Chromophoric Dissolved Organic Matter (CDOM)

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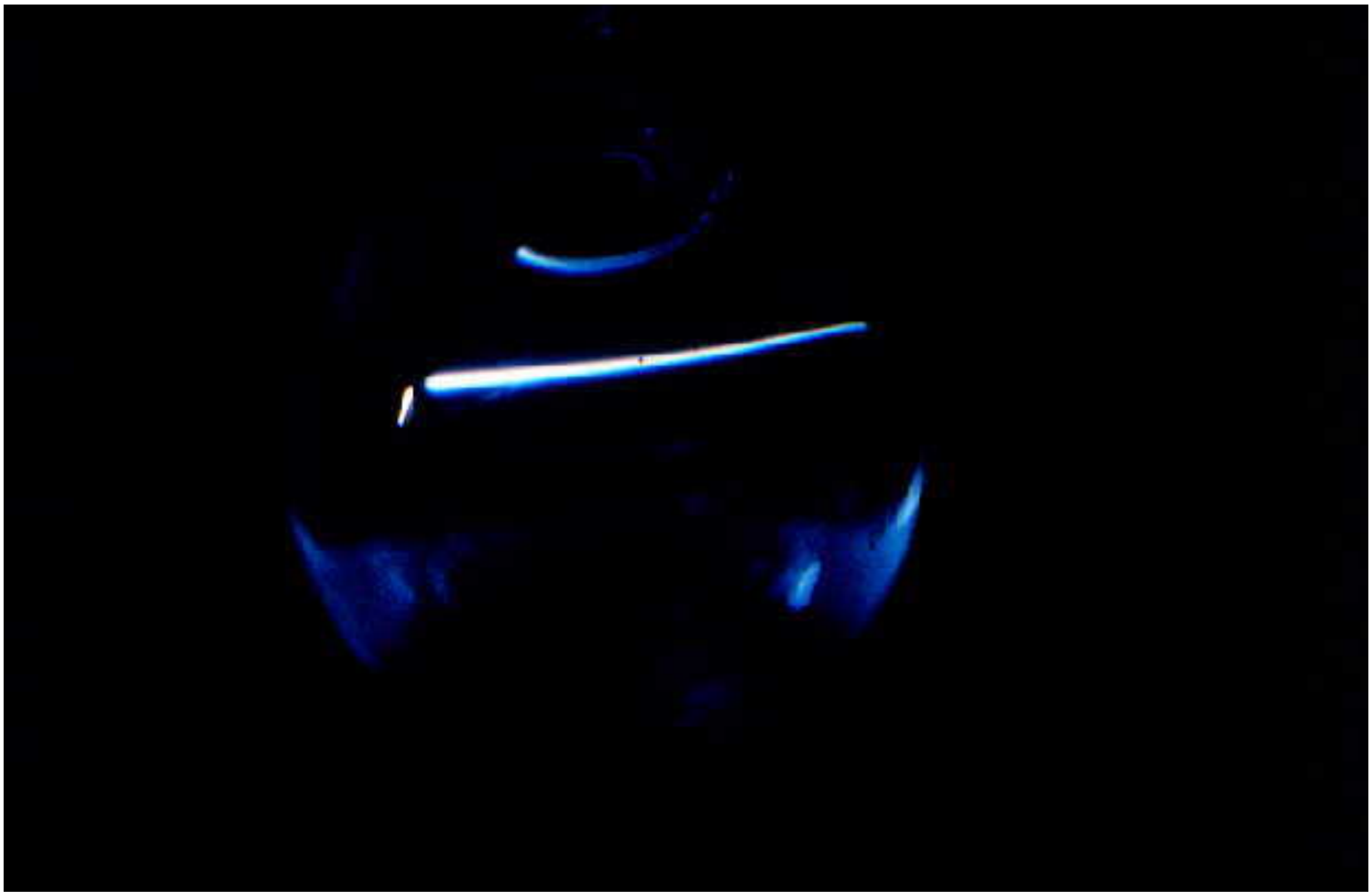
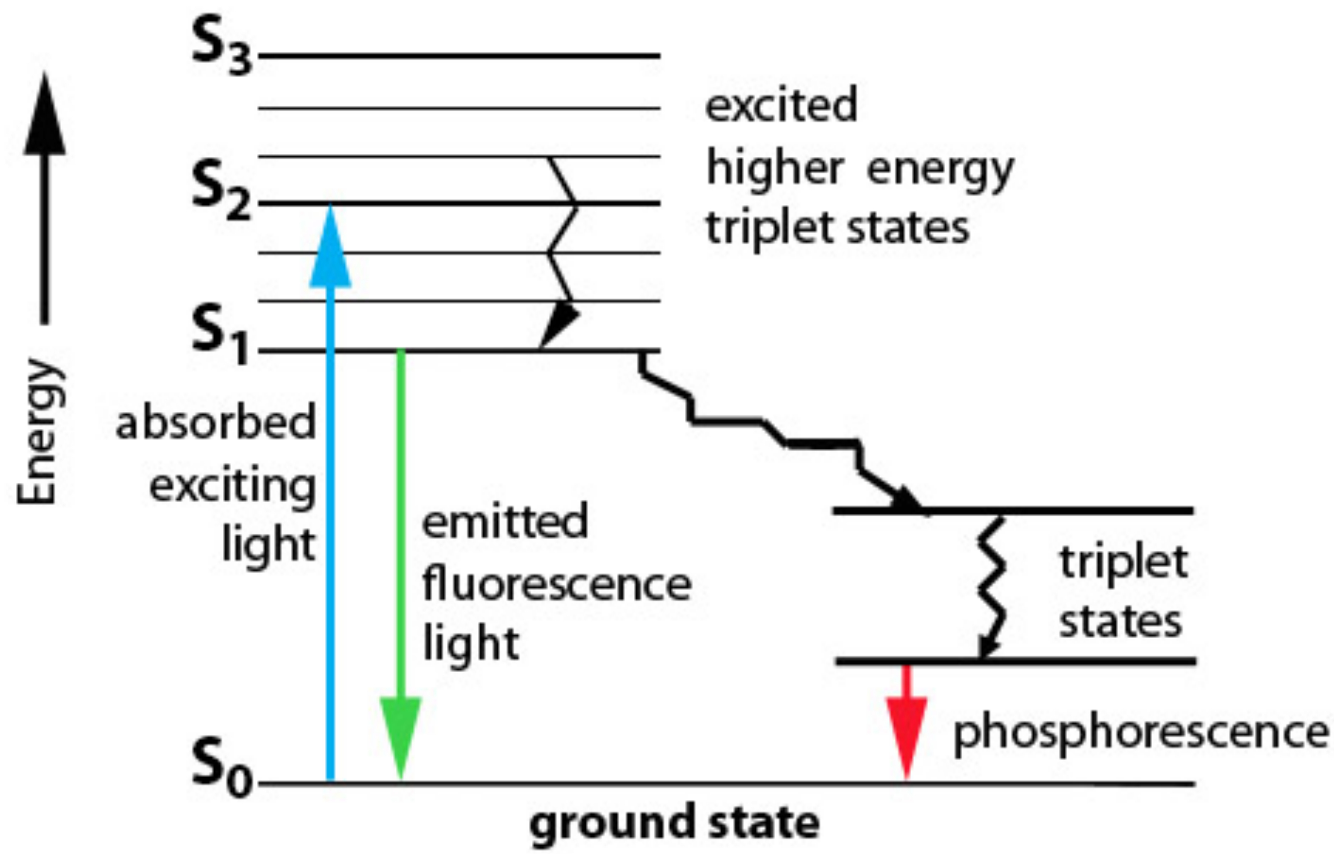
Initial Observations

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

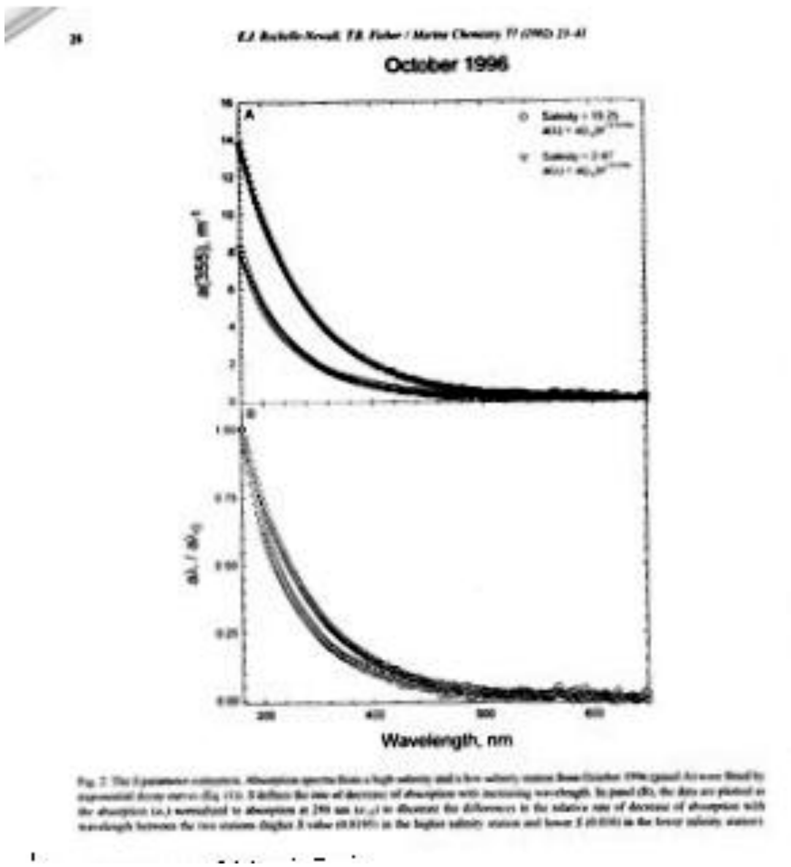
Fluorescence of Seawater



Jablonski Diagram



Spectra



Rochelle-Newall & Fisher, 2002

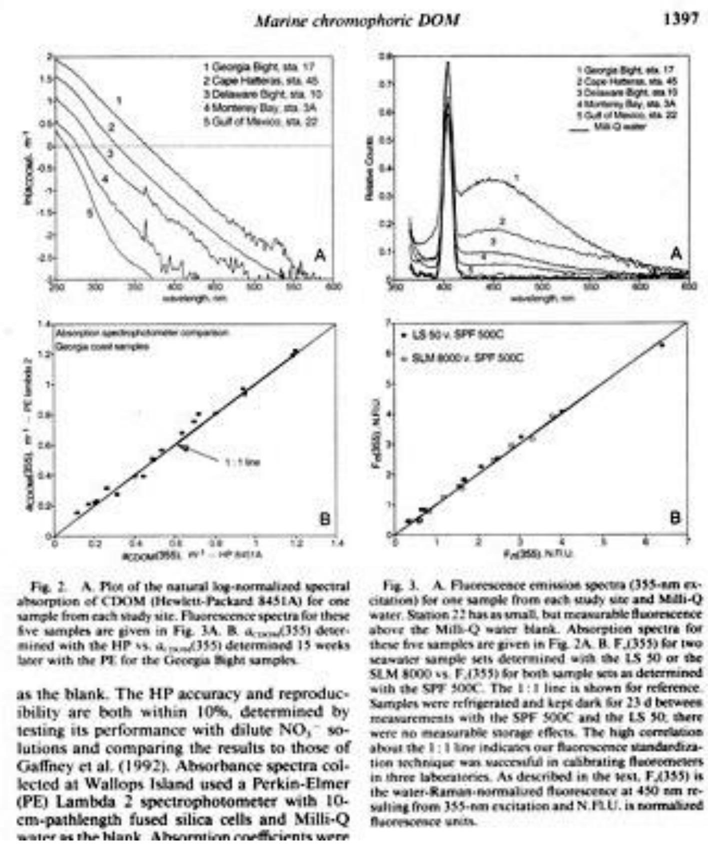

Marine chromophoric DOM 1397

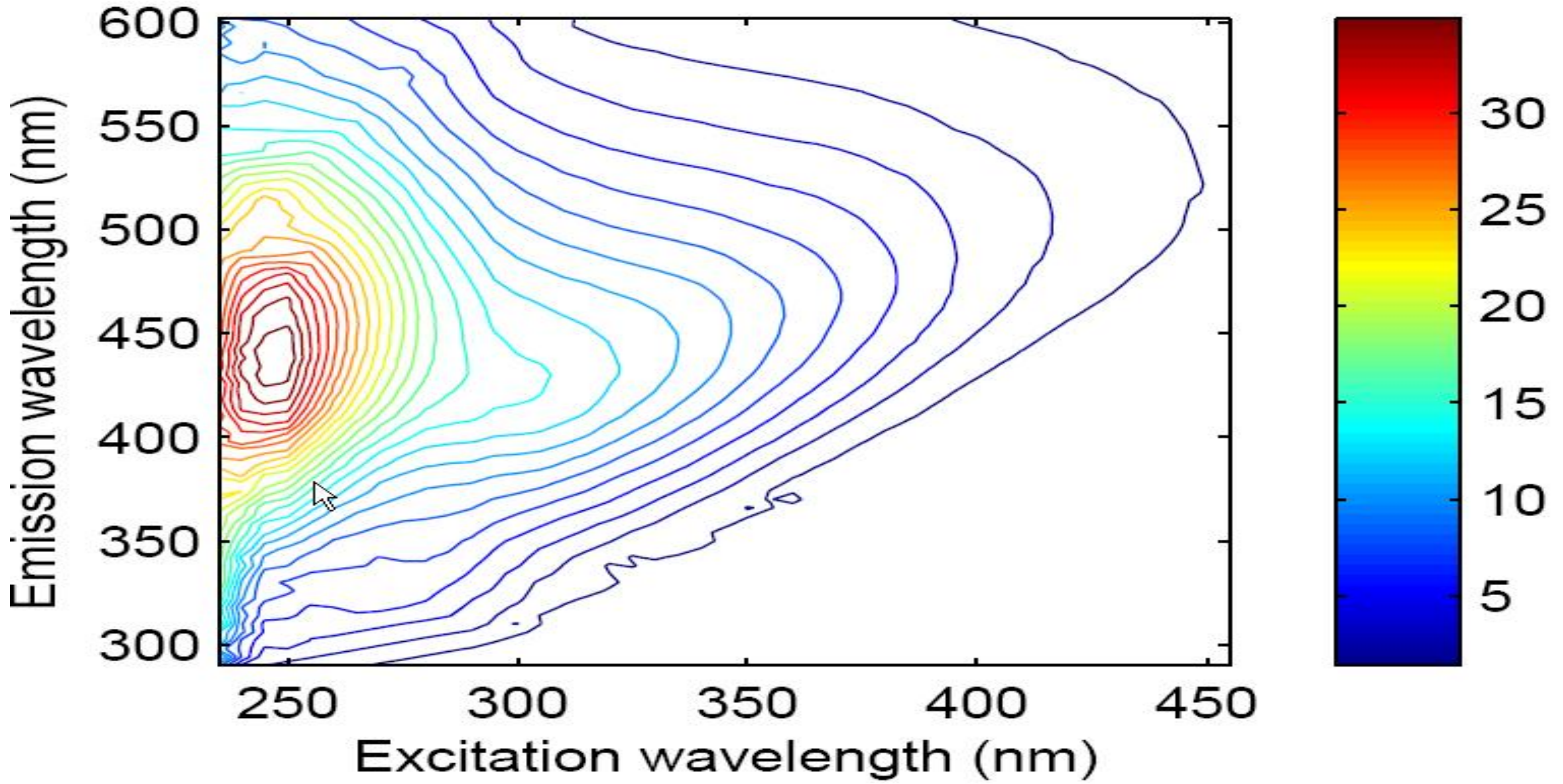
Fig. 2. A. Plot of the natural log-normalized spectral absorption of CDOM (Hewlett-Packard 8451A) for one sample from each study site. Fluorescence spectra for these five samples are given in Fig. 3A. B. $a_{CDOM}(355)$ determined with the HP vs. $a_{CDOM}(355)$ determined 15 weeks later with the PE for the Georgia Bight samples.

Fig. 3. A. Fluorescence emission spectra (355-nm excitation) for one sample from each study site and Milli-Q water. Station 22 has as small, but measurable fluorescence above the Milli-Q water blank. Absorption spectra for these five samples are given in Fig. 2A. B. $F_n(355)$ for two seawater sample sets determined with the LS 50 or the SLM 8000 vs. $F_n(355)$ for both sample sets as determined with the SPF 500C. The 1 : 1 line is shown for reference. Samples were refrigerated and kept dark for 23 d between measurements with the SPF 500C and the LS 50; there were no measurable storage effects. The high correlation about the 1 : 1 line indicates our fluorescence standardization technique was successful in calibrating fluorometers in three laboratories. As described in the text, $F_n(355)$ is the water-Raman-normalized fluorescence at 450 nm resulting from 355-nm excitation and N.FLU. is normalized fluorescence units.

