Mannino, Dyda and Herses

Biogeochemical and Optical Analysis of Coastal DOM for Satellite Retrieval of Terrigenous DOM in the U.S. Middle Atlantic Bight

Estuaries and coastal ocean waters experience a high degree of variability in the composition and concentration of particulate and dissolved organic matter (DOM) as a consequence of riverine/estuarine fluxes of terrigenous DOM, sediments, detritus and nutrients into coastal waters and associated phytoplankton blooms. Our approach integrates biogeochemical measurements (elemental content, molecular analyses), optical properties (absorption) and remote sensing to examine terrestrial DOM contributions into the U.S. Middle Atlantic Bight (MAB). We measured lignin phenol composition, DOC and CDOM absorption within the Chesapeake and Delaware Bay mouths, plumes and adjacent coastal ocean waters to derive empirical relationships between CDOM and biogeochemical measurements for satellite remote sensing application. Lignin ranged from 0.03 to 6.6 ug/L between estuarine and outer shelf waters. Our results demonstrate that satellite-derived CDOM is useful as a tracer of terrigenous DOM in the coastal ocean.
Biogeochemical and Optical Analysis of Coastal DOM for Satellite Retrieval of Terrigenous DOM in the U.S. Middle Atlantic Bight

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\textbf{Funding:} NASA Ocean Biology \& Biogeochemistry, Interdisciplinary Science, Carbon Cycle Science Programs

Outline

• Objectives
• CDOM:DOC Relationships
• Lignin Distributions
• Lignin:CDOM Relationships
• Satellite algorithm development for CDOM, DOC and Lignin Phenols
Objectives

- Link chemical and optical properties of DOM
- Link DOM optical/chemical properties to in situ radiometry
- Develop satellite algorithms for CDOM, DOC and Terrigenous DOM (Lignin Phenols).
- Identify processes that regulate distributions of CDOM, DOC and Lignin Phenols
- Apply field and satellite data to track and quantify fluxes of terrigenous and marine carbon within the continental margin along northeastern U.S.

GOAL: Investigate and quantify the contribution and impact of riverine carbon to continental margins and beyond
Field Sampling Stations

**Gulf of Maine**
- April 26-30, 2007
- May 26-28, 2007
- June 6-8, 2007

**New York Bight**
- May 5-9, 2007
- Nov. 10-14, 2007
- July 21-24, 2008
- May 19-21, 2009

**Southern MAB**
- March 30-April 1, 2005
- July 26-30, 2005
- May 9-12, 2006
- July 2-6, 2006

**Ches. Bay Plume**
- May 27, 2005
- Nov. 3, 2005
- Sep. 6, 2006
- Nov. 28, 2006
- March 19, 2007
- April 23, 2007
- July 3, 2007
- Aug. 16, 2007

**Lower CB:** July 2004 to May 2006
Outline

• Objectives

• **CDOM:DOC Relationships**

• Lignin Distributions

• Lignin:CDOM Relationships

• Satellite algorithm development for CDOM, DOC and Lignin Phenols
• Interannual consistency in DOC to $a_{\text{CDOM}}$ relationships
Regional & Seasonal DOC: $a_{CDOM}$ Relationships

- DOC per unit $a_{CDOM}$ increases from N to S: differences in source materials, such as more colored terrestrial DOM exported to the GoM due to the absence of large estuaries where the DOM can be degraded.
- Seasonal shift in DOC to $a_{CDOM}$ relationships from accumulation of DOC from NCP and photooxidation of CDOM between spring and fall.
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- Lignin:CDOM Relationships
- Radiometry:CDOM Relationships
- Satellite-derived CDOM, DOC, Lignin
Chesapeake MAB Lignin Stations

Lower Chesapeake Bay: July 04, Sept. 04, Oct. 04, Nov. 04, Jan. 05, May 05

SMAB
March 30-April 1, 2005
July 26-30, 2005
May 9-12, 2006
July 2-6, 2006

CB Plume
May 27, 2005
Nov. 3, 2005
Sep. 6, 2006
Nov. 28, 2006
Freshwater Discharge into Delaware Bay and Chesapeake Bay

Data courtesy of USGS
Lignin Source & Degradation Parameters

- S:V
- C:V

Angiosperm
- woody
- non-woody

Gymno
- woody
- non-woody

Data points from:

- DB_Nov02
- B02_July05
- B03_May06
- D04_Nov06
- CBM04_Oct04
- CBM07_May06

- DB_July03
- D01_May05
- B04_July06

- B01_Apr05
- D02_Nov05
- D03_Sep06
- CBM02_July04
- CBM05_Nov04

- CBM03_Sep04
- CBM06_Jan05
Terrigenous DOC Estimates

\[ \frac{[\text{Lignin/DOC}]_O}{[\text{Lignin/DOC}]_R} \times 100 \]
proportion of ocean to river lignin yields
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aCDOM versus Lignin Phenols

\[ y = 1.374x^{0.809} \]
\[ R^2 = 0.851 \]

\[ y = 0.476x^{0.816} \]
\[ R^2 = 0.822 \]
Lignin Phenol to SUVA$_{254}$ Relationships

