Chromophoric Dissolved Organic Matter (CDOM) In The Global Ocean

Norm Nelson, Dave Siegel, UCSB

Outline

- CDOM: Definitions, rationale, methodology, research questions
- CDOM distribution and dynamics in the global ocean
  - Sources & sinks
- CDOM – climate connections

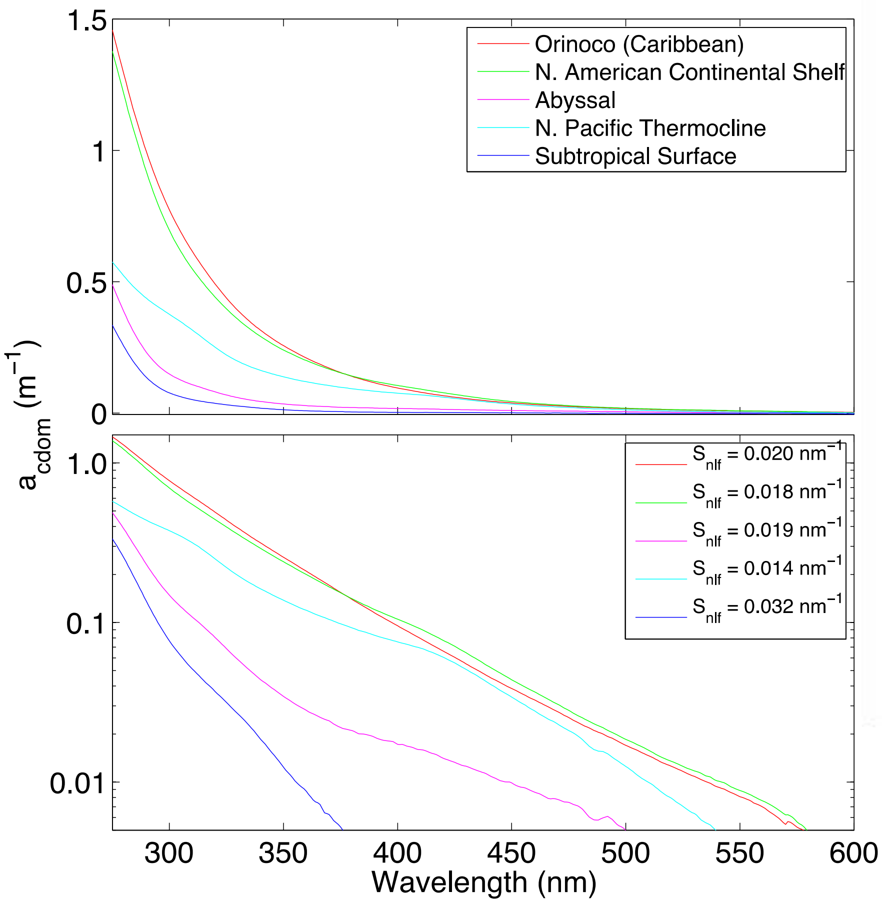
What is CDOM?

- **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

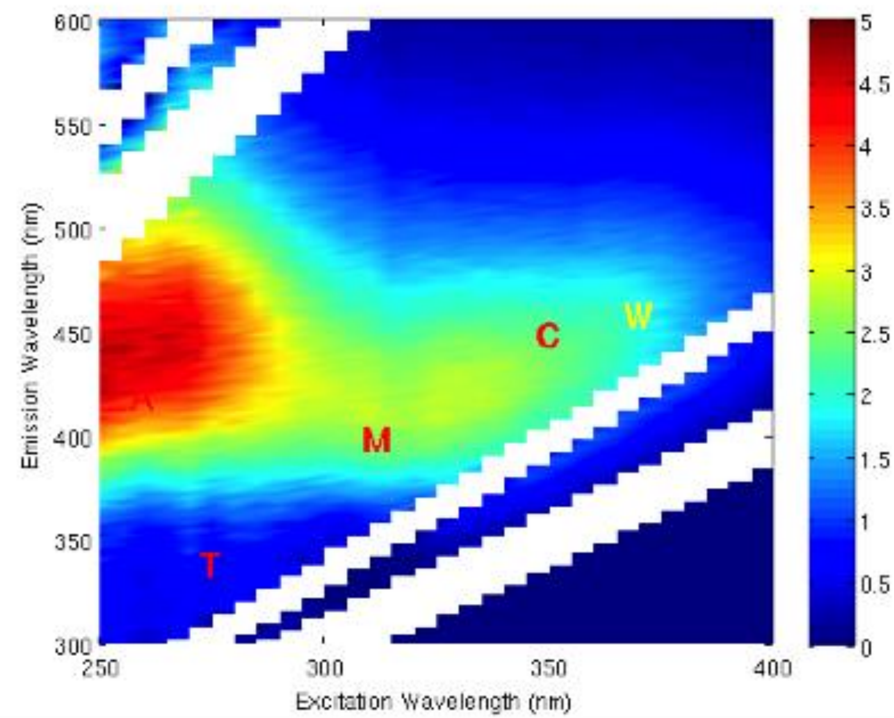
Why should we care about CDOM?

- 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



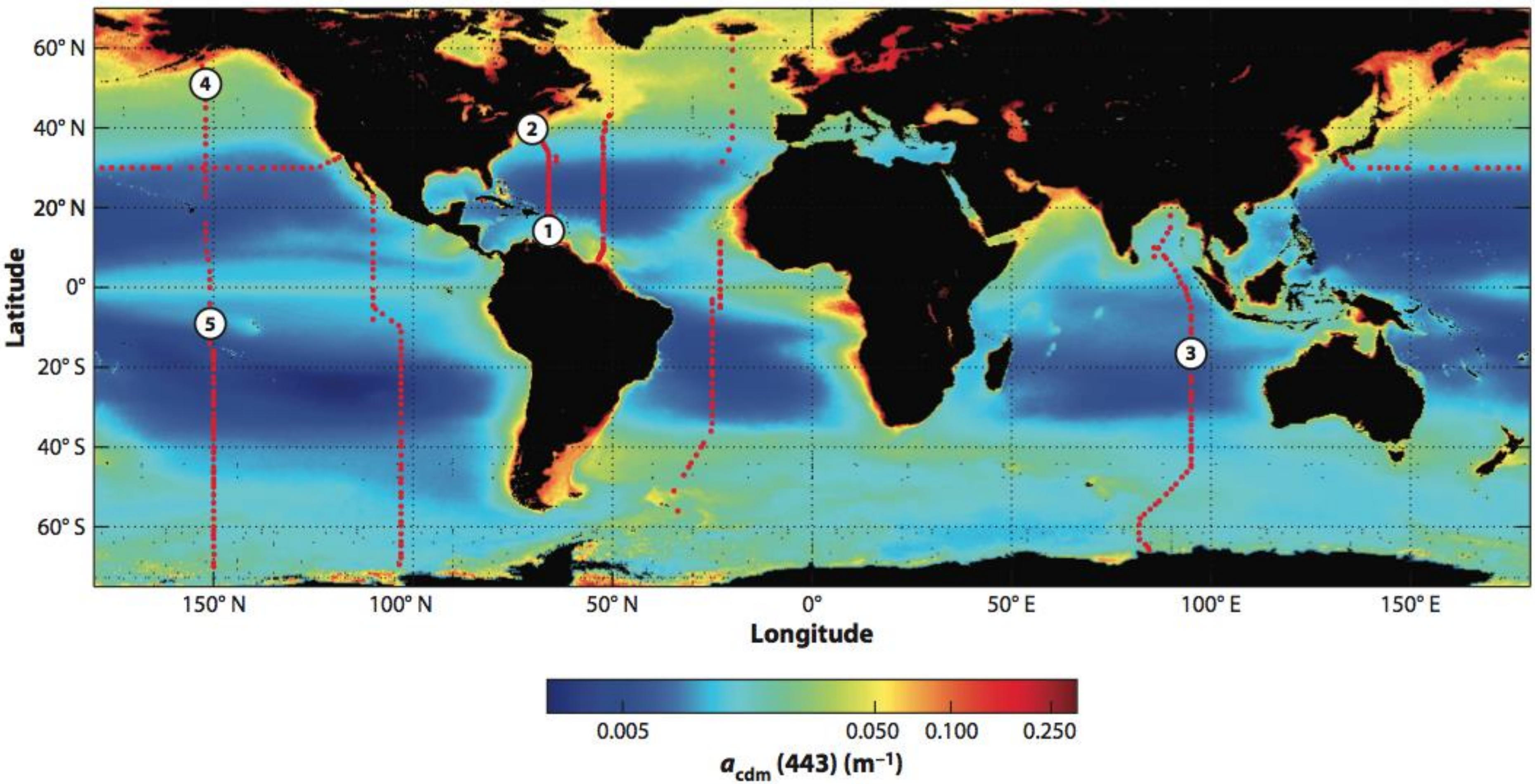
UV-Vis Absorption Spectroscopy



Fluorescence Spectroscopy
(Excitation-Emission Matrix)

Nelson & Siegel [2013] ARMS

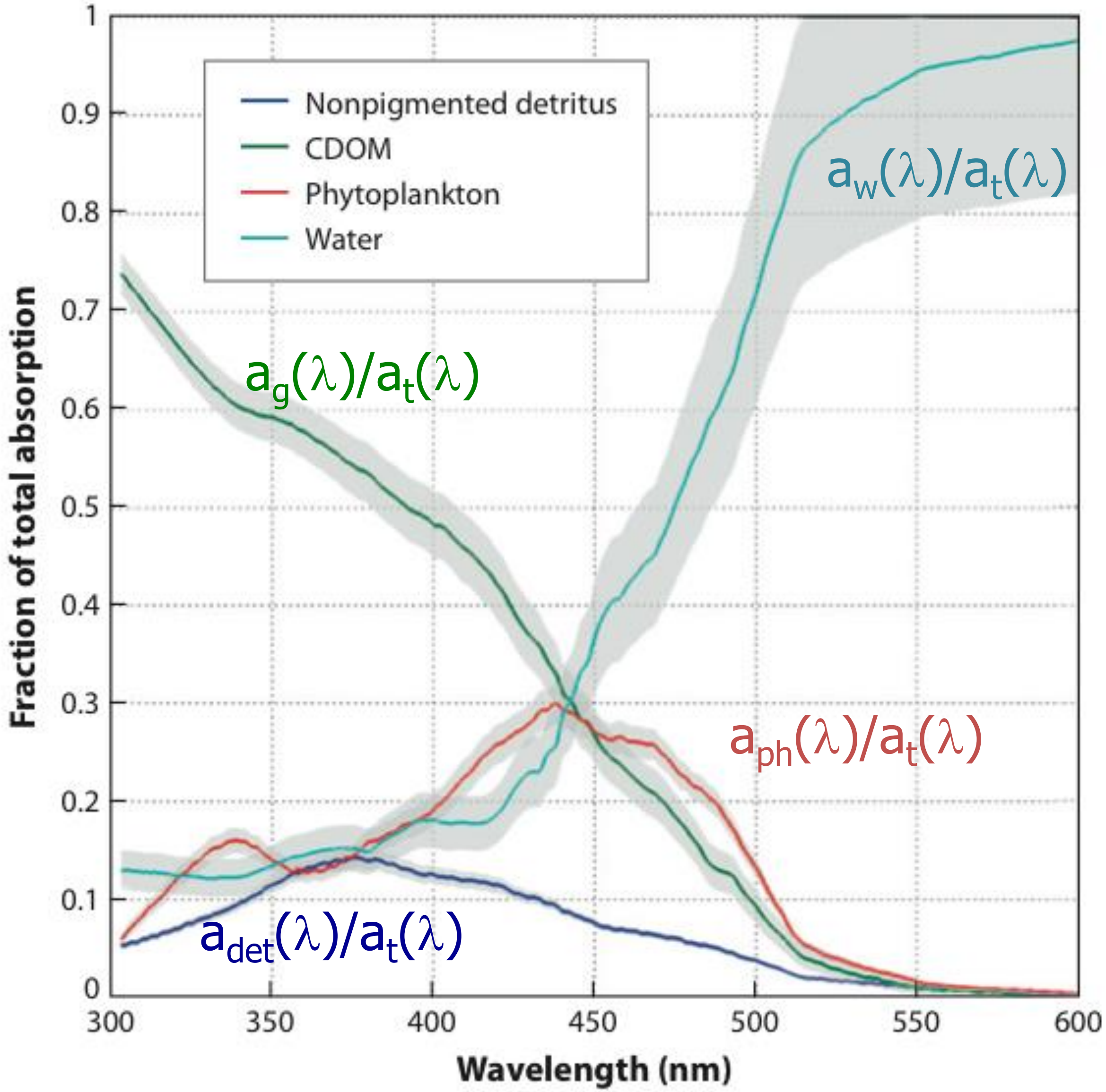
Global CDOM Data Set



CLIVAR/Repeat Hydrography Surveys

Nelson & Siegel [2013] ARMS

Contribution to Spectral Absorption



Surface samples from all three oceans

Nelson & Siegel *AnnRevMarSci* [2013]

Global CDOM Data

- CDOM is the most important for λ < 440 nm
- Water dominates for λ > 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

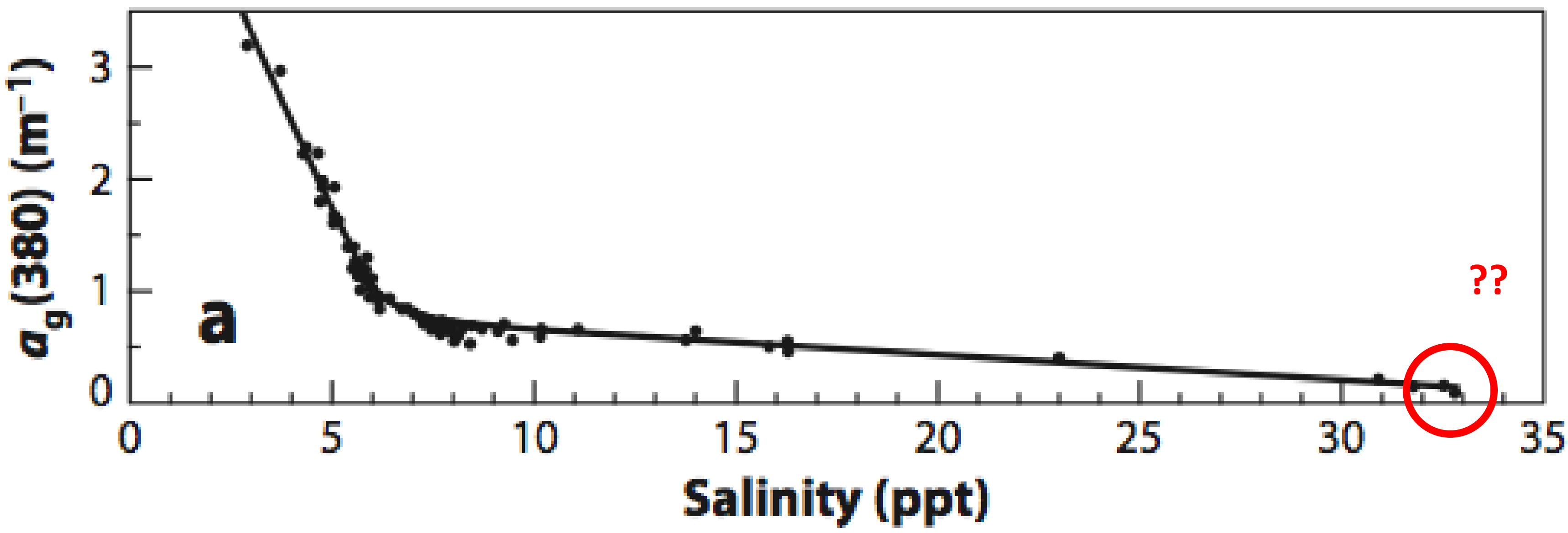
  First optical oceanographers worked in the Baltic Sea

  Hence CDOM was termed gelbstoff

- They found that gelbstoff drives water clarity & was obviously related to land-ocean exchange