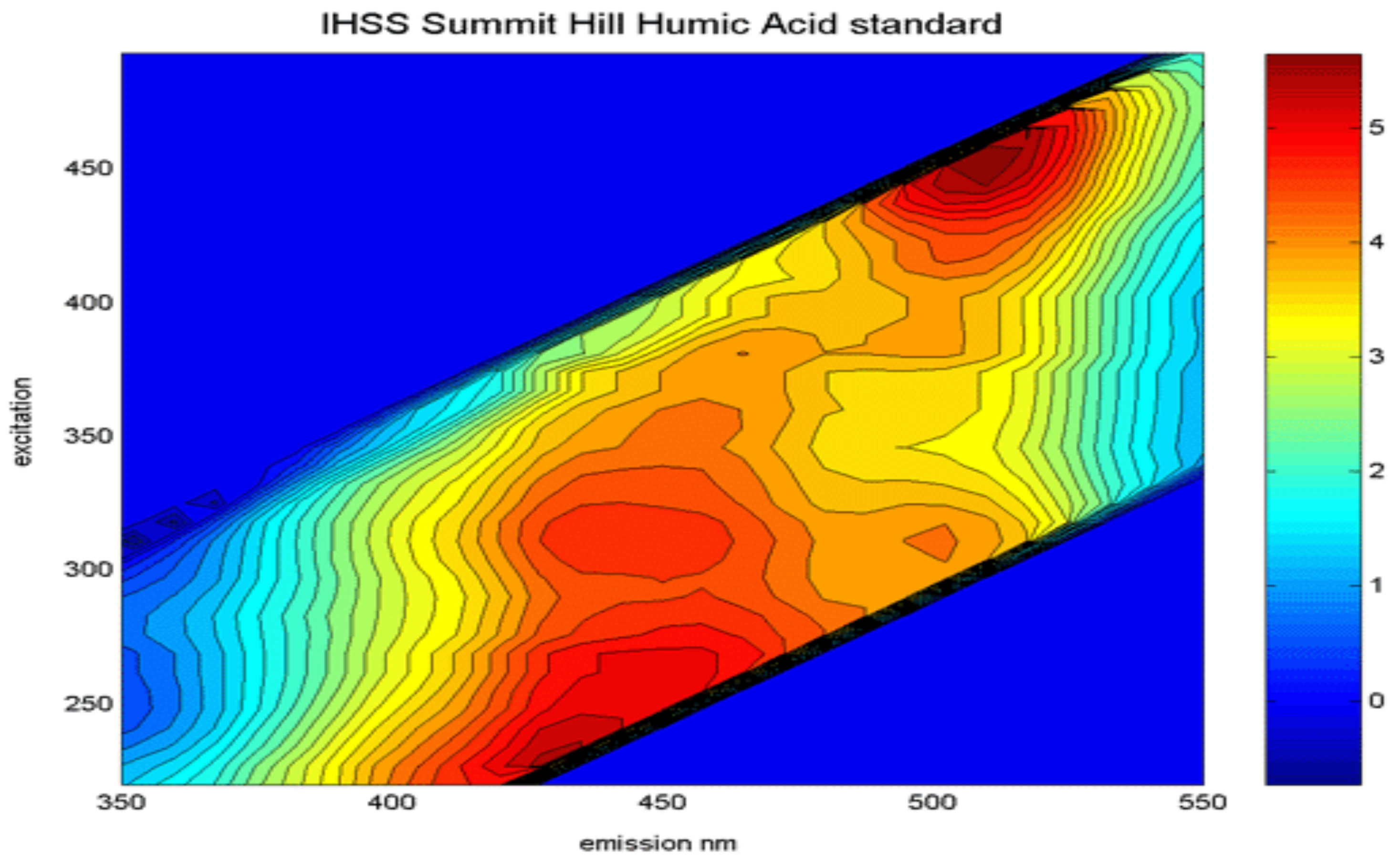
as the blank. The HP accuracy and reproducibility are both within 10%, determined by testing its performance with dilute NO_3^- solutions and comparing the results to those of Gaffney et al. (1992). Absorbance spectra collected at Wallops Island used a Perkin-Elmer (PE) Lambda 2 spectrophotometer with 10-cm-pathlength fused silica cells and Milli-Q water as the blank. Absorption coefficients were

Hoge, Vodacek and Blough, 1993

Seawater Excitation-Emission Matrix (EEM)



Humic EEM



IHSS Summit Hill Humic Acid standard
excitation
emission nm
350
400
450
500
550
250
300
350
400
450
0
1
2
3
4
5

You can see it

Distributions

- Varies in surface waters

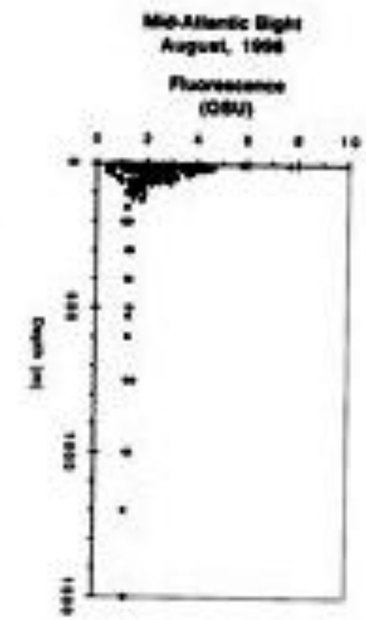
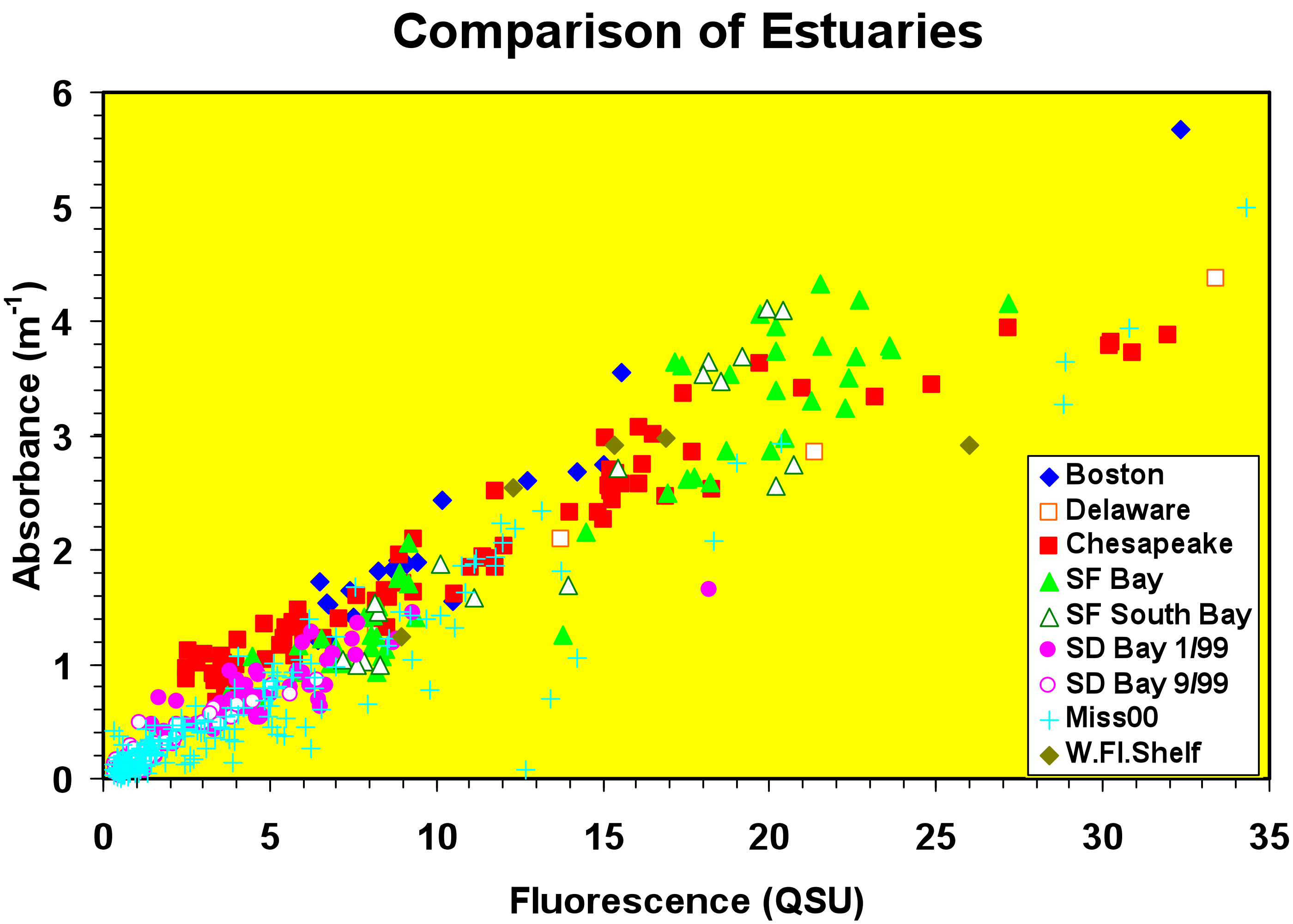
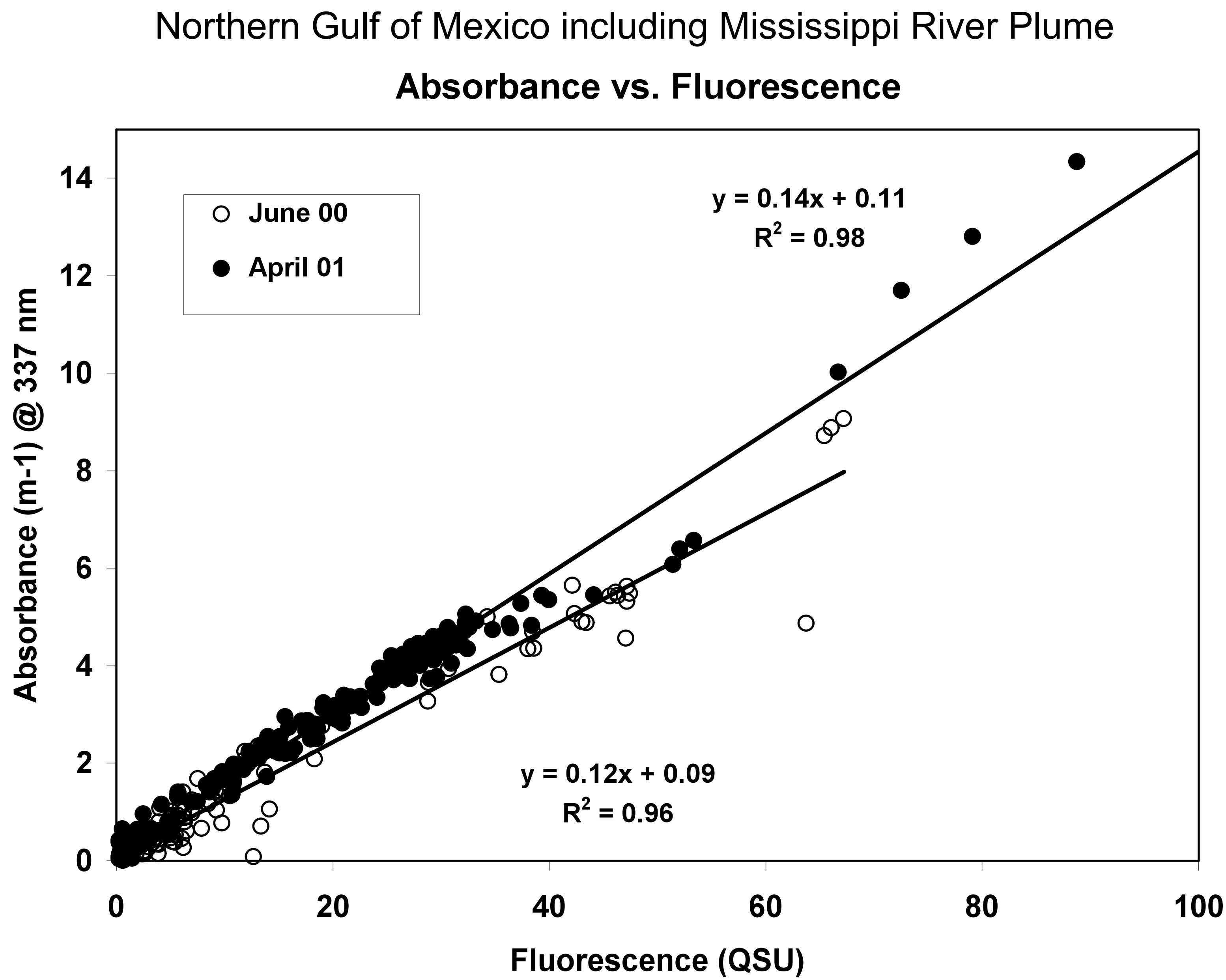


Fig. 4. A compilation of all filtered bottle fluorescence measurements vs depth on the RV Seward Johnson, August 1996.

Chen, 1992

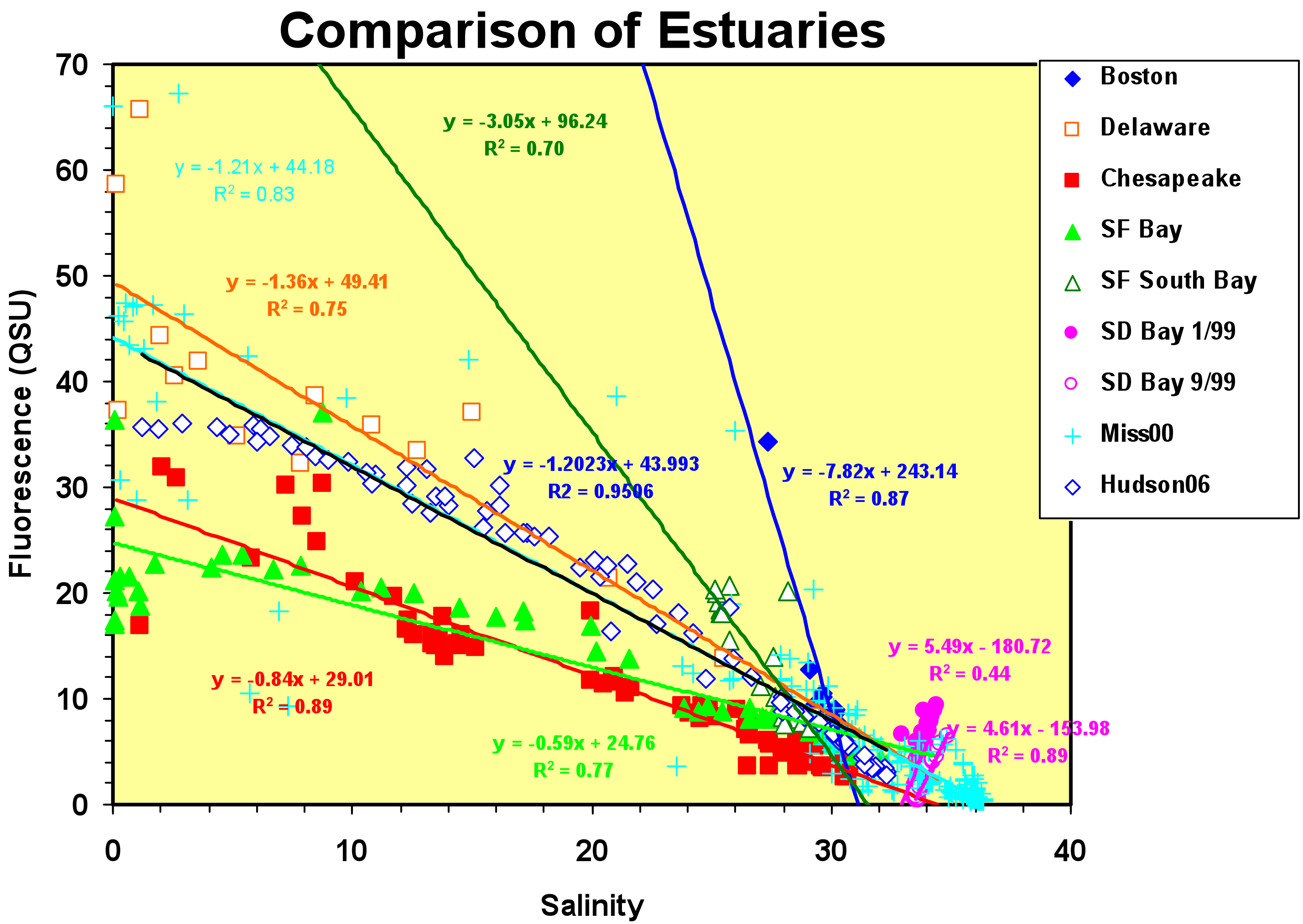
Fluorescence vs. Absorbance

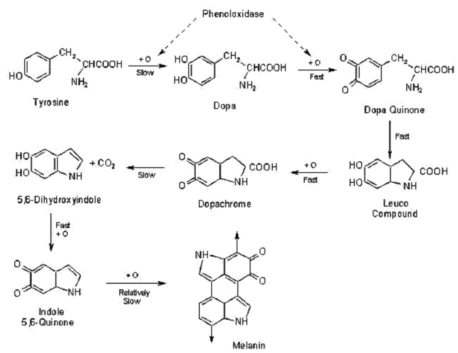




Northern Gulf of Mexico including Mississippi River Plume
Absorbance vs. Fluorescence
June 00
April 01
y = 0.14x + 0.11
R^2 = 0.98
y = 0.12x + 0.09
R^2 = 0.96
Absorbance (m-1) @ 337 nm
Fluorescence (QSU)
0
2
4
6
8
10
12
14
0
20
40
60
80
100

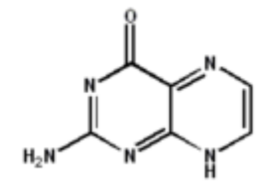
US Estuaries-CDOM



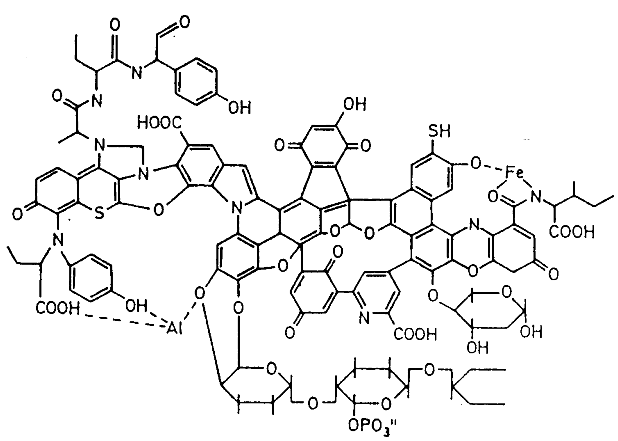


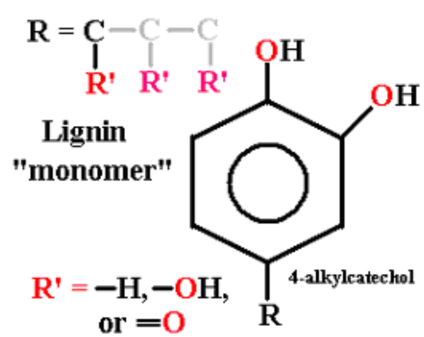
What is it?

