Chromophoric Dissolved Organic Matter (CDOM)

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Initial Observations

- Von Kurt Kalle, 1949 (Fluorescence)
- Bricaud, 1981 (Absorption Spectrum)
- Chen, 1992 (Ocean FDOM Cycle)
- Coble, 1996 (EEMS)
Fluorescence of Seawater
Jablonski Diagram

- $S_0$: ground state
- $S_1$: excited state for fluorescence
- $S_2$: excited state for phosphorescence
- $S_3$: excited state for triplet states

The diagram shows the absorption of light (blue arrow) and the emission of light (green arrow) from the ground state ($S_0$) to excited states ($S_1$, $S_2$, $S_3$). The green arrow represents fluorescence, while the red arrow represents phosphorescence. The black arrows indicate the transition to triplet states.
Spectra

Rochelle-Newall & Fisher, 2002

Hoge, Vodacek and Blough, 1993
Seawater Excitation-Emission Matrix (EEM)
Humic EEM
You can see it
Distributions

- Varies in surface waters

Chen, 1992
Fluorescence vs. Absorbance

Comparison of Estuaries

Absorbance (m$^{-1}$) vs. Fluorescence (QSU)
Northern Gulf of Mexico including Mississippi River Plume

Absorbance vs. Fluorescence

- **June 00**
- **April 01**

Equations:
- $y = 0.14x + 0.11$  \( R^2 = 0.98 \)
- $y = 0.12x + 0.09$  \( R^2 = 0.96 \)
What is it?

- Melanoidins (Proteins and Carbohydrates)
- Humics (Degradation Products)
- Flavins and Pterins (coral natural products)
- Lignin Phenols
Chemical Characterization

• Isolation
  – Humics
  – HMW DOM
• NMR
• IR
• MS
• 1-30% DOM
• ???
Figure 1 Map of locations sampled for survey of FDOM distribution and typical vertical profiles of fluorescence intensity. Right inset: Vertical profiles of fluorescence intensity at 50° 00’ N (open circles) and 30° 00’ N (open squares). Left inset: Vertical profiles of fluorescence intensity at 0° 05’ N (crosses), 20° 00’ S (open circles) and 50° 00’ S (open squares). Scales of depth (y axis) were different between ranges of 0–300 m and 400–6,000 m.
Pacific Ocean

Figure 2: Contour maps of fluorescence intensity and AOU along the transects at 160° W and 170° W. a, b, Levels of fluorescence intensity (a) and AOU (b). Contour maps were illustrated using Ocean Data View®.

Yamashita and Tanoue, 2008
Why do we care?
Why do we care?

• Inherent optical properties of seawater
  – See bottom, subs
  – Remote sensing of Chl
  – Light availability for primary productivity
  – Energy Budget

• Proxy for dissolved organic carbon (DOC)
  – Trace freshwater DOM in coastal ocean
  – High resolution
  – Trace other CDOM sources

• Biogeochemical processes

• Photochemistry
The Global Carbon Cycle

- Pools: $10^{15}$ gC, fluxes: $10^{15}$ gC/year

- Land plants: 560
- GPP: 120
- $R_p$: 60
- $R_D$: 60
- Net destruction of vegetation: 0.9
- Fossil fuels: 6
- Atmospheric pool: 750 + 3.2/year

- Rivers: 0.4 DOC, 0.4 DIC

- Soils: 1500

- Oceans: (38,000)
  - 36,000 inorganic
  - 1,000 DOC
  - 3 POC

- Reactive marine sediments: 3000
- Fossil fuels: > 5000

- Burial: 0.1

- > 10,000,000 sediments
- > 90,000,000 earth’s crust
Sea Surface Color

CZCS (Nimbus-7 Nov. 78 - June 86)
Labile vs Refractory

- LMW vs HMW
- Photo reactive
Sources
Sources

- Soils
- Plants
- Wetlands
- Phytoplankton
- Zooplankton
- Sediments
- Diagenesis (humification, photo/bio processes)
- Photolytic release from particles
Rivers

Fig. 5. DOC – salinity correlation for the Bristol Channel and Severn Estuary during 1978.
Arctic Rivers

- Terrestrial biomarkers

Figure 6. Salinity correlations at 12 m water depth. (a) $a_{312}$ versus salinity, (b) DOC versus salinity, (c) lignin phenols versus salinity, (d) BER1 versus salinity, (e) BER2 versus salinity, and (f) BER3 versus salinity. End-members identified include Atlantic (stations 1–8), Archipelago (stations 10–49), Mackenzie River plume (stations 54–59), and mixing regions (stations 50–52 and 60–61).