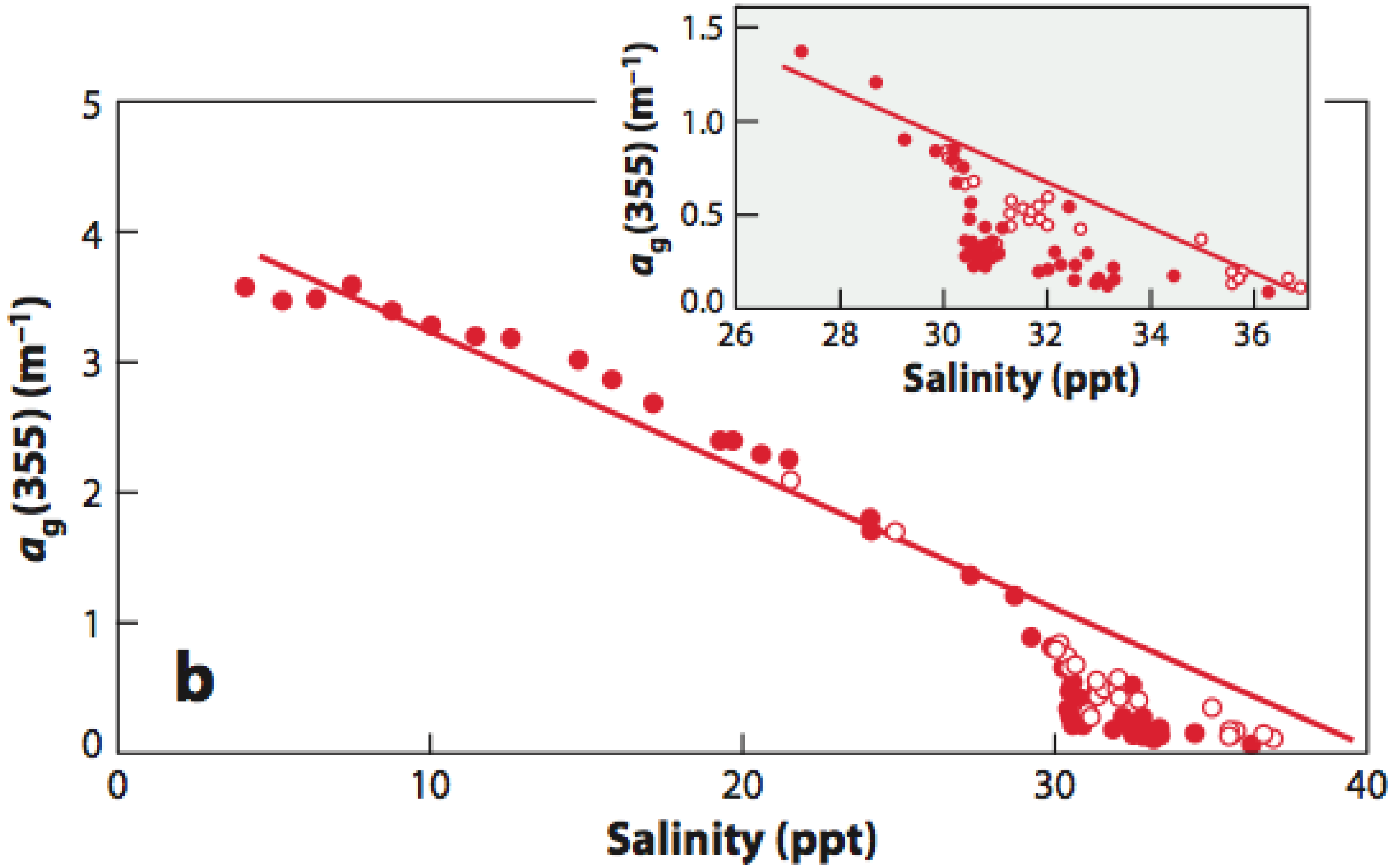
  Results in CDOM = f(Salinity)

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 <u>allochthonous</u>)?
  - Or are internal (i.e., <u>autochthonous)</u> sources important?
  - Need to know the time/space CDOM distribution

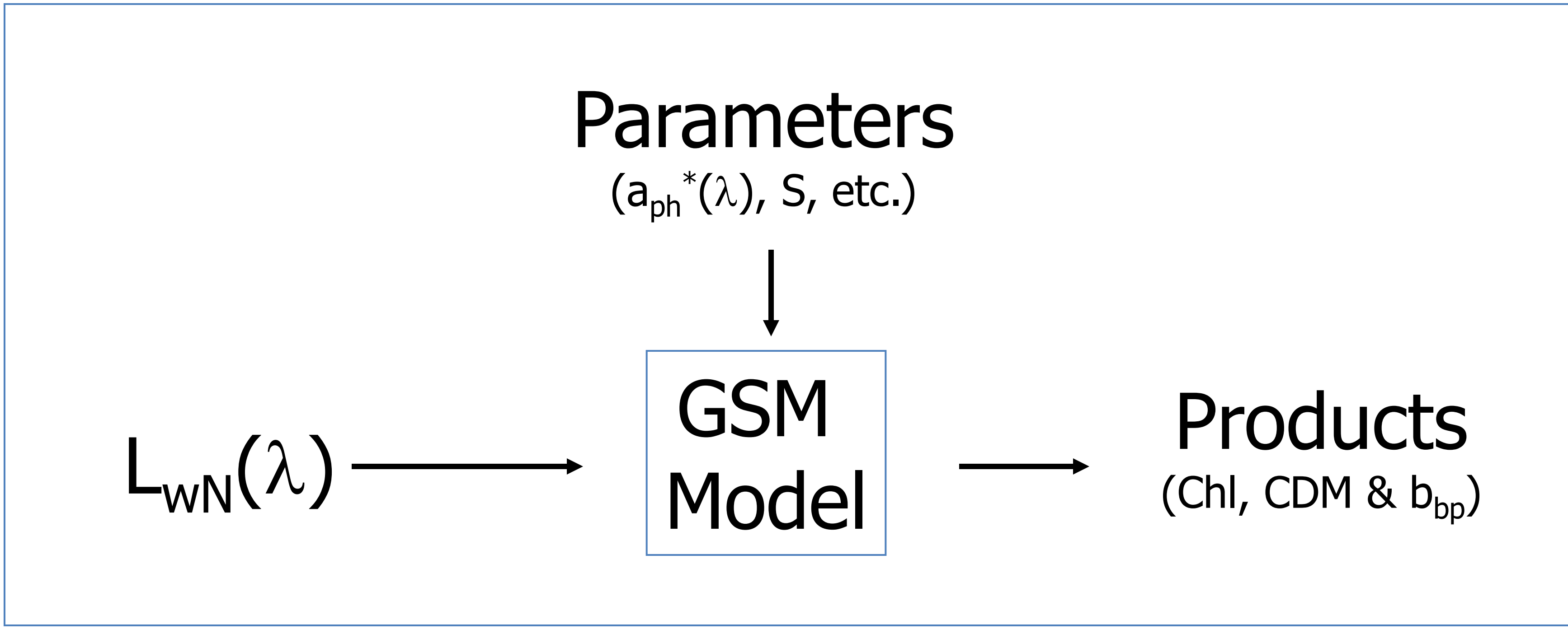
The Global CDOM Distribution

- 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 $L_{wN}(\lambda)$ & 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 $a_{det}(440) << a_g(440)$

The GSM Ocean Color Model



- Problems
  - Only first order understanding
  - Parameterizations are imperfect

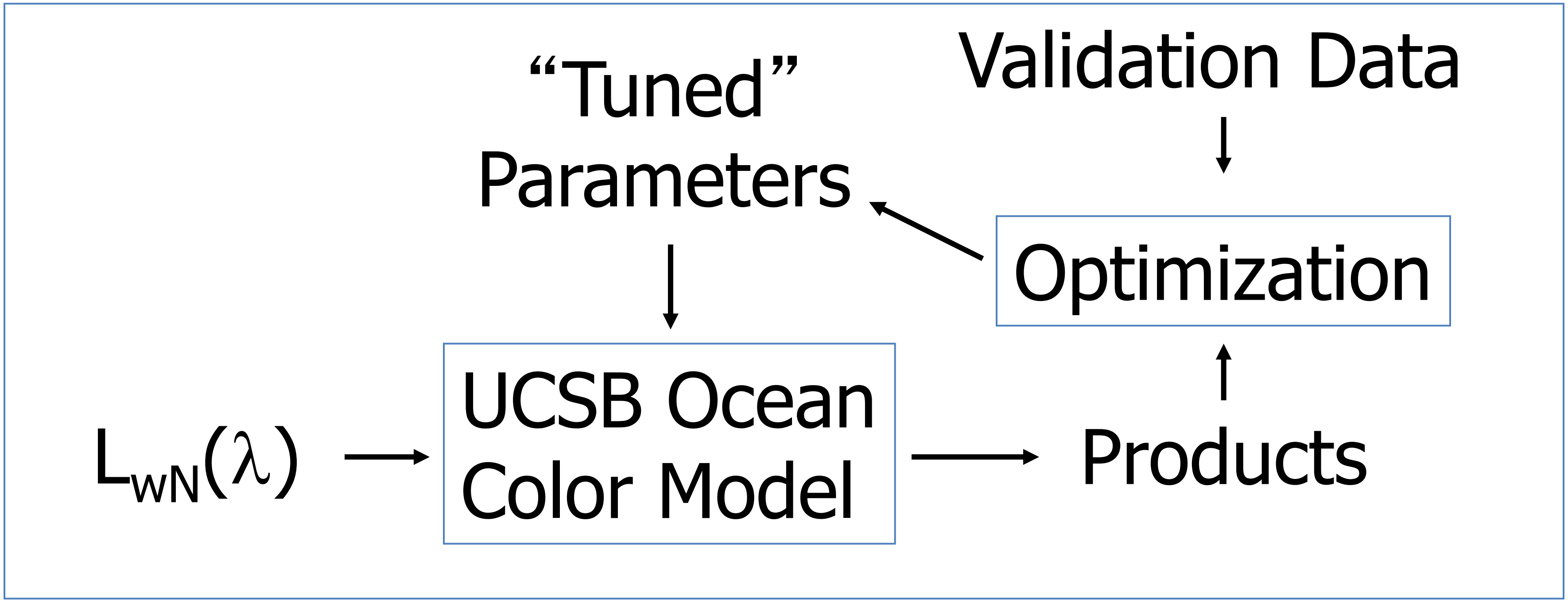
Garver & Siegel, JGR [1997]

Optimizing the GSM Model

Compiled a global $L_{wN}(\lambda)$ & validation data set

Used it to "tune" the parameters in the model

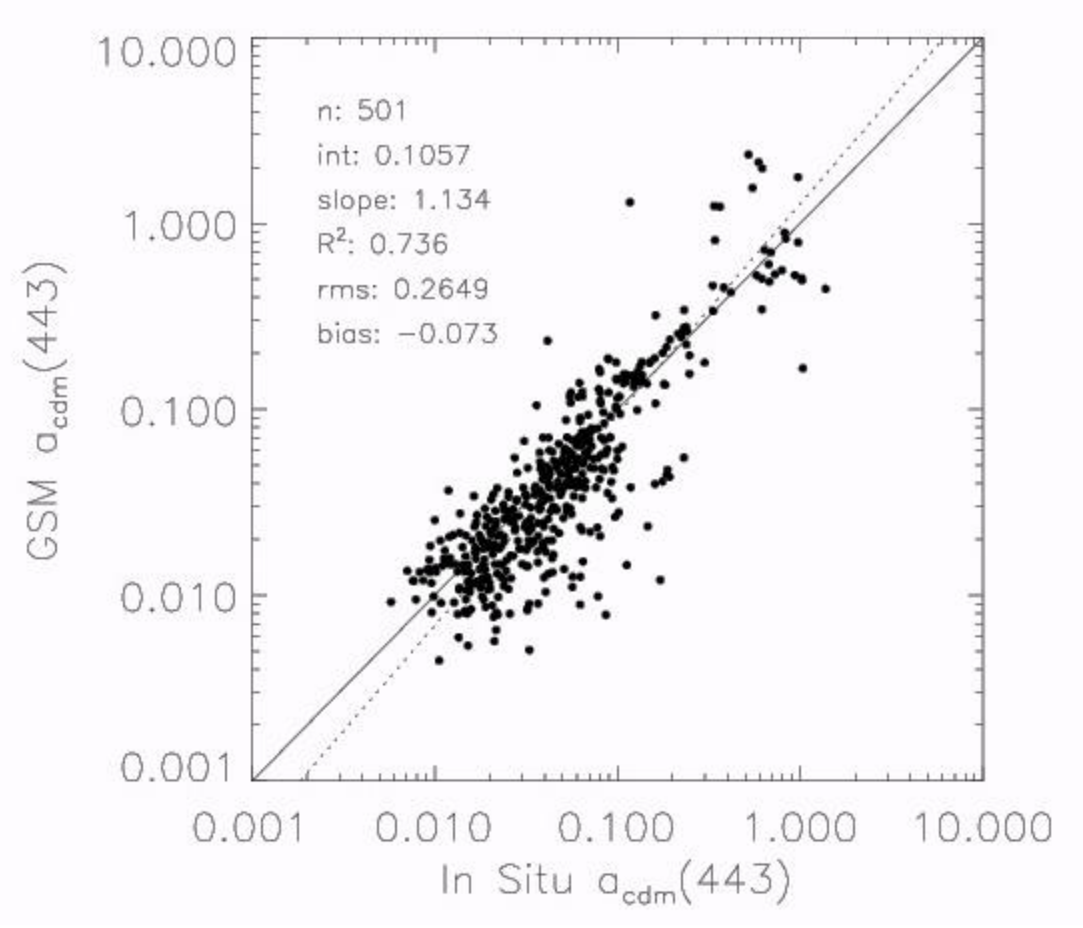
Maritorena *et al*. [2002] AO (... the GSM01 model)



GSM2.0 is now under going testing

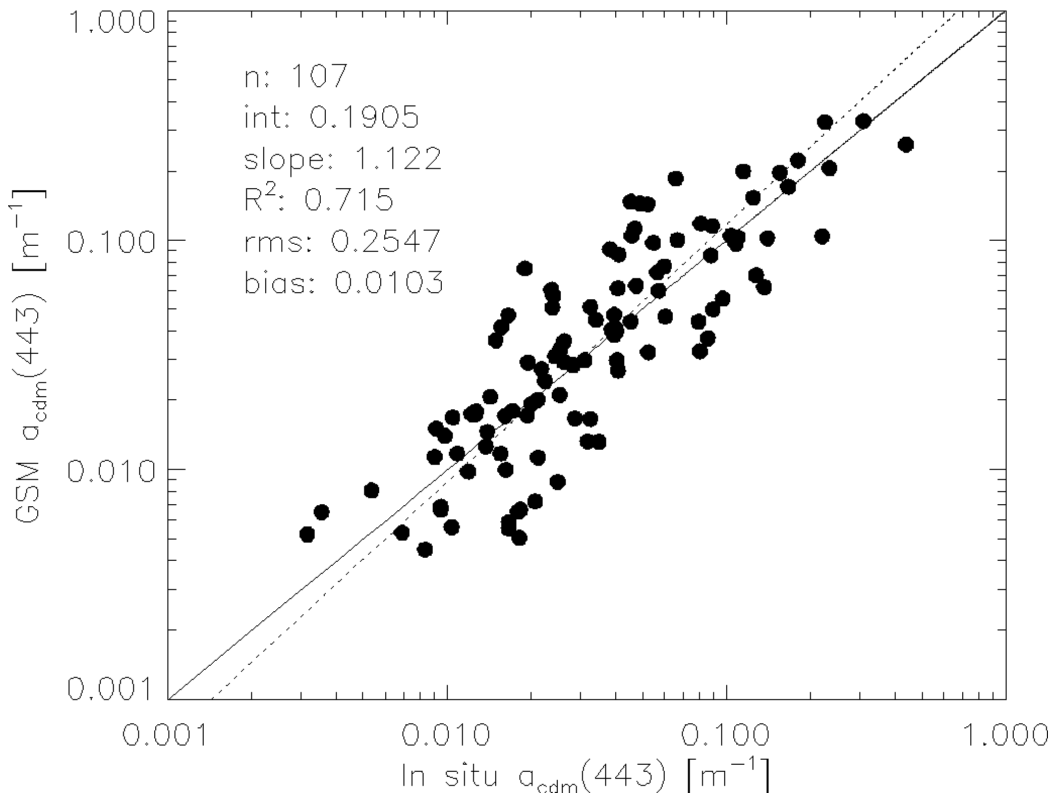
Does this all work??

- 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



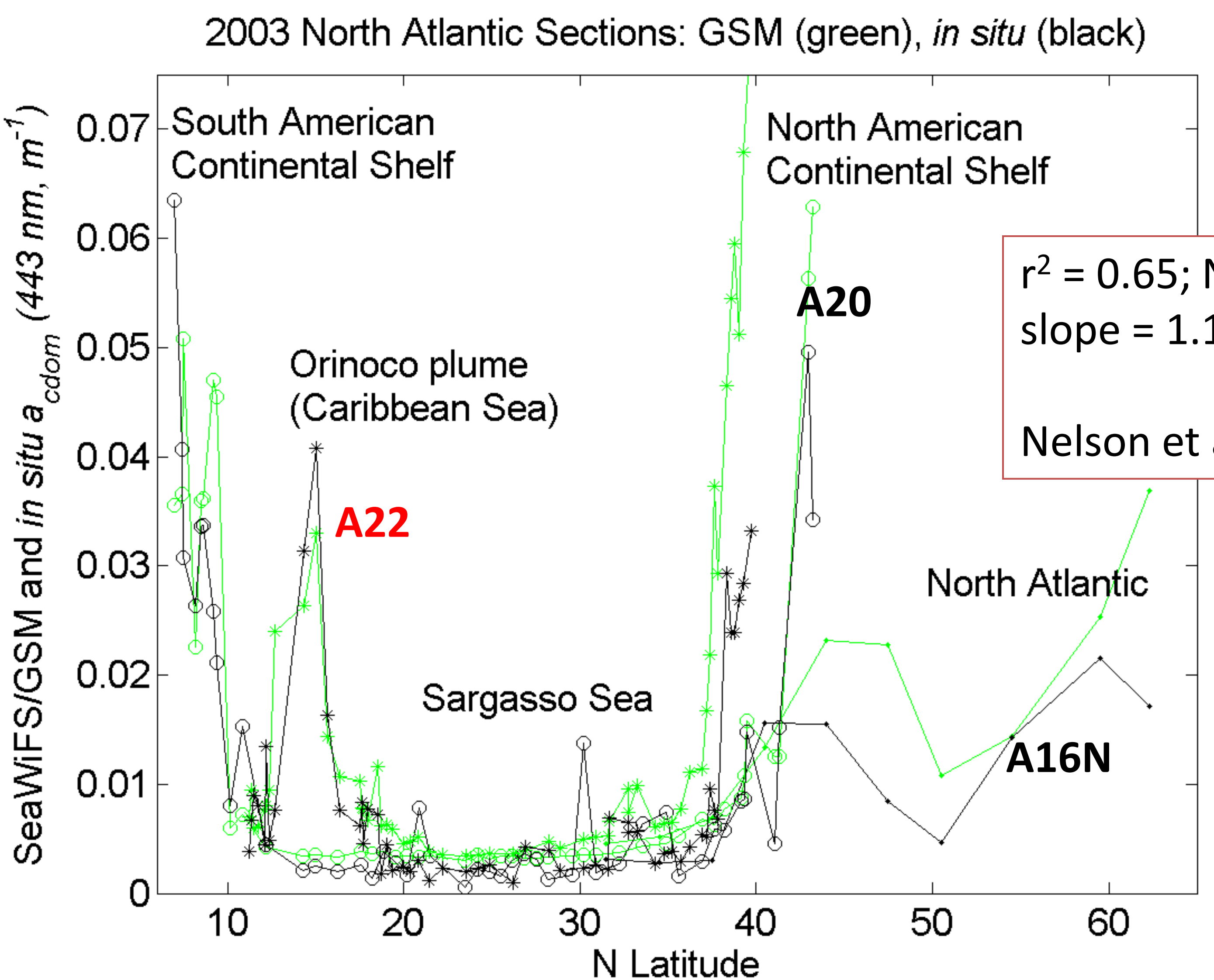
Does this all work??