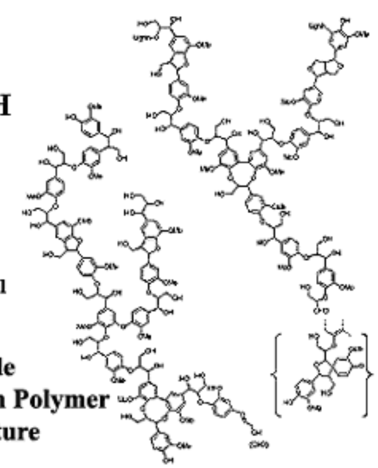
- Melanoidins (Proteins and Carbohydrates)
- Humics (Degradation Products)
- Flavins and Pterins (coral natural products)



- Lignin Phenols







Sample Lignin Polymer Structure

Chemical Characterization

- Isolation
  - Humics
  - HMW DOM
- NMR
- IR
- MS
- 1-30% DOM
- ???

Ocean Distribution

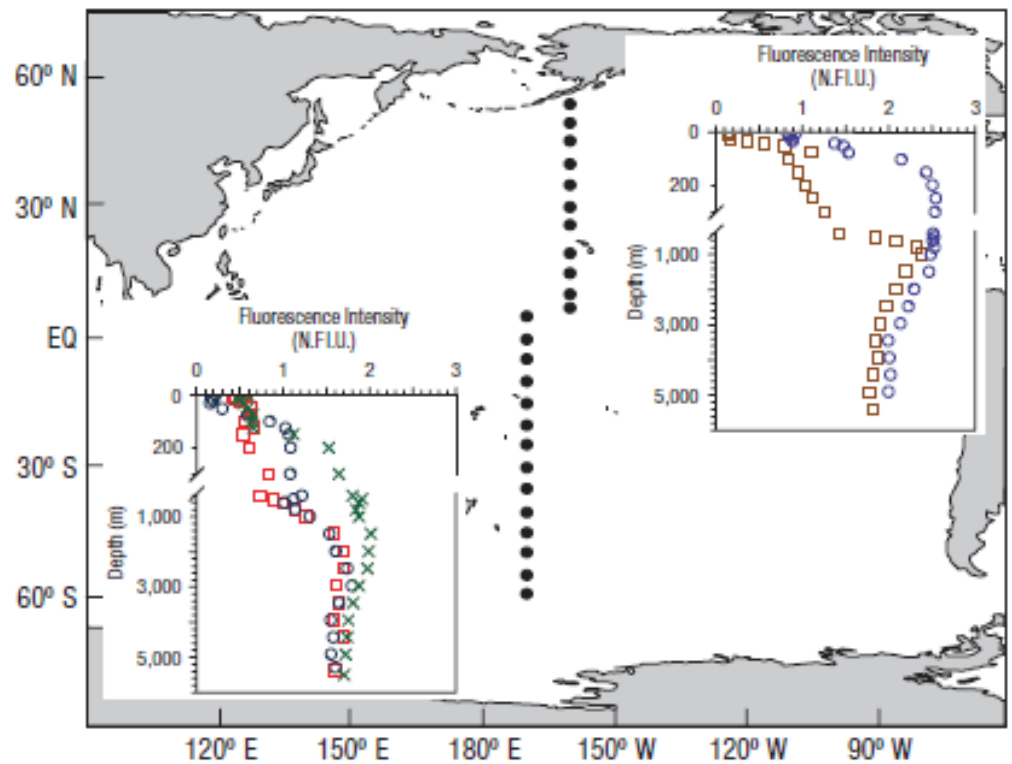


Figure 1 Map of locations sampled for survey of FDOM distribution and typical vertical profiles of fluorescence intensity. Right inset: Vertical profiles of fluorescence intensity at 50° 00′ N (open circles) and 30° 00′ N (open squares). Left inset: Vertical profiles of fluorescence intensity at 0° 05′ 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.

Yamashita and Tanoue, 2008

Pacific Ocean

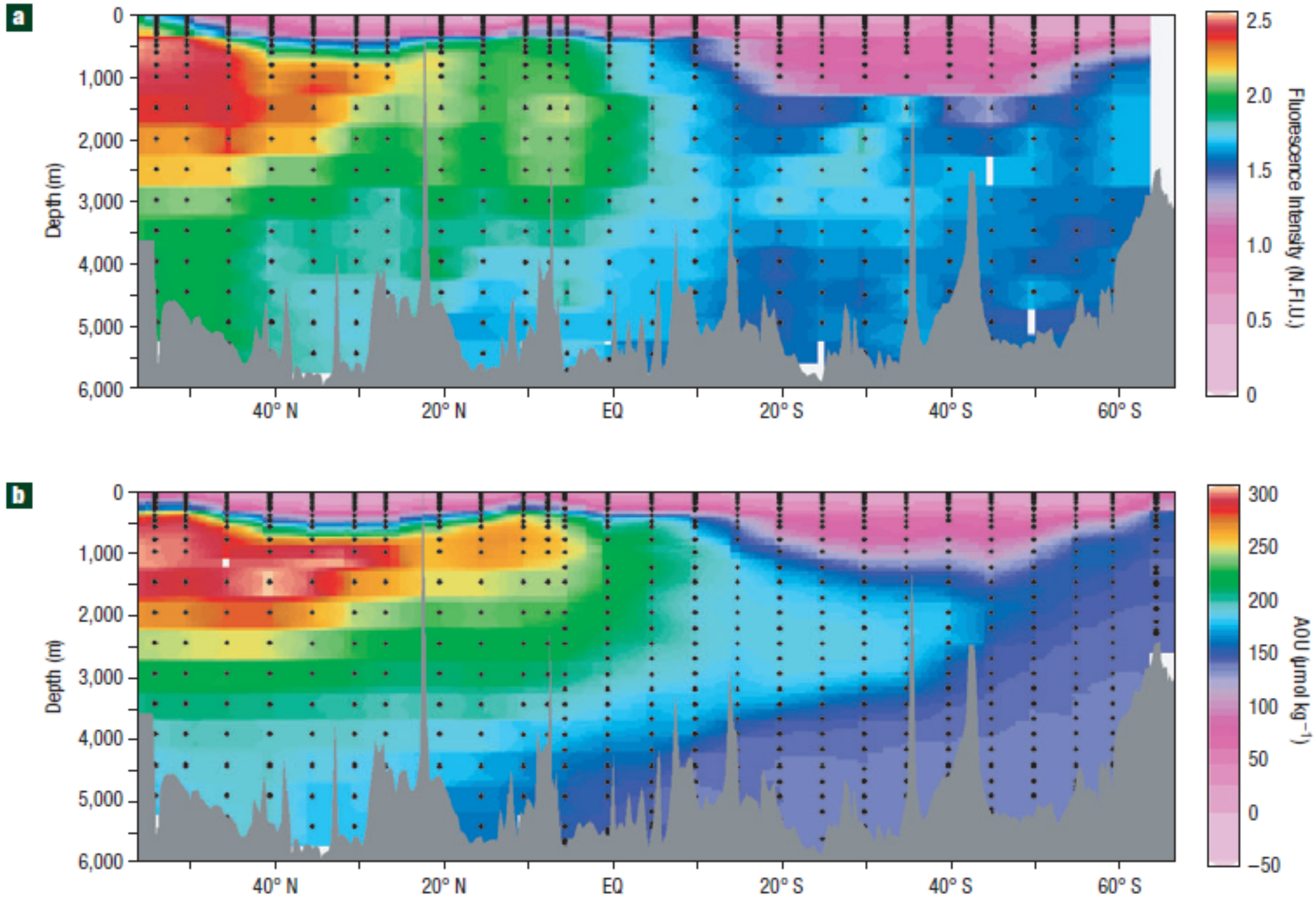


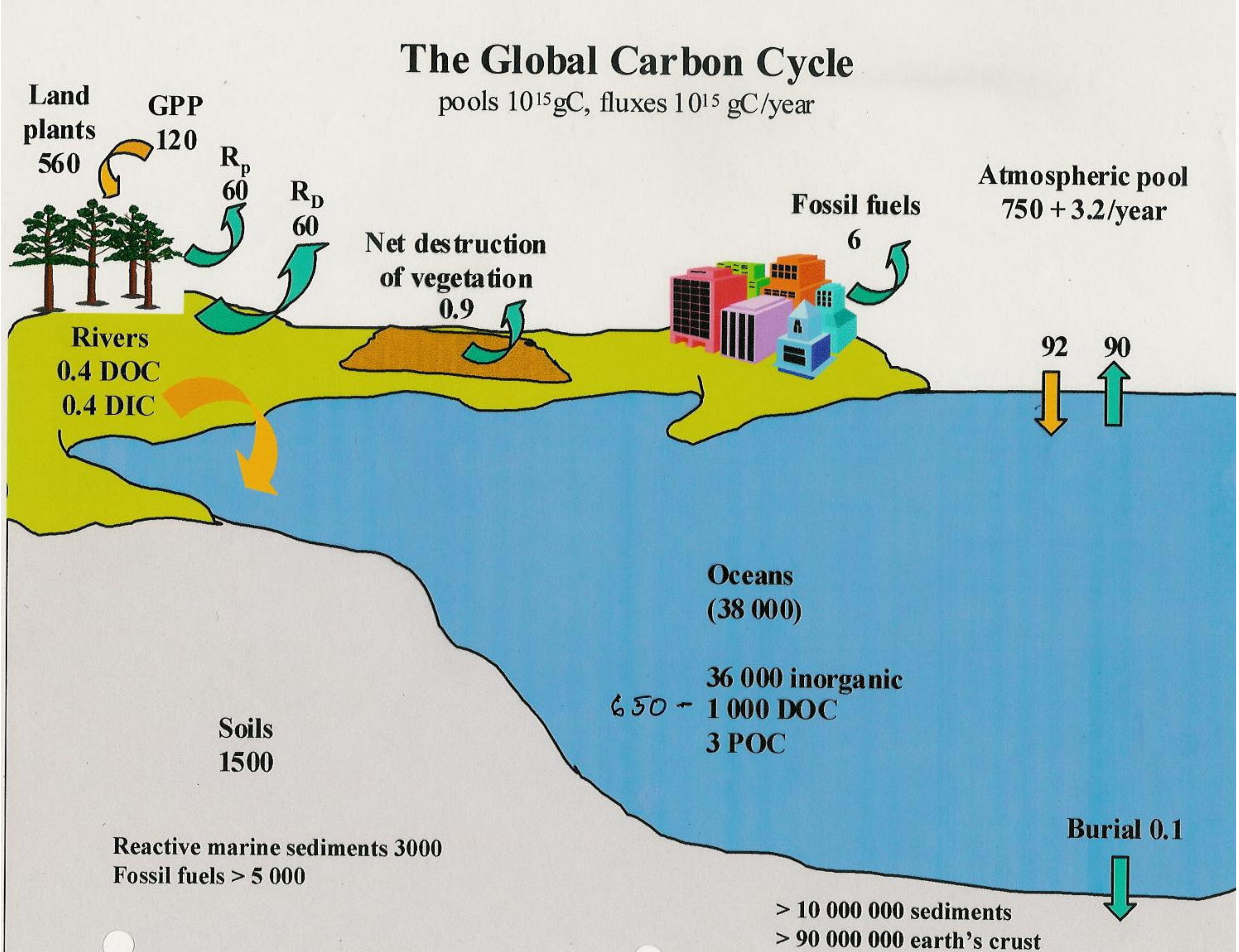
Figure 2 Contour maps of fluorescence intensity and AOU along the transects at 160° W and 170° W. a,b, Levels of fluorescence intensity (**a**) and AOU (**b**). Contour maps were illustrated using Ocean Data View[26].

Yamashita and Tanoue, 2008

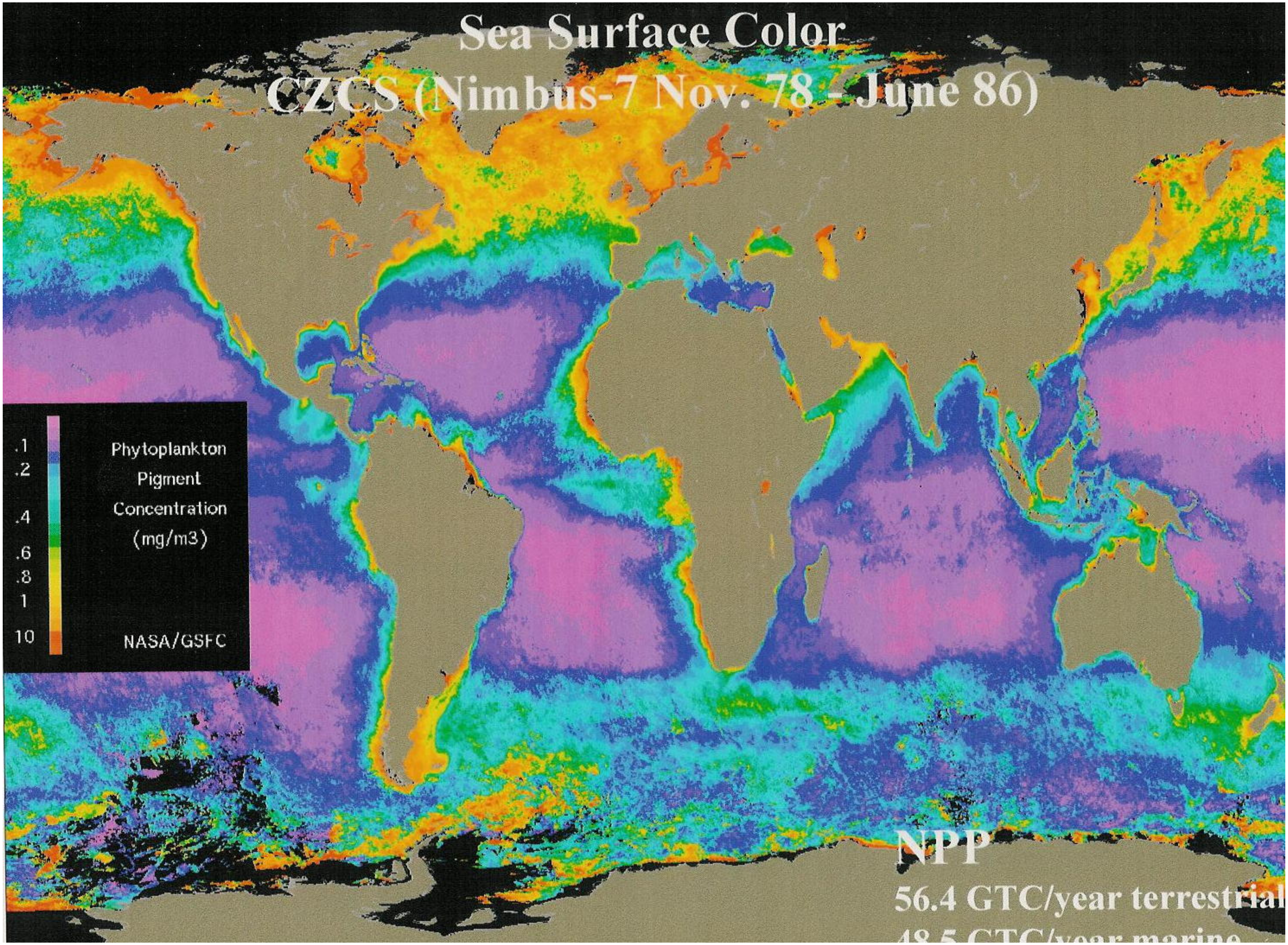
Why do we care?