Walker et al., 2009
Conservative Mixing

- CDOM vs Salinity

*Fig. 1. Mixing diagram for a dissolved constituent, with a higher concentration in freshwater than in seawater (e.g. CDOM) (adapted from Lis, 1978).*
Parker River Estuary, Plum Island
Ecosystems LTER

July
50% *In Situ*

August
70% *In Situ*

September
89% *In Situ*
CDOM Fluorescence vs Salinity
August 2002: Upstream, surface
'True' and Apparent fresh water end-member CDOM concentrations

<table>
<thead>
<tr>
<th>Month</th>
<th>True</th>
<th>Apparent</th>
<th>% in-situ production</th>
</tr>
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<tbody>
<tr>
<td>July</td>
<td>33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>September</td>
<td>35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>November</td>
<td>20</td>
<td></td>
<td></td>
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<tr>
<td>December</td>
<td>13</td>
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</table>
CDOM Fluorometer and Density

On north-south line at 89.85° W : June 25 2000(Ln22)

Color contours : CDOM/QSU
Contour lines : $\sigma_0$ (kg/m$^3$)
CDOM-Salinity Curve for North-South Line at 89.85°W
June 25 2000 (Ln22)
Miss ‘07--Sub-Surface CDOM Production =15% of River
Mississippi 2000: Line 14
CDOM Fluorescence/QSU vs. salinity
Mississippi 2000: Line 26
CDOM Fluorescence/V vs. salinity

[Graph showing data points scattered across a 2D axis with labeled axes: Cdom Fluorescence/QSU on the y-axis and Salinity/PSU on the x-axis. A color bar indicates depth in meters.]

Depth/m
31
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0

Salinity/PSU
31
33
35

Cdom Fluorescence/QSU
Phytoplankton

- Cultures
- Not proportional to Chl or cell counts
- Microbial source

Rochelle-Newell & Fisher, 2002
Hudson River Estuary
Hudson River Estuary
June, 2004 (Sewage)
CDOM Sinks

- Photodegradation
- Microbial degradation
- Photo/Bio degradation
- Aggregation/sinking
Flocculation

Figure 3. Humic acid carbon as a function of salinity. The standard error of the mean is 5%. The humic acid concentration at 30% in the Delaware Bay has been measured to be anomalously high in three surveys suggesting that the measurement is valid. It may represent a seaward source of humic acid to the Bay.
Incubations
Plume CDOM Degradation (Hudson)

Incubation:
- Photodegradation rates are maximal (surface water rates)
- Bacterial degraded plume CDOM very quickly
- Plume CDOM were degraded about half in 4 days.

Wei Huang, 2010
The DOC lost during incubation includes the addition from phytoplankton production, bacterial degradation and photochemical transformation.

Incubation

DOC Degradation of Hackensack Endmember
October 2006

DOC = 481+69*exp(-0.05*t)

$R^2 = 0.94$

Unfiltered, clear bottle incubations
• Biological combined with photochemical degradation

Miller and Moran, 1997
Possible Sources and Sinks

- Photochemical Transformation
- Bacterial Degradation
- Flocculation
- Phytoplankton Production
- Addition from marsh, sewage et al.
What application could you use CDOM measurements for?

• Draw a Concept Map
• CDOM in the middle
• What are the connections?
• What are the major concepts?

• Design a research project based on your knowledge of CDOM
Arctic Ocean

• Tracing terrestrial inputs into the ocean

Walker et al., 2009
PARAFAC

- Principle Components
- 3-9 components
- Excitation and Emission (Contours)
- >60 samples

Walker et al., 2009
Coastal Dynamics

• Time Series
• Sensor Networks
• Models
Boston Harbor

60 m resolution
72 hour prediction
Hudson River Estuary
June, 2004 (Sewage)
Model with ‘schmutz’: Possibly associated with Port Richmond POTW
Modeling-Summary

- CDOM added to existing observatory/predictive physical model
- High resolution measurements ground-truth model
- New sources and source strengths can be discovered
- Boston Harbor is being modeled as well

Blumberg and Geogas, unpubl.
Estimating CDOM concentration with hydrograph and landuse variables at Neponset River Watershed

\[ y = 0.306 \ln(Q) - 0.226 \ln(S) + 0.043w + 0.06d + 0.06f + 0.15a + 0.085\text{wet} + 0.725 \]
Remote Sensing: Field Measurements--CDOM and Spectra

Mini-shuttle

Applied Spectral Devices Spectro-Radiometer
Field Data: Spectra, CDOM contents

Along cruise route
Results: model evaluation

- Functional Linear Analysis
- With str1 and str2 as dummy variables, $R^2=0.8635$
- Without dummy variables, $R^2=0.8415$
CDOM detection from EO1-Hyperion for Atchafalaya River

Quasi-Analytical Algorithm

EO1-Hyperion images (220 bands, )
The CDOM “gang”
Tangent Based App. End Member vs. Time

Based on Linear Fit for S>28 PSU

- AEM_T/QSU
- Neponset stream flow at dam

Hours after 0000, 20 Aug 02

Stream flow/m³s⁻¹
Surface (River Plume)

Subsurface CDOM max

Line 20--June, 2000
Subsurface CDOM Max

Surface Plume

A

B

mm 0 to 320 is averaged on

bathemp

2250.0=2

log m Q

250.0=2

10

5

0

0 300 320 340 360 380 400 420 440

mm, Reversal

21.2

mm

Log m Q

10

5

0

0 300 320 340 360 380 400 420

mm, Reversal
EEMs of Surface and Subsurface CDOM
CDOM

- **Quantity of CDOM**
  - Comprises a significant fraction of DOM
  - Controls the optical properties of natural water
  - Affects remote sensing of surface water

- **Quality of CDOM**
  - Initiates biochemical & photochemical process
  - Can trace multiple sources of DOM
  - Indicates land cover changes