



# CDOM on CLIVAR

## Ocean Optics and Biogeochemistry on the U.S. CO<sub>2</sub>/CLIVAR Repeat Hydrography Project

**Norm Nelson, Dave Siegel, Craig Carlson  
Chantal Swan, Stu Goldberg, Stéphane Maritorea  
*UC Santa Barbara***

Ocean Color Research Team 2007

# Outline

- Objectives
- Background on global CDOM research -- prior results summary
- Background on CLIVAR/CO<sub>2</sub> Repeat Hydrography Project
- CDOM Project Activities on CLIVAR -- Measurements and Methods
- Some Results from Atlantic and Pacific
- Ongoing and future activities

# The inevitable “Why CDOM” slide

- Light absorption by CDOM in the blue & UV is comparable to or greater than particle absorption in many open ocean regimes -- CDOM dynamics differ from particle (phytoplankton) dynamics.
- CDOM has a major impact upon ocean color -- influences retrieval of chlorophyll, penetration of PAR and UV to depth
- CDOM sensitizes photochemical reactions involving climate-relevant atmospheric trace gases (DMS, OCS, CO)

# More “Why CDOM”

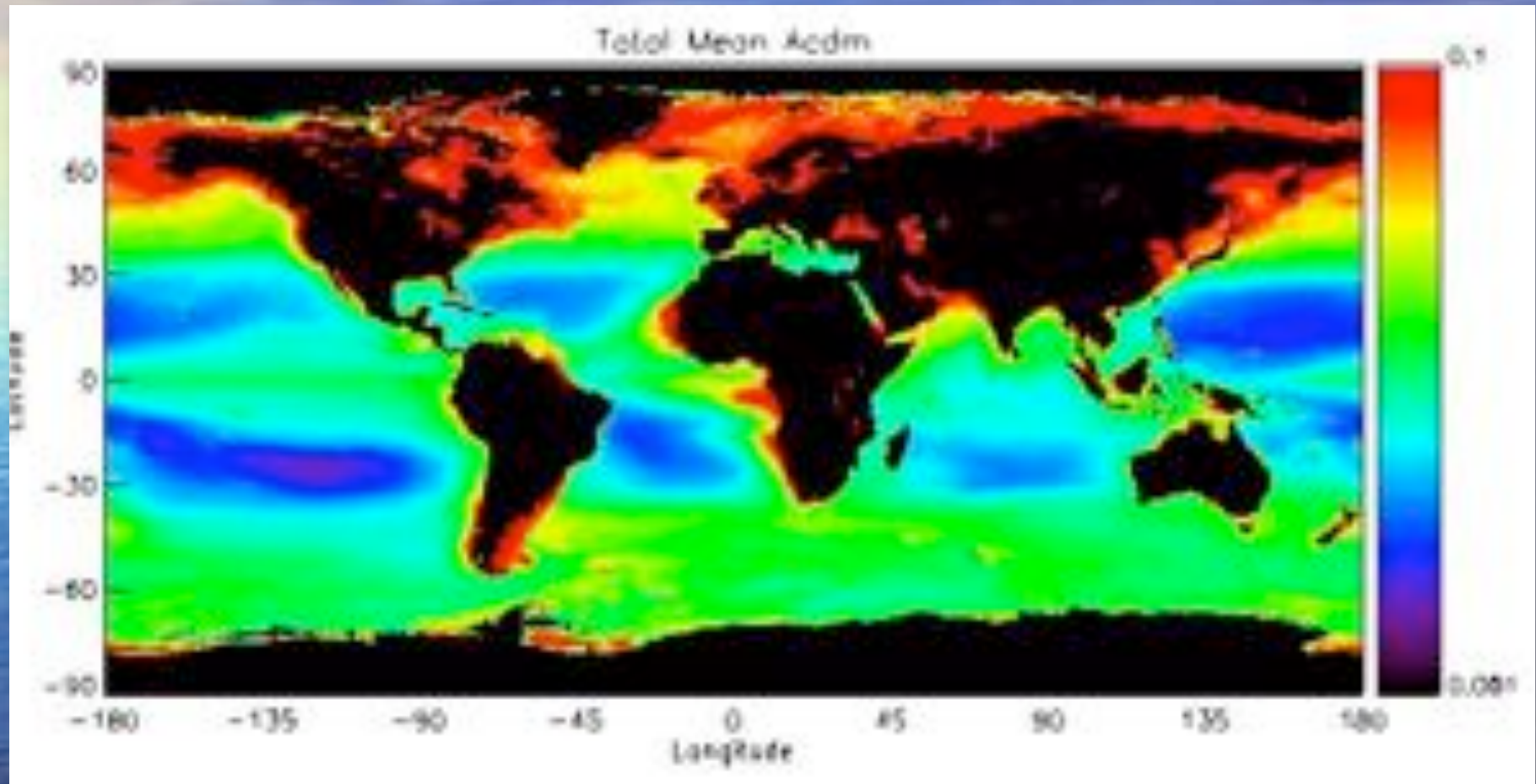
- CDOM reflects a (small) portion of the DOM pool with dynamics that differ from the DOM pool overall. This suggests the use of CDOM characteristics as an indicator of DOM diagenetic state.
- CDOM is found at all depths in the ocean and has very slow dynamics, further suggesting its application as a tracer of circulation and water mass renewal. Only deep ocean tracer so far with a remotely-sensible surface boundary condition ...
- It's the most important stuff in the ocean

# UCSB Global CDOM Project

## Goals

- Quantify global distribution of CDOM  
*Surface, intermediate, and deep water*
- Determine physical and biological factors controlling CDOM distribution
- Apply knowledge gained to problems of ocean circulation and DOM characterization and cycling
- Collect calibration and validation data for ocean color models

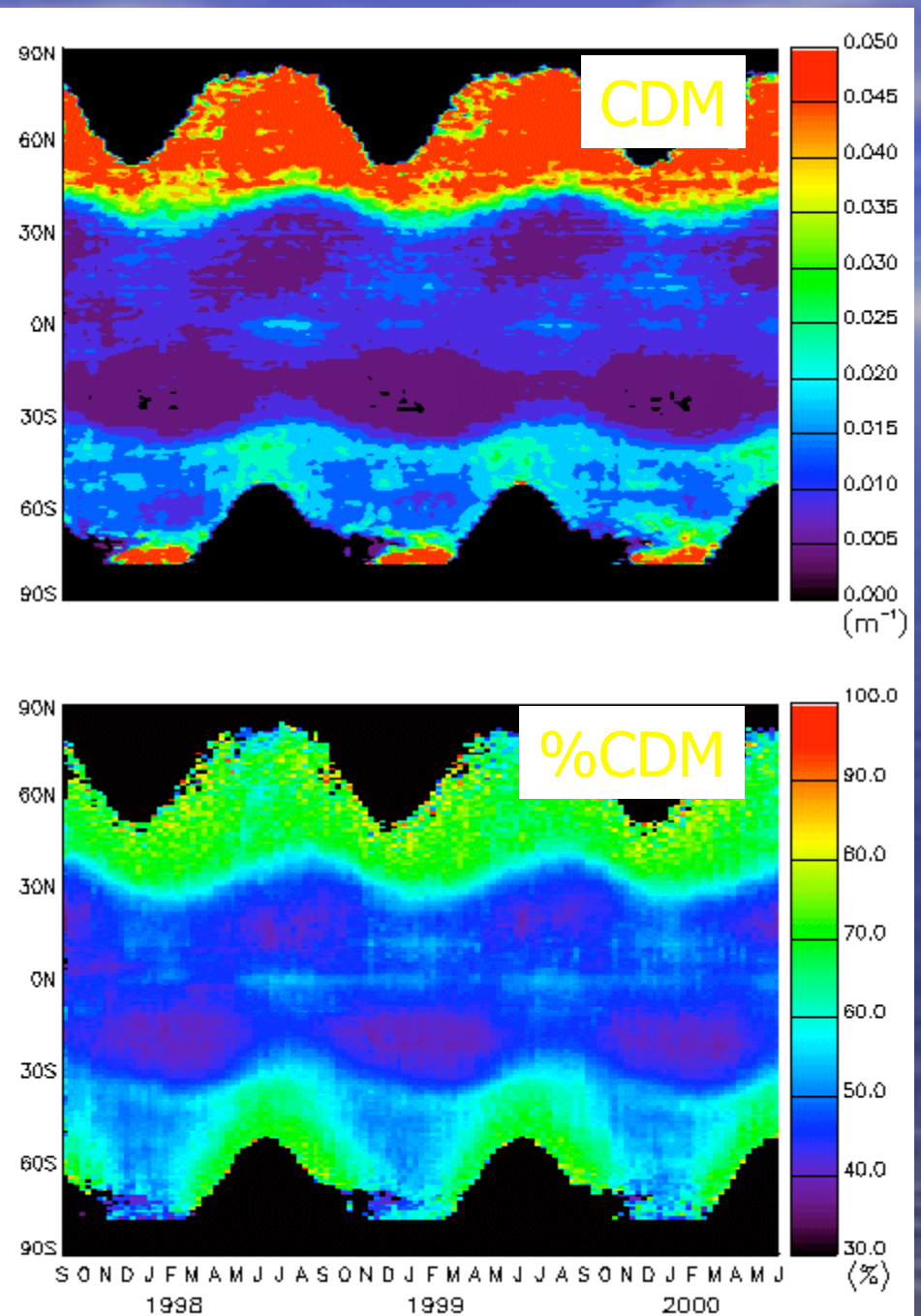
# Global CDOM (CDM) Distribution



Siegel et al. [2005] JGR

# Seasonal CDOM Cycle

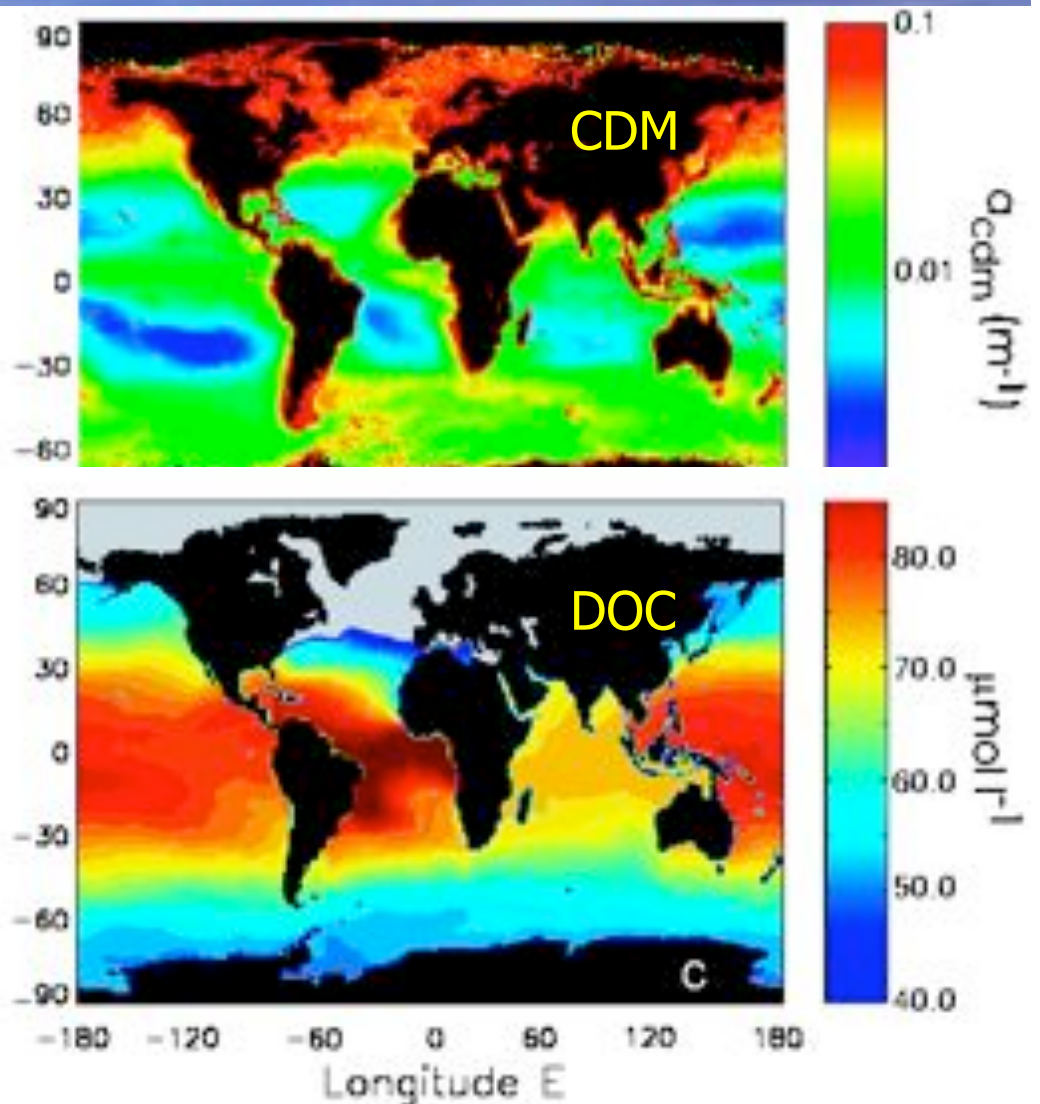
- Seasonal changes at most latitudes
- Lower in summer
- Reduced in tropics
- Higher towards poles
- Hemispheric asymmetry