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



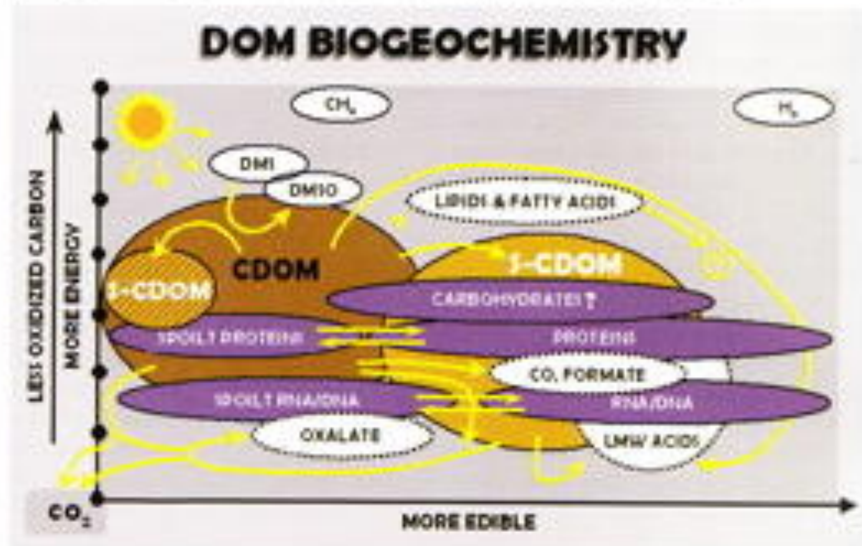
The Global Carbon Cycle
pools 10^{15}gC, fluxes 10^{15} gC/year
Land plants 560
GPP 120
R_p 60
R_D 60
Net destruction of vegetation 0.9
Fossil fuels 6
Atmospheric pool 750 + 3.2/year
Rivers 0.4 DOC 0.4 DIC
92
90
Oceans (38 000)
36 000 inorganic
650 ← 1 000 DOC
3 POC
Soils 1500
Reactive marine sediments 3000
Fossil fuels > 5 000
Burial 0.1
> 10 000 000 sediments
> 90 000 000 earth's crust


Sea Surface Color
CZCS (Nimbus-7 Nov. 78 - June 86)
.1
.2
.4
.6
.8
1
10
Phytoplankton
Pigment
Concentration
(mg/m3)
NASA/GSFC
NPP
56.4 GTC/year terrestrial

Labile vs Refractory

- LMW vs HMW
- Photo reactive

Cartoon 1. Sunburnt DOM: food availability and quality. This plot depicts some possible roles of light in altering the energy content (vertical axis) and bioavailability (horizontal axis) of CDOM molecules commonly found in aquatic environments. *Purple*: biomacromolecules; *dark brown*: fresh CDOM; *light brown*: S-CDOM (partially photooxidized and bleached); *hatched*: S-CDOM of lowered reactivity (not a well-established pool); *white*: low molecular weight (LMW) photoproduct molecules of low or no photoreactivity, but of high biogeochemical significance. (Methane and hydrogen are also shown to exemplify the range of the energy scale). Dotted or dashed boundaries surround molecular classes of low or no photoreactivity, but high biological significance. The yellow arrows indicate likely or known phototransformations. The indirect photodegradation of lipids to unknown materials is included (arrow leading to a question mark).



Sources

Sources

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

Rivers

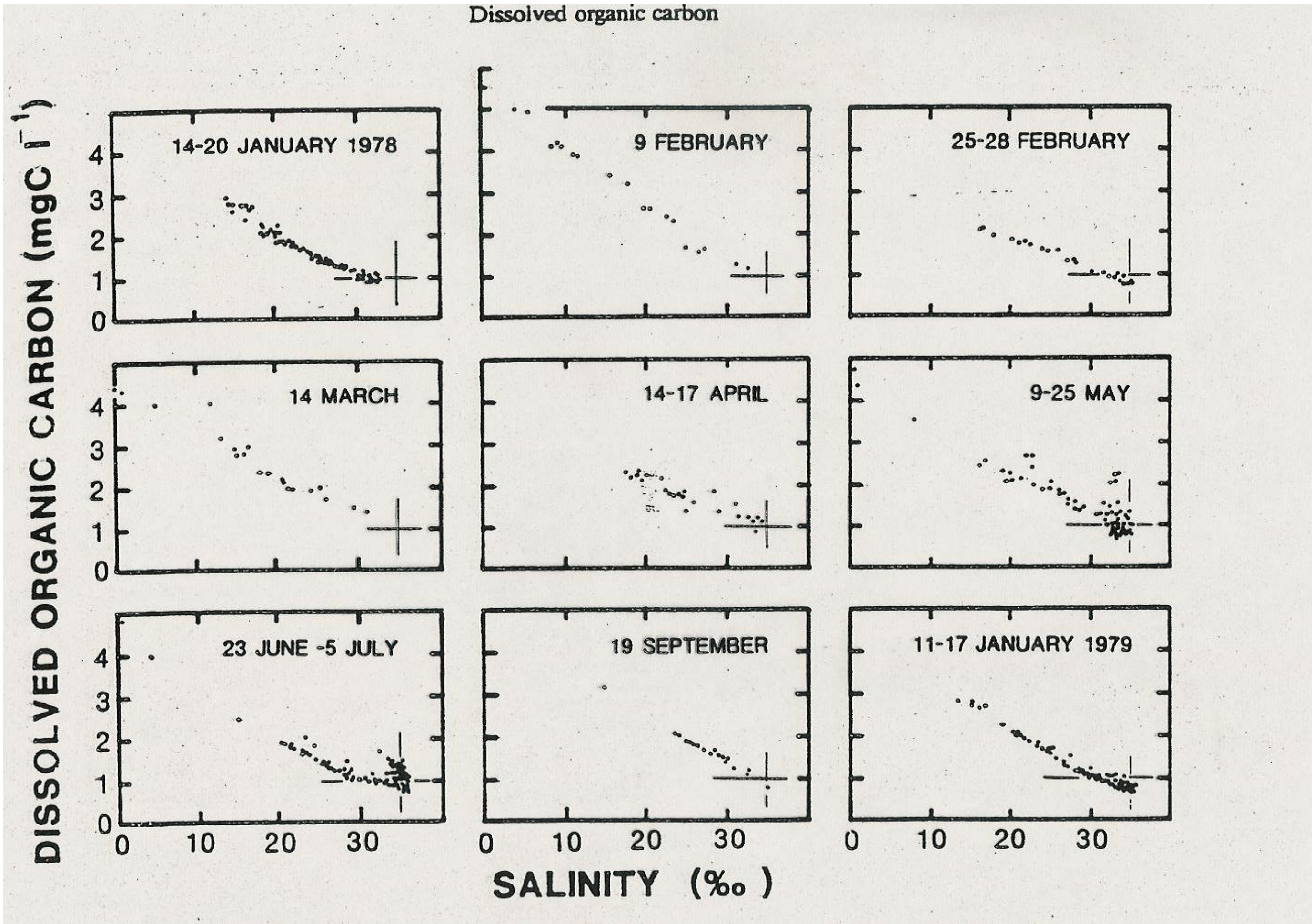
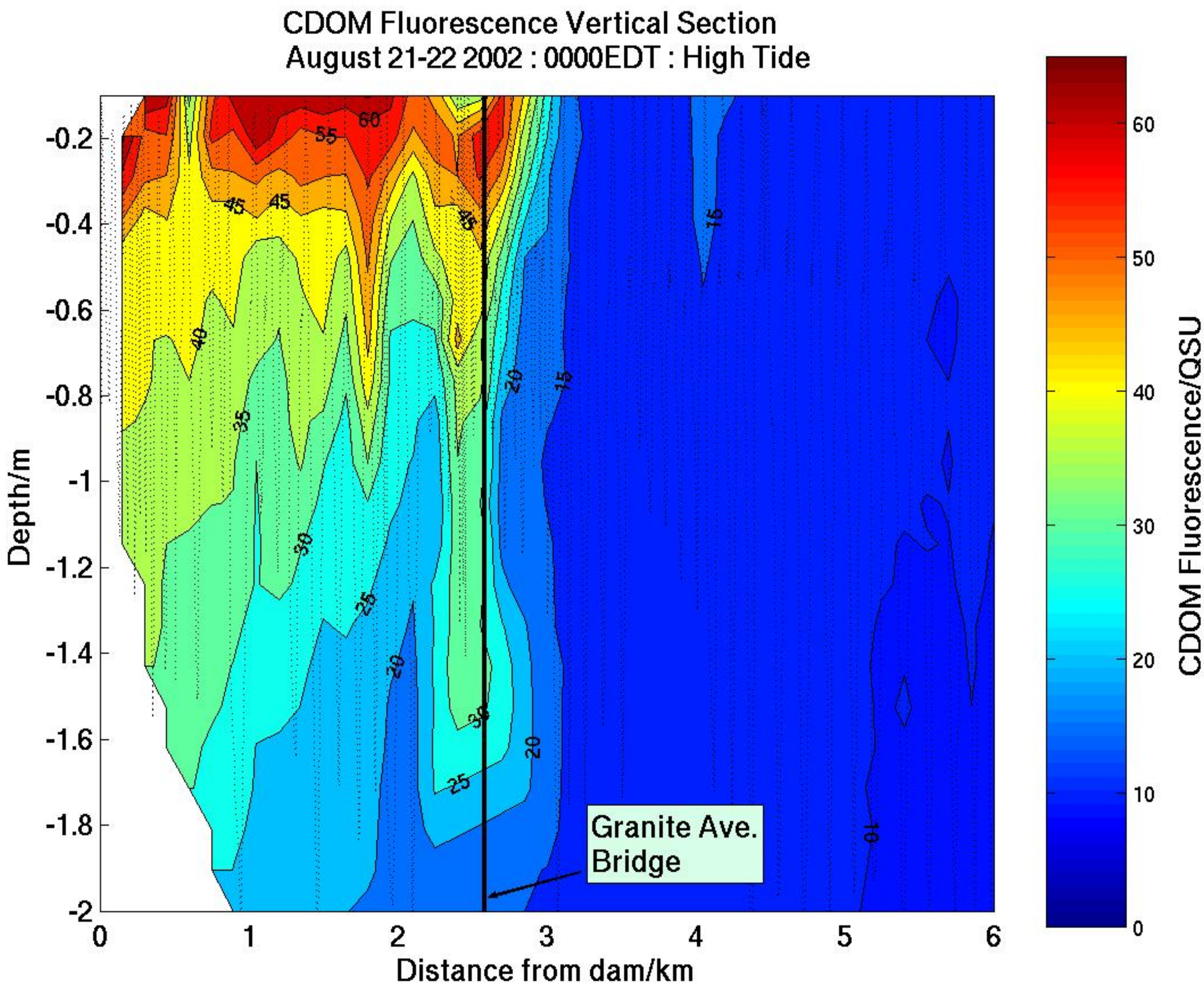
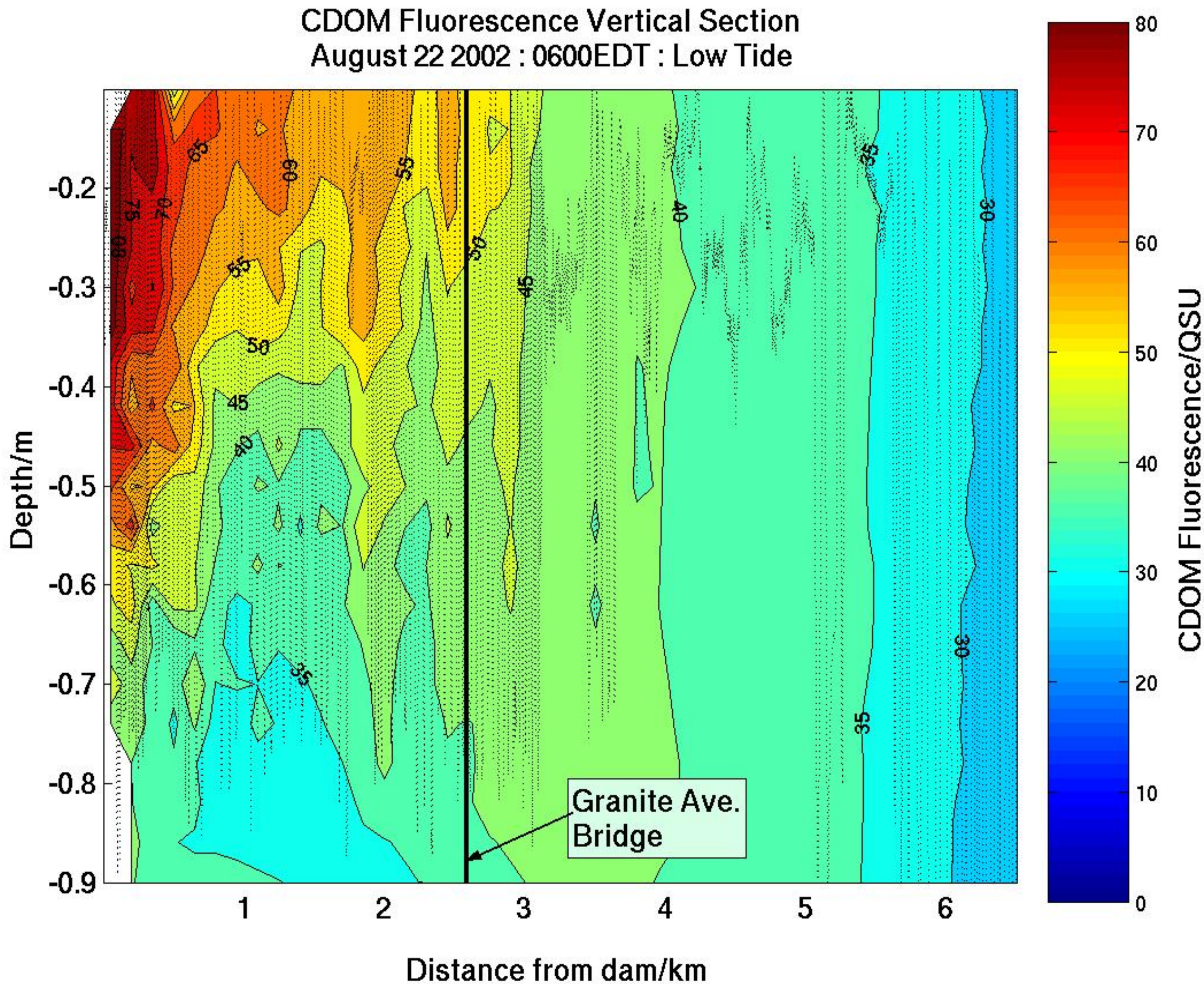


FIG. 5. DOC – salinity correlation for the Bristol Channel and Severn Estuary during 1978.



