) \) (1 from Johannessen and Miller [2001], 6 from Bélanger et al. [2006] and 6 from White et al. [2010]) and the spectral dependencies of \( \Xi^{\text{Exp}}(\lambda) \) derived from the 38 photochemical experiments conducted as part of this study. These 494 estimates yielded the average value \( \bar{B} = 0.706 \) used in this study, with a standard deviation \( s = 0.076 \).
Figure A.1 Linear relationship between DOC concentration and total dissolved lignin phenols (mol C units) in the Mississippi River (MR) and Atchafalaya River (AR). This relationship is used to calculate the seasonal values of discharge-weighed TDLP$_9$-C, which are used to calculated tDOC concentrations in the shelf mixed layer.

\[ \text{TDLP}_9 = 0.00862 \times [\text{DOC}] - 1.4903 \]

\[ R^2 = 0.82 \]
Figure A.2 Illustration of the variables involved in the calculation of $\Xi_{290-490}^{\text{Exp}}$. The controlled illumination conditions of the irradiation setup allow the assumption that the average cosine of incident irradiance is equal to one. (a) The incident downwelling irradiance decreases with depth within the cell as a result of the total attenuation by water and CDOM, a process called self-shading. (b) The absorption coefficient of CDOM decreases during irradiation as a result of photobleaching. Self-shading and photobleaching need to be taken into account in order to calculate $\Xi_{290-490}^{\text{Exp}}$ accurately.
Figure A.3 Irradiance measurement acquired with the spectroradiometer, $E_d^{\text{spectrorad}}(\lambda)$, and other variables used to calculate the downwelling irradiance $E_d(0^-, \lambda)$ incident at the top of the irradiation solution and below the top window of the quartz cell.
Figure A.4 Comparison of the spectral dependence of $\Xi_{\text{ML}}(\lambda)$ and $\Xi_{\text{Exp}}(\lambda)$. The spectral dependence of $\Xi_{\text{Exp}}(\lambda)$ shown here is an average from 38 photomineralization experiments.
Table A.1 Discharge-weighted average lignin yield of the freshwater discharged over each season’s freshwater filling time.

<table>
<thead>
<tr>
<th>Season</th>
<th>$\text{TDLP}<em>g\text{-C}</em>{\text{M-ARS}}$ (%DOC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>0.458</td>
</tr>
<tr>
<td>Summer</td>
<td>0.489</td>
</tr>
<tr>
<td>Fall</td>
<td>0.430</td>
</tr>
<tr>
<td>Winter</td>
<td>0.388</td>
</tr>
</tbody>
</table>
APPENDIX B
SUPPLEMENTARY FIGURES
Figure B.1 Stations where samples were collected and analyzed for DOC, CDOM and lignin measurements. Data collected from these stations were used to establish the relationship between $S_{275-295}$ and TDL$P_9$-C (see Fig. 4.1a). Surface water samples were acquired in the Gulf of Ob in September 2005 and during several field expeditions to the Arctic Ocean between 2008 and 2010. The field expeditions included the Circumpolar Flaw Lead (CFL) system study in the Amundsen Gulf and Beaufort Sea during July and August 2008 (Leg 10), the Nansen and Amundsen Basin Observational System (NABOS) program along the Eurasian shelves during October 2008, the Malina research program in the Beaufort Sea in August 2009, and the Impacts of Climate on the Eco-Systems and Chemistry of the Arctic Pacific Environment (ICESCAPE) program in the Chukchi Sea during June and July 2010. Stations are grouped by research program.
Figure B.2 Stations where remote-sensing reflectances and CDOM absorption coefficients were measured. Data collected from these stations were used to develop the $S_{275-295}$ algorithm (see Fig. 4.1b). Optical profiles and surface water samples were acquired as part of the Malina research program in the Beaufort Sea in August 2009 and the Impacts of Climate on the Eco-Systems and Chemistry of the Arctic Pacific Environment (ICESCAPE) program in the Chukchi Sea during June and July 2010. Stations are grouped by research program.
Figure B.3 Routing and distribution of Mackenzie River runoff between 2002 and 2005. The Mackenzie River runoff was predominantly eastward toward the Canadian Arctic Archipelago from 2002 to 2005. The $S_{275-295}$ algorithm was implemented using 4-km resolution, yearly-binned, MODIS Aqua ocean color. The Mackenzie River is labeled (4). The contour line represents the 2000-m isobath and outlines the Canada Basin.
Figure B.4 Routing and distribution of Mackenzie River runoff between 2006 and 2011. The Mackenzie River runoff was repeatedly routed northwestward to the Canada Basin between 2006 and 2011. The \( S_{275-295} \) algorithm was implemented using 4-km resolution, yearly-binned, MODIS Aqua ocean color. The Mackenzie River is labeled (4). The contour line represents the 2000-m isobath and outlines the Canada Basin.
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Requestor: Mr Cedric G Fichot
Contact’s Name (if different): Cedric G. Fichot
Institution: University of South Carolina
Department: Marine Science
Mailing Address: 308 Charbonneau Columbia, SC 29210 USA
Telephone: 706-254-1629 Fax: 803-777-6610
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