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



Siegel et al. [2005] JGR

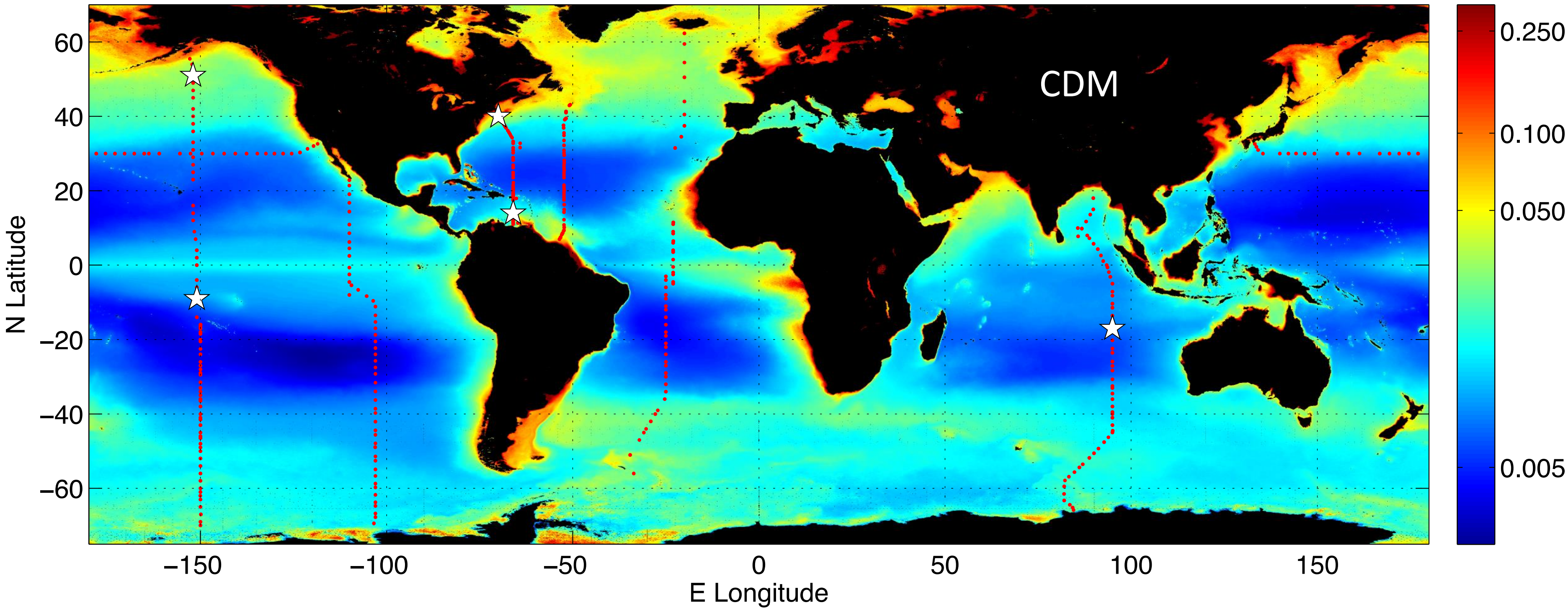
Surface CDOM & SeaWiFS



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

Nelson et al. [2007]

CDOM: where (surface)?



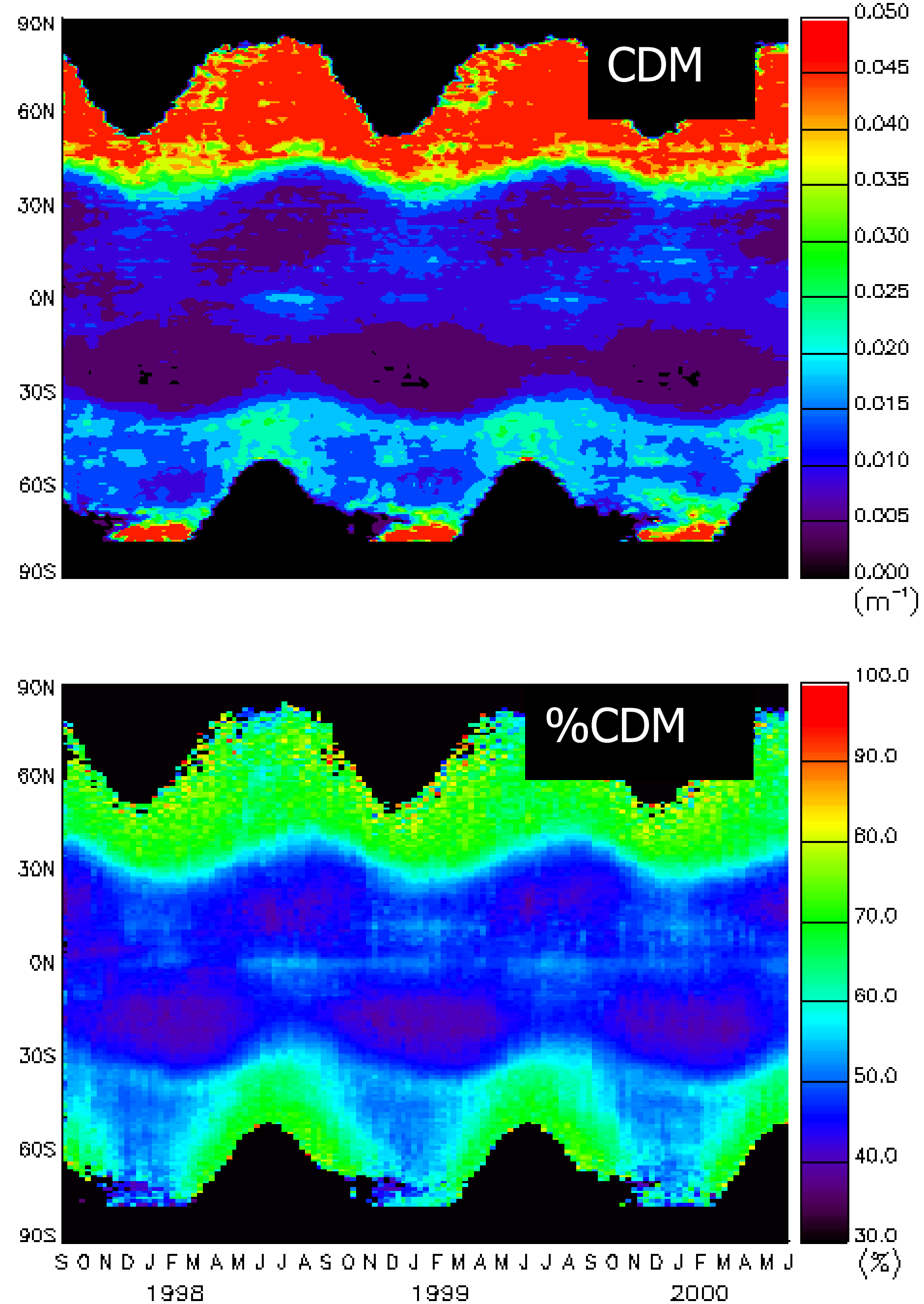
Nelson & Siegel [2013] ARMS

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

Seasonal Surface CDOM Cycle

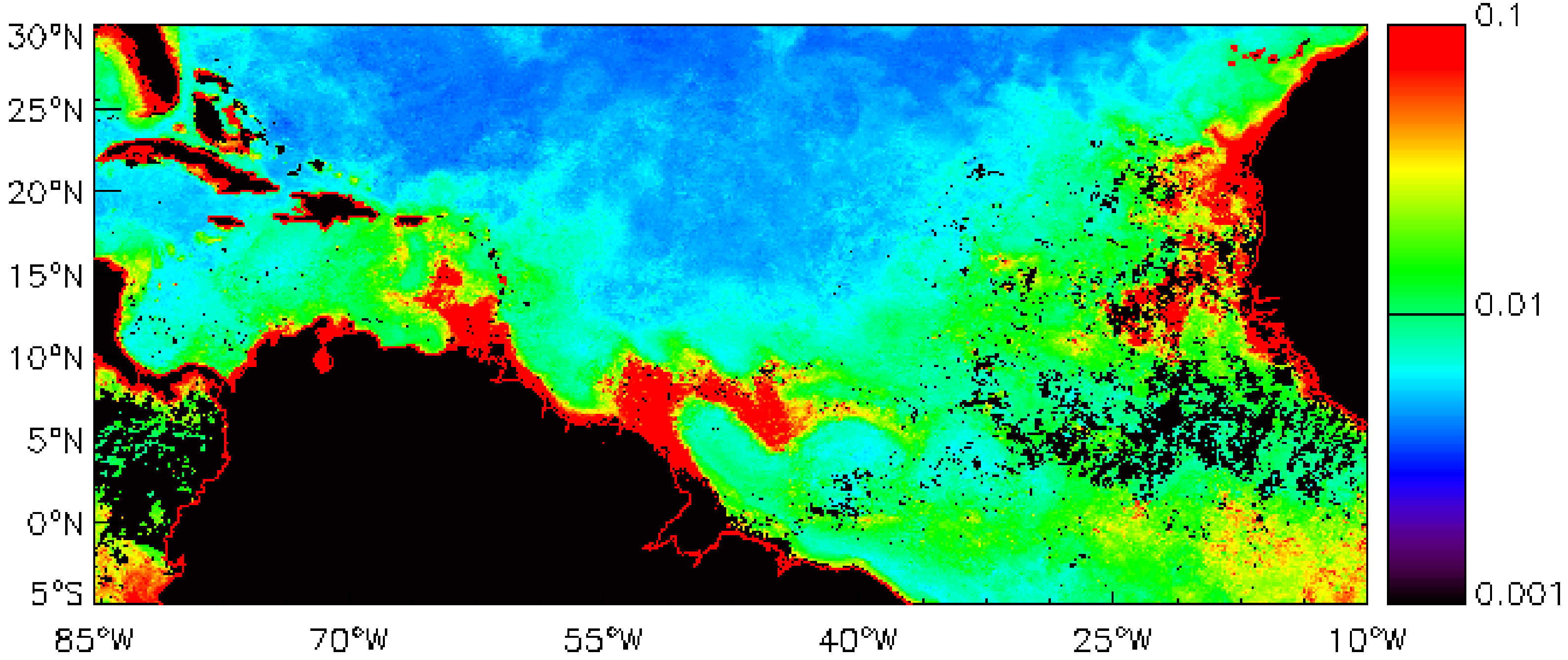
- Seasonal changes at most latitudes
- Lower in summer
- Reduced in tropics
- Higher towards poles
- Hemispheric asymmetry

$$\%CDM = 100*CDM/(CDM+a_{ph}(440))$$
where $a_{ph}(440) = f(Chl)$



Role of Rivers

Large River Outflows…



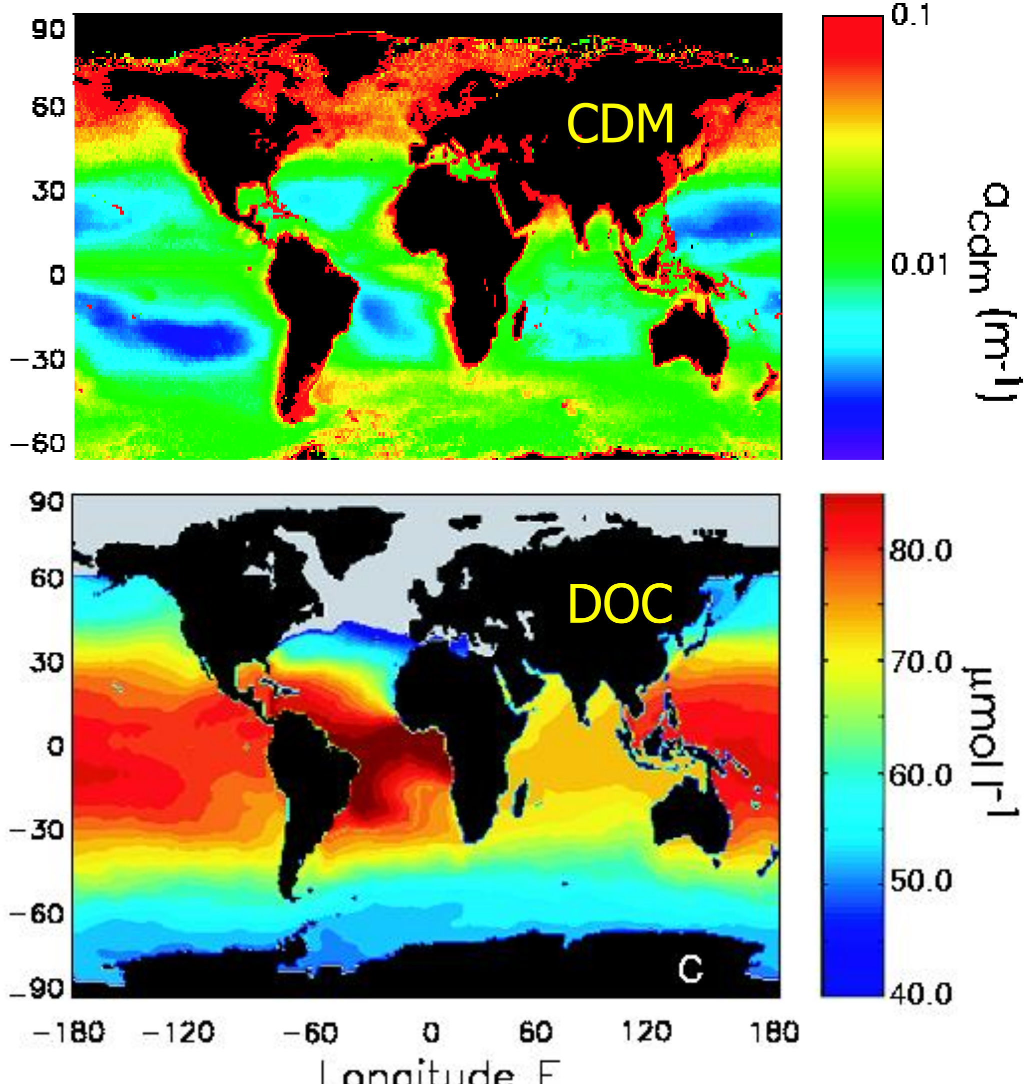
Maximum annual change due to global rivers is 0.005 m^{-1}

River inputs are just not important on a global scale

Siegel et al. [2002]

