Chromophoric Dissolved Organic Matter (CDOM) In The Global Ocean

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Outline

• CDOM: Definitions, rationale, methodology, research questions

• CDOM distribution and dynamics in the global ocean
  – Sources & sinks

• CDOM – climate connections
What is CDOM?

• Chromophoric Dissolved Organic Matter: *Operational definition*: Passes submicron filter, absorbs light in the solar wavebands

• Some fraction is also fluorescent (absorbs UV, emits blue light) – important for characterization

• **What’s it made of?** Largely uncharacterized. Includes proteins/amino acids, possibly pigment degradation products, “humic materials” and secondary metabolites like lignin phenols

• CDOM is a characteristic of DOM rather than a discrete family of compounds
  – CDOM is a part of the open ocean DOM pool
Why should we care about CDOM?

- Dominates light availability for $\lambda < 450$ nm
  Huge role in marine photo-processes
- CDOM is often related to DOC in many coastal oceans, but **NOT** in the open ocean
- Precursor for photochemical rxn’s
  Emission of trace gas (DMS, COS, CO, CO$_2$)
  Bioavailability of trace metals (Fe, Mn, Cu, etc.)
- A natural tracer of water mass exchange
  CDOM may be a good index of DOM diagentic state
Quantifying and characterizing CDOM

UV-Vis Absorption Spectroscopy

Fluorescence Spectroscopy (Excitation-Emission Matrix)

Nelson & Siegel [2013] ARMS
Global CDOM Data Set

CLIVAR/Repeat Hydrography Surveys

Nelson & Siegel [2013] ARMS
Contribution to Spectral Absorption

Surface samples from all three oceans
Global CDOM Data

- CDOM is the most important for $\lambda < 440$ nm
- Water dominates for $\lambda > 440$ nm
- Only near 440 nm does phytoplankton have a dominate role (& then equal with water & CDOM)
- Detritus is small part of $a_t(\lambda)$ budget (<15%)
- CDOM is the most important optical property
Where does ocean CDOM come from?

- Historically, only terrestrial discharge sources were considered.
  First optical oceanographers worked in the Baltic Sea.
  Hence CDOM was termed gelbstoff.

- They found that gelbstoff drives water clarity & was obviously related to land-ocean exchange.
  Results in $\text{CDOM} = f(\text{Salinity})$.
Observations from the Baltic Sea

After Jerlov [1953]
Example From Delaware Bay

Does Open Ocean CDOM = 0??

After Del Vecchio & Blough [2006]
Where does ocean CDOM come from?

- Simple mixing analyses suggest near zero CDOM at oceanic salinities

- What are the oceanic CDOM sources?
  - Is it simply mixing of terrestrial waters (i.e., the sources are allochthonous)?
  - Or are internal (i.e., autochthonous) sources important?
  - Need to know the time/space CDOM distribution
The Global CDOM Distribution

- There are relatively few quality field observations of CDOM in the global ocean
- If CDOM dominates the optics, it should be a big part of the ocean color signal
- We should be able to use satellite ocean color sensors to quantify CDOM globally
The GSM Ocean Color Model

- Relationship between $L_w N(\lambda)$ & surface ocean inherent optical properties is known
- Component spectral shapes are constant – only their magnitudes vary
- Solve least-squares problem for 3 components
  - Water properties are known
  - Nonlinear processes are ignored
  - Retrieves Chl, CDM ($=a_g(440) + a_{det}(440)$) & BBP ($=b_{bp}(440)$)
  - Assume $a_{det}(440) \ll a_g(440)$
The GSM Ocean Color Model

Parameters
(a_{ph}^{*}(\lambda), S, etc.)

\[ L_{WN}(\lambda) \]

GSM Model

Products
(Chl, CDM & b_{bp})

• Problems
  – Only first order understanding
  – Parameterizations are imperfect

Garver & Siegel, JGR [1997]
Optimizing the GSM Model

Compiled a global $L_{WN}(\lambda)$ & validation data set
Used it to “tune” the parameters in the model
Maritorena et al. [2002] AO (... the GSM01 model)

UCSB Ocean Color Model

Validation Data
"Tuned" Parameters

$L_{WN}(\lambda)$

Optimization

Products

GSM2.0 is now under going testing
Does this all work??

- Algorithm alone...
- Matchup with NOMAD data (IOCCG IOP report; Lee et al. 2006)
- Model-data fits are pretty good – though not excellent
- GSM01 is optimized for all 3 retrievals
Does this all work??