$R^2 = 0.81$
$Sy.x = 0.47$
$n = 70$

$R^2 = 0.68$
$Sy.x = 0.38$
$n = 57$
$S_{CDOM(275:295)}$ versus Lignin Phenols

$R^2 = 0.95$

$Sy.x = 0.226$

$n = 66$
\( S_{CDOM(275:295)} \) versus Lignin Yields

\[ R^2 = 0.76 \]
\[ \text{Sy.x} = 0.015 \]
\[ n = 66 \]
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Types of Algorithms

- Band ratios (ex. OC4)
- Semi-analytical (ex. GSM01, QAA, GIOP)
- IOP based algorithms (DOC from CDOM)
- Multivariate algorithms
- Machine Learning
  - Neural networks
  - Vector support machines
  - Gaussian process models
CDOM Algorithm Development

\[ \frac{R_{rs(412)}}{R_{rs(547)}} \]

\( a_{CDOM}(412) \text{ (m}^{-1}) \)

- Southern MAB
- Gulf of Maine
- Hudson Plume
- Exp. One-Phase Decay Model

\[ R^2 = 0.95 \]
\[ \text{Sy.x} = 0.076 \]
\[ n = 153 \]

in situ remote sensing reflectance (Rrs) band ratios versus \( a_{CDOM} \)

\[ \frac{R_{rs(380)}}{R_{rs(555)}} \]

\( a_{CDOM}(380) \text{ (m}^{-1}) \)

- in situ observations
- 3rd Order Polynomial Model

\[ R^2 = 0.95 \]
\[ \text{Sy.x} = 0.064 \]
\[ n = 151 \]
Validation of SeaWiFS CDOM Algorithms

\[ y = 0.781x - 0.005 \quad R^2 = 0.532 \]

\[ y = 0.827x + 0.026 \quad R^2 = 0.649 \]

APD = Absolute Percent Difference
DOC: $a_{\text{CDOM}}$ Correlation with Wavelength
Relevance to CDOM & DOC algorithms

DOC can be derived from wide range of $a_{\text{CDOM}}(\lambda)$

Credit: Aron Stubbins for idea for this plot
DOC 2004
Monthly Composites - MODIS-A 4km
**Terrigenous DOM from Space - AGU 2007**

**Mississippi River Plume**

Lignin Phenols (μg L⁻¹)  
May 16, 2000

\[ X = (Y + 0.346) / 1.034 \]

\[ r = 0.99 \]

Hernes & Benner 2003

Lignin Phenols: APD = 10 ± 8.8%
## DOC and CDOM Yields

<table>
<thead>
<tr>
<th>Drainage Area</th>
<th>% Drainage of Contiguous US</th>
<th>% DOC Flux vs. Mississippi</th>
<th>DOC yield (gC m² yr⁻¹)</th>
<th>CDOM yield (a_{350}) (yr⁻¹)</th>
<th>DOC Load (kg yr⁻¹)</th>
<th>CDOM Load (a_{350}) (m² yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atchafalaya</td>
<td>3.3</td>
<td>56.6</td>
<td>4.92</td>
<td>10.6</td>
<td>1.19 X 10⁹</td>
<td>2.56 X 10¹²</td>
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<tr>
<td>Columbia</td>
<td>9.1</td>
<td>19.2</td>
<td>0.61</td>
<td>0.93</td>
<td>4.04 x 10⁸</td>
<td>6.16 x 10¹¹</td>
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<tr>
<td>Mississippi</td>
<td>40.1</td>
<td>100</td>
<td>0.72</td>
<td>1.25</td>
<td>2.10 x 10⁹</td>
<td>3.65 x 10¹²</td>
</tr>
<tr>
<td>Potomac</td>
<td>0.4</td>
<td>2.11</td>
<td>1.48</td>
<td>2.62</td>
<td>4.43 x 10⁷</td>
<td>7.84 x 10¹⁰</td>
</tr>
<tr>
<td>South Atlantic Bight</td>
<td>4.3</td>
<td>45.4</td>
<td>3.04</td>
<td>7.43</td>
<td>9.55 x 10⁸</td>
<td>2.33 x 10¹²</td>
</tr>
<tr>
<td>Susquehanna</td>
<td>1.0</td>
<td>3.97</td>
<td>1.17</td>
<td>1.75</td>
<td>8.23 x 10⁷</td>
<td>1.23 x 10¹¹</td>
</tr>
</tbody>
</table>

Source: Rob Spencer, in prep.
Summary

- Relationships of optical properties ($a_{CDOM}$ and S) with biogeochemical variables (DOC and lignin phenols) are robust and driven primarily by terrestrial contributions into coastal waters.
- Black carbon contributions also likely (Mannino et al. 2004).
- Satellite-derived lignin phenol distributions (DOM) are within reach now, but would be more robust with UV-capable satellite sensors.
- Currently need to extrapolate CDOM parameters from the UV to satellite radiometry in the visible.
- Much more problematic for $S_{275:295}$