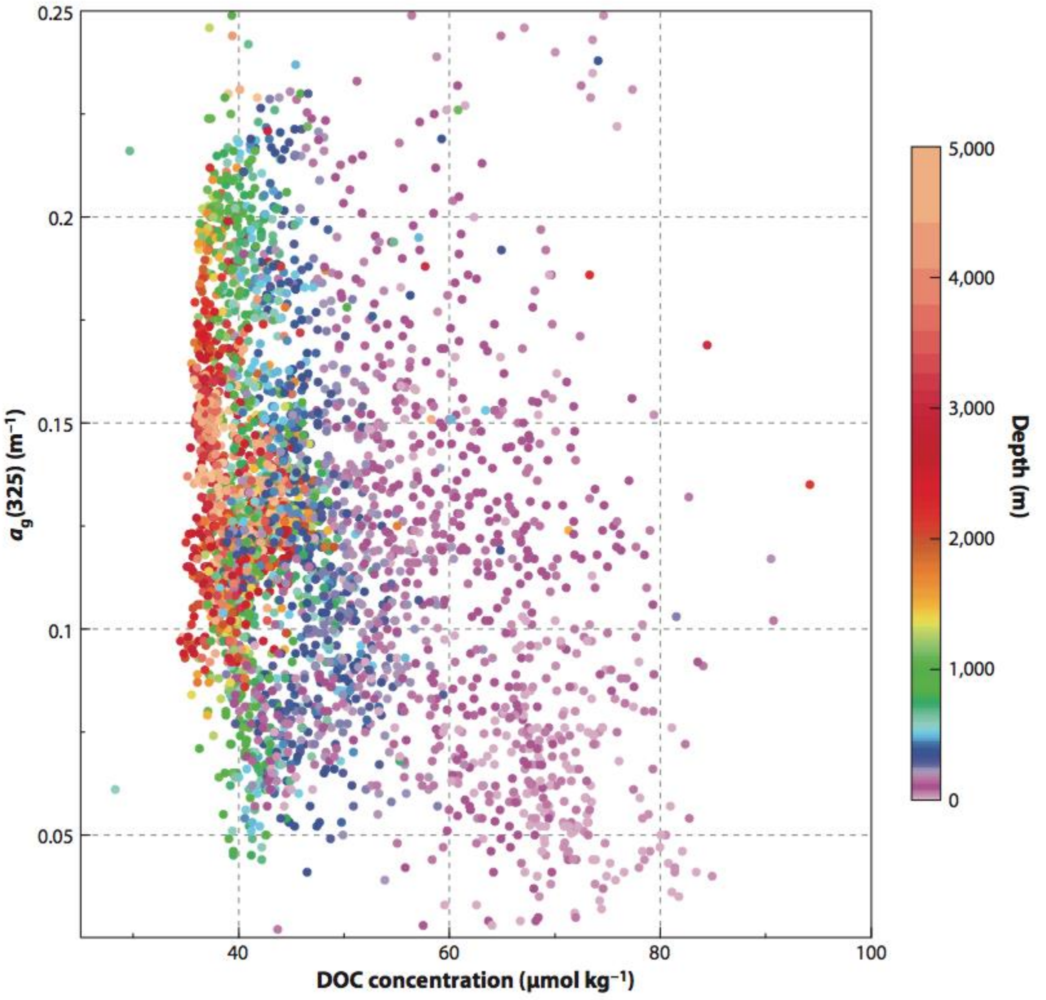
Global CDOM & DOC

- CDOM ≠ 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

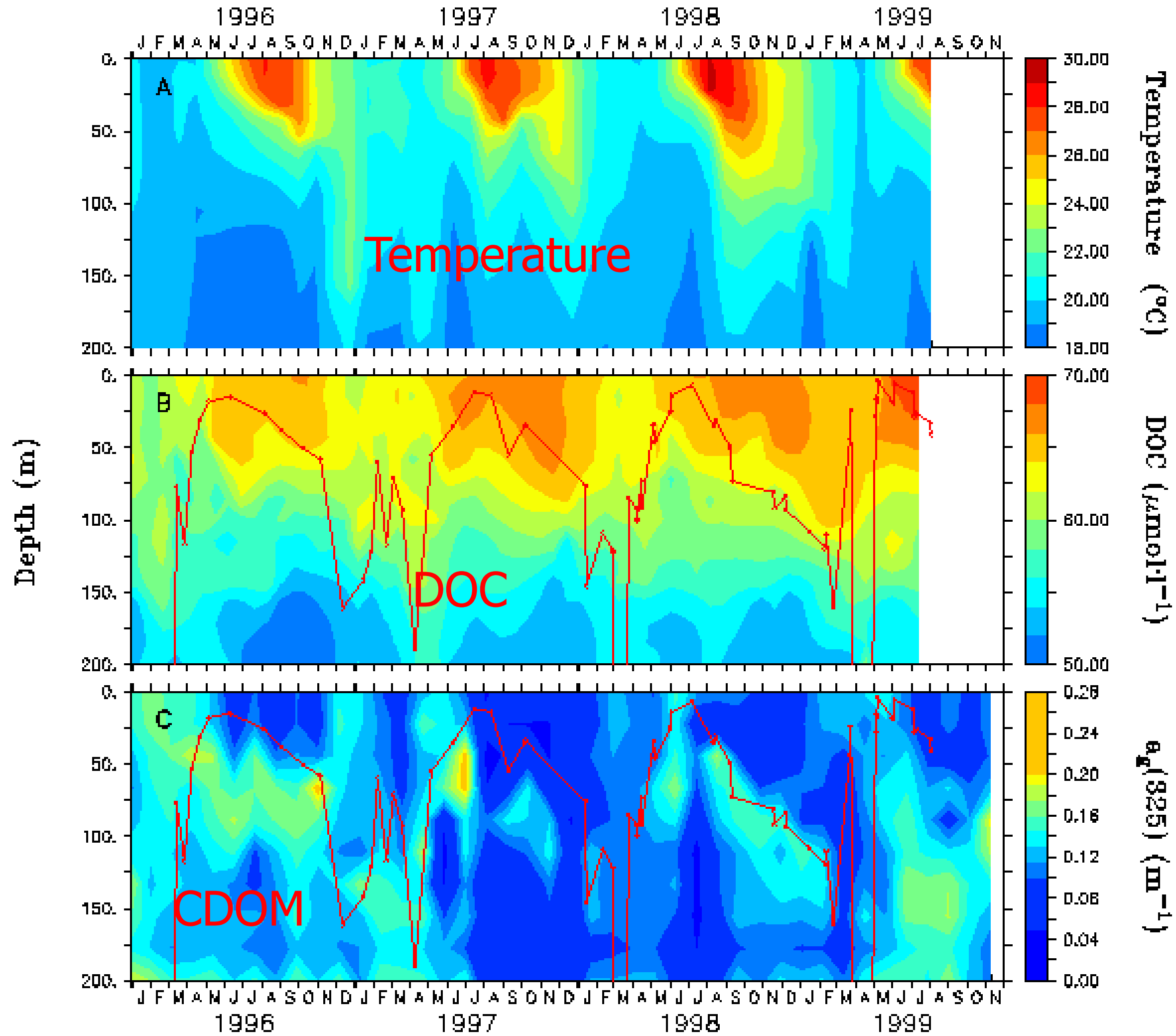
(after Nelson et al. 1998)

Seasonal cycle

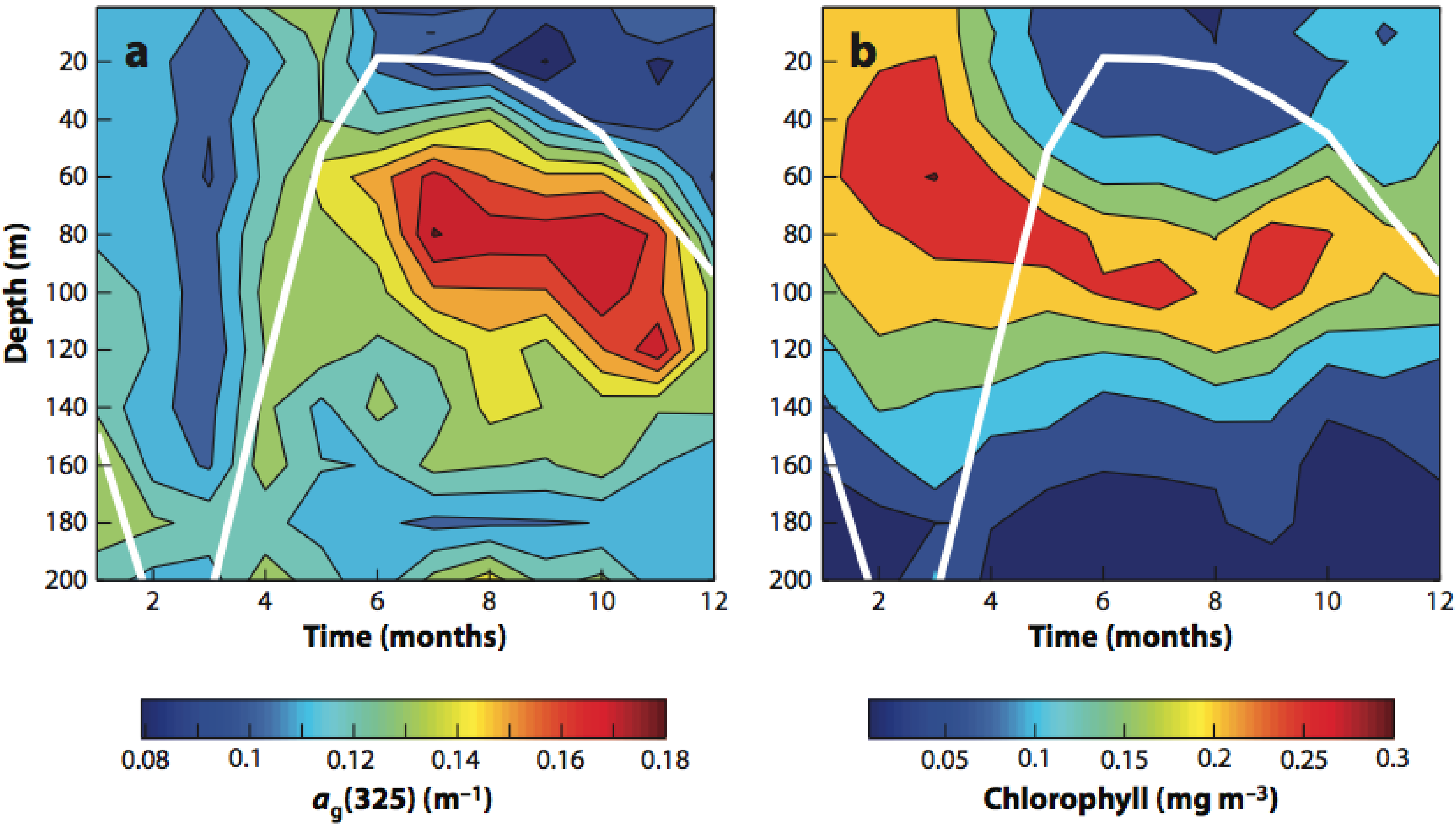
CDOM ≠ DOC

CDOM ≠ POC

CDOM ≠ Chl



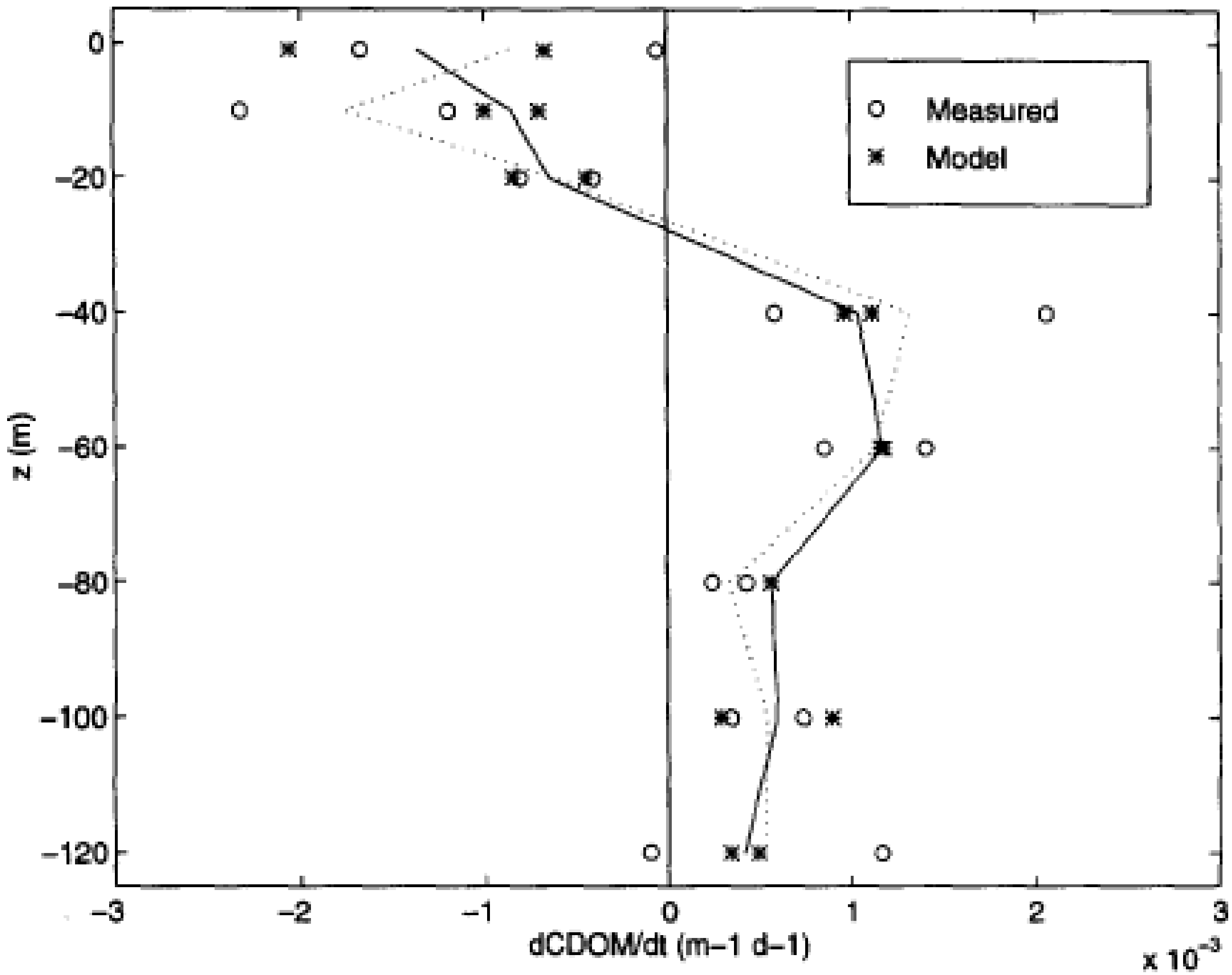
Seasonal Cycle of CDOM at BATS



Nelson & Siegel (2013)

Net Production of CDOM

Summer – Spring CDOM



BATS data

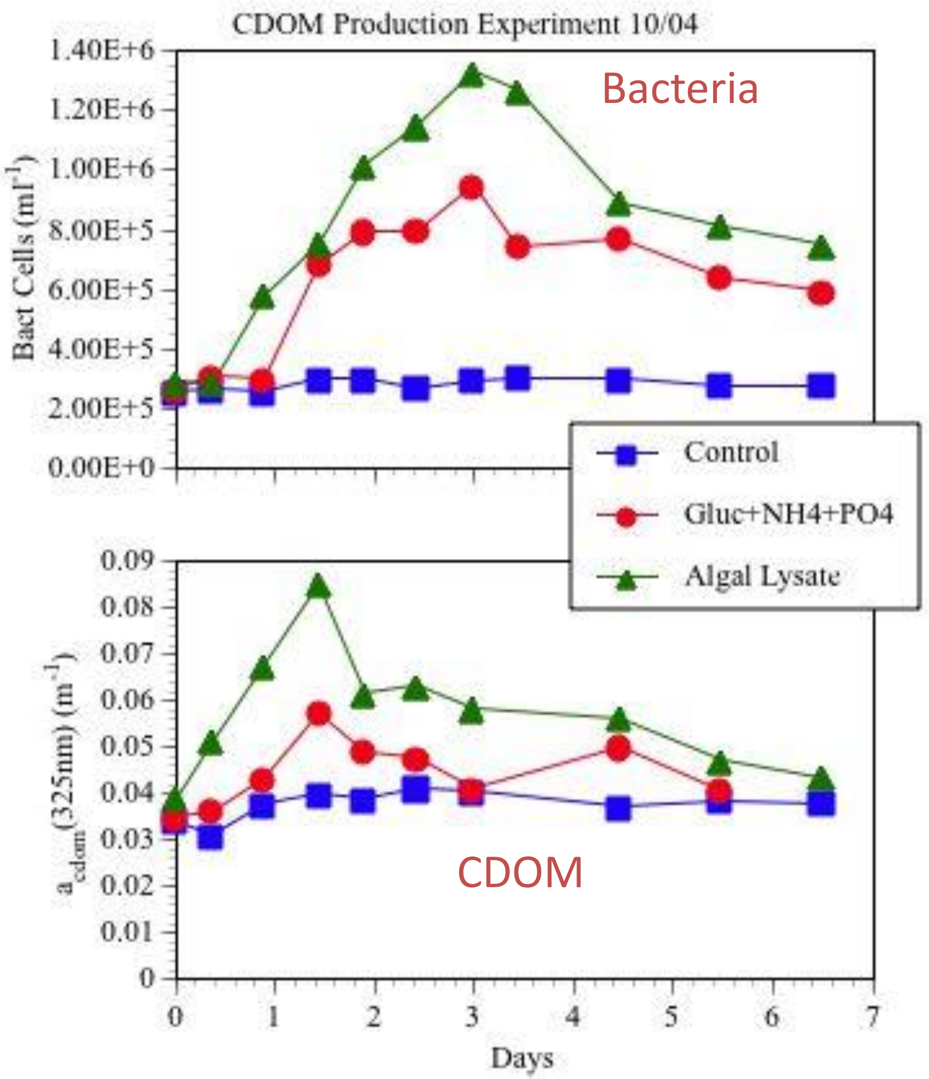
Sargasso Sea

(Nelson et al. 1998)

Production max at 40-60 m

Similar to the bacterial production

Microbial Production of CDOM

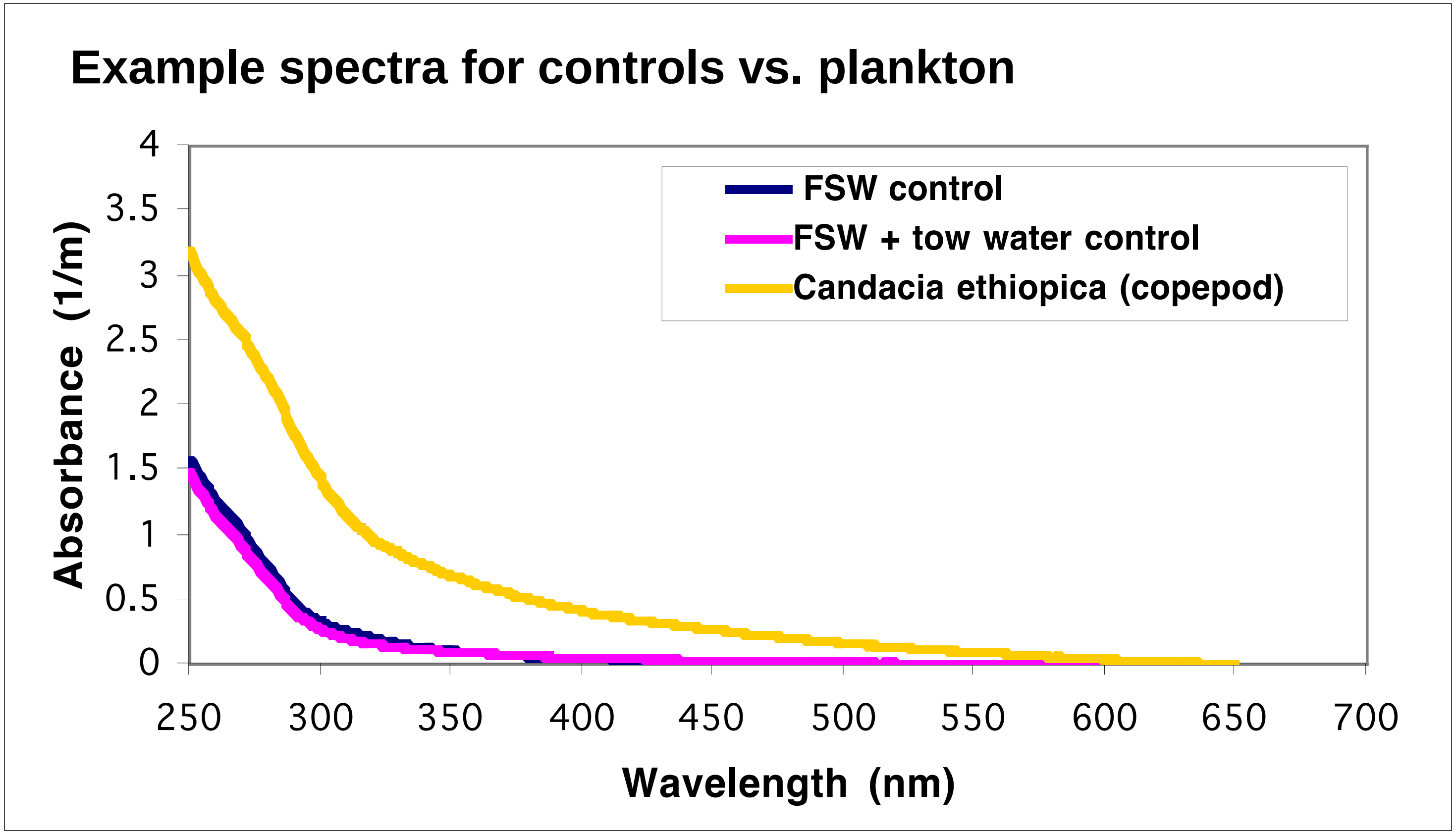


Microbes produce long-lived CDOM

Experiments from BATS 60m water by Nelson & Carlson

After Nelson et al. [2004] Mar. Chem.

Zooplankton & CDOM



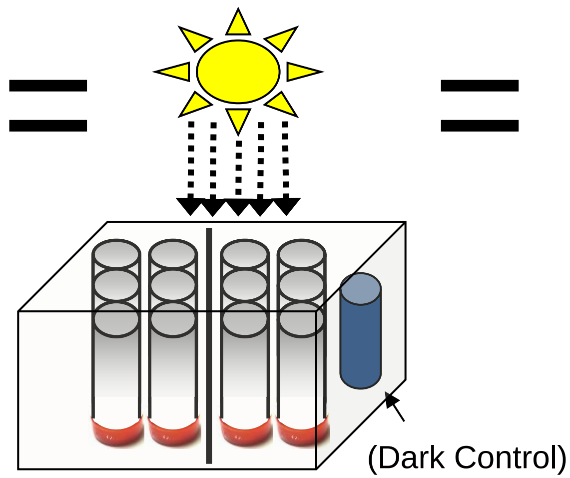
8 hour excretion experiments from Sargasso Sea

Steinberg et al. [2004] - MEPS

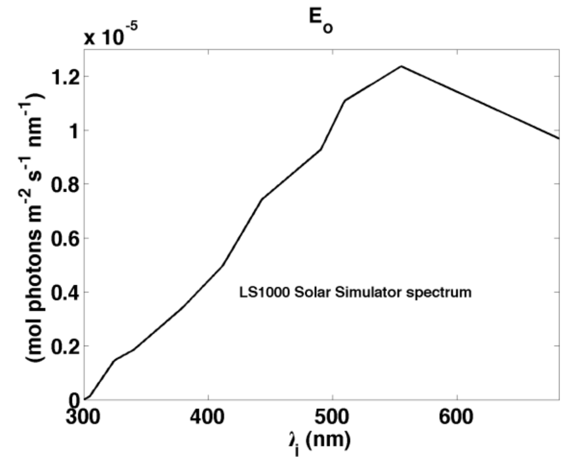
CDOM Photolysis

Experimental Design:

Solar Light Co. LS1000 Solar Simulator



Collimated beam simulates spectrum and intensity of terrestrial irradiance

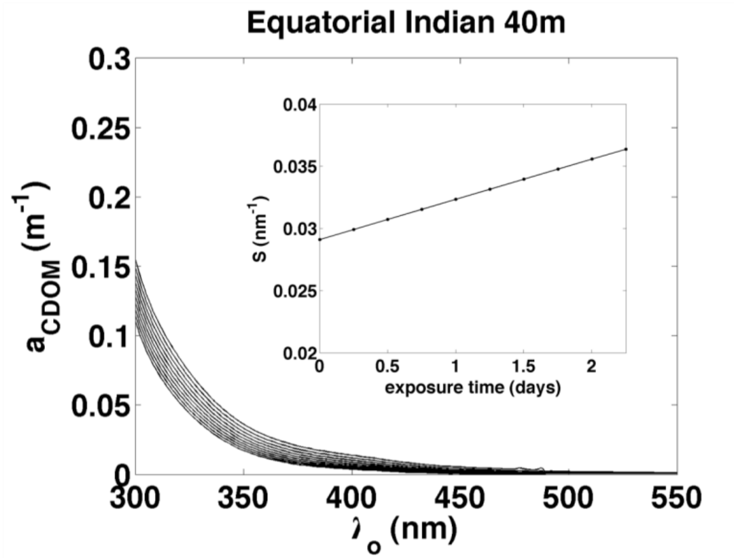


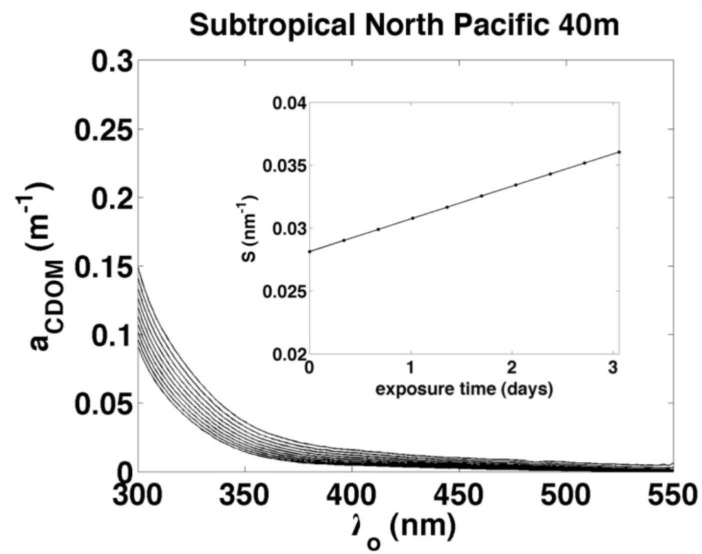
- Time course of CDOM absorption = photolysis rate = $da_{CDOM}(\lambda_o)/dt$
- 2 days in simulator ≈ 7 days in surface ocean ≈ **35 days* in mixed layer**

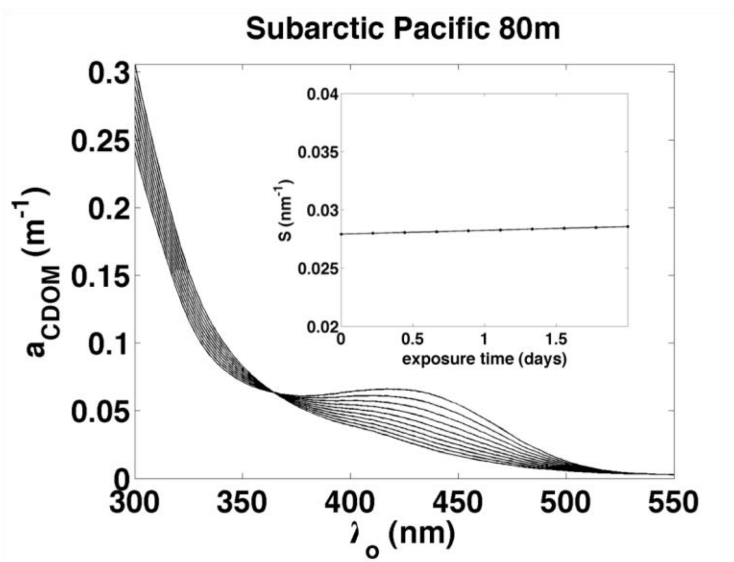
*estimate based on daily insolation at 325nm, MLD, and CDOM/light attenuation in mid-Atlantic in winter

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…

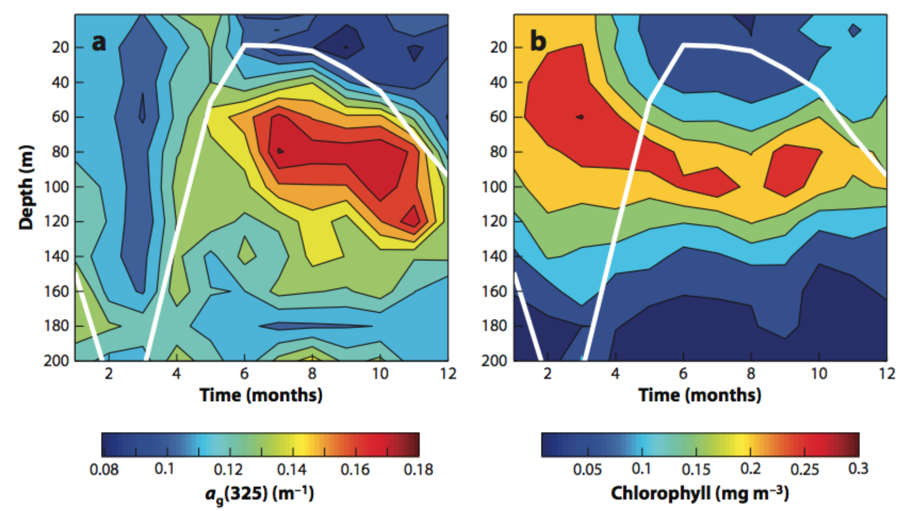
Swan et al. [2012] DSR-1

Seasonal CDOM Cycle at BATS

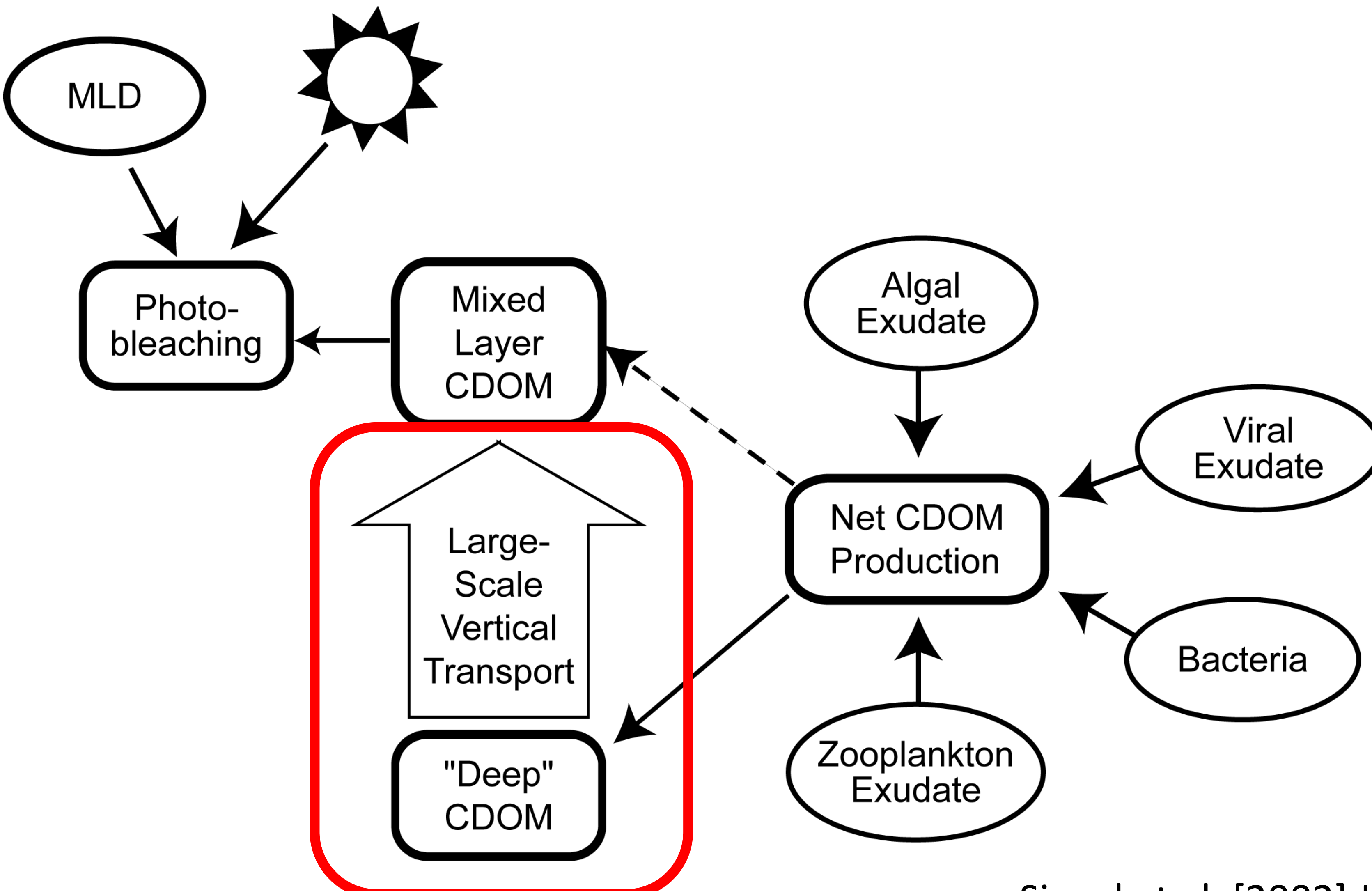
Links mixing, photolysis & production

- 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

  [CDOM] << [DOM]



Surface Ocean CDOM Dynamics

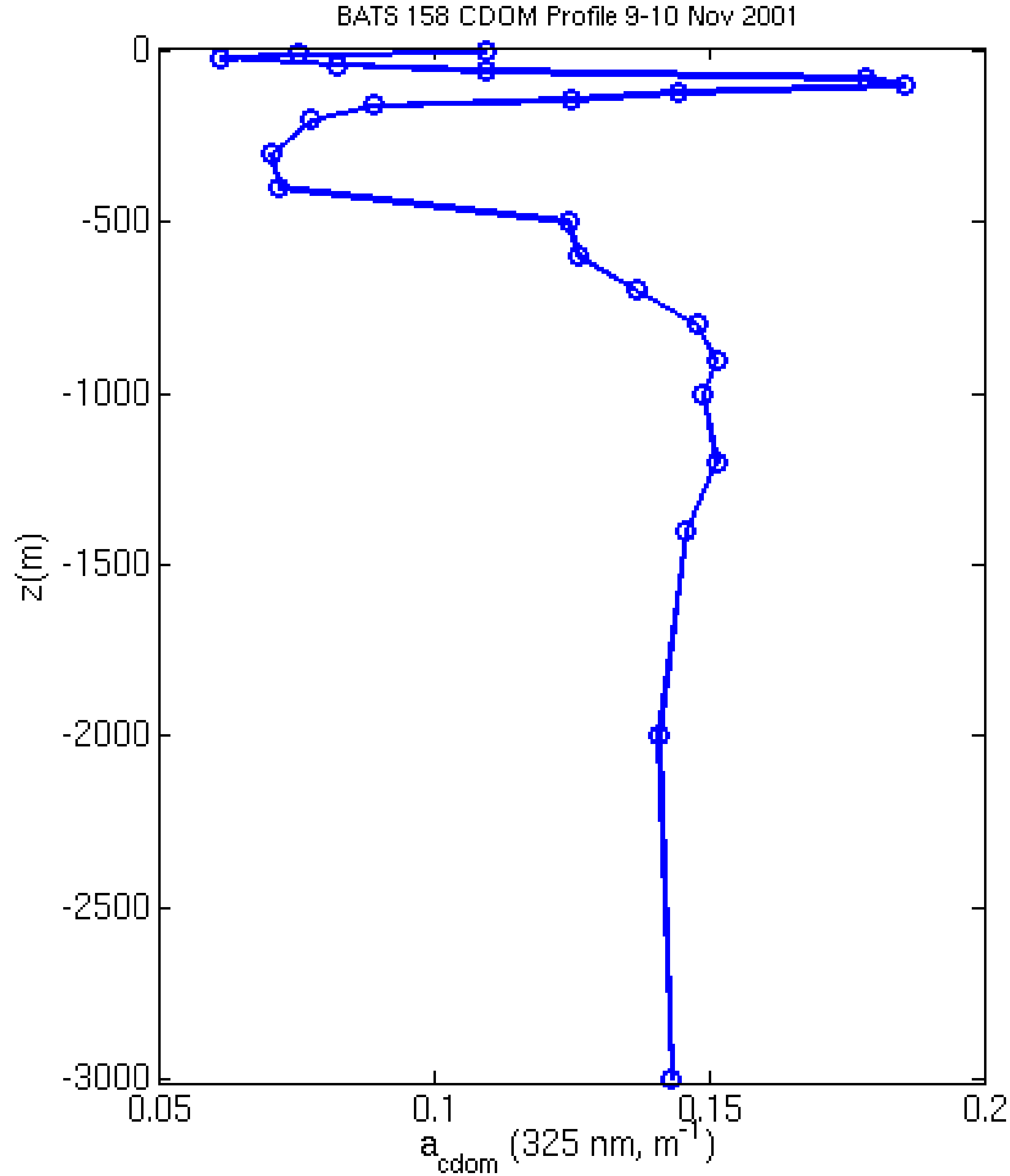


Siegel et al. [2002] JGR

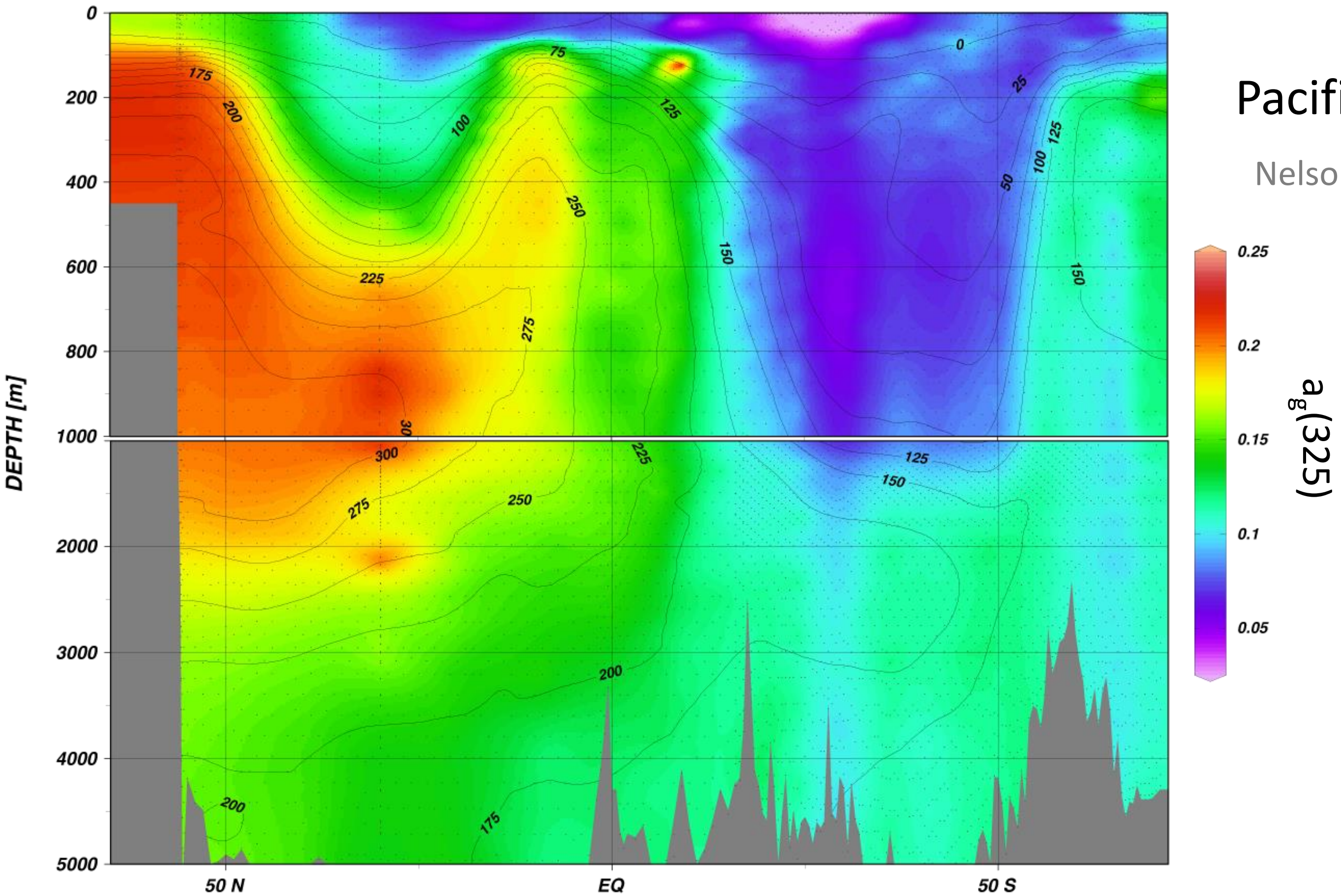
CDOM: where (ocean interior)?

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)?

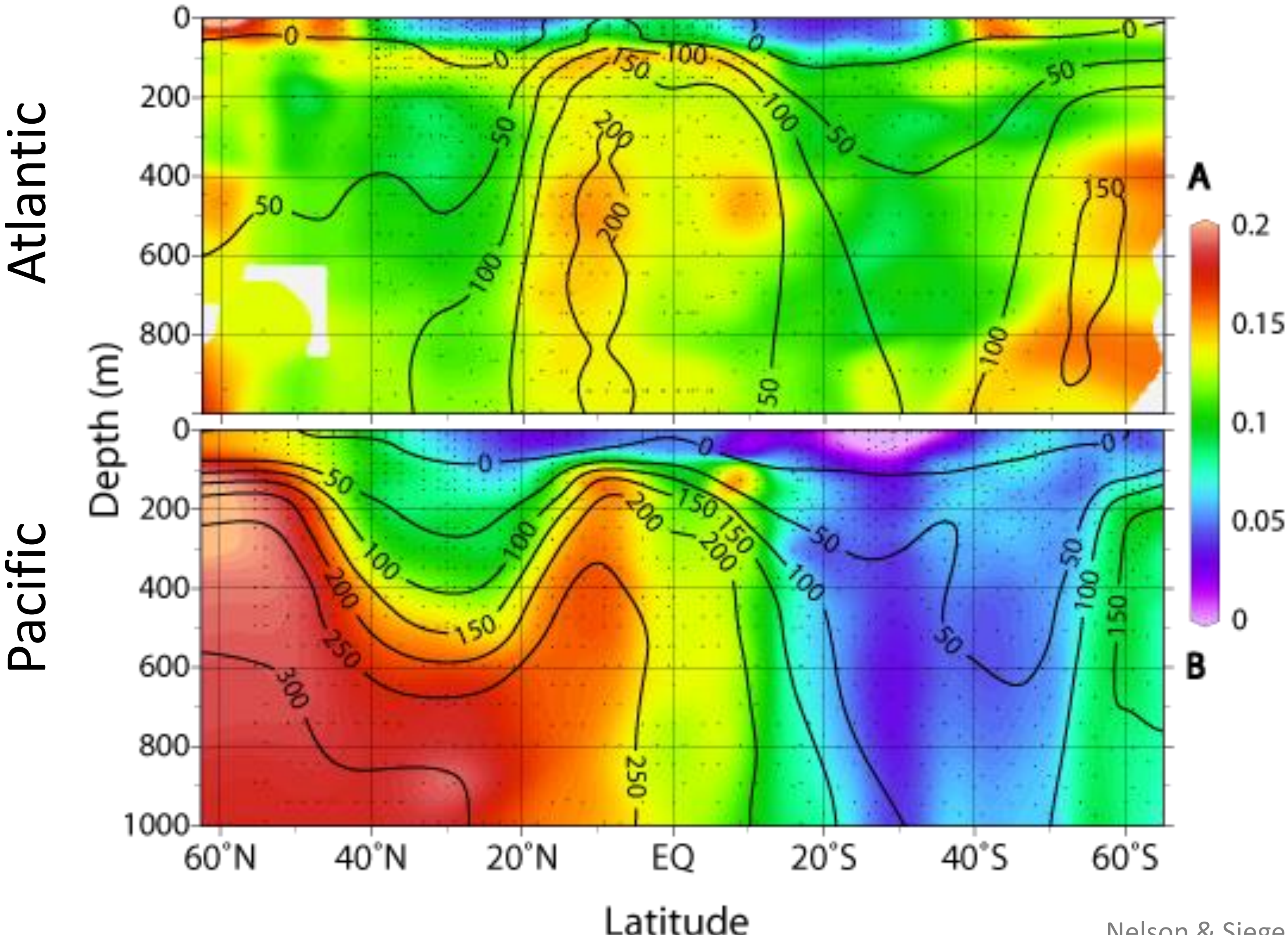


Pacific (P16 N/S) section

Nelson & Siegel [2013] ARMS

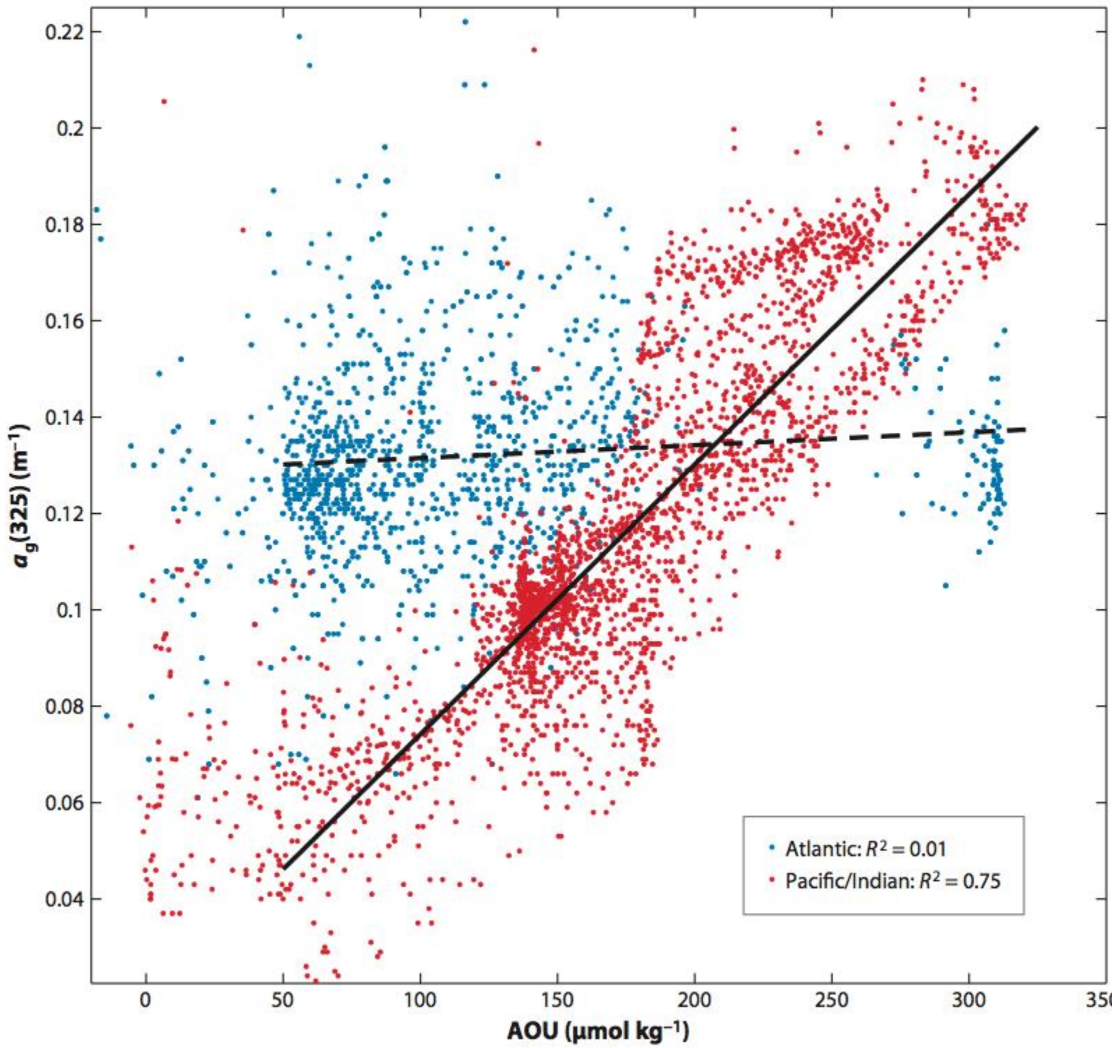
- Near surface in productive regions
- Increases in the main thermocline
- Connection to overturning circulation apparent

AOU and CDOM



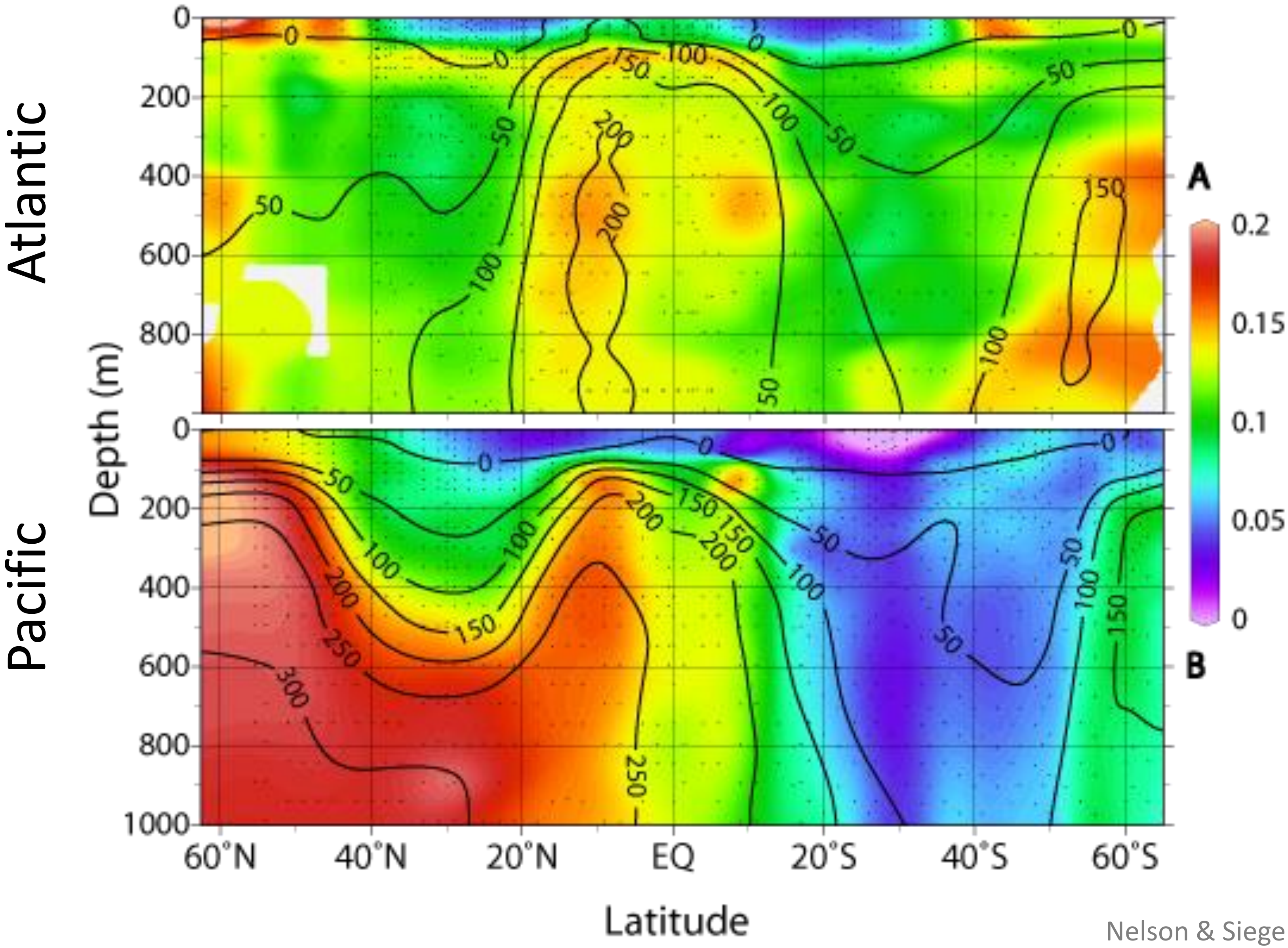
Nelson & Siegel [2013]

AOU and CDOM



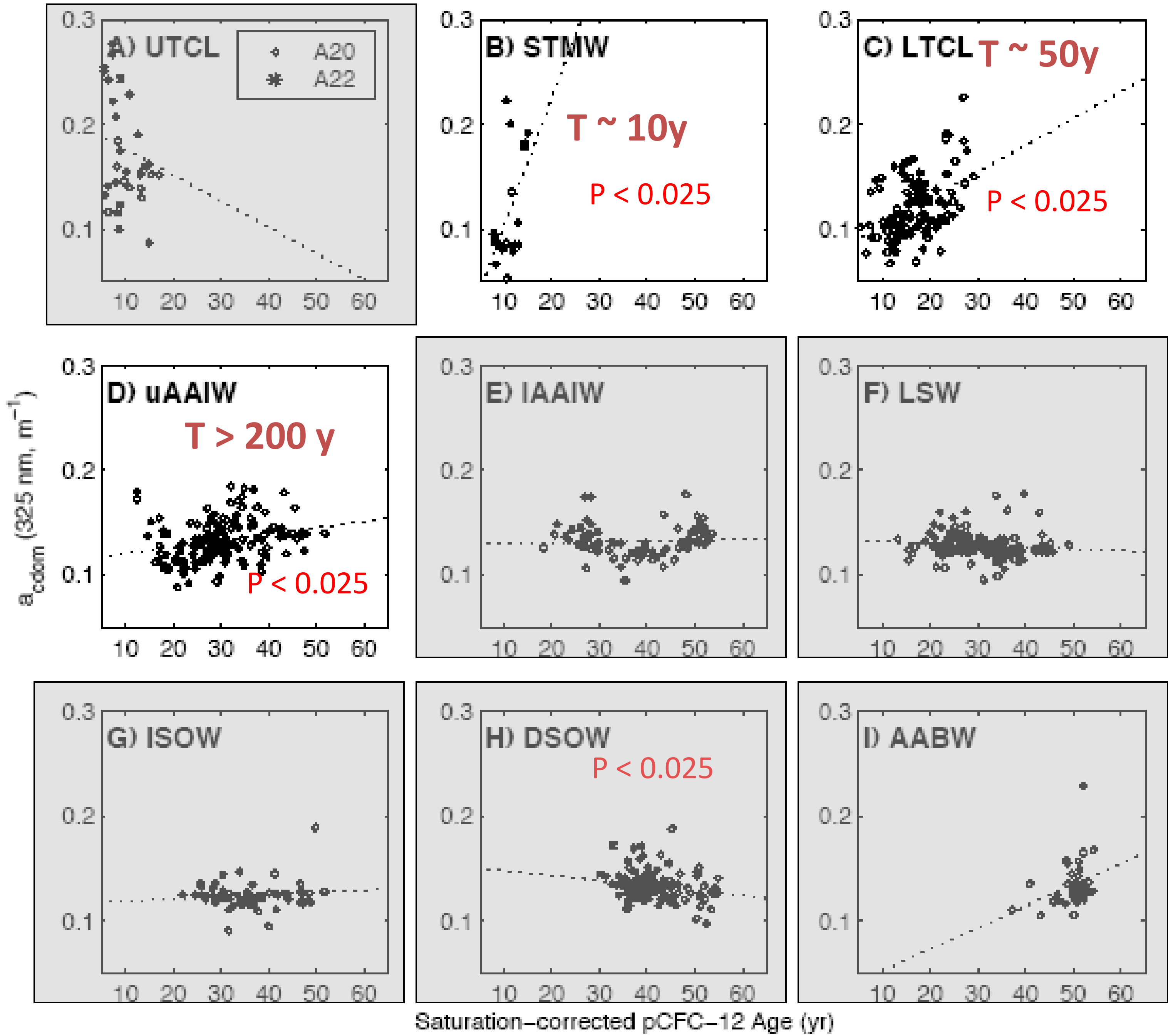
Nelson et al. [2013]

Why do AOU & CDOM Correspond?



Nelson & Siegel [2013]

CFC-estimated Age vs. CDOM



Nelson et al. [2007] DSR-I

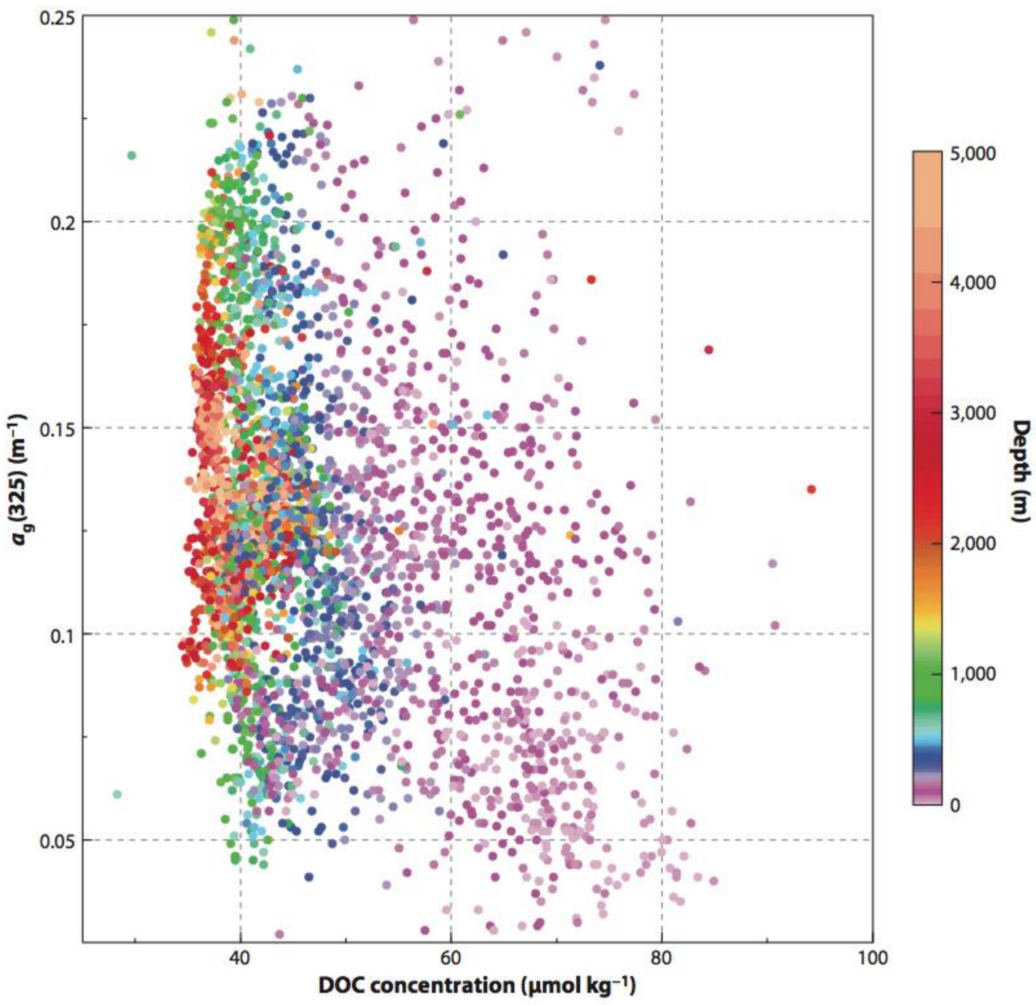
Time scales of Deep Ocean CDOM Cycling

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

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

T_{bio} for deep ocean formation of long-lived CDOM must be O(100 years).

CDOM ≠ DOC in the Open Ocean



Nelson & Siegel [2013]

CDOM & DOC

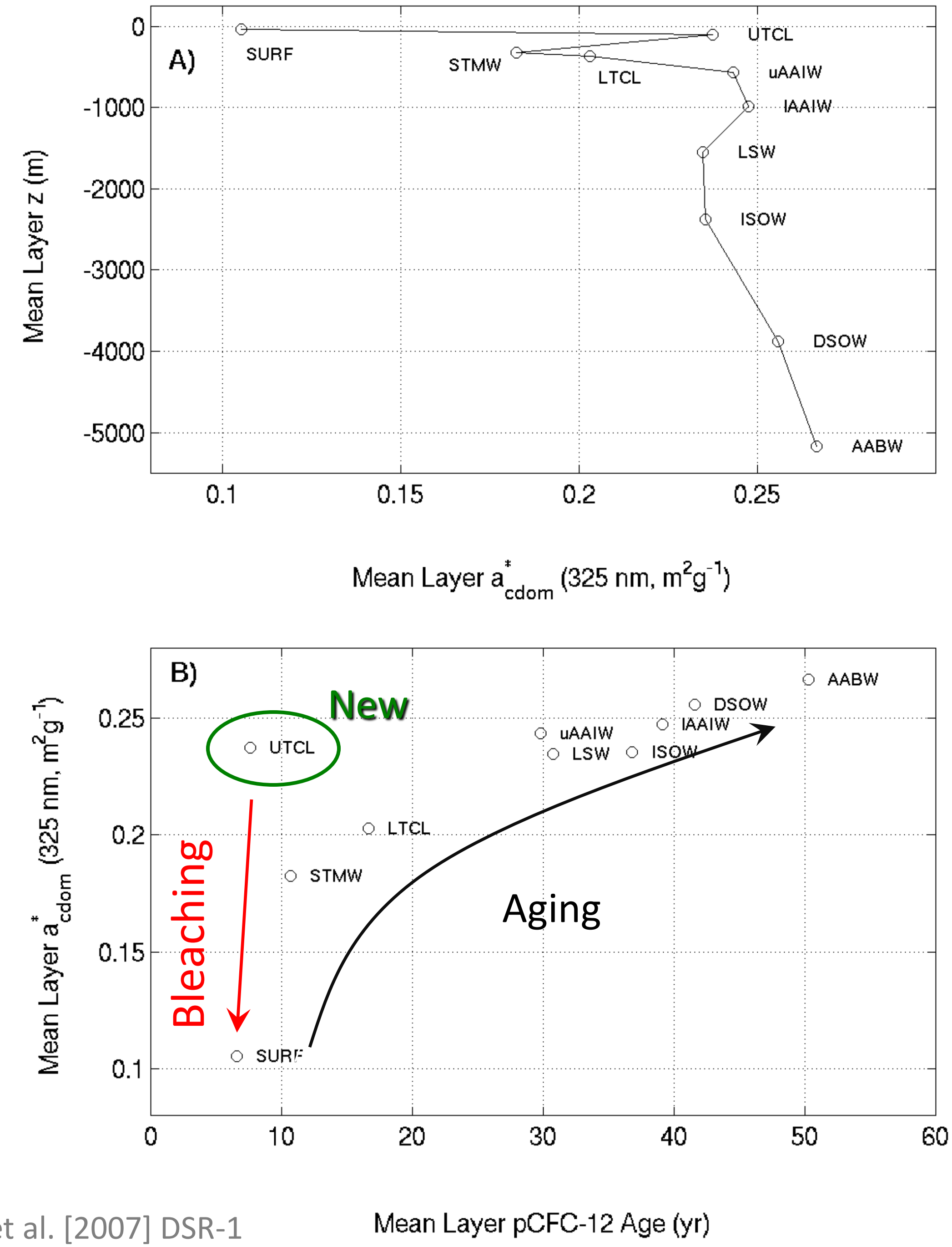
Generally uncorrelated except in coastal regions

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

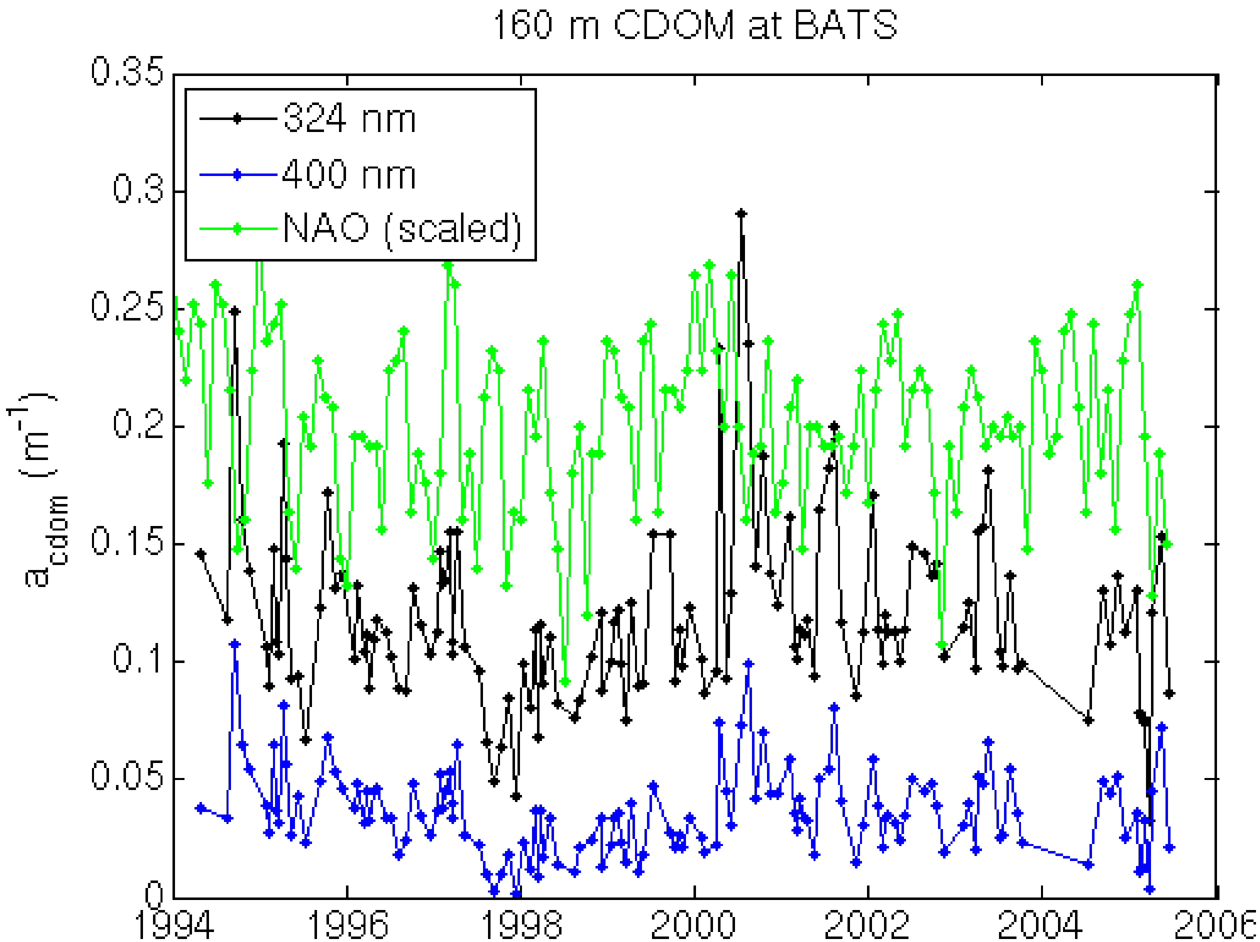
- CDOM distributions are consistent with hydrographic & transient tracer patterns
- Ventilation & net BGC production are the two dominant processes
- CDOM mirrors AOU. As organic C is consumed, a colored dissolved byproduct is formed (?).
- Time scales of long-lived, deep water CDOM production are many 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.

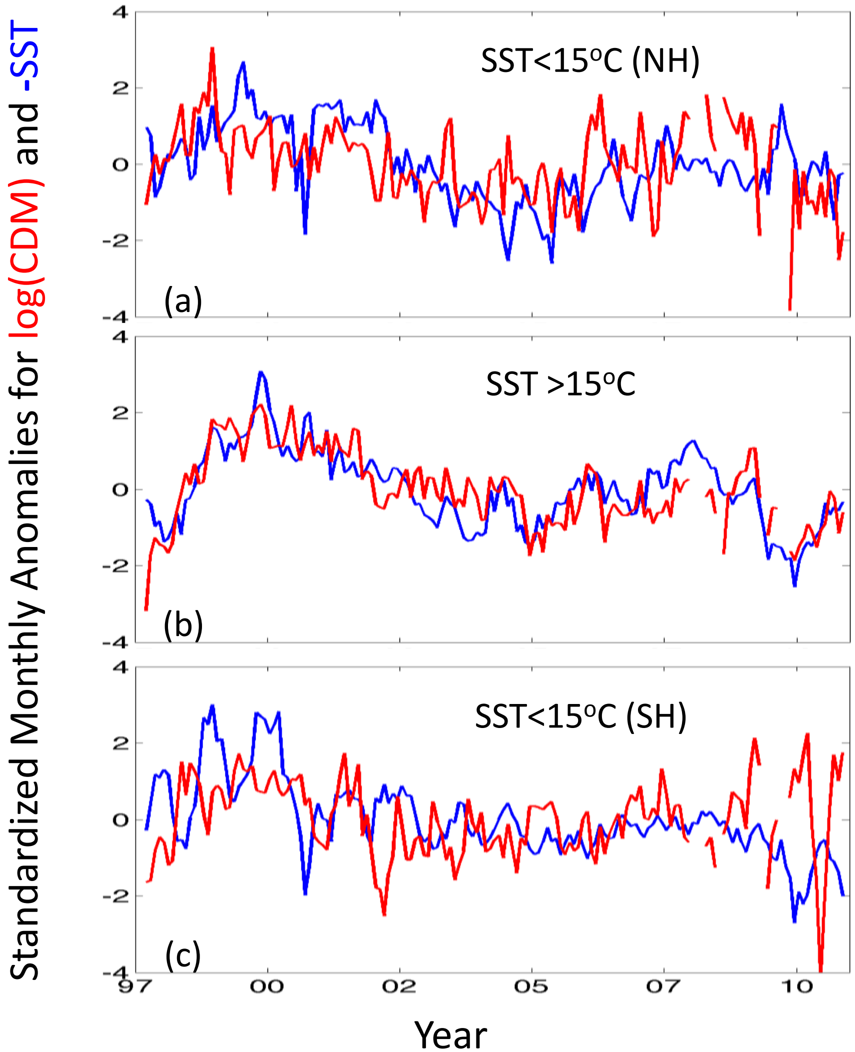
- Trends in CDOM abundance at the surface have implications for important biogeochemical processes.

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

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

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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 fluorescese.

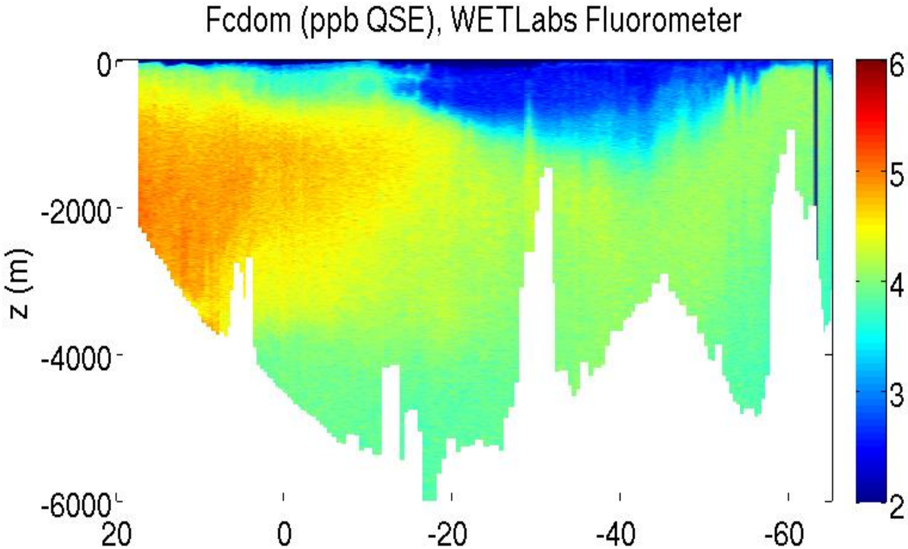
- Thus, FDOM is a subset of CDOM & FDOM may be a useful index of DOM quality.

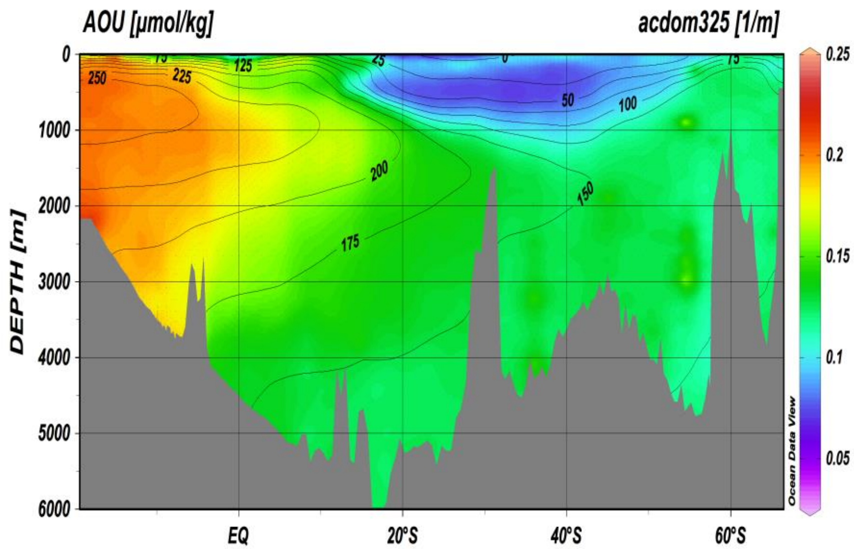
- Two approaches for characterizing FDOM

  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

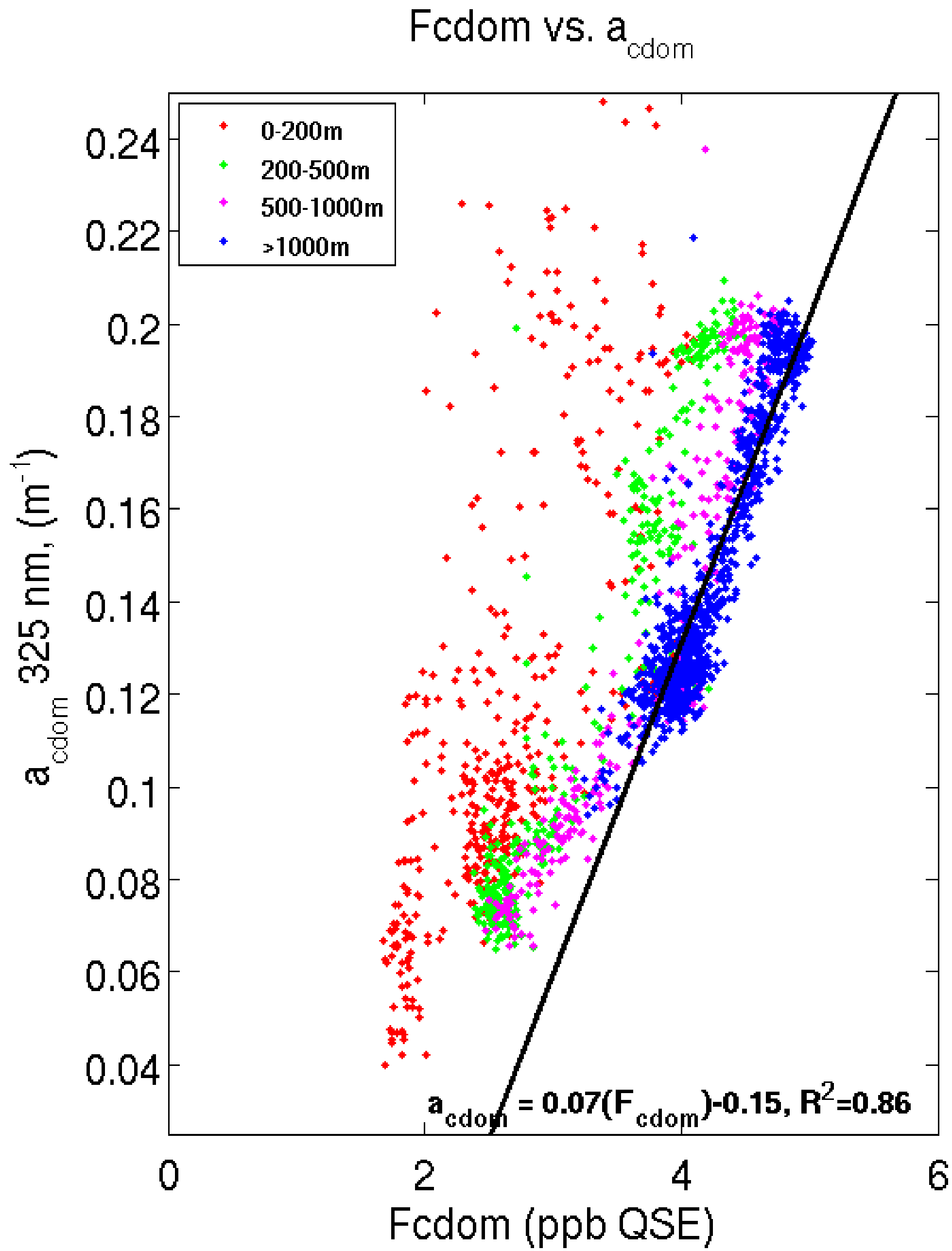
CLIVAR I8/I9

Good correspondence between WETLabs fluorescence & $a_g(325)$ over entire depth range

CDOM and F_{cdom}

(WETLabs ECO)

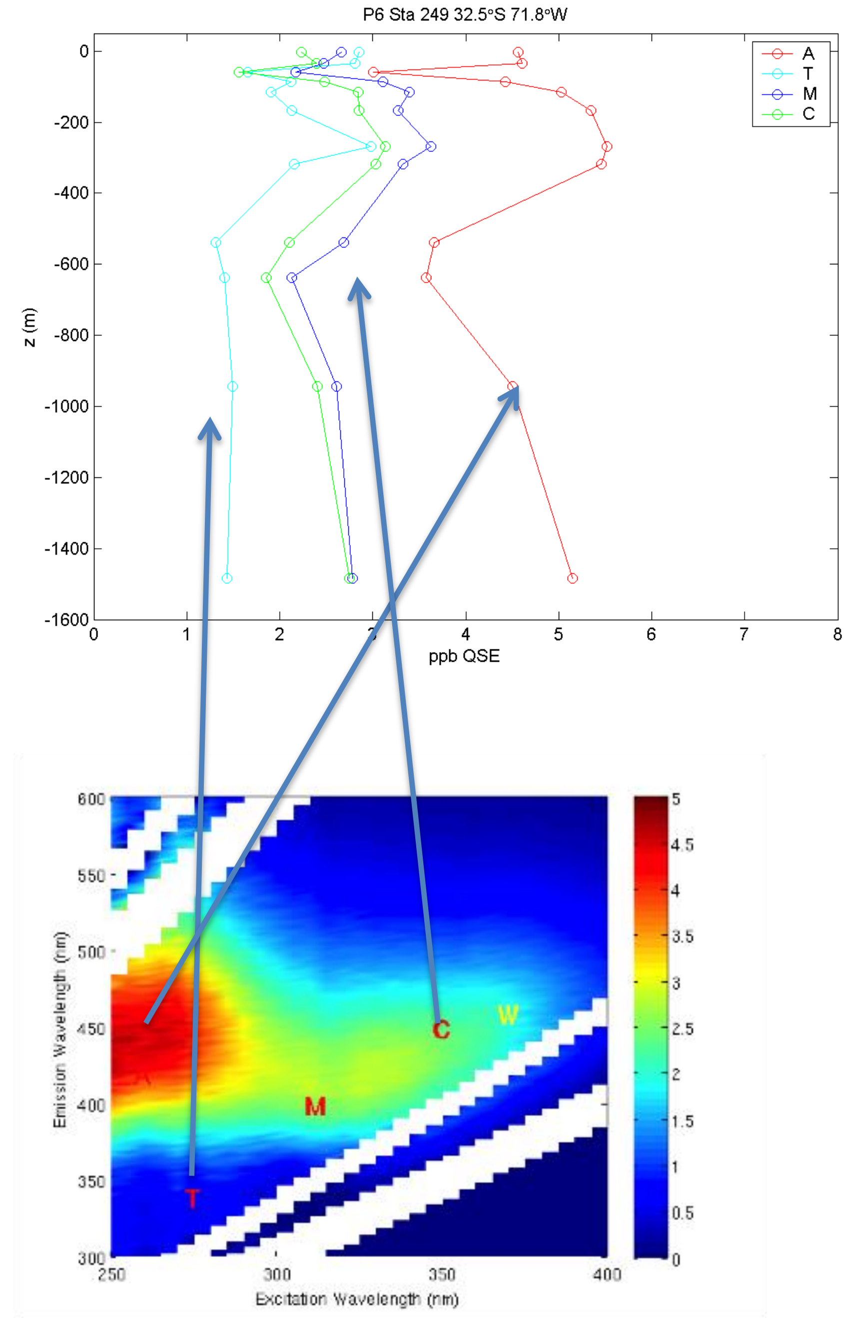
- Largely uncorrelated shallower than 1000m
- Indicates different CDOM composition in surface and sub-thermocline waters
- **CDOM fluorescence does not equal CDOM absorption**
- **Suggests $N_{fluorophores} < N_{chromophorces}$**



CDOM and F_{cdom}

(EEM Spectroscopy)

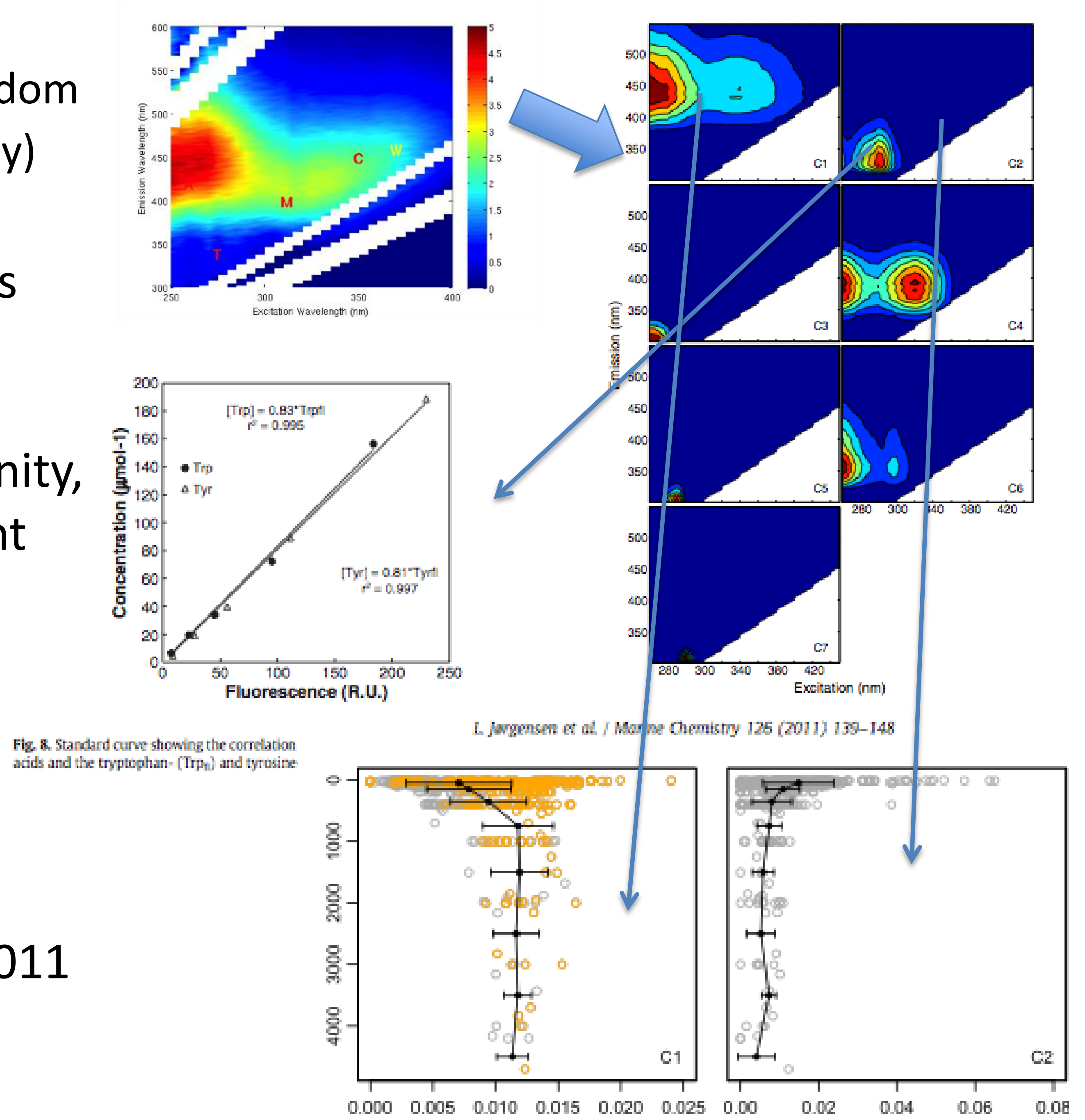
- “Protein-like” fluorescence shows different profiles than “humic” fluorescence
- “Humic” fluorescence has similar depth profiles from different parts of the matrix
- More sophisticated analysis (PARAFAC) reveals additional patterns that correlate to other compositional indicators (e.g. Jørgensen et 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

Outline

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- CDOM distribution and dynamics in the global ocean
- CDOM – climate connections
- Research frontiers

Thank You for Your Attention!!

Thanx to Norm Nelson, Chantal Swan, Julia Gauglitz, Jon Klamberg, Stéphane Maritorena, Craig Carlson, Dennis Hansell, Stu Goldberg, Bryan Franz, Chuck McClain, Mike Behrenfeld and many others…