- Independent global match-up data set of SeaWiFS & CDM observations
- Regression is pretty good ($r^2 = 71\%$)

Siegel et al. [2005] JGR
2003 North Atlantic Sections: GSM (green), \textit{in situ} (black)

- South American Continental Shelf
- North American Continental Shelf
- Orinoco plume (Caribbean Sea)
- Sargasso Sea
- North Atlantic

$r^2 = 0.65; N = 111$
Slope = 1.16

Nelson et al. [2007]
CDOM: where (surface)?

- Coastal areas, river outflows
- High productivity open areas, depleted in central gyres
- Coastal and equatorial upwelling areas are elevated
- Large north/south asymmetry

Nelson & Siegel [2013] ARMS
Seasonal Surface CDOM Cycle

- Seasonal changes at most latitudes
- Lower in summer
- Reduced in tropics
- Higher towards poles
- Hemispheric asymmetry

\[\%\text{CDM} = 100 \times \frac{\text{CDM}}{\text{CDM} + a_{\text{ph}}(440)}\]
where \(a_{\text{ph}}(440) = f(\text{Chl})\)
Role of Rivers

Large River Outflows...

Maximum annual change due to global rivers is 0.005 m\(^{-1}\)
River inputs are just not important on a global scale

Siegel et al. [2002]
Global CDOM & DOC

- CDOM $\neq$ DOC
- Completely different
  Tropics vs. high latitudes
  Subtropical gyres
- Different processes driving CDOM & DOC

Siegel et al. [2002] JGR
CDOM ≠ DOC in the Open Ocean

CLIVAR/Repeat Hydrography Surveys

Nelson & Siegel [2013]
Summary of Satellite CDOM

- Large latitudinal trends (low in tropics)
- Large seasonal trends (low in summer)
- Ocean circulation structures are apparent
  - CDOM follows basin-scale upwelling patterns
- Rivers are small, proximate sources
- CDOM is not related to DOC (simply)

These are global surface CDOM values ...

What are the roles of vertical processes??
Seasonal Cycles of CDOM at BATS

BATS - Sargasso Sea
(after Nelson et al. 1998)

Seasonal cycle
CDOM ≠ DOC
CDOM ≠ POC
CDOM ≠ Chl
Seasonal Cycle of CDOM at BATS

Nelson & Siegel (2013)
Net Production of CDOM

Summer – Spring CDOM

BATS data
Sargasso Sea
(Nelson et al. 1998)

Production max at 40-60 m

Similar to the bacterial production
Microbial Production of CDOM

Microbes produce long-lived CDOM

Experiments from BATS 60m water by Nelson & Carlson

Zooplankton & CDOM

Example spectra for controls vs. plankton

8 hour excretion experiments from Sargasso Sea
Steinberg et al. [2004] - MEPS
CDOM Photolysis

**Experimental Design:**

- Time course of CDOM absorption = photolysis rate = \( da_{CDOM}(\lambda_o)/dt \)

- 2 days in simulator \( \approx 7 \) days in surface ocean \( \approx 35 \) days* in mixed layer

*estimate based on daily insolation at 325nm, MLD, and CDOM/light attenuation in mid-Atlantic in winter

Swan et al. [2012] DSR-1
CDOM spectral changes during irradiation

Values of $a_g(\lambda)$ generally decrease
Spectral slopes ($S$) usually increase
A peak near 430 nm is sometimes seen in HNLC waters
Not sure why...

Swan et al. [2012] DSR-1
Seasonal CDOM Cycle at BATS

Links mixing, photolysis & production

- Low summer ML CDOM due to bleaching
- Shallow summer max of CDOM production
- Mixing homogenizes the system
- Surface CDOM will look like Chl
- Again, not related to DOC

\[ [\text{CDOM}] \ll [\text{DOM}] \]
CDOM: where (ocean interior)?

BATS station, 31.7N 64.7W

- Surface bleaching
- Near surface maxima (local production)
- Minima in the subtropical mode waters
- Increase in the main thermocline
CDOM: where (ocean interior)?

- Near surface in productive regions
- Increases in the main thermocline
- Connection to overturning circulation apparent

Pacific (P16 N/S) section
Nelson & Siegel [2013] ARMS
AOU and CDOM

Nelson & Siegel [2013]
AOU and CDOM

Nelson et al. [2013]
Why do AOU & CDOM Correspond?