CDOM Fluorescence Vertical Section
August 21-22 2002 : 0000EDT : High Tide
Depth/m
Distance from dam/km
CDOM Fluorescence/QSU
Granite Ave.
Bridge
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
-1.6
-1.8
-2
0
1
2
3
4
5
6
60
50
40
30
20
10
0



CDOM Fluorescence Vertical Section
August 22 2002 : 0600EDT : Low Tide
Depth/m
Distance from dam/km
CDOM Fluorescence/QSU
Granite Ave.
Bridge

Arctic Rivers

- Terrestrial biomarkers

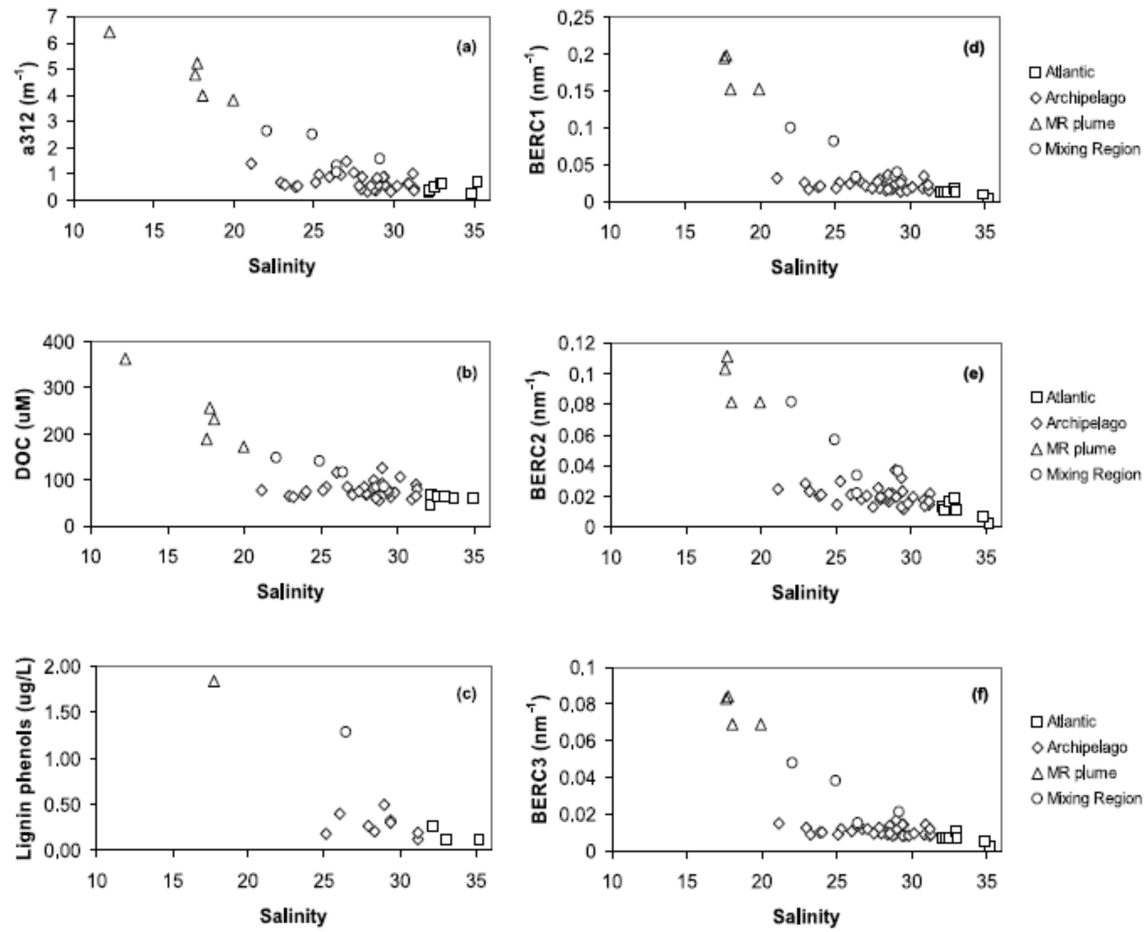
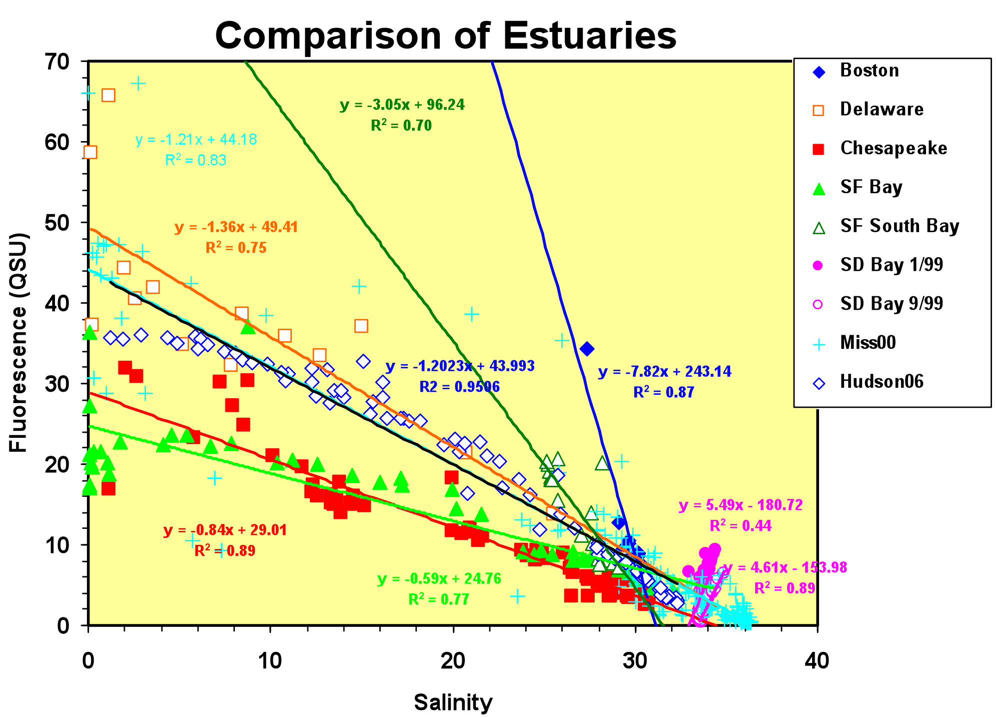


Figure 6. Salinity correlations at 12 m water depth. (a) a_{312} verses salinity, (b) DOC verses salinity, (c) lignin phenols verses salinity, (d) BERC1 verses salinity, (e) BERC2 verses salinity, and (f) BERC3 verses salinity. End-members identified include Atlantic (stations 1–8), Archipelago (stations 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



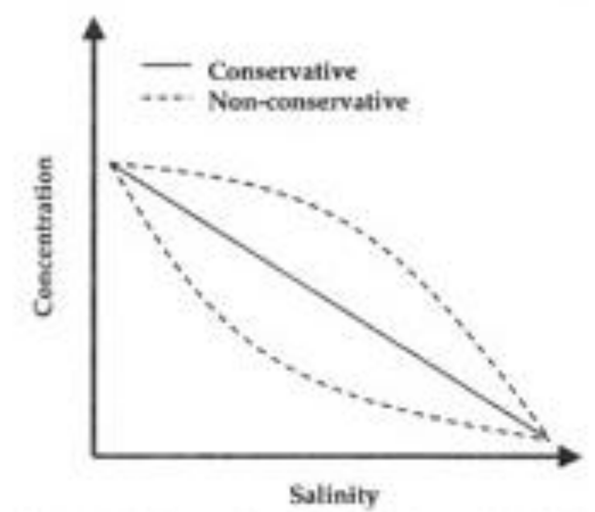
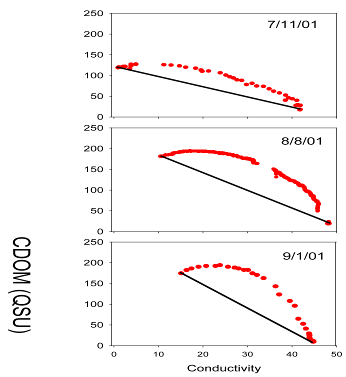


Fig. 1. Mixing diagram for a dissolved constituent, with a higher concentration in freshwater than in seawater (e.g. CDOM) (adapted from Liss, 1976).