# 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 Dynamics at BATS

BATS data

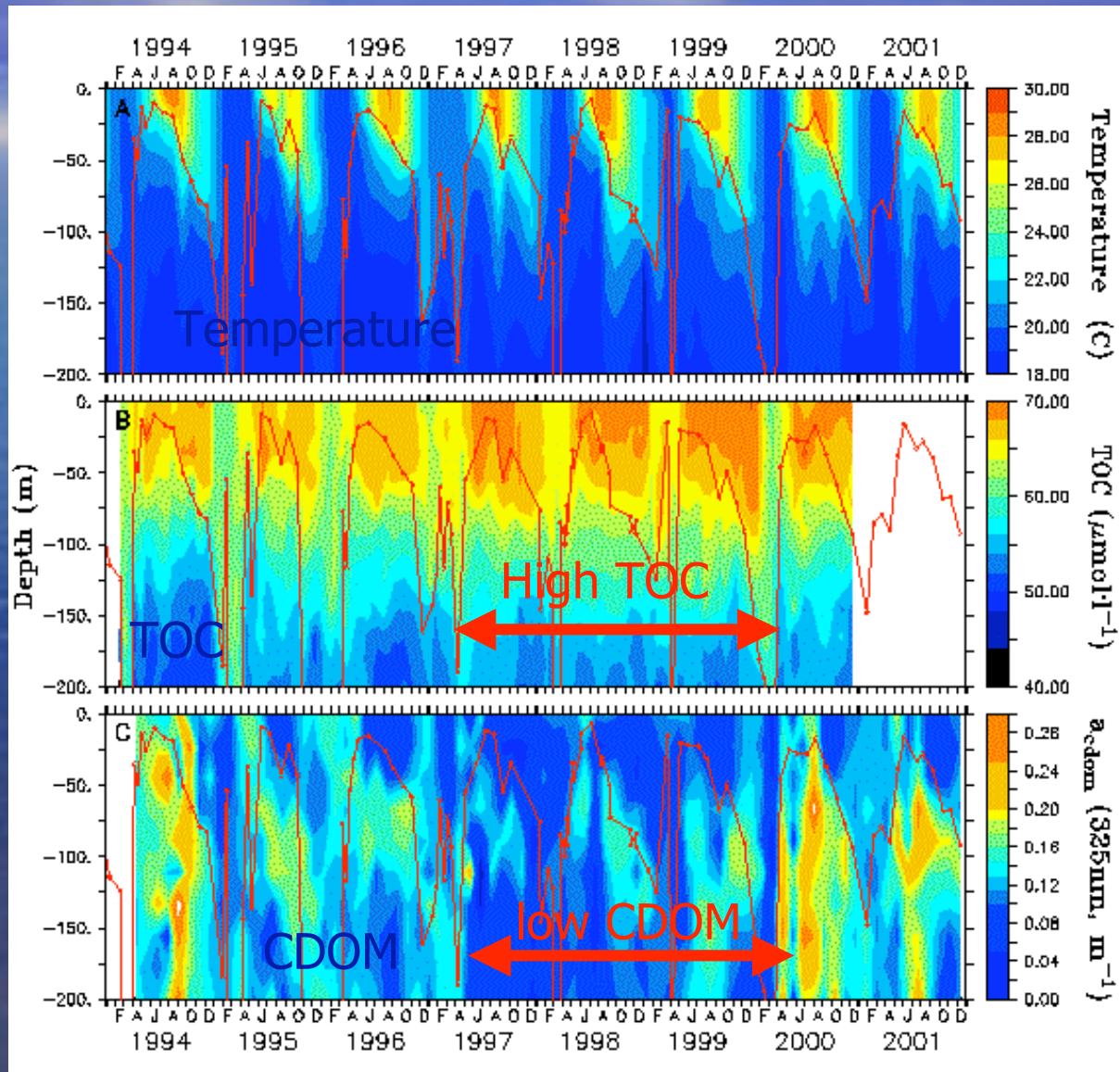
Temp/TOC/CDOM

Control of CDOM

profile related to  
bleaching and local  
production

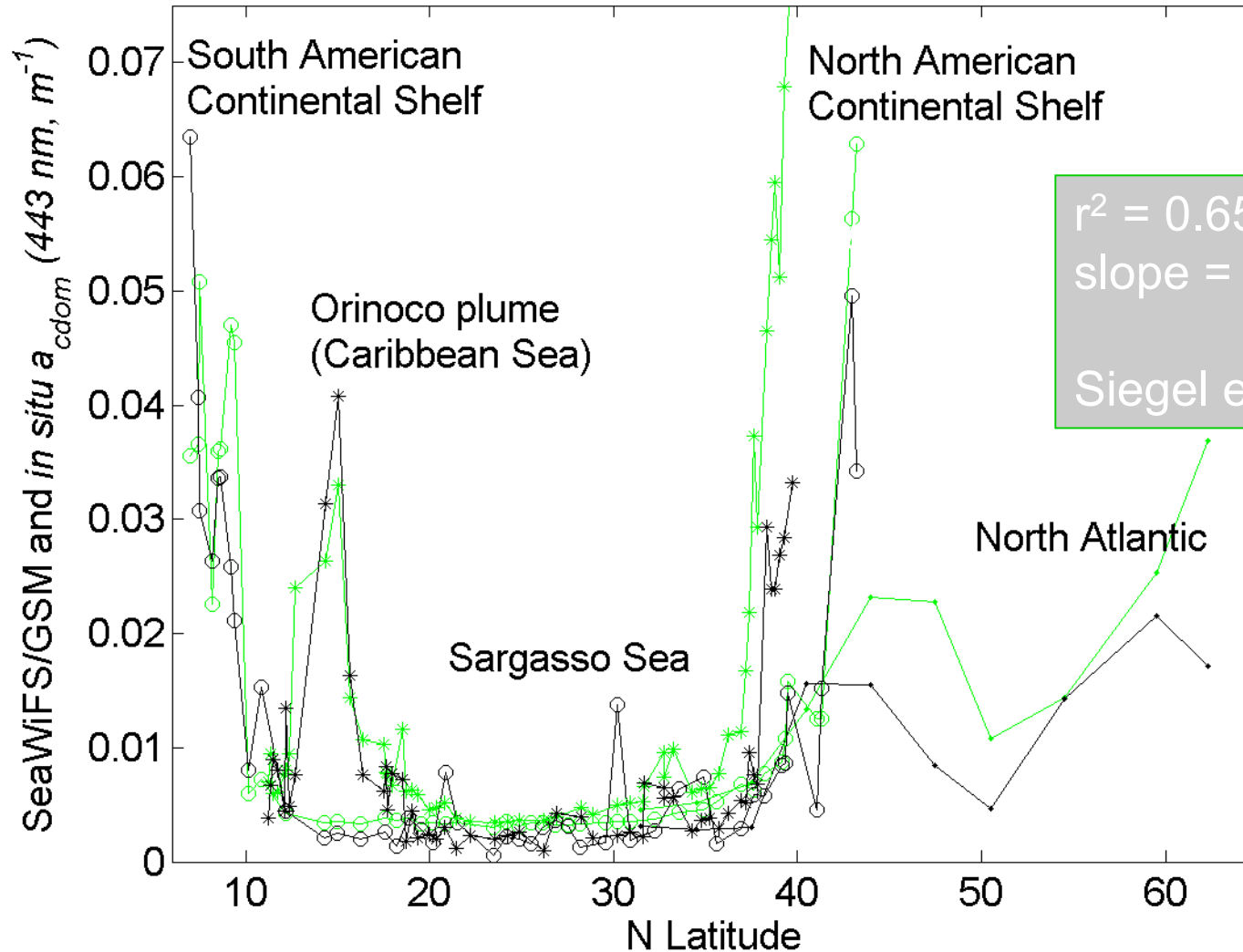
CDOM low from  
1997-1999

Related to water  
mass renewal?



# Surface CDOM & SeaWiFS

2003 North Atlantic Sections: GSM (green), *in situ* (black)



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

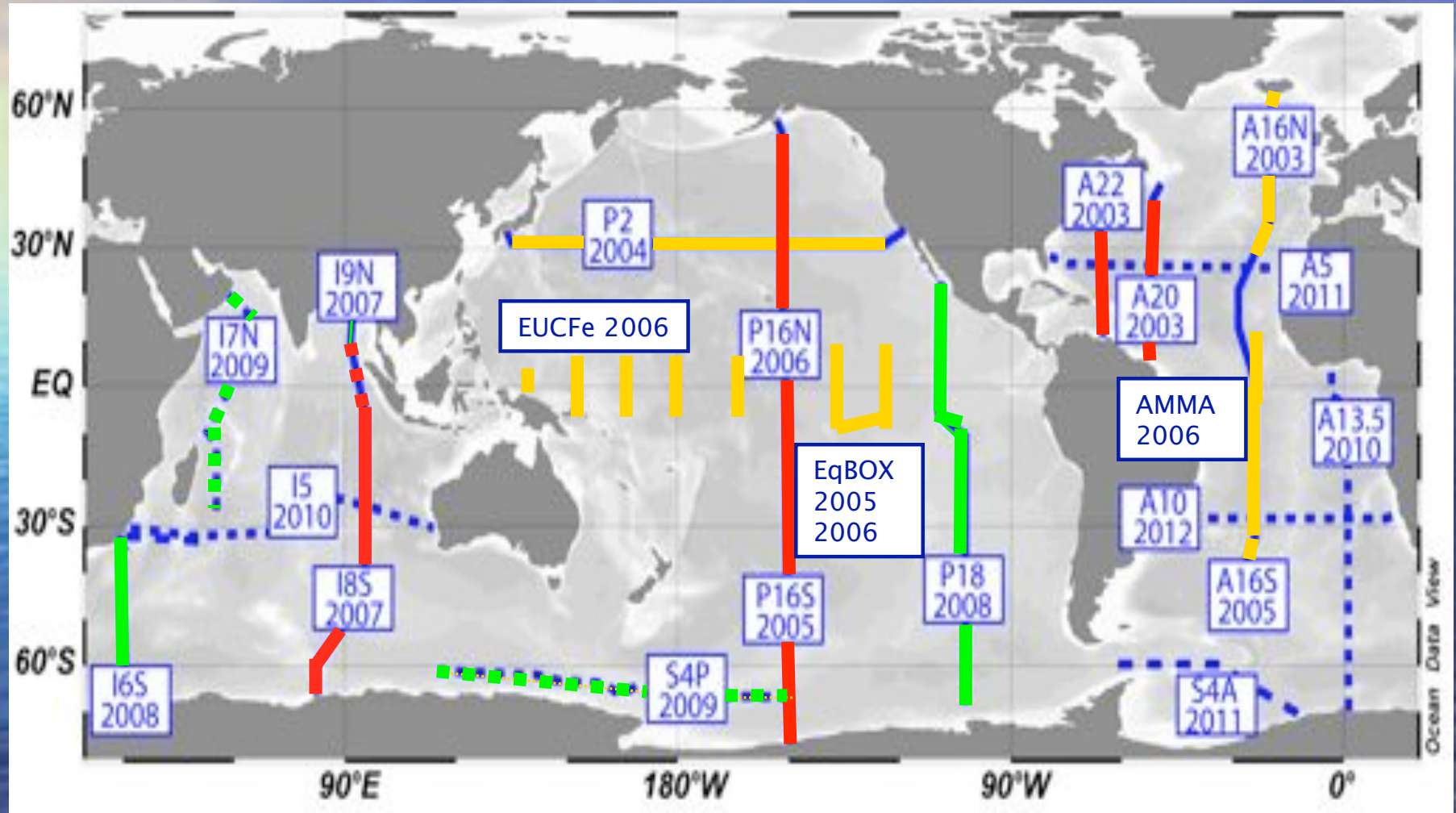
Siegel et al. [2005] JGR

# U.S. CLIVAR/CO<sub>2</sub> Repeat Hydrography Project

<<http://ushydro.ucsd.edu/>>

- Document in time and space, changes in ocean properties and circulation related to climate change
- Core measurements include T-S-O<sub>2</sub>, nutrients, DIC, DOC/N, CFC, He/<sup>3</sup>H, currents
- Repeat selected WOCE Hydrography Project sections with new technology and new measurements including **trace metals, pH, and CDOM and other ocean color related parameters** -- Stations every 30-60 nmi along sections.

# Global CDOM Project Sections



# UCSB Global CDOM Project Measurements & Methods *Once Daily Bottle Samples*

- CDOM Profile (surface - bottom)
- Chlorophyll Profile (top 250m)
- HPLC Samples (surface)  
(NASA Chls/carotenoids, UNH MAA)
- Particulate Absorption Sample (surface)
- DOM quality profile (top 1000m)
- Bacterial counts (full) & BP (top 250)



# UCSB Global CDOM Project Measurements & Methods *Occasional Bottle Samples*



- Large-volume (~2L) samples for CDOM dynamics experiments
  - Photobleaching (Chantal Swan, NASA Grad Student Fellowship)
  - Microbial CDOM Production/Consumption
  - POC/PON for transmissometer calibration

# UCSB Global CDOM Project Measurements & Methods *Profiling instruments*

- On Main Sampling Rosette (every cast)
  - WETLabs ECO CDOM Fluorometer
  - WETLabs C-Star Beam c meter (TAMU)
- Once daily radiometric profile
  - Satlantic MicroPro II with UV and visible  $E_d/L_u$ ,  
SMSR deck reference



# UCSB Global CDOM Project Measurements & Methods *CDOM Analysis At Sea*

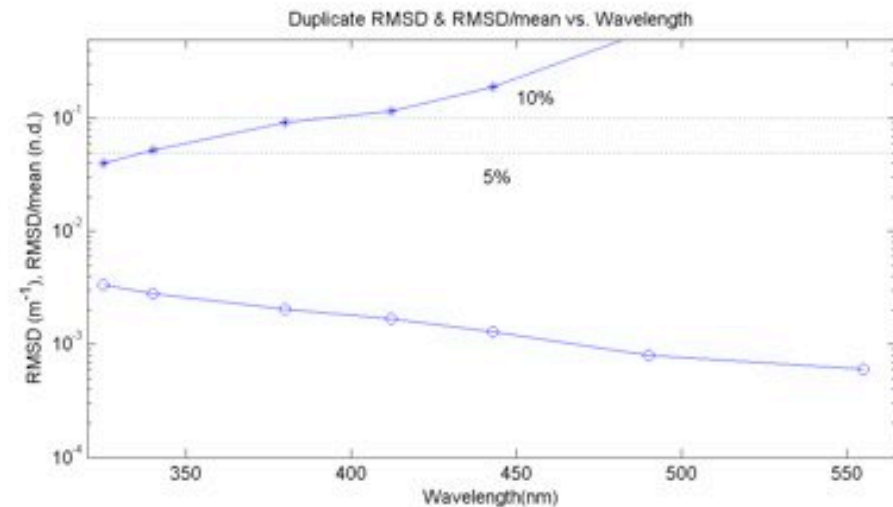
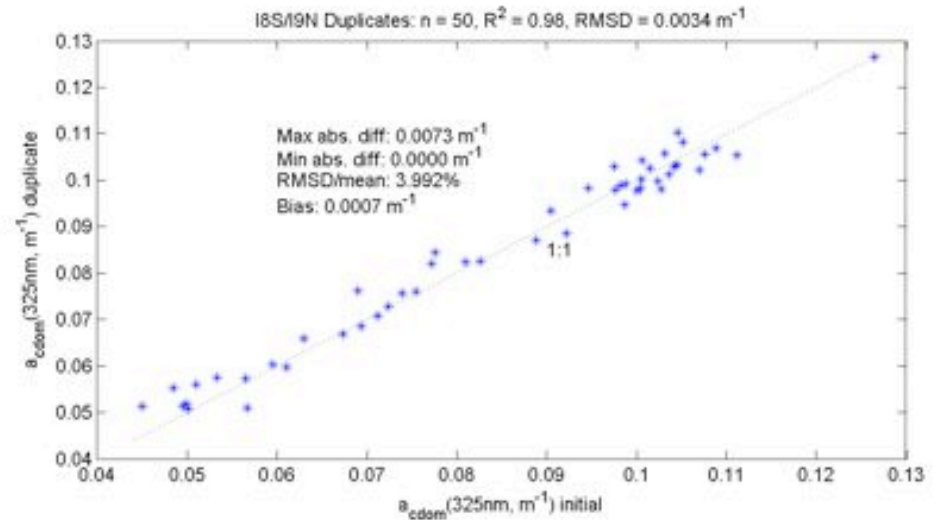
- 200 cm Liquid Waveguide Absorption Cell (UltraPath, WPI Inc)
- Single-beam spectrophotometer with D<sub>2</sub> & Tungsten-halogen light sources, diode-array spectrometer detector
- Fast, low sample volume (2 min/sample, 30-60 ml)
- Issues with blanks (refractive index correction, purity of open ocean water can exceed that of best pure water)



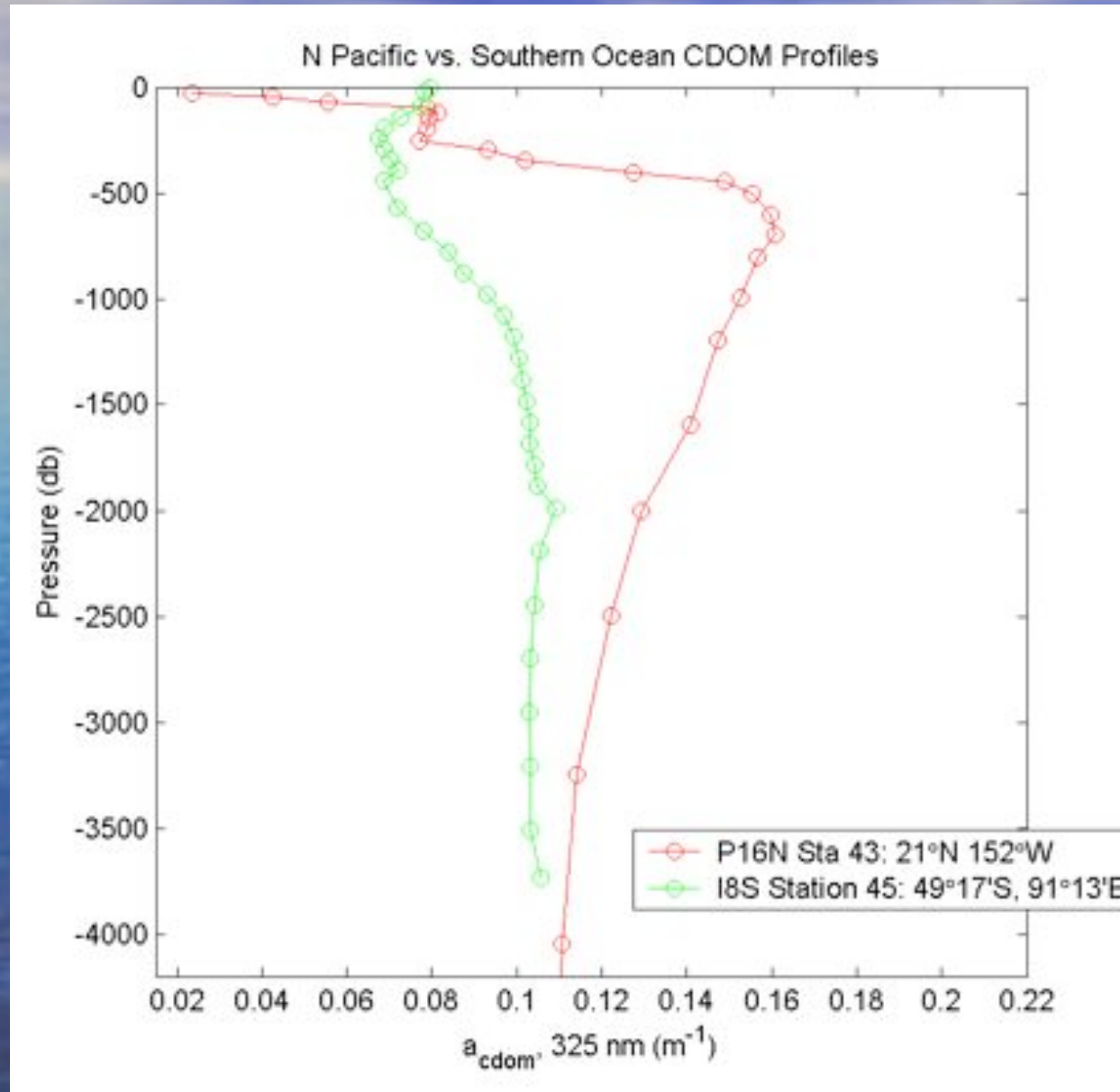


# UltraPath Precision

- Duplicate sample analysis (same Niskin)
- RMS difference at 325 nm:  $0.0034 \text{ m}^{-1}$
- This is  $\sim 4\%$  of mean
- RMS/Mean is between 5 and 10% between 300 and 400 nm
- Longer wavelengths are not as good



# UltraPath Example CDOM Profiles

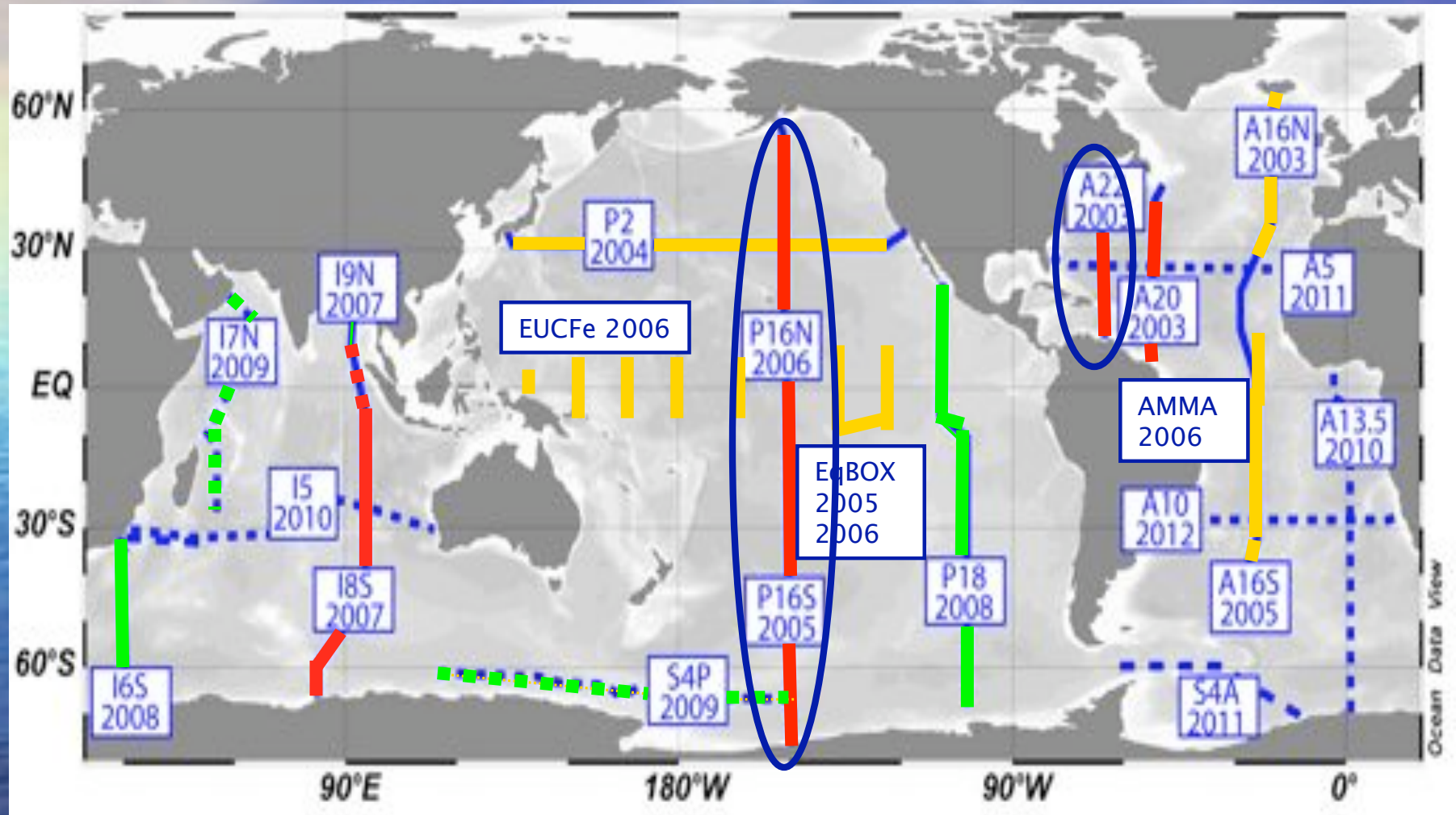


# Selected Project Results

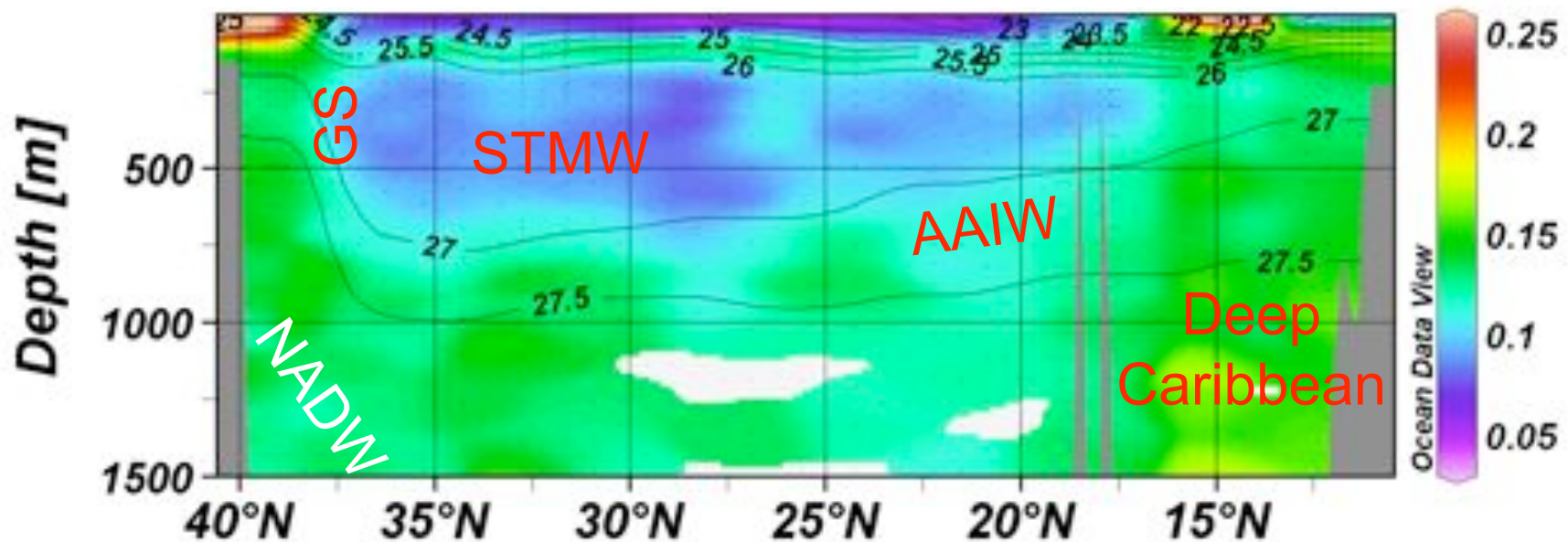
## Distribution of CDOM

- N. Atlantic (S.A. -> N.A. shelves, subtropical)
- Pacific (Antarctic->Alaska)
  
- CDOM in the upper 1000m
- CFC (ventilation age tracer)
- Apparent Oxygen Utilization (quantifies remineralization, a known CDOM source in surface waters)

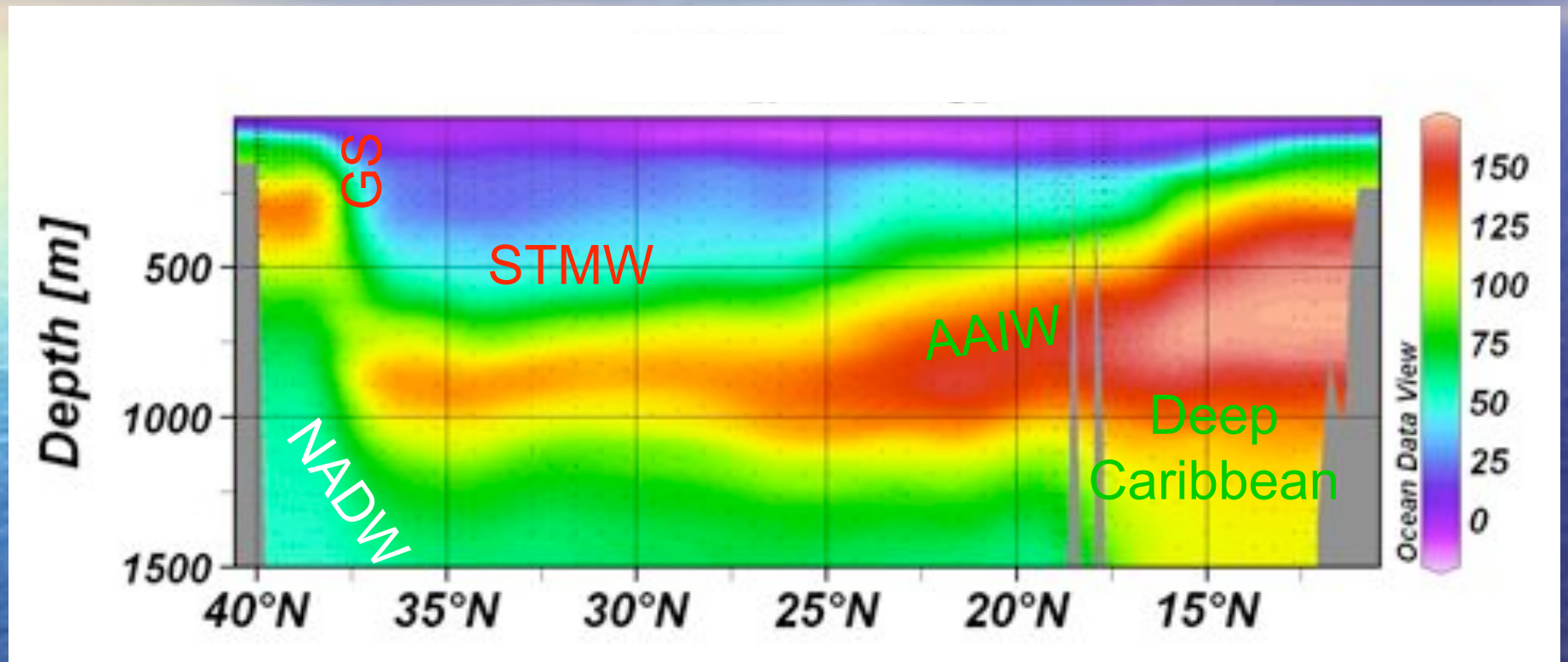
# Results from A22 and P16



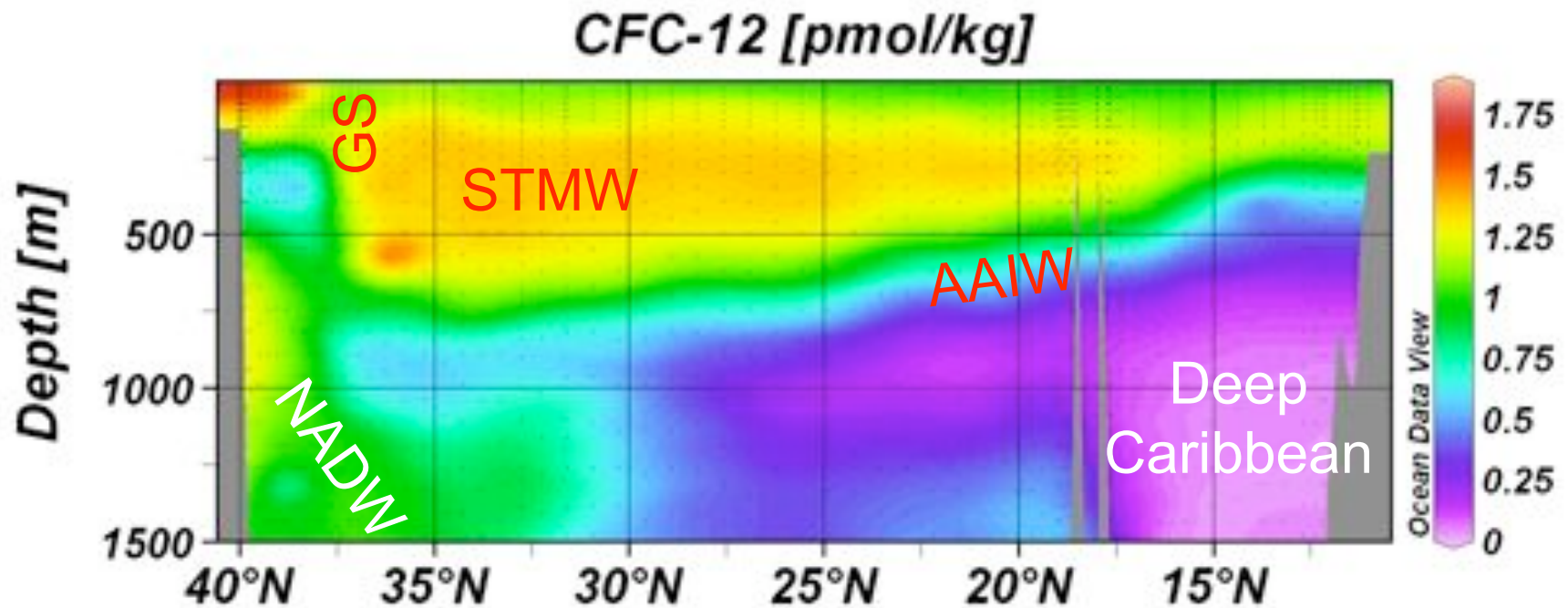
# Atlantic A22 CDOM



# Atlantic A22 AOU



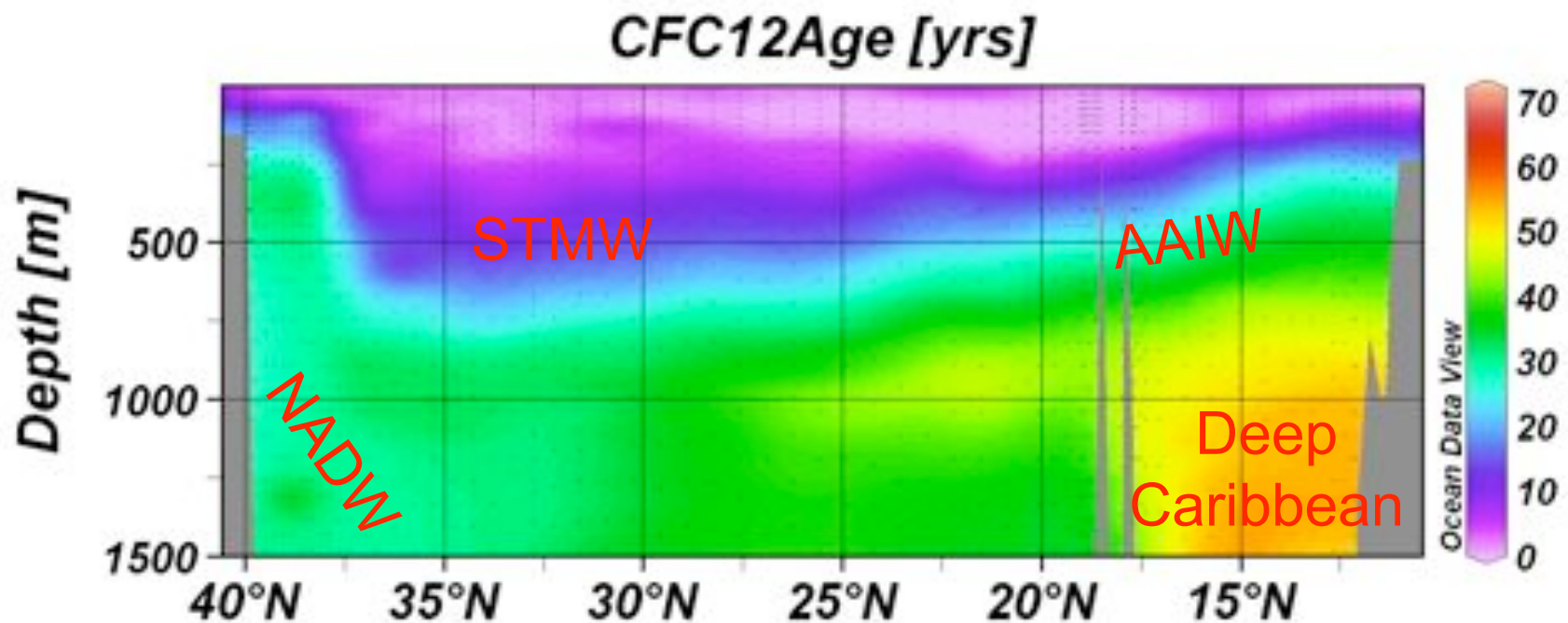
# A22 CFC-12 Concentrations



High CFC's – recently ventilated waters

Low CFC's – old water

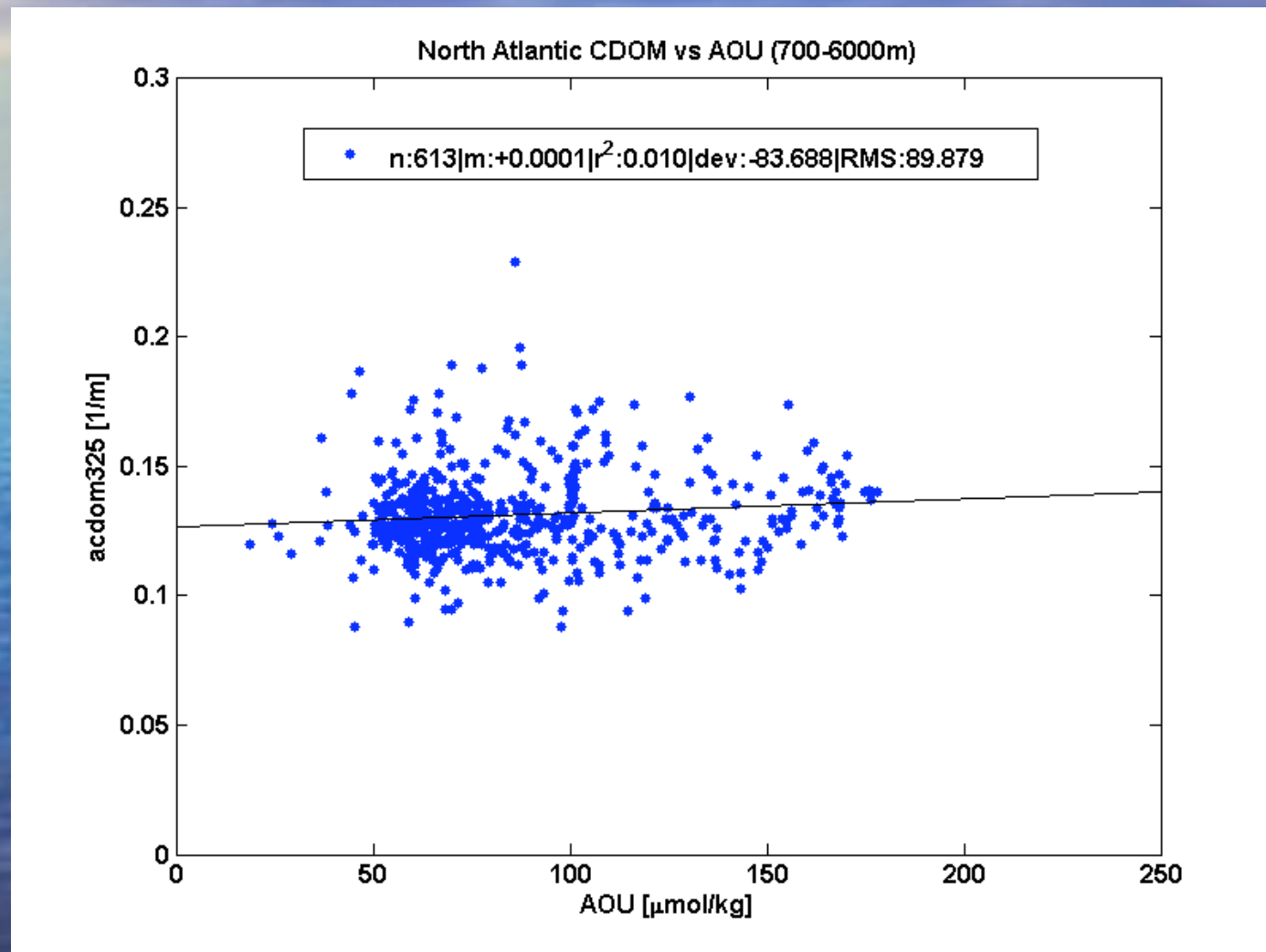
# Atlantic A22 CFC-12 Age



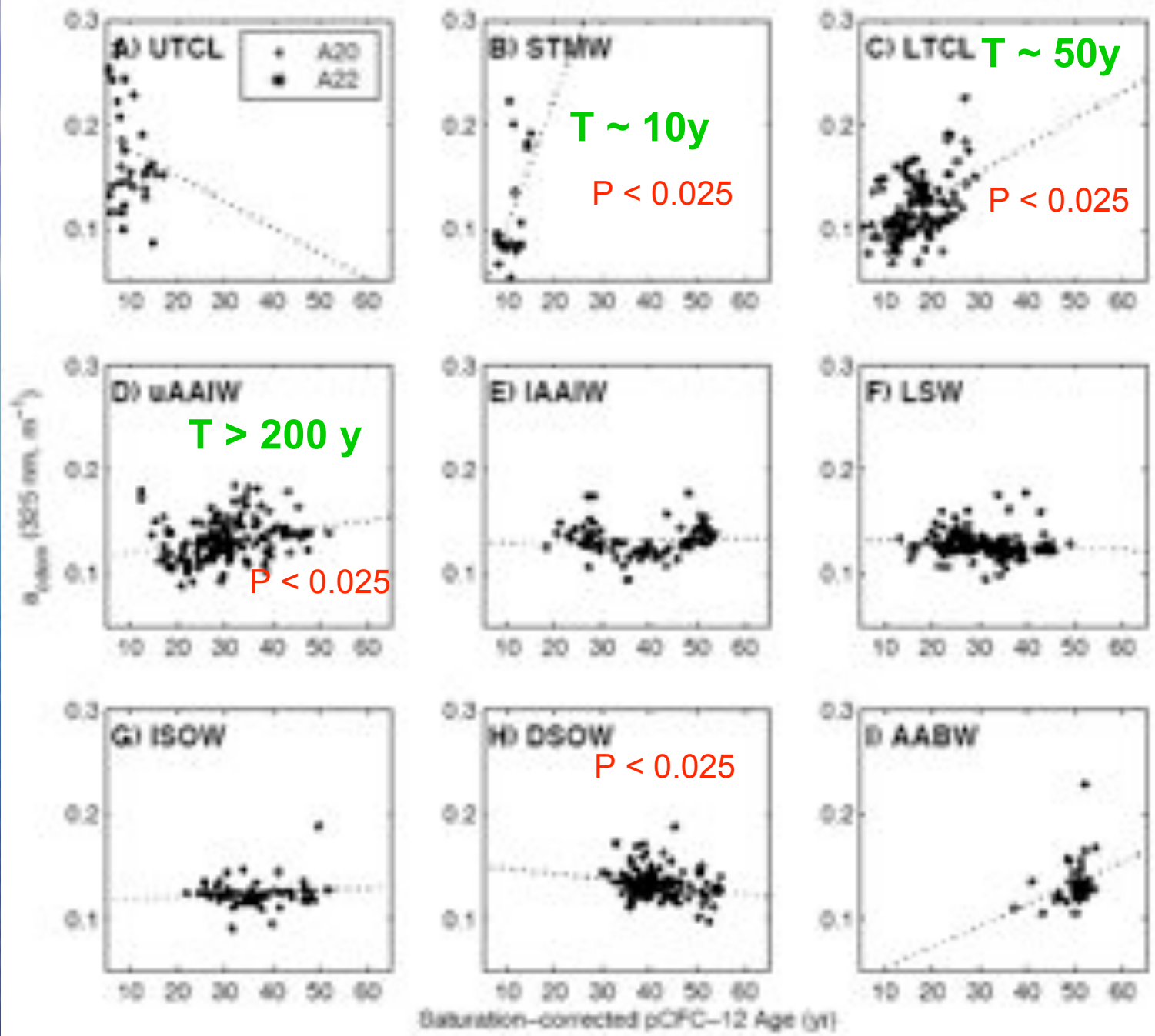
Age calculations by Bill Smethie & Samar Khatiwala [LDEO]



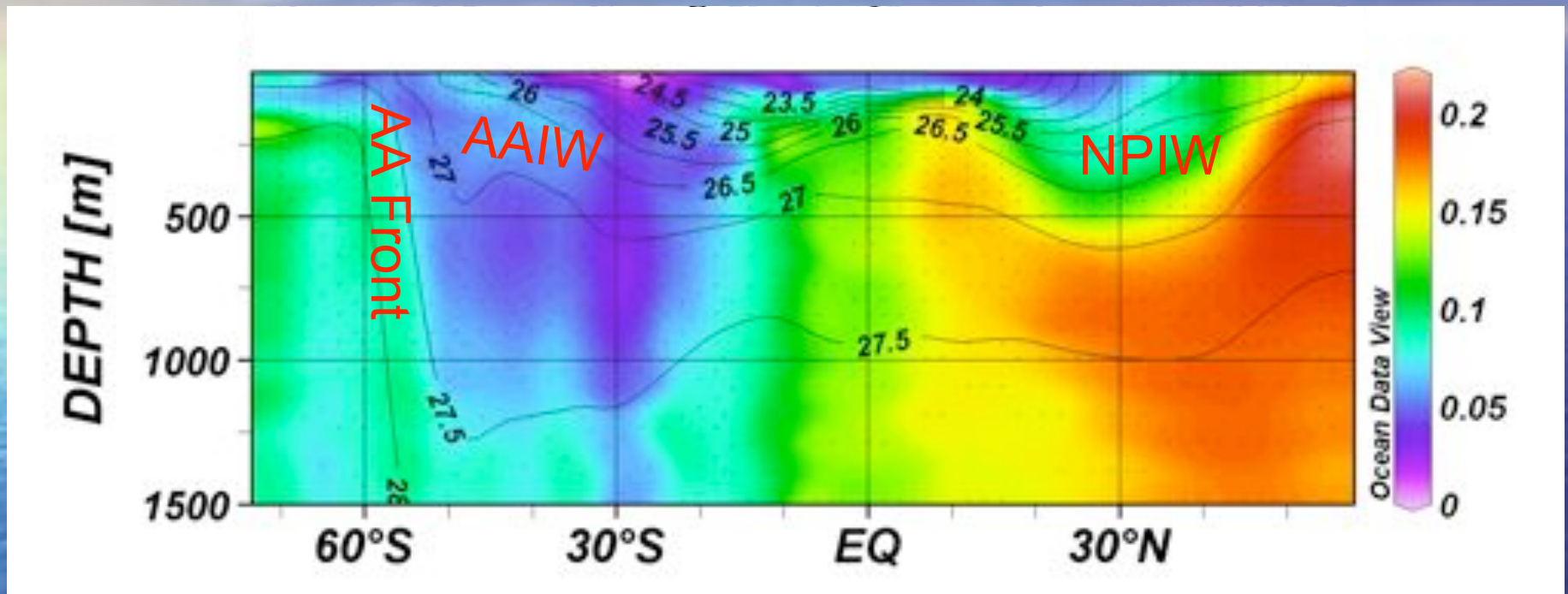
# North Atlantic AOU vs. CDOM



# Age vs. CDOM

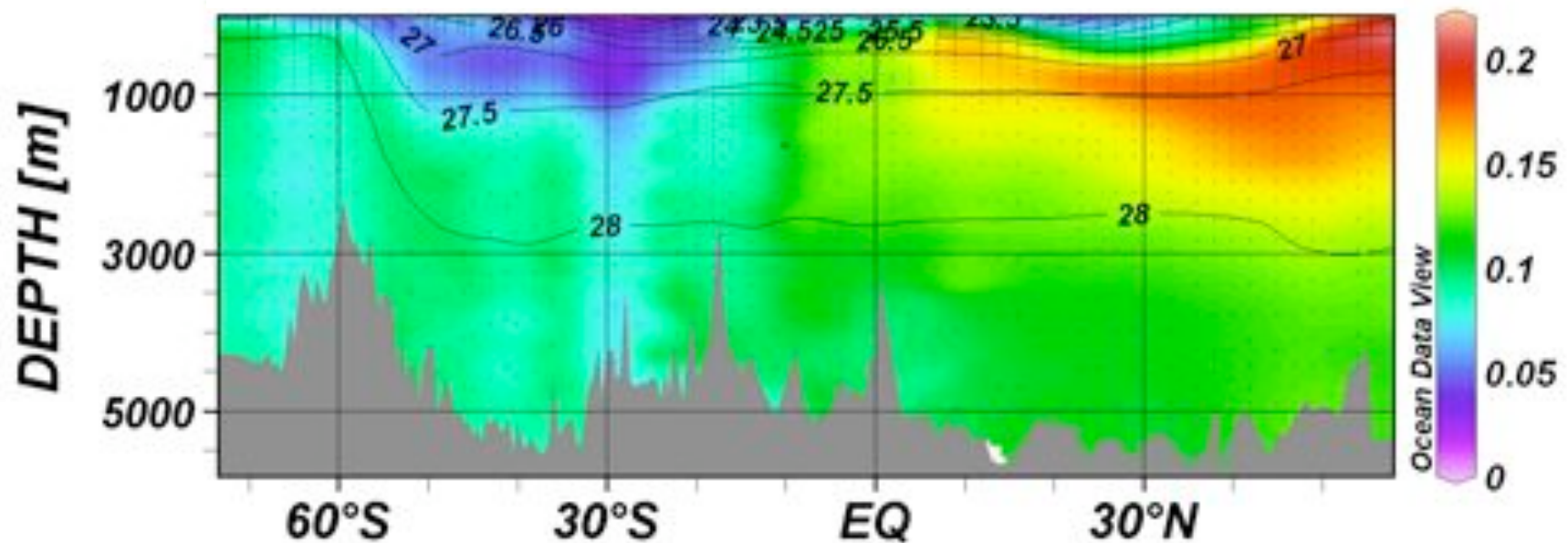


# Pacific P16 CDOM



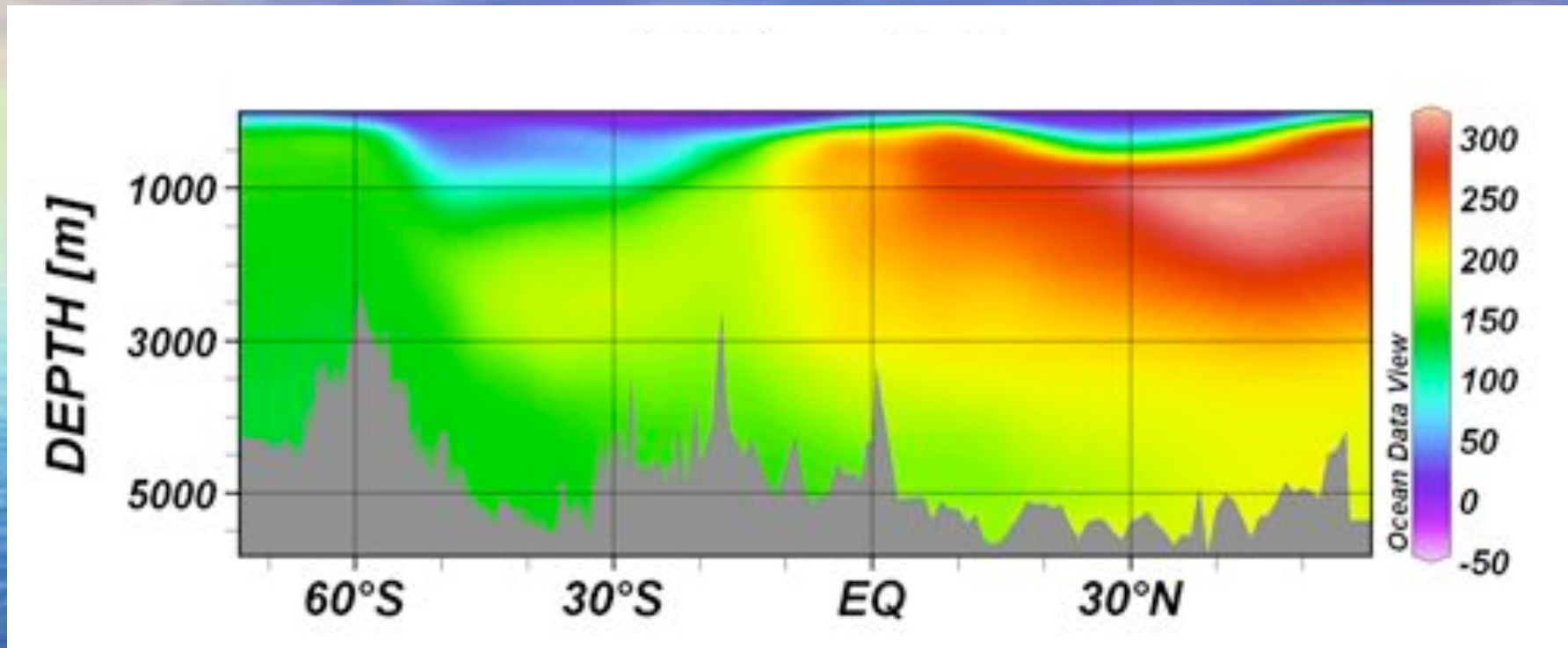
- Low CDOM in SH subtropical gyre
- Very high in NH thermocline
- Some subducting water mass signatures are seen in CDOM

# Pacific P16 CDOM



- SH Subtropical CDOM low extends thru upper 1000 m
- High CDOM in NH thermocline

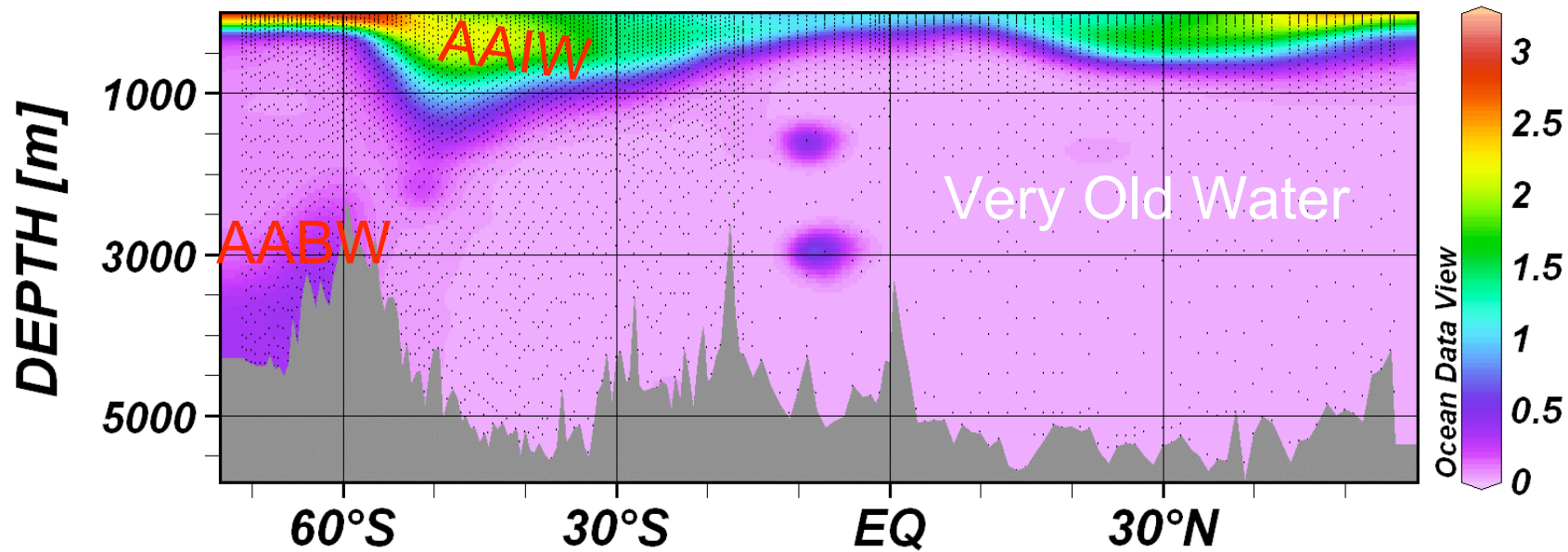
# Pacific P16 AOU



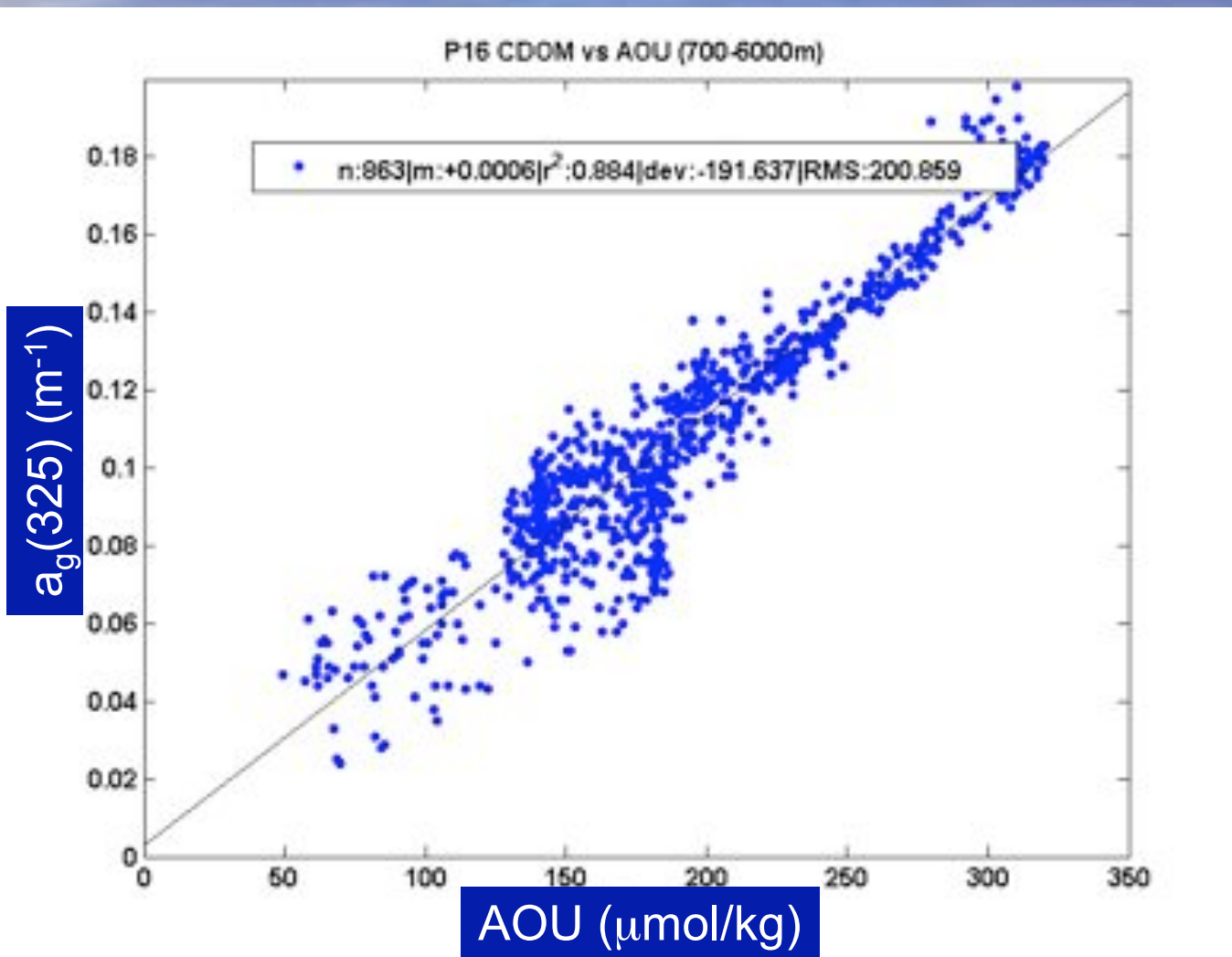
Apparent Oxygen Utilization =  $O_{2\text{sat}} - O_2$

Measure of *past* remineralization of organic carbon

# Pacific P16 CFC-12



# Pacific AOU vs. CDOM



# Atlantic vs. Pacific CDOM

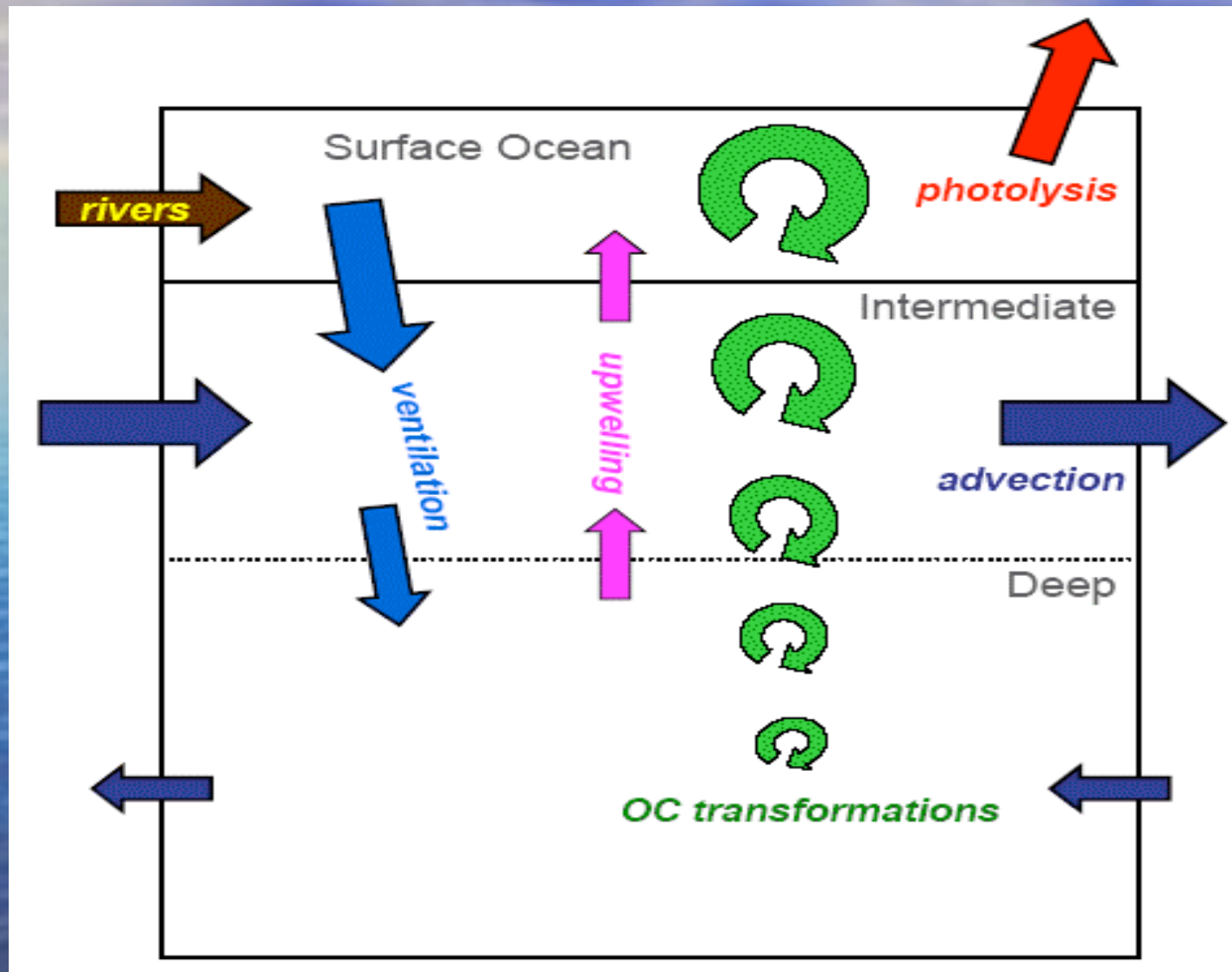
- Significant spatial and depth gradients
- CDOM distribution is relatable to water mass distribution

But ...

- Atlantic profiles do not show remineralization-correlated accumulation of CDOM like in the N. Pacific



# CDOM Conceptual Model - Ocean Scale



# CDOM Conceptual Model - Whole Ocean Scale

It's a simple ratio of time scales -  $T_{\text{phys}}/T_{\text{bio}}$

Small  $T_{\text{phys}}/T_{\text{bio}}$

Slow ventilation & Fast biology

\* Pacific Ocean

Large  $T_{\text{phys}}/T_{\text{bio}}$

Fast ventilation & Slow biology

\* North Atlantic Ocean

# Selected Project Results

## North Atlantic CDOM/DOM Diagenesis

*Nelson et al. Deep-Sea Res. I in press*

*<doi:10.1016/j.dsr.2007.02.006>*

- CFC age estimation based on atmospheric CFC history and % saturation at origin (Smethie and Khatiwala, LDEO)
- CDOM and CFC Age compared by water mass component
- DOC-Specific absorption of CDOM

$$a_{\text{cdom}}^*(325)$$

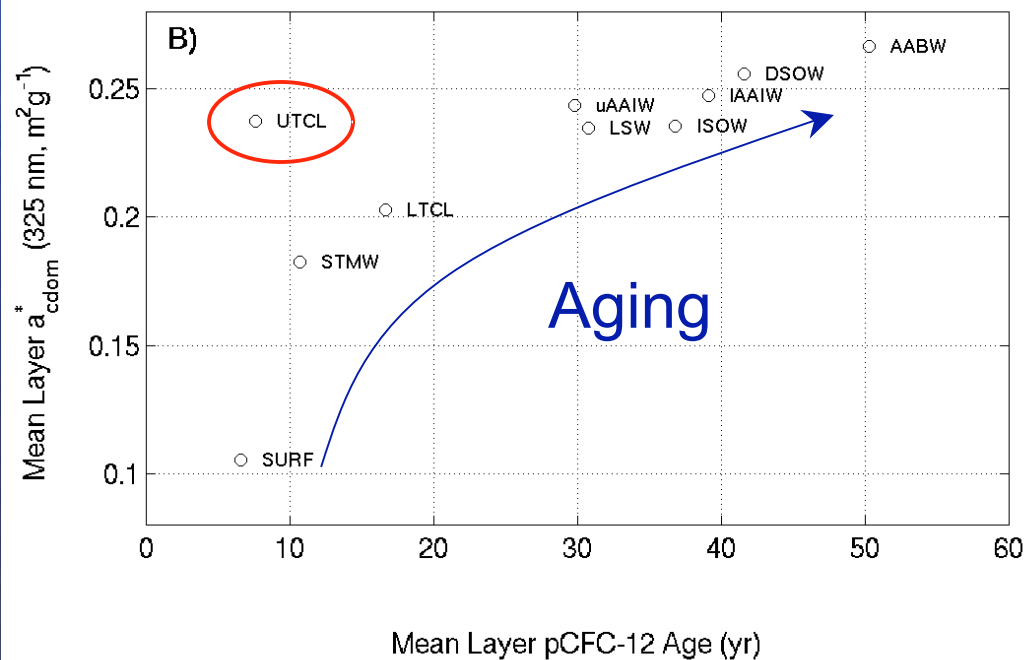
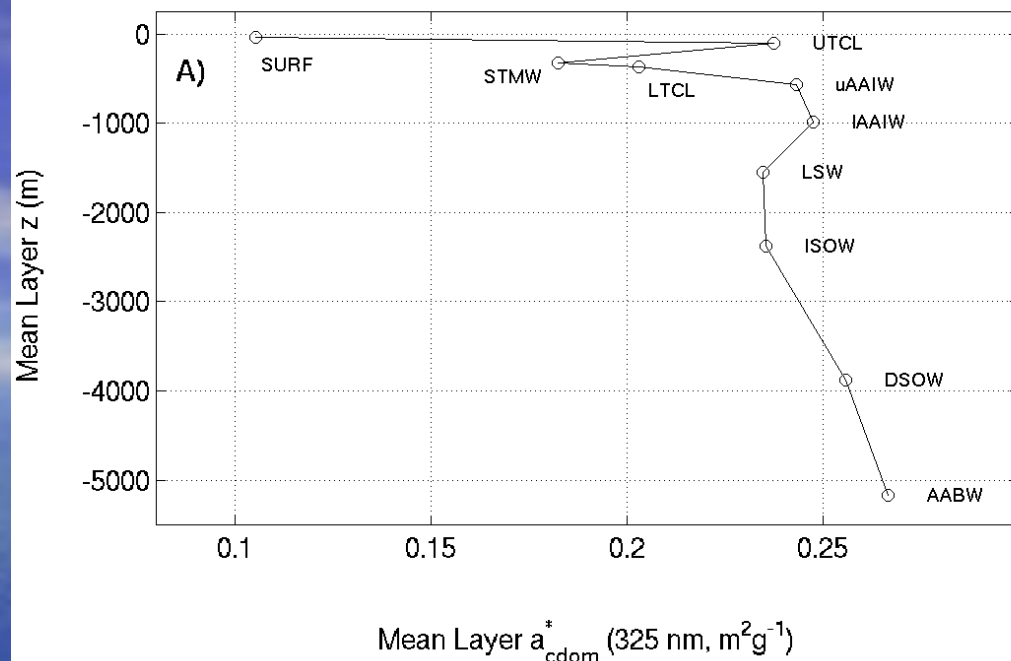
$$a_{\text{cdom}}^* = \text{CDOM} / \text{DOC}$$

(units  $\text{m}^2\text{g}^{-1}$ )

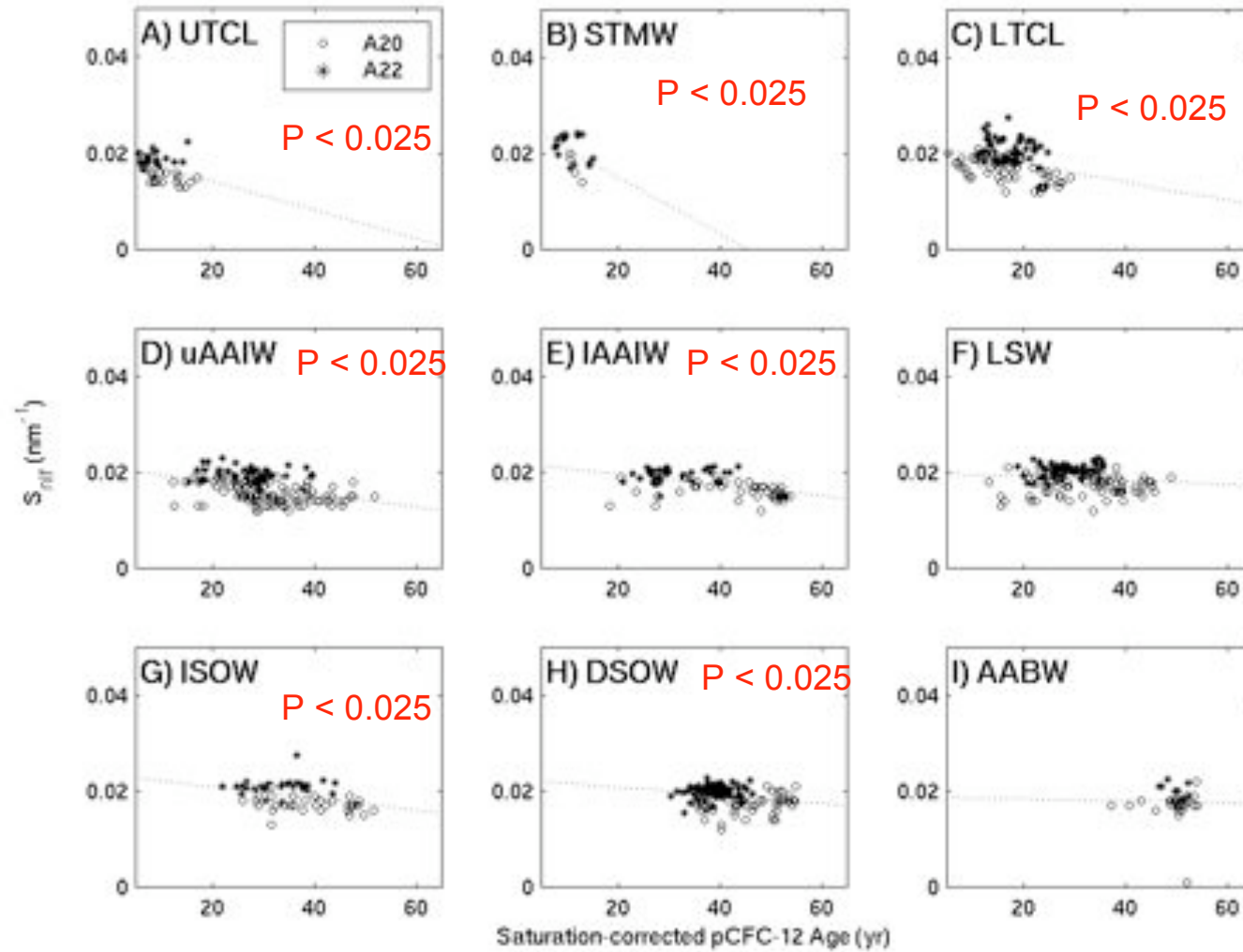
Upper layers bleaching  
& production signals

$a_{\text{cdom}}^*$  increases w/  
depth & age

CDOM is more  
recalcitrant than bulk  
DOC



# Diagenesis of CDOM spectral characteristics



# Summary

- Global CDOM distribution reflects not only local input, production and removal processes but also larger-scale features of ventilation and remineralization.
- CDOM represents a (small) portion of the DOM pool that resists remineralization on decadal time scales and is therefore useful as a semiconservative circulation tracer and indicator of DOM diagenesis.

# Ongoing and future work

- Completion of global survey (see map) (in collaboration with GSFC cal/val group)
- Photobleaching of CDOM at open ocean concentrations (Chantal Swan)
- Relationships between DOM quality/composition (e.g. carbohydrate composition) and CDOM (Stu Goldberg)
- CDOM characterization using fluorometric techniques -- archived and new samples, profiling (ECO) and (lab) spectrofluorometers

# Acknowledgments



- NASA OBB & NSF Chem Oce
- CLIVAR/CO2 Repeat Hydro Program  
(*Jim Swift, Lynne Talley, Dick Feely, Rik Wanninkhof, Rana Fine*)
- UCSB Field Teams: Dave Menzies, Jon Klamberg, Meredith Meyers, Ellie Wallner, Meg Murphy
- Bill Landing (FSU) and Chris Measures (UHI) (Water samples @ sea)
- Ru Morrison & Mike Lesser, UNH (MAA analysis)
- Bill Smethie, Samar Khatiwala, LDEO (CFC Age analysis)
- Dennis Hansell & Team, U Miami (Sampling and collaboration)
- Wilf Gardner and Team, TAMU (C-Star transmissometer)
- Mike Behrenfeld and Team, OSU (Equatorial BOX project)
- Erica Key and Team, U Miami (AMMA-RB 2006)
- Jim Murray and Team, UW (EUCFe 2006)
- *R/Vs Brown, Knorr, Revelle, Melville, Thompson, Ka'i, Kilo Moana*



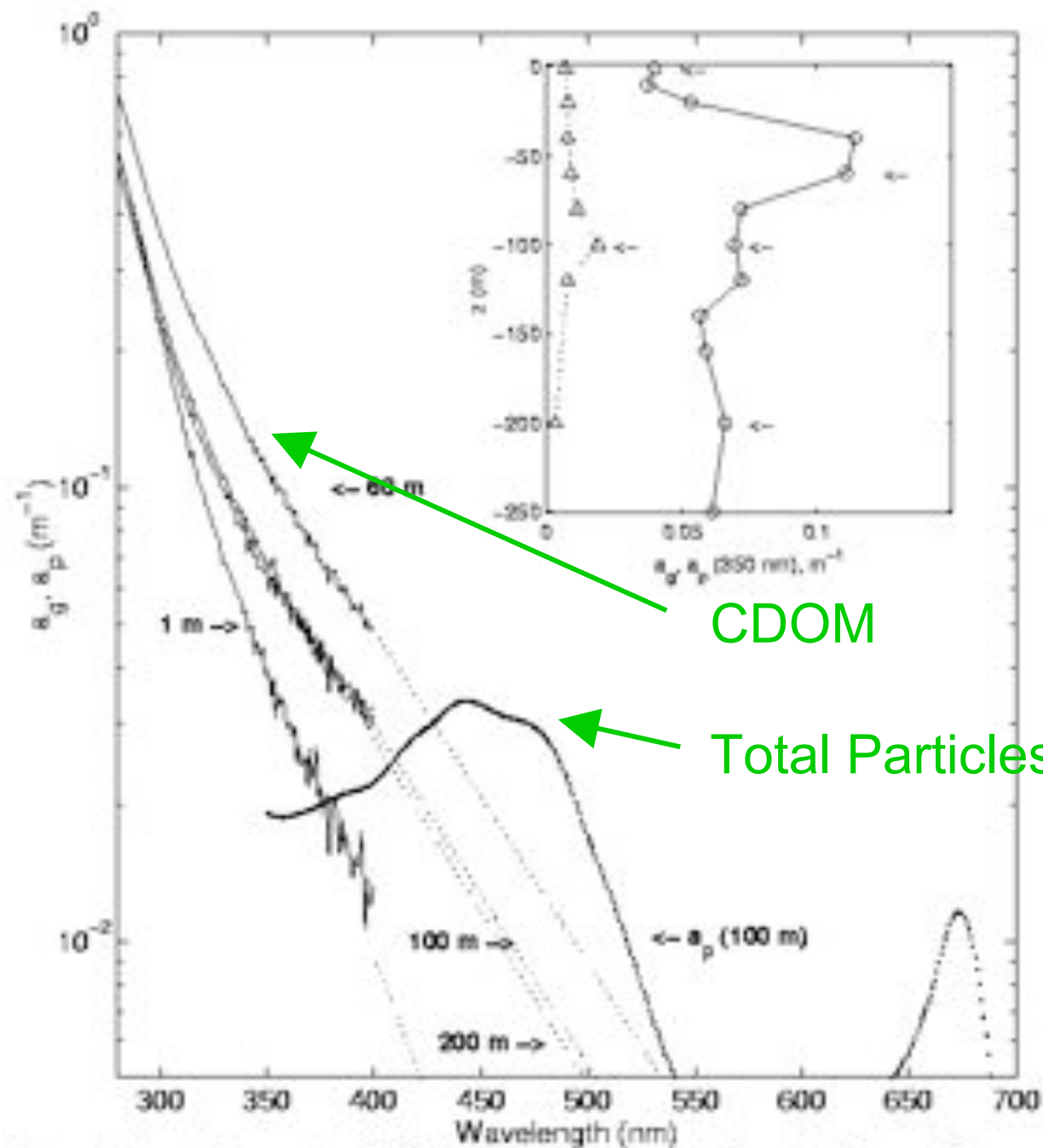


Extra Slides

# Sargasso Sea

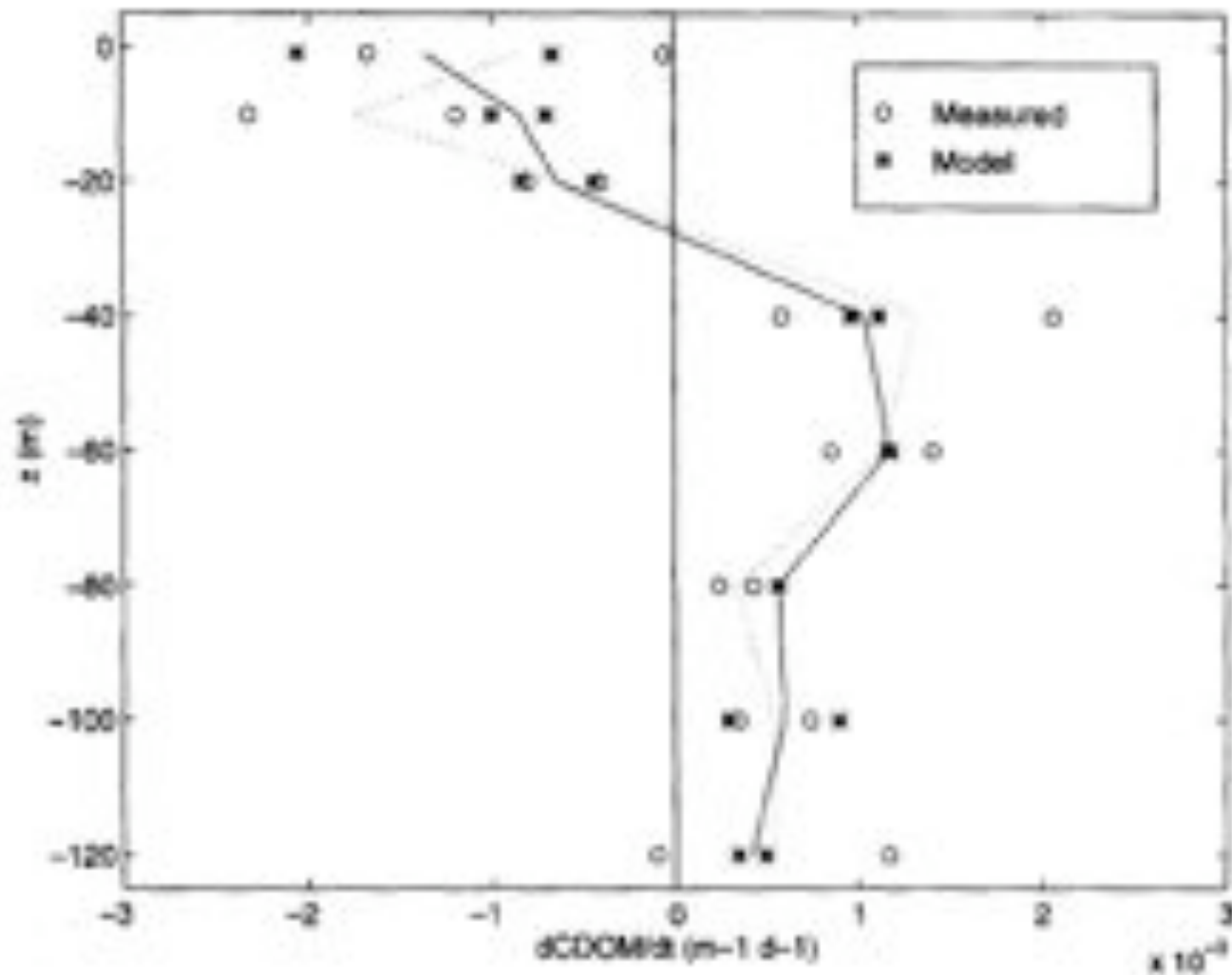
(open ocean;  
summer-time)

Nelson et al [1998]



# Net Production of CDOM

Summer – Spring CDOM



BATS data

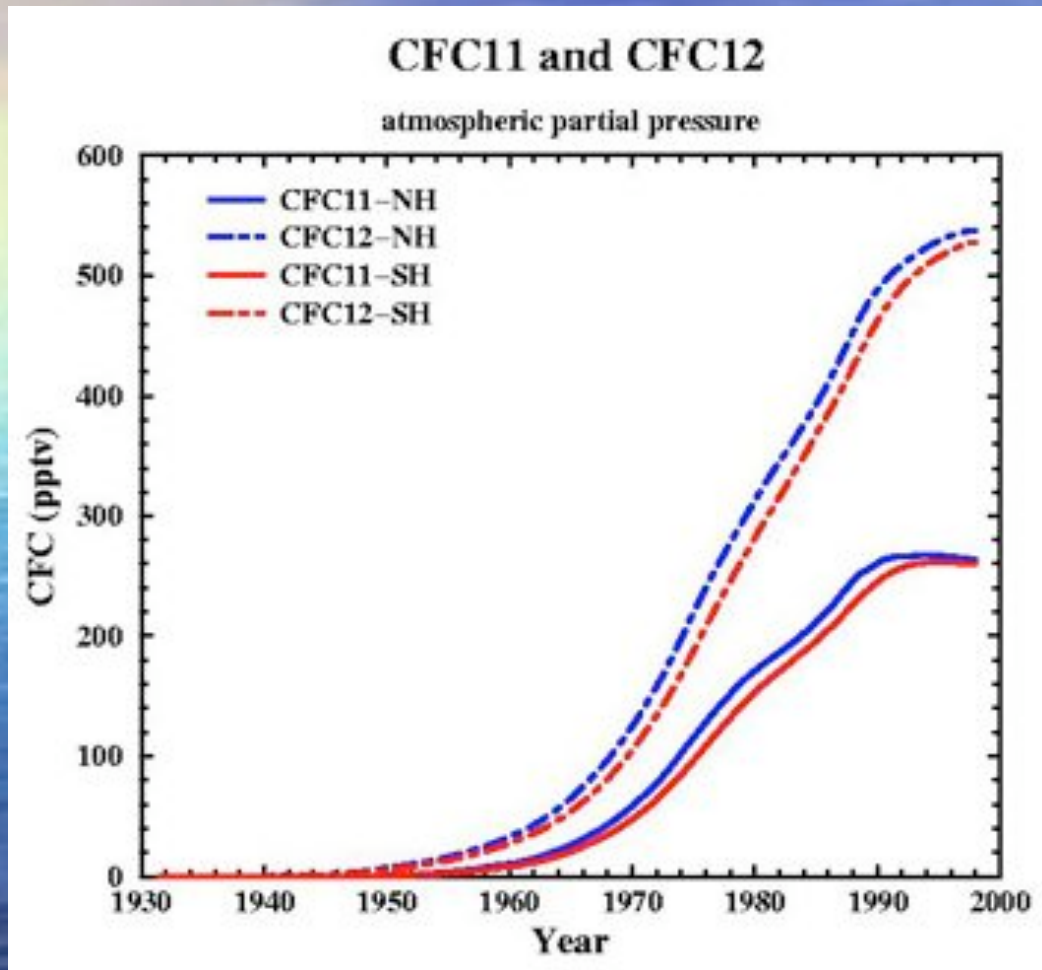
Sargasso Sea

(Nelson et al. 1998)

Production max  
at 40-60 m

Similar to the  
bacterial  
production

# CFC's as Transient Tracers



Mixing with ocean imprints ventilated waters w/ CFC levels

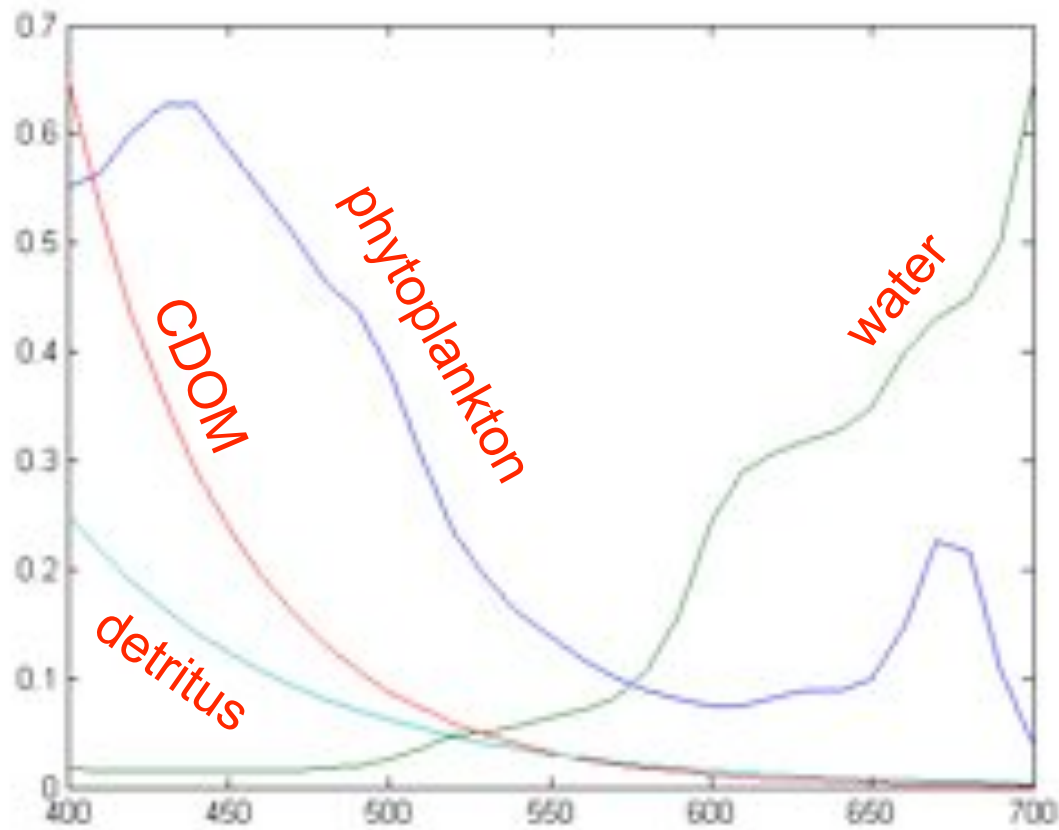
Provides a ventilation "age" for water mass

Atmospheric CFC's are now dropping

Good for O<sub>3</sub> hole

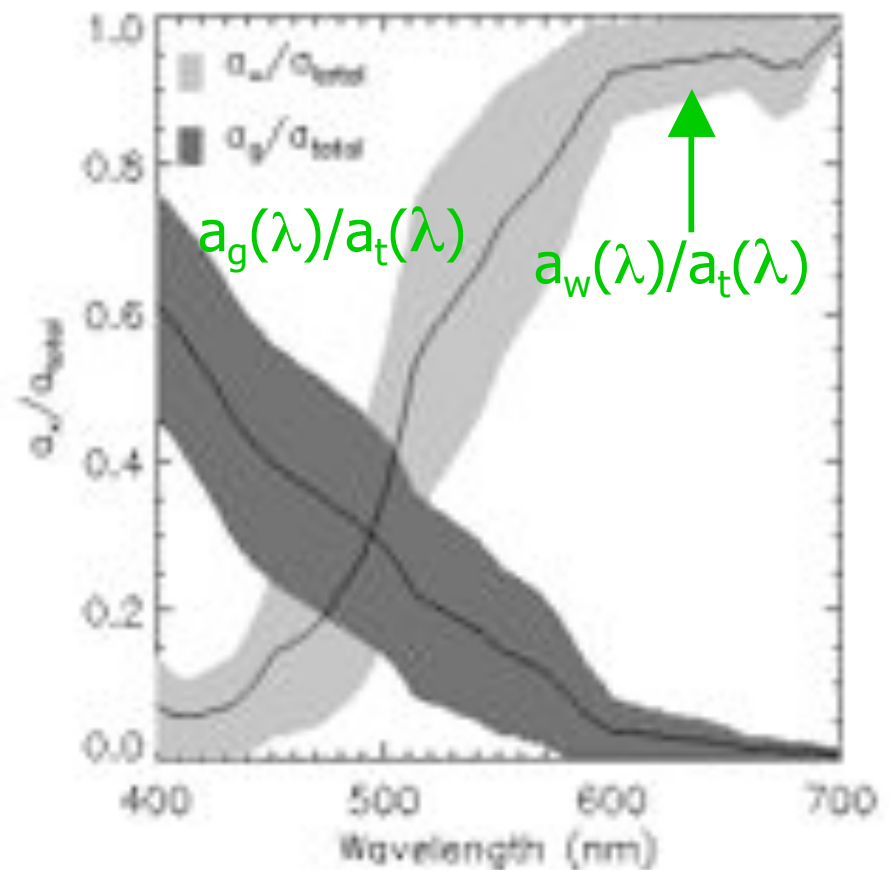
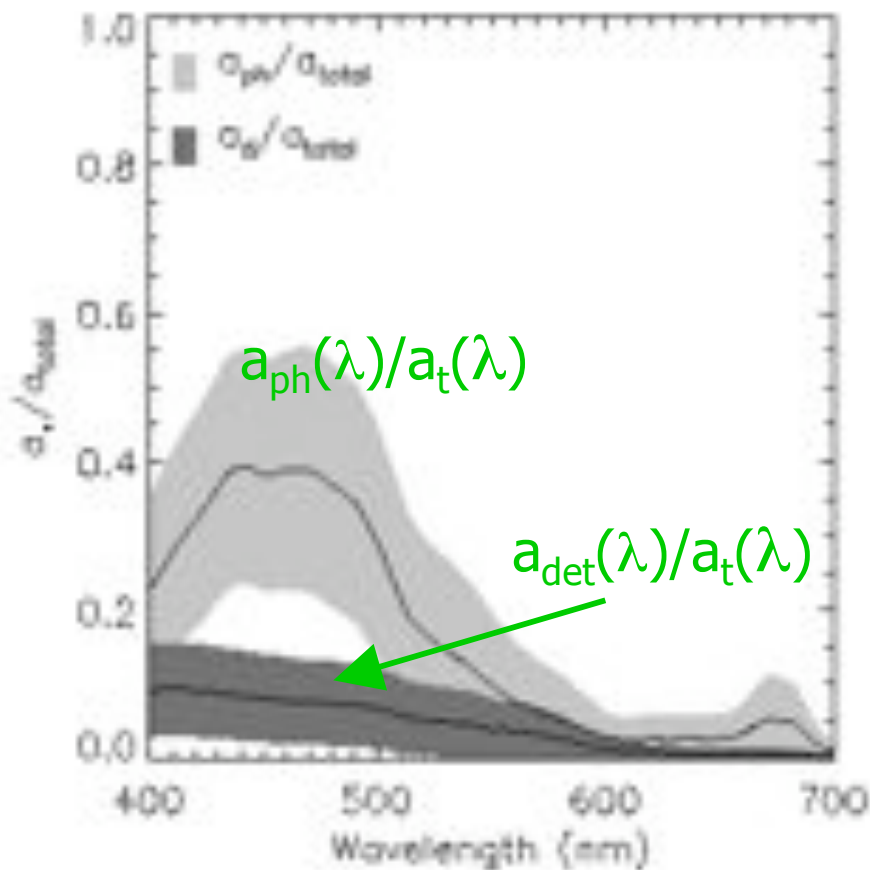
Bad for tracer work...

# Light Absorption Spectral Shapes



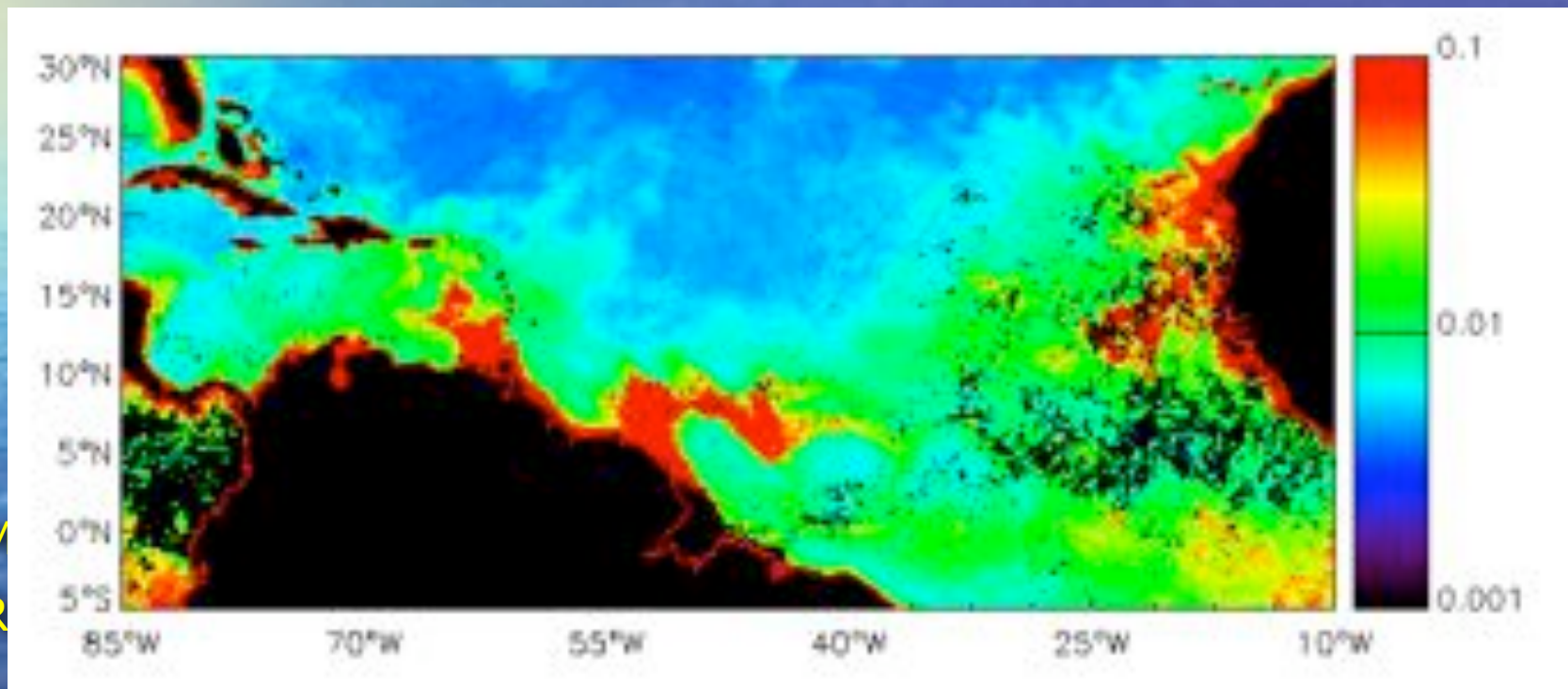
Wavelength (nm)

# Relative Spectral Contributions



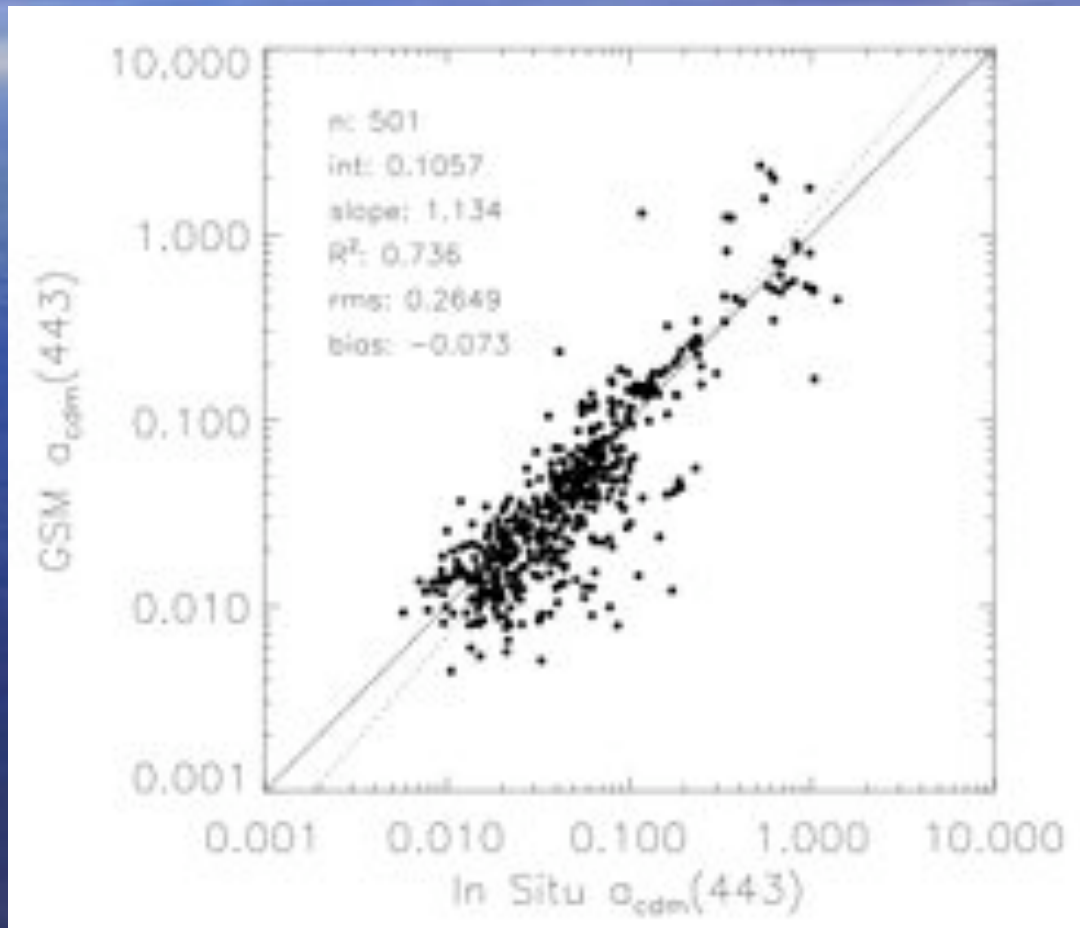
# Role of Rivers

Large River Outflows...



# Does this all work??

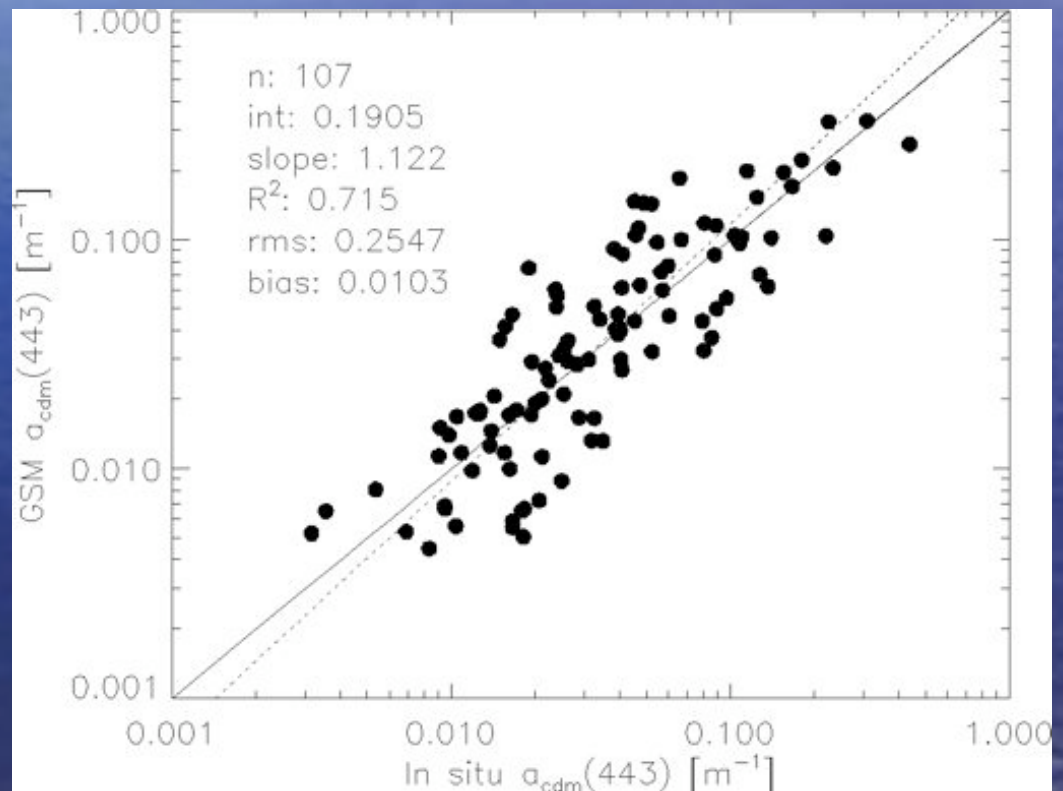
- Matchup with NOMAD data (IOCCG IOP report; Lee et al. 2006)
- Model-data fits are pretty good – though not excellent
- GSM01 is optimized for all 3 retrievals



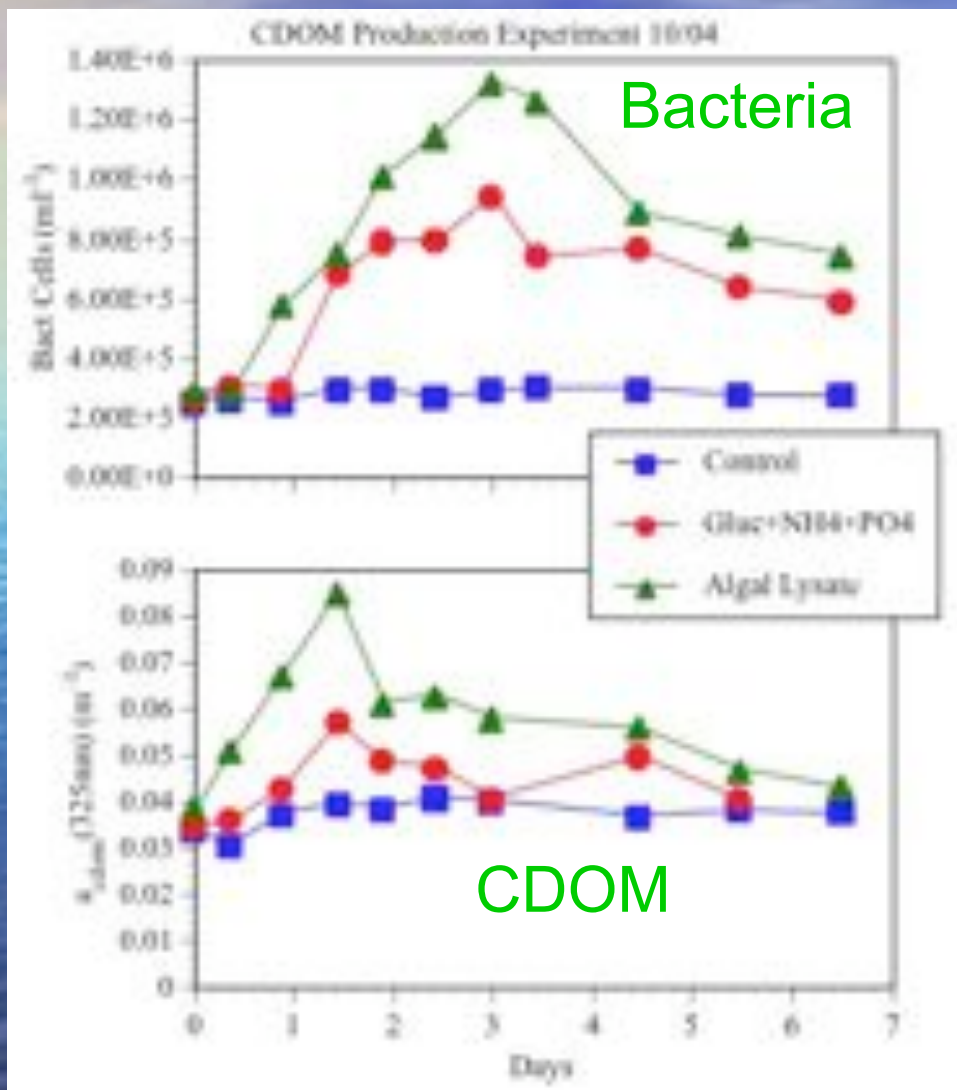


# Does this all work??

- Independent global match-up data set of SeaWiFS & CDM observations
- Regression is good, not great



# Microbial Production of CDOM

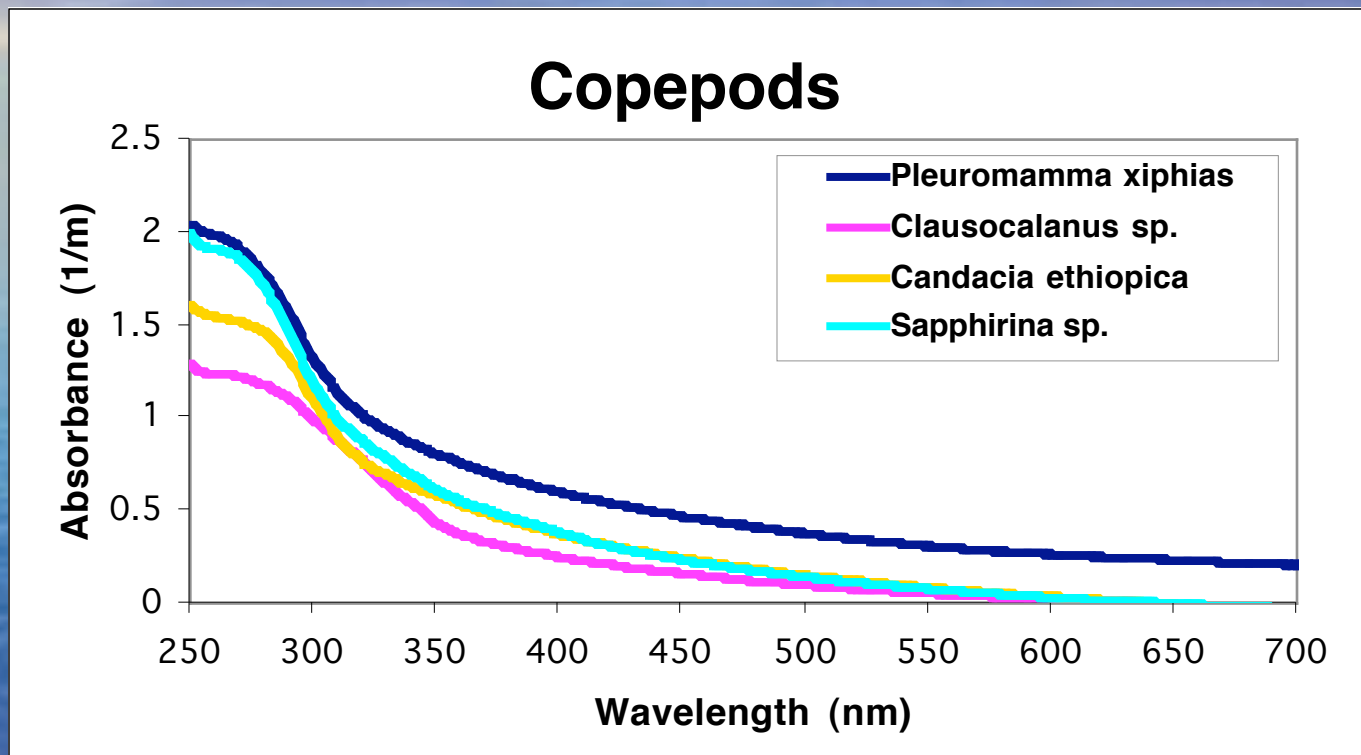


Microbes produce long-lived CDOM

Experiments from BATS 60m water by Nelson & Carlson

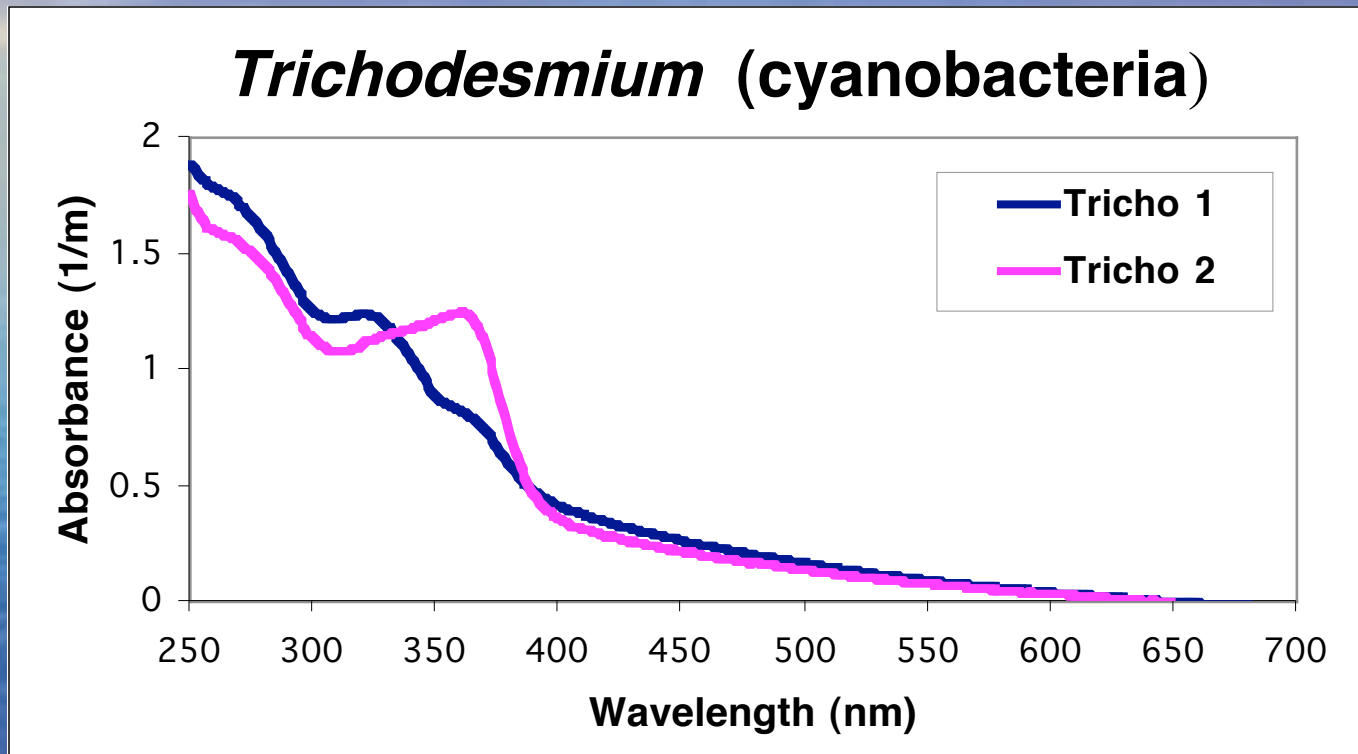
After Nelson et al. [2004]

# Zooplankton & CDOM



Debbie Steinberg, Norm Nelson & Craig Carlson (MEPS 2004)

# Trichodesmium & CDOM



**Debbie Steinberg, Norm Nelson & Craig Carlson (2004)**