Nelson & Siegel [2013]
CFC-estimated Age vs. CDOM

Nelson et al. [2007] DSR

- UTCL: $T \sim 10\text{y}$, $P < 0.025$
- STMW: $T \sim 50\text{y}$, $P < 0.025$
- LTCL: $T > 200\text{y}$, $P < 0.025$

Saturation-corrected pCFC-12 Age (yr)
Time scales of Deep Ocean CDOM Cycling

Ratio of time scales $\Rightarrow T_{\text{phys}} / T_{\text{bio}}$

- Large $T_{\text{phys}} / T_{\text{bio}}$
  Slow ventilation & Fast biology
  $\Rightarrow$ Biogeochemical control $\Rightarrow$ Pacific

- Small $T_{\text{phys}} / T_{\text{bio}}$
  Fast ventilation & Slow biology
  $\Rightarrow$ Ventilation control $\Rightarrow$ North Atlantic

$T_{\text{bio}}$ for deep ocean formation of long-lived CDOM must be $O(100 \text{ years})$. 
CDOM ≠ DOC in the Open Ocean

Nelson & Siegel [2013]
CDOM & DOC

Generally uncorrelated except in coastal regions

Coastal ocean
• DOC-specific absorbance depends upon source water

Open ocean
• DOC-specific absorbance is low in bleached water but increases with age of the water – new chromophores? CDOM less labile than bulk DOM?

Nelson et al. [2007] DSR-1
Deep Ocean CDOM

- CDOM distributions are consistent with hydrographic & transient tracer patterns
- Ventilation & net BGC production are the two dominant processes
- CDOM mirrors AOU. As organic C is consumed, a colored dissolved byproduct is formed (?).
- Time scales of long-lived, deep water CDOM production are many decades to centuries
- CDOM ≠ DOC – but their ratio provides clues to deep ocean DOM cycling
CDOM – Climate Connections

• Time series from in situ (BBOP) and satellite (SeaWiFS/MODIS) observations show connections to climate oscillators like NAO and ENSO.

• Trends in CDOM abundance at the surface have implications for important biogeochemical processes.
Decadal scale trends - CDOM at BATS

Nelson unpublished
Decadal scale trends – global surface CDOM

- CDM retrievals from SeaWiFS mission, GSM algorithm
- Decadal-scale variations, overall decline, well correlated with temperature increase
- Has implications for photobiology (increased UV penetration), photochemistry

Nelson & Siegel [2013] ARMS
CDOM – Climate Connections

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Research Frontiers

• **Now**: New characterization tools are providing insight into the composition of CDOM and how processes such as bleaching and new production change it.

• **Future**: Techniques such as ultrahigh resolution mass spectroscopy allow identification of chromophores and their reactions in the ocean.
DOM Fluorescence - FDOM

• Photons need to be absorbed for DOM to fluoresce.

• Thus, FDOM is a subset of CDOM & FDOM may be a useful index of DOM quality.

• Two approaches for characterizing FDOM

  Single-channel CDOM fluorometers that can be deployed in situ.

  Excitation-emission matrix spectroscopy (EEMS) allows identification of categories of fluorophores.
In Situ CDOM Fluorescence

WETLabs In Situ CDOM fluorometer (370 nm excitation & 460 emission)

Section from Bay of Bengal to Antarctica

CLIVAR I8/I9

Good correspondence between WETLabs fluorescence & $a_g(325)$ over entire depth range
CDOM and $F_{\text{cdom}}$ (WETLabs ECO)

- Largely uncorrelated shallower than 1000m
- Indicates different CDOM composition in surface and sub-thermocline waters
- CDOM fluorescence does not equal CDOM absorption
- Suggests $N_{\text{fluorophores}} < N_{\text{chromophorces}}$

\[
a_{\text{cdom}} = 0.07(F_{\text{cdom}}) - 0.15, \quad R^2 = 0.86
\]
CDOM and $F_{cdom}$
(EEM Spectroscopy)

- “Protein-like” fluorescence shows different profiles than “humic” fluorescence
- “Humic” fluorescence has similar depth profiles from different parts of the matrix
- More sophisticated analysis (PARAFAC) reveals additional patterns that correlate to other compositional indicators (e.g. Jørgensen et al. 2011)
CDOM and $F_{cdom}$
(EEM Spectroscopy)

- PARAFAC reveals fluorescence patterns that correlate to salinity, AOU, fluorescent amino acids, terrestrial?

(Jørgensen et al. 2011
*Marine Chemistry*)
Current / Future Research Prospects

• Open questions:
  • Origin of Arctic / subpolar CDOM – tracer of terrestrial DOM input to the global ocean?
  • Relationships among CDOM, DOC & DOC quality?
  • What controls the extent of the “bathtub ring”? 
  • **Improved quantification** of CDOM is required – standards (e.g. DOC reference material) should be developed.
  • **CDOM characterization** will yield information on reactions, rates, and lifetime of DOM in the deep ocean.
  • **General circulation models** will incorporate CDOM dynamics, improving climate – DOM connections
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• Research frontiers
Thank You for Your Attention!!

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