Parker River Estuary, Plum Island Ecosystems LTER

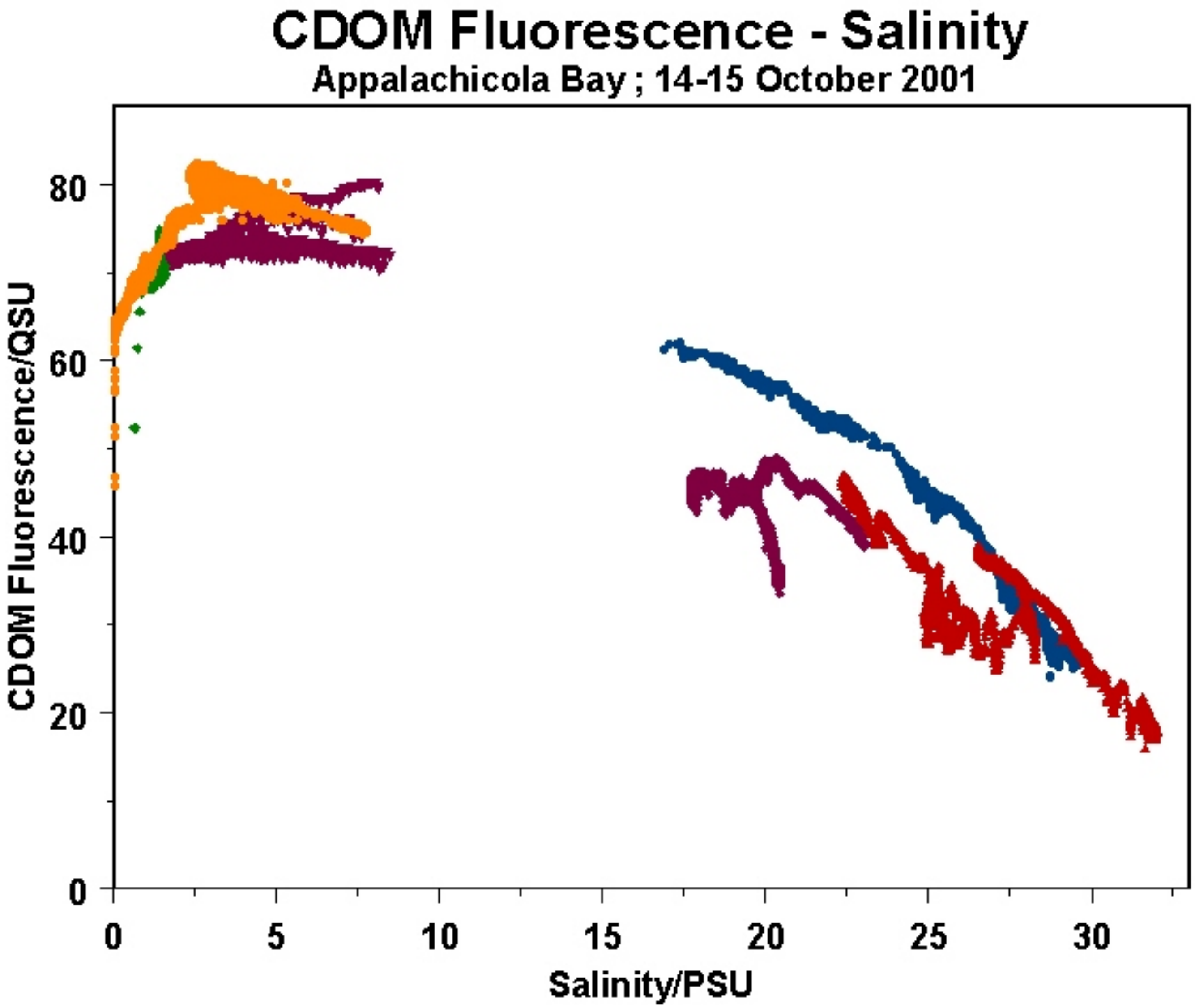


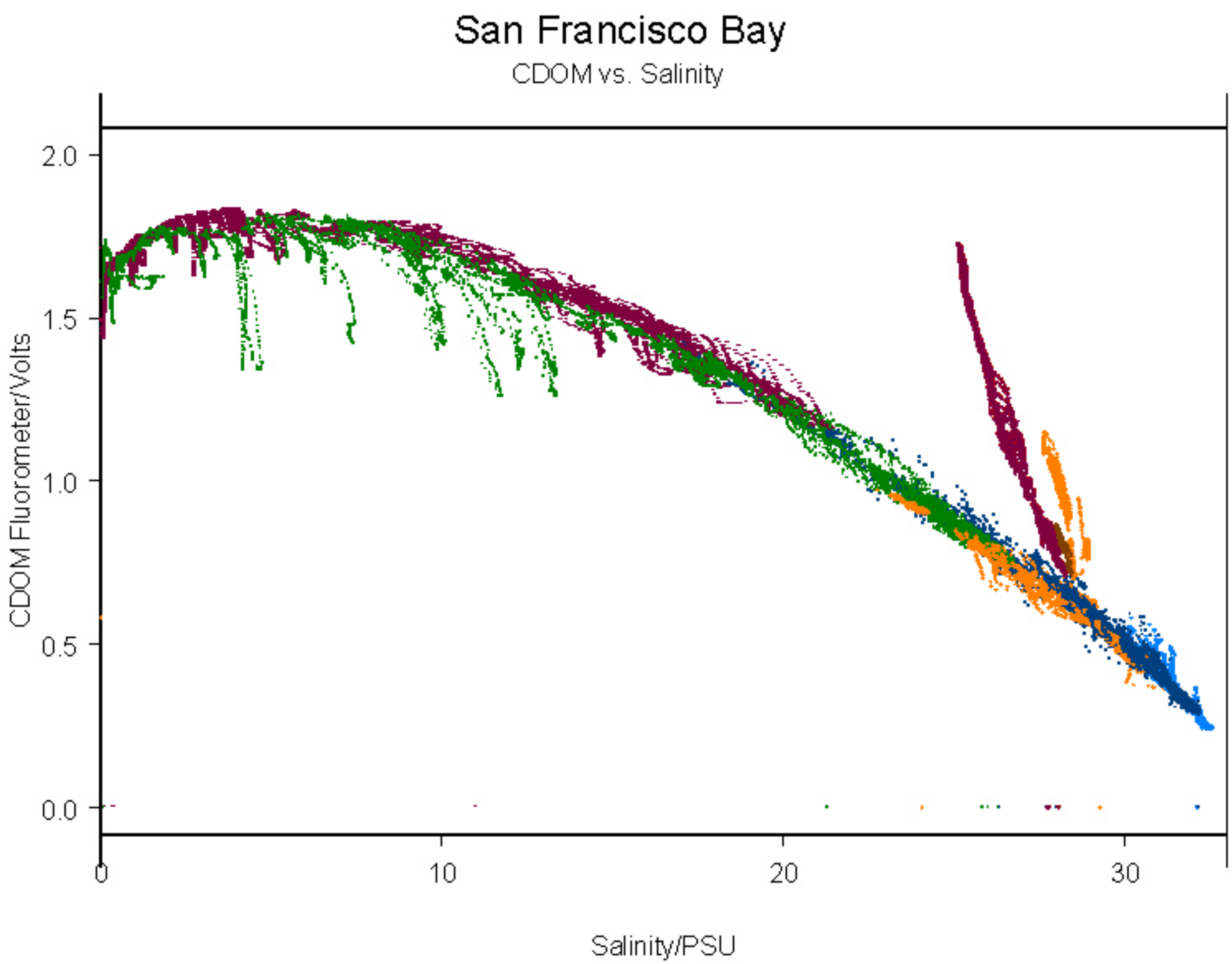
July
50% *In Situ*

August
70% *In Situ*

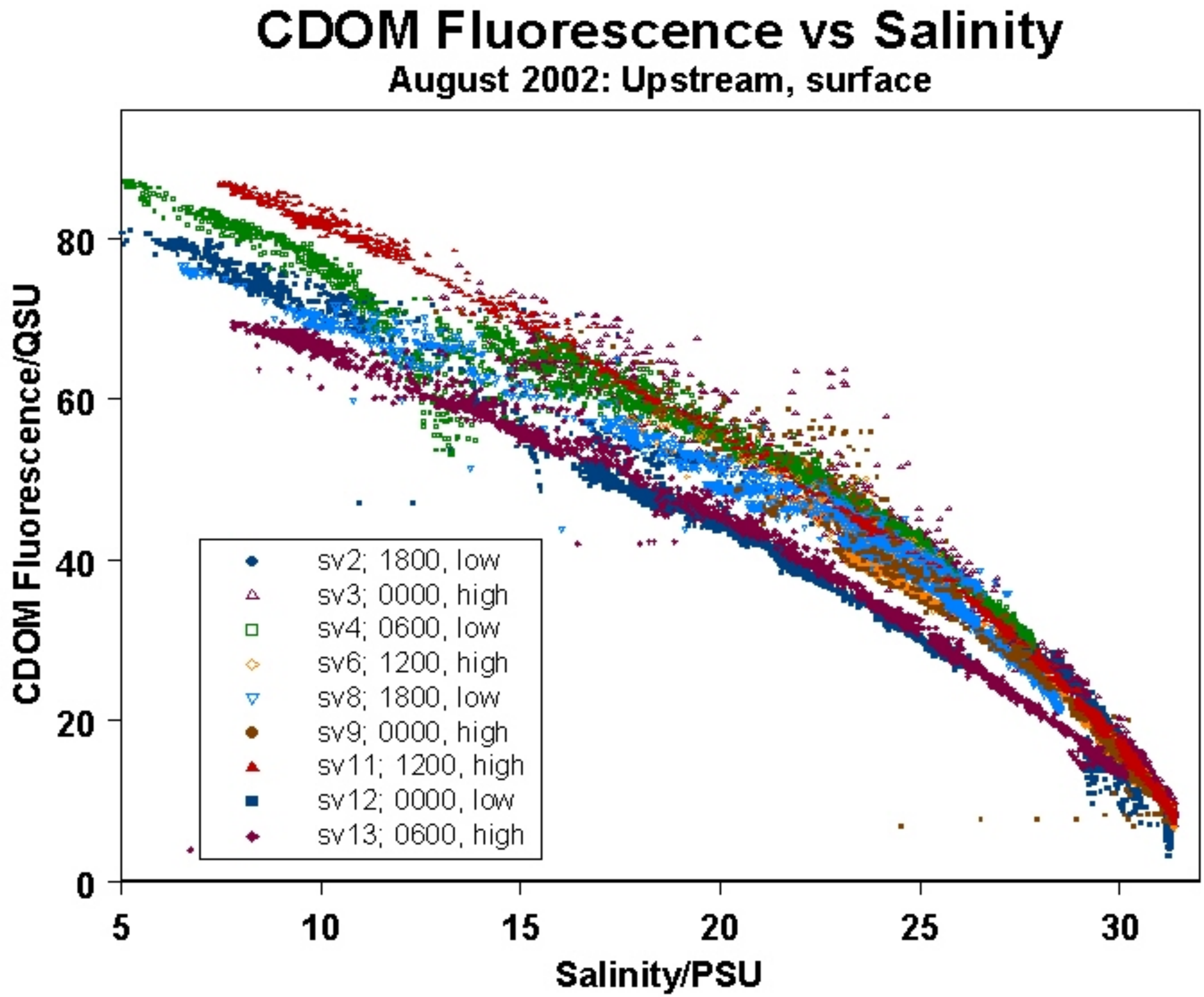
September
89% *In Situ*

Apalachicola Bay



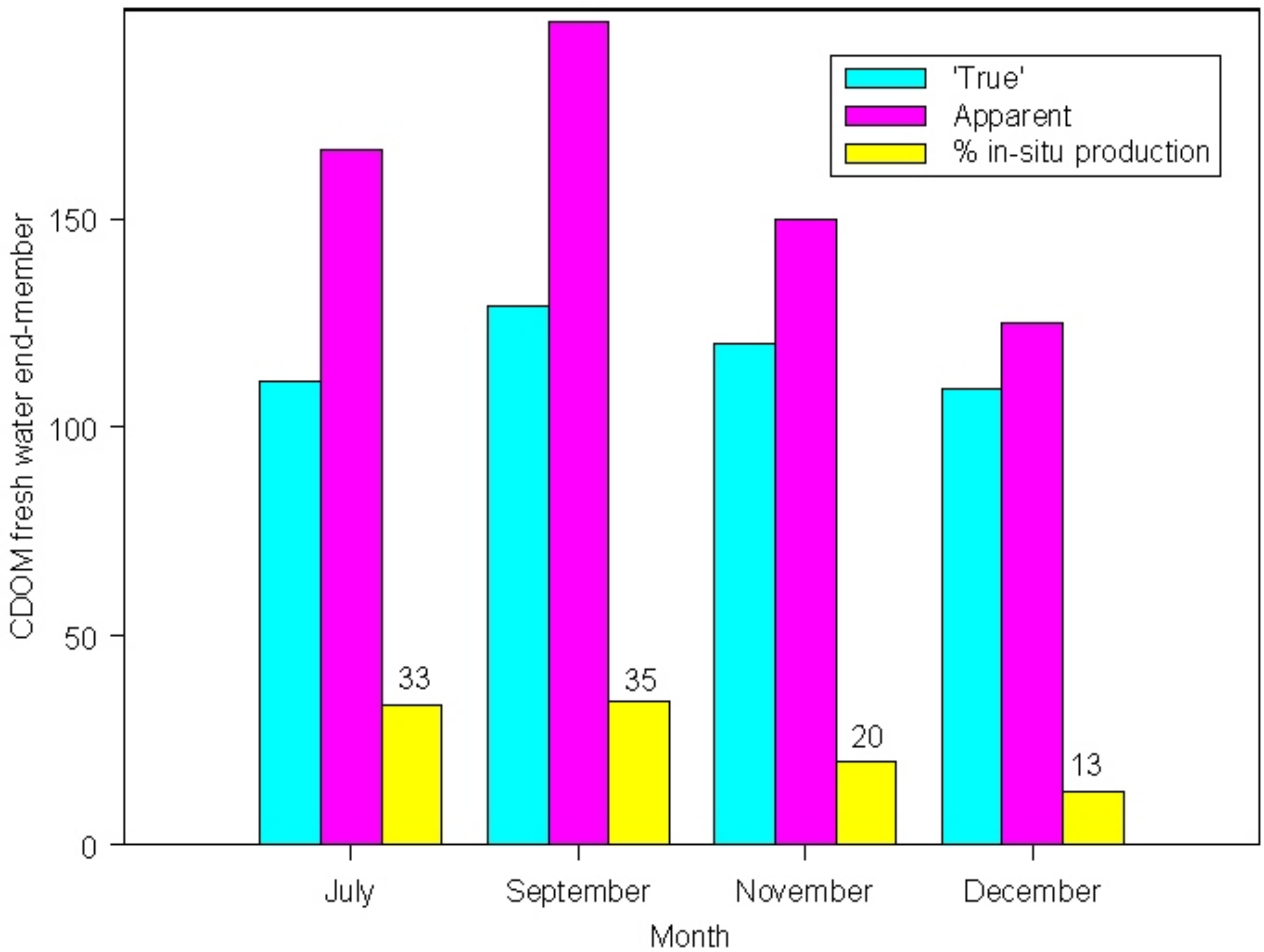


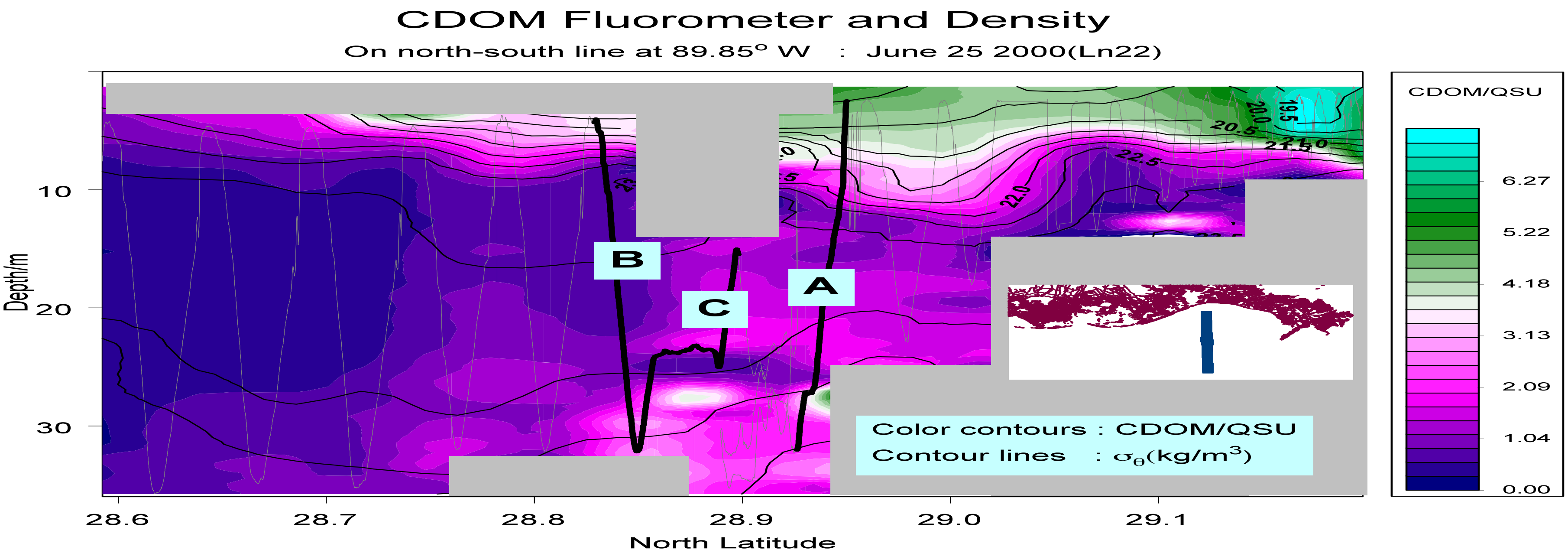
San Francisco Bay
CDOM vs. Salinity
CDOM Fluorometer/Volts
2.0
1.5
1.0
0.5
0.0
0
10
20
30
Salinity/PSU



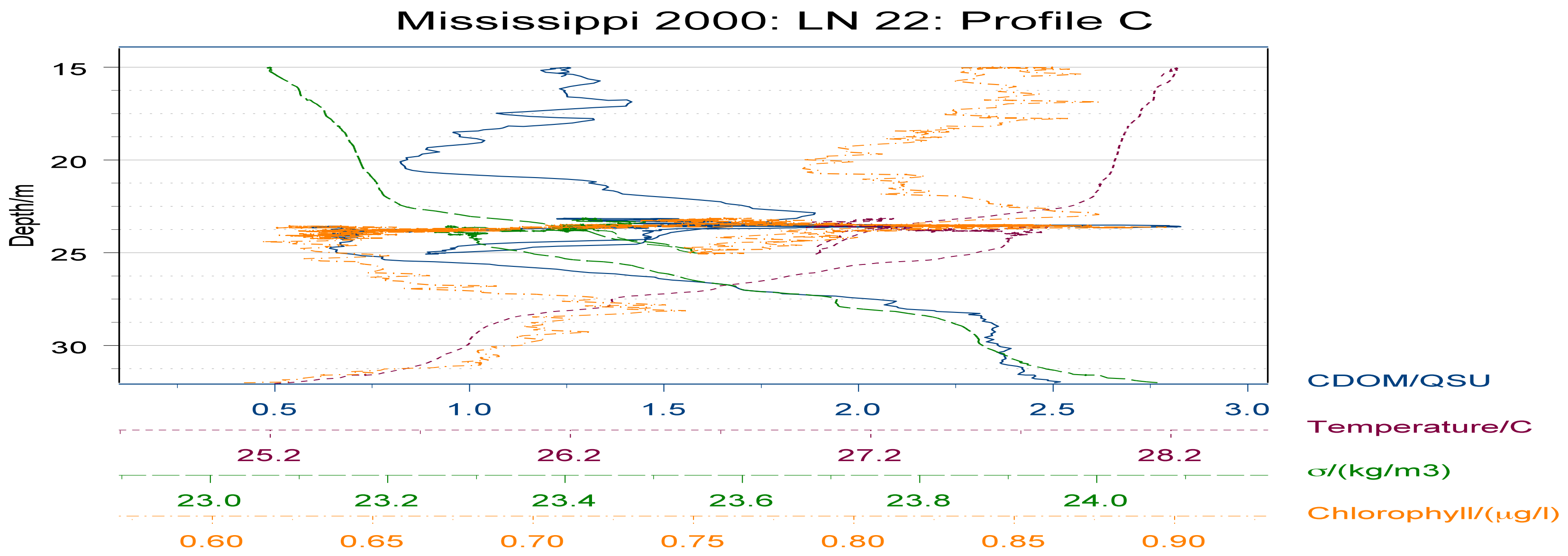
CDOM Fluorescence vs Salinity
August 2002: Upstream, surface
CDOM Fluorescence/QSU
0
20
40
60
80
5
10
15
20
25
30
Salinity/PSU
sv2; 1800, low
sv3; 0000, high
sv4; 0600, low
sv6; 1200, high
sv8; 1800, low
sv9; 0000, high
sv11; 1200, high
sv12; 0000, low
sv13; 0600, high

'True' and Apparent fresh water end-member CDOM concentrations





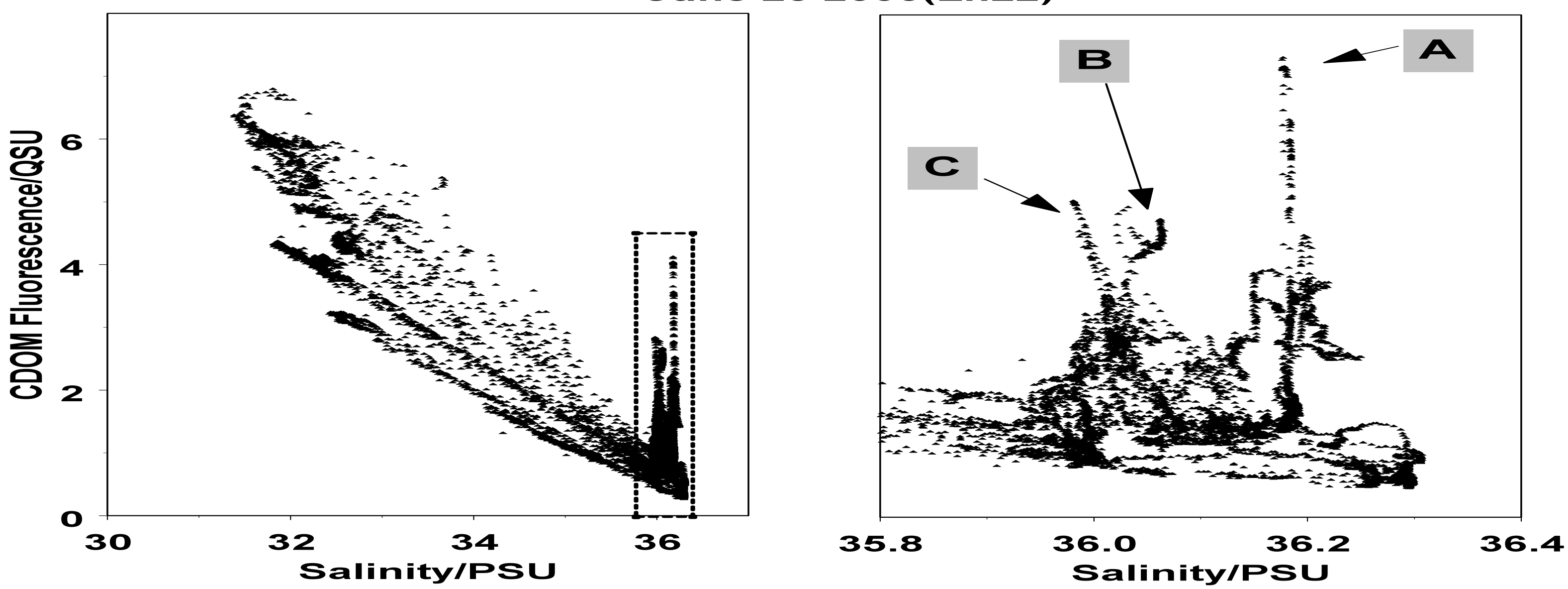
CDOM Fluorometer and Density
On north-south line at 89.85° W : June 25 2000(Ln22)
Depth/m
10
20
30
28.6
28.7
28.8
28.9
29.0
29.1
North Latitude
B
C
A
Color contours : CDOM/QSU
Contour lines : σθ(kg/m3)
CDOM/QSU
6.27
5.22
4.18
3.13
2.09
1.04
0.00



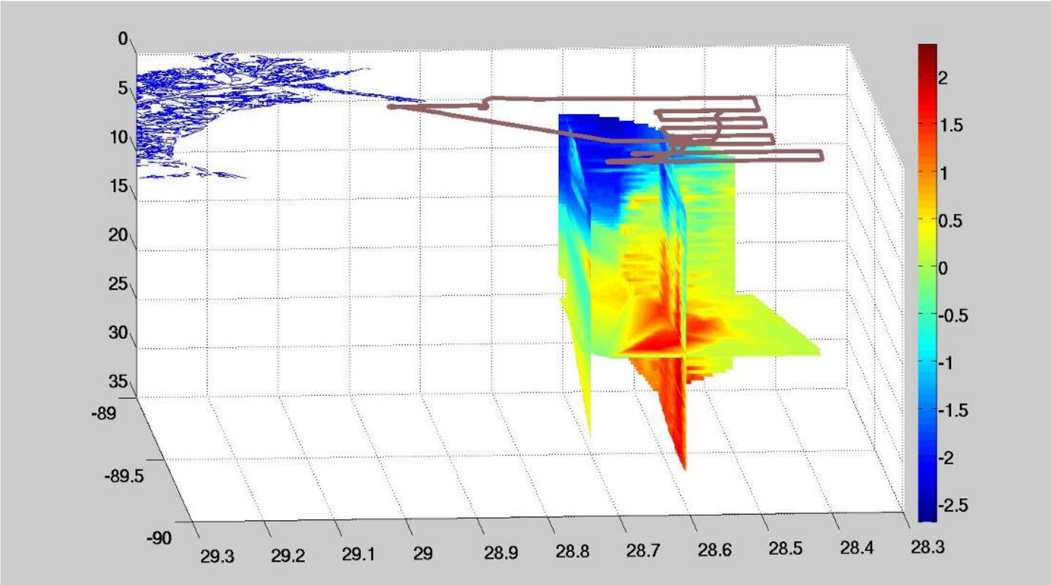
Mississippi 2000: LN 22: Profile C
Depth/m
15
20
25
30
0.5
1.0
1.5
2.0
2.5
3.0
CDOM/QSU
25.2
26.2
27.2
28.2
Temperature/C
23.0
23.2
23.4
23.6
23.8
24.0
σ/(kg/m3)
0.60
0.65
0.70
0.75
0.80
0.85
0.90
Chlorophyll/(μg/l)

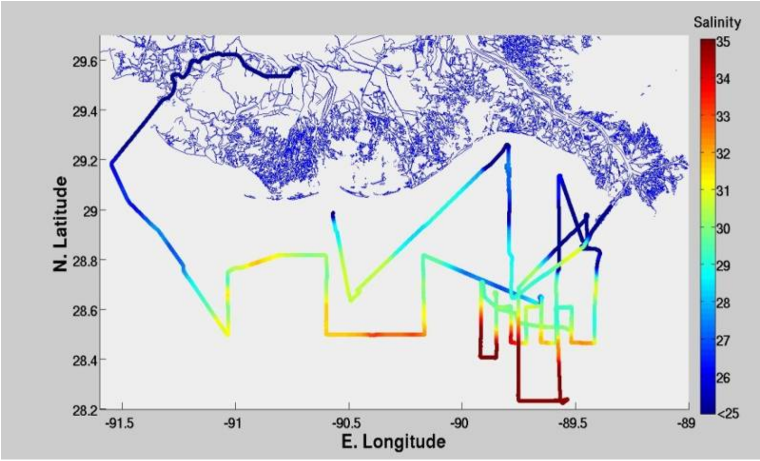
CDOM-Salinity Curve for North-South Line at 89.85^{o}W

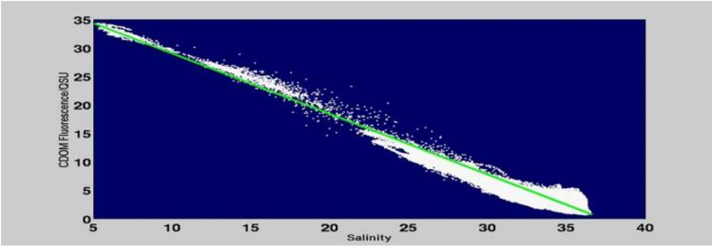
June 25 2000(Ln22)

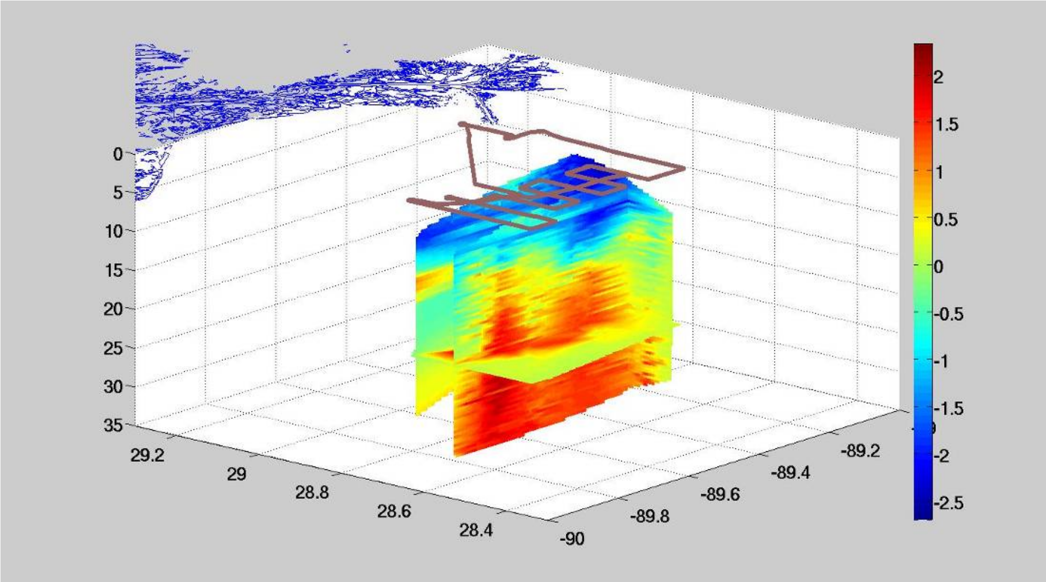


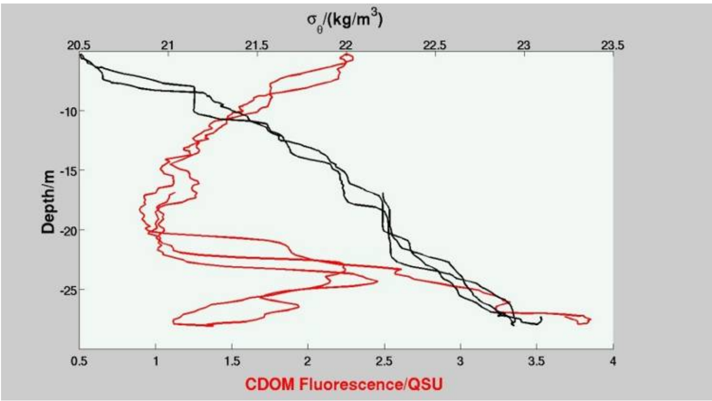
Miss '07--Sub-Surface CDOM Production =15% of River



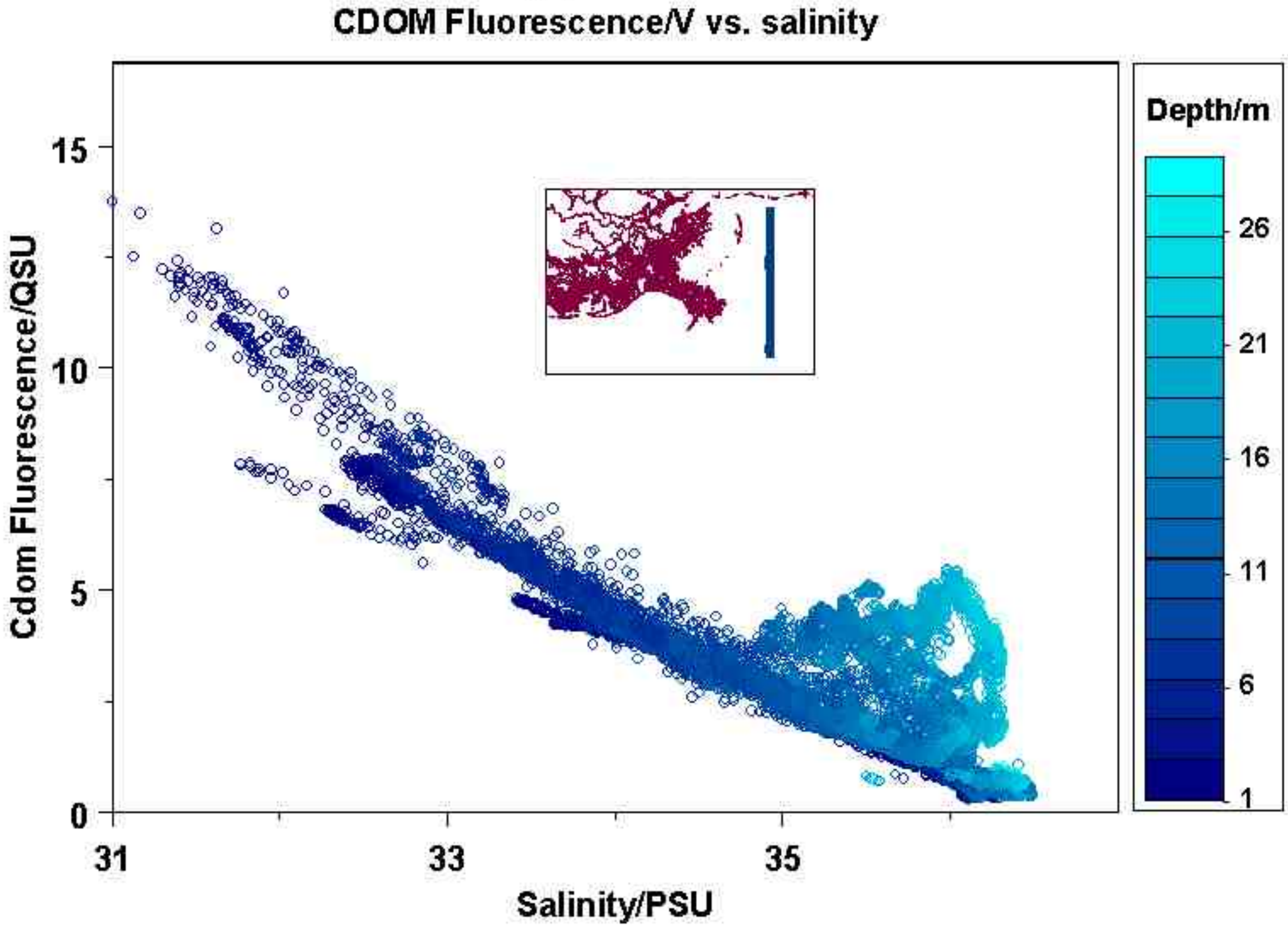


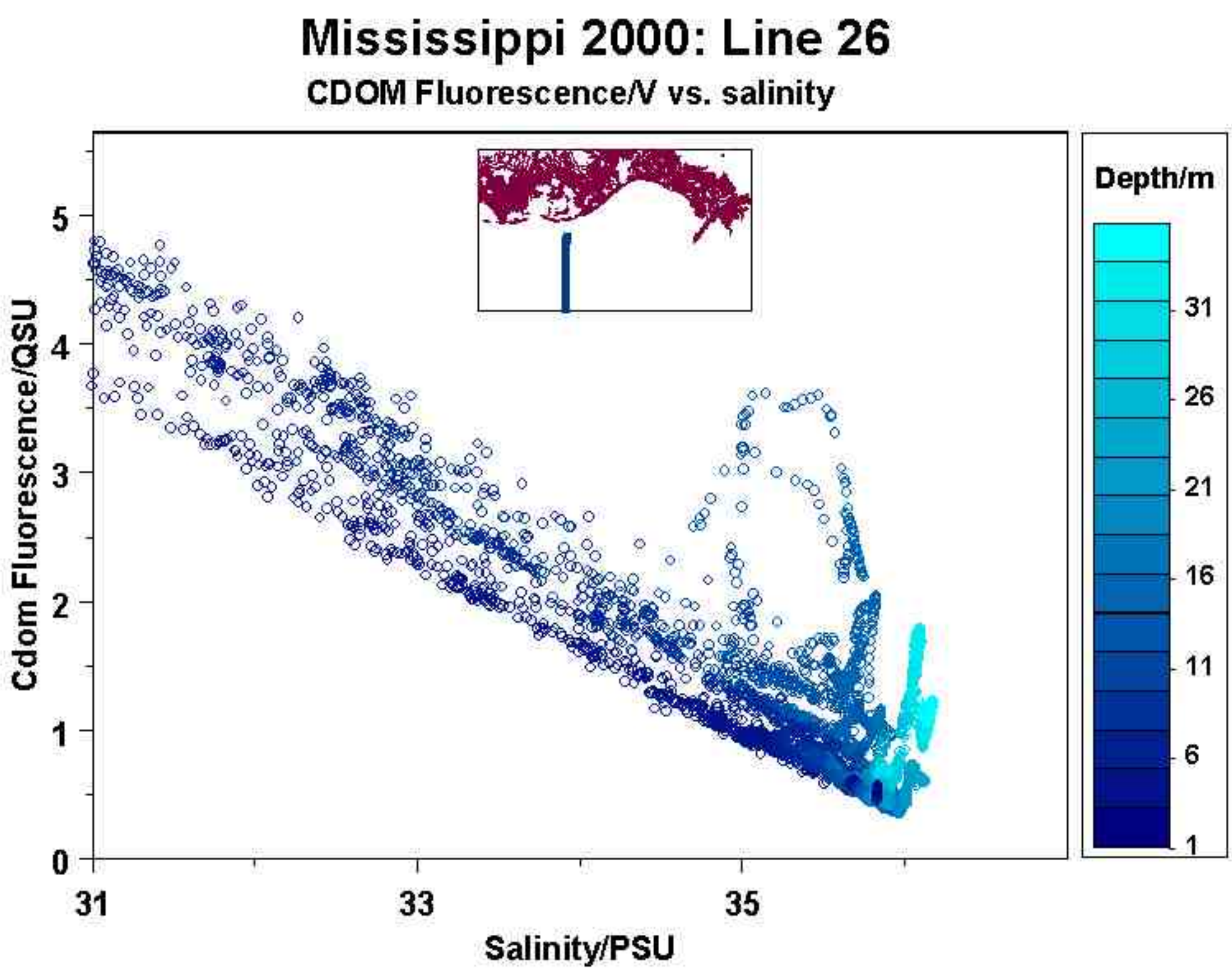






Mississippi 2000: Line 14

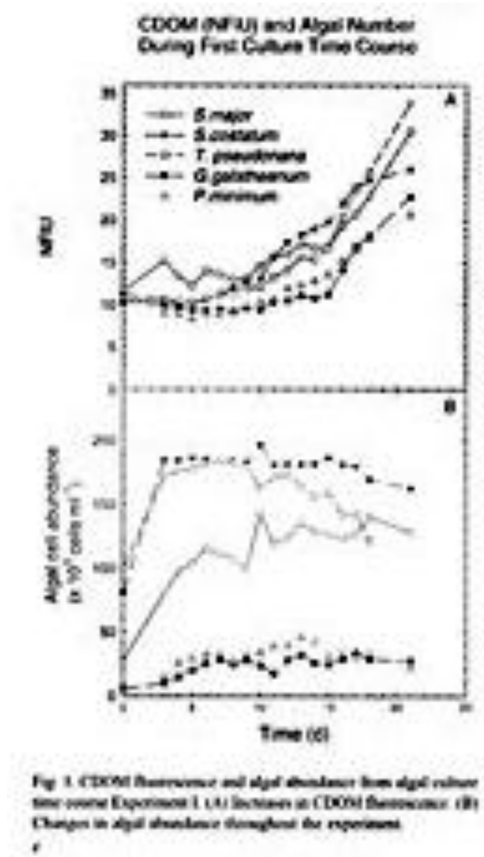




Mississippi 2000: Line 26
CDOM Fluorescence/V vs. salinity
Cdom Fluorescence/QSU
0
1
2
3
4
5
31
33
35
Salinity/PSU
Depth/m
1
6
11
16
21
26
31

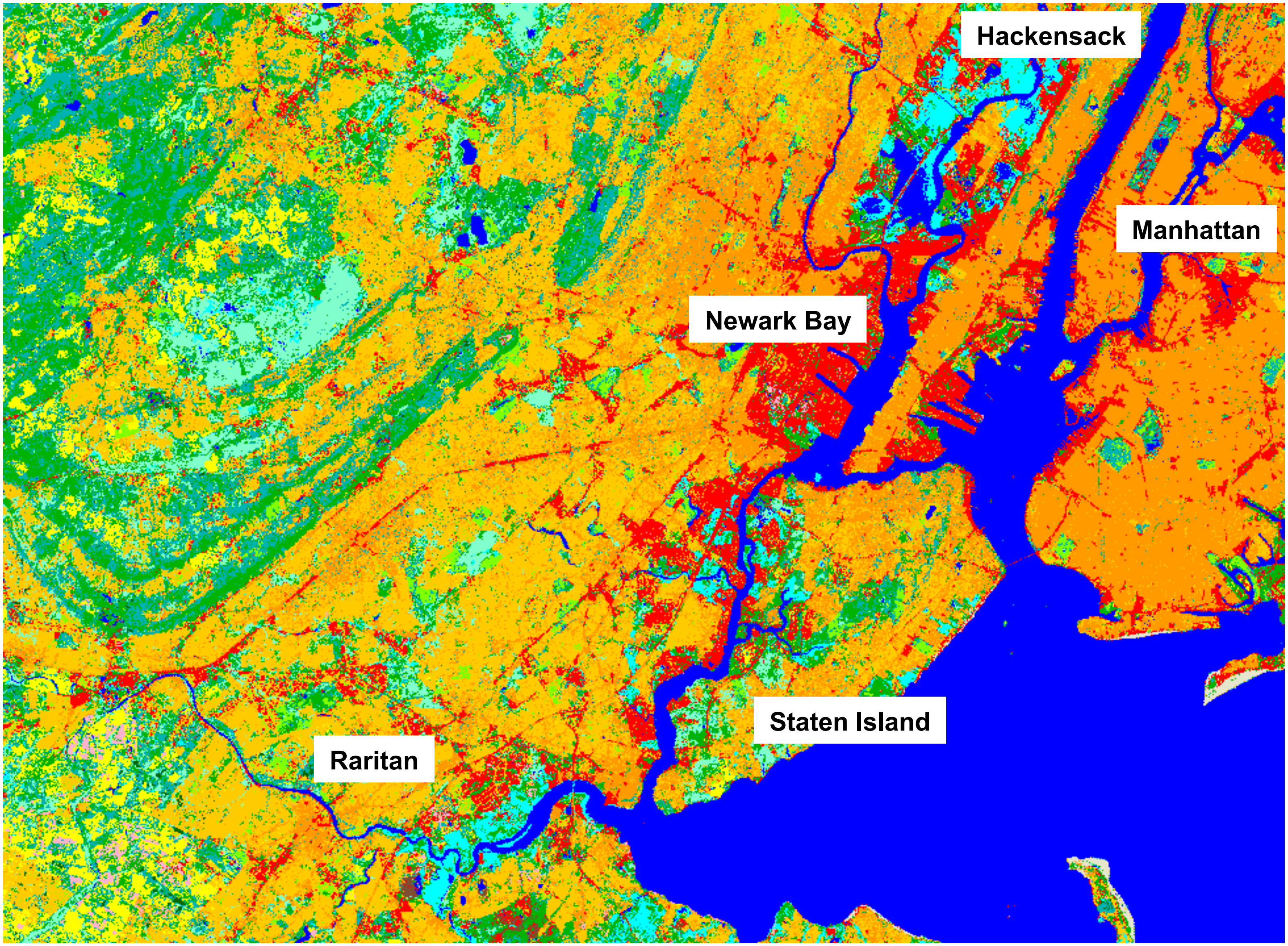
Phytoplankton

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

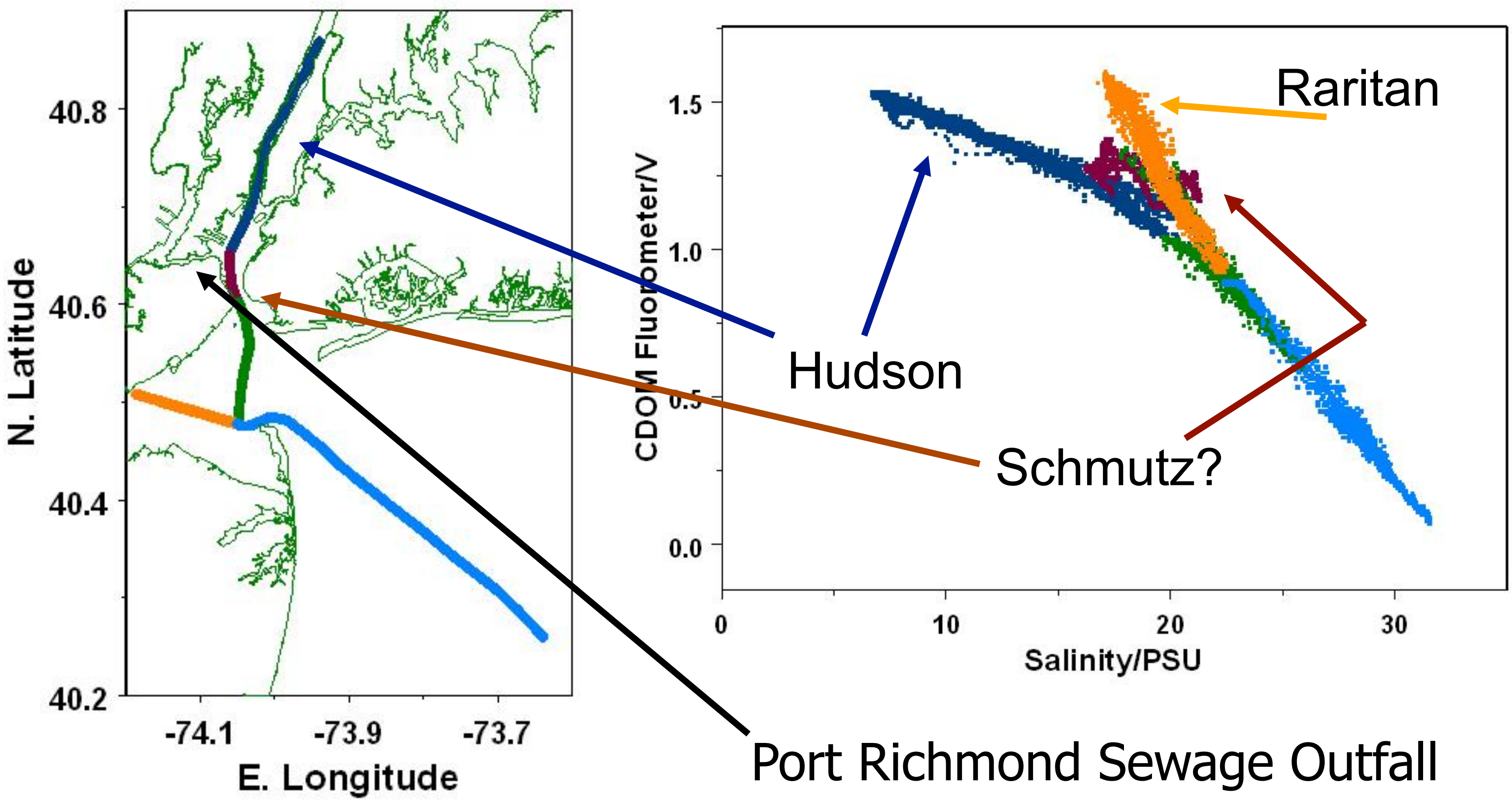


Rochelle-Newell & Fisher, 2002

Hudson River Estuary



Hudson River Estuary
June, 2004 (Sewage)



CDOM Sinks

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

Flocculation

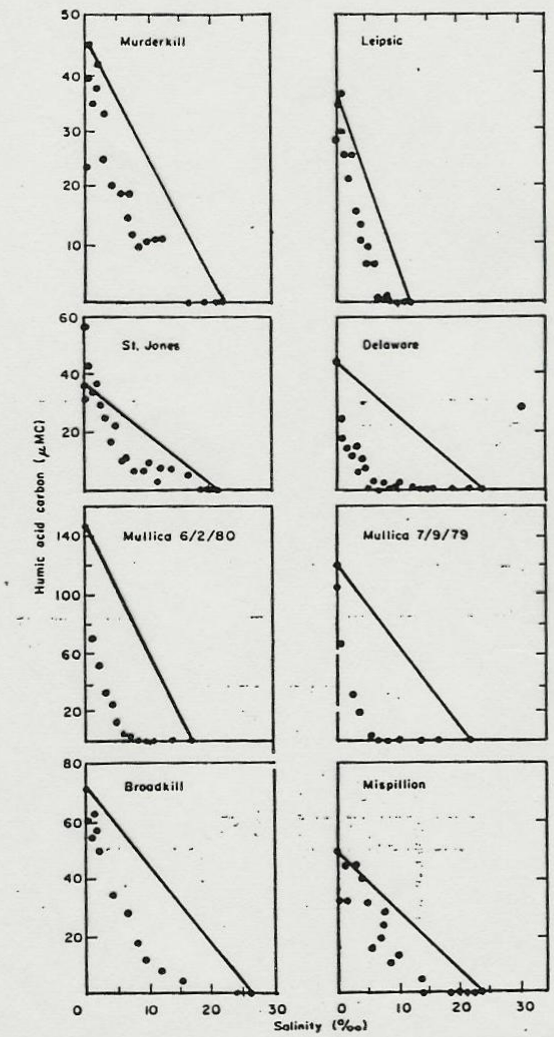
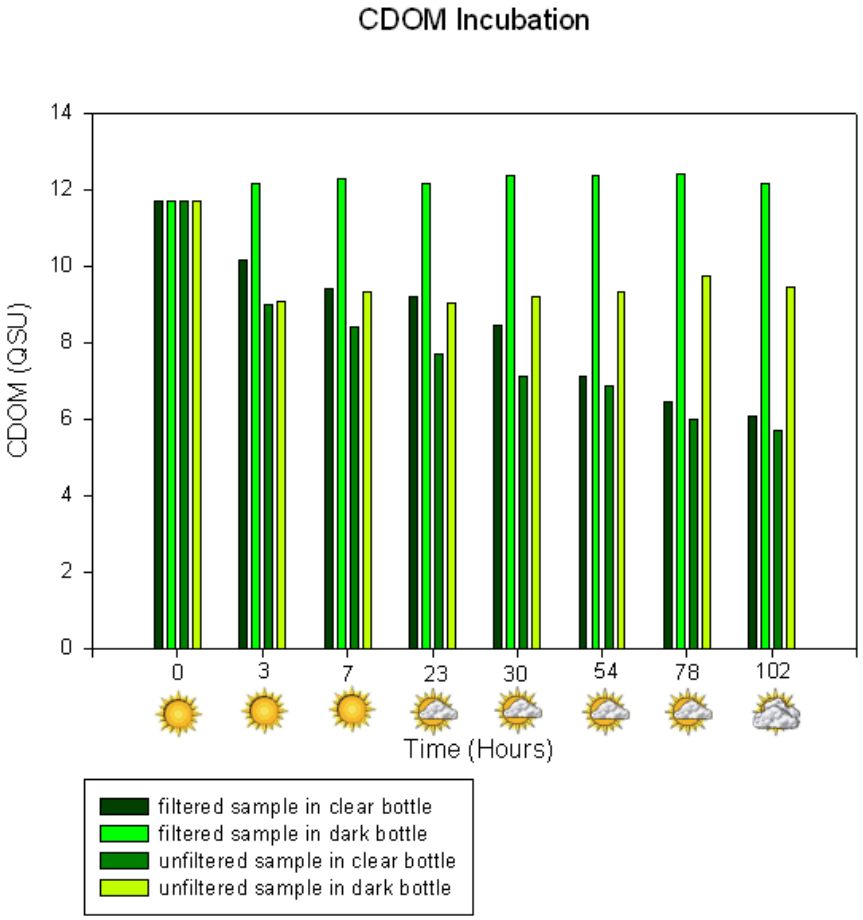
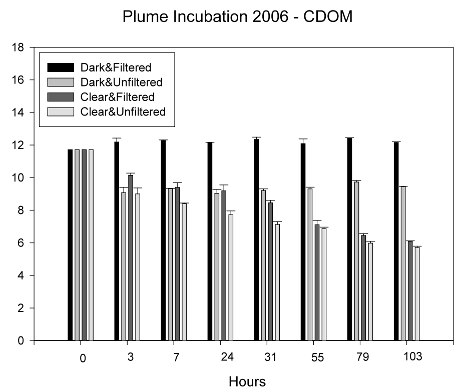


Figure 3. Humic acid carbon as a function of salinity. The standard error of the mean is 5%. The humic acid concentration at 30‰ in the Delaware Bay has been measured to be anomalously high in three surveys suggesting that the measurement is valid. It may represent a seaward source of humic acid to the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

Incubations



Plume CDOM Degradation (Hudson)

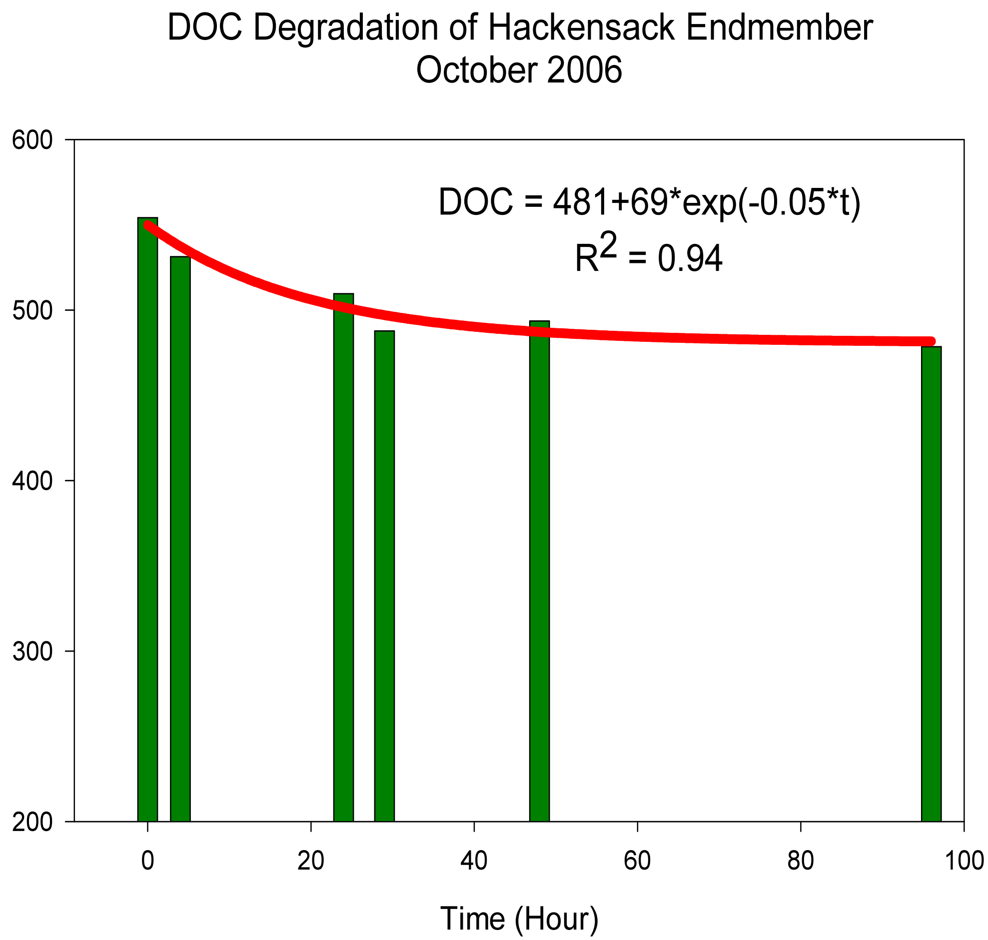


Incubation:

- 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

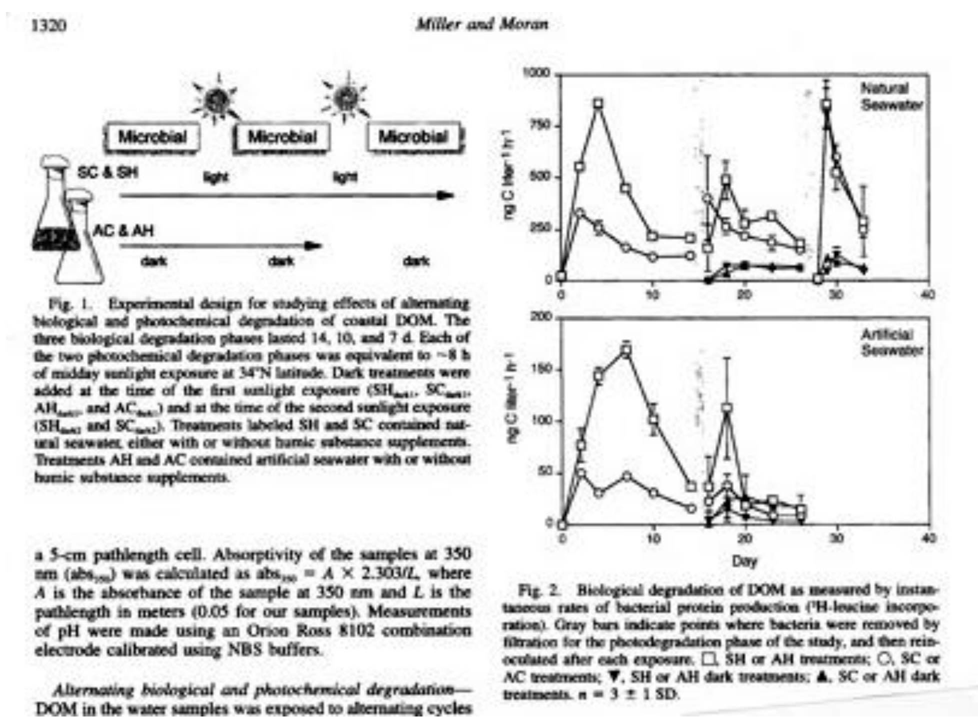
Incubation



Unfiltered, clear bottle incubations

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

- Biological combined with photochemical degradation



1320 *Miller and Moran*

Fig. 1. Experimental design for studying effects of alternating biological and photochemical degradation of coastal DOM. The three biological degradation phases lasted 14, 10, and 7 d. Each of the two photochemical degradation phases was equivalent to ~8 h of midday sunlight exposure at 34°N latitude. Dark treatments were added at the time of the first sunlight exposure (SH_{dark1}, SC_{dark1}, AH_{dark1}, and AC_{dark1}) and at the time of the second sunlight exposure (SH_{dark2} and SC_{dark2}). Treatments labeled SH and SC contained natural seawater, either with or without humic substance supplements. Treatments AH and AC contained artificial seawater with or without humic substance supplements.

Fig. 2. Biological degradation of DOM as measured by instantaneous rates of bacterial protein production (^{3}H-leucine incorporation). Gray bars indicate points where bacteria were removed by filtration for the photodegradation phase of the study, and then reinoculated after each exposure. □, SH or AH treatments; ○, SC or AC treatments; ▼, SH or AH dark treatments; ▲, SC or AH dark treatments. $n = 3 \pm 1$ SD.

a 5-cm pathlength cell. Absorptivity of the samples at 350 nm (abs_{350}) was calculated as $abs_{350} = A \times 2.303/L$, where A is the absorbance of the sample at 350 nm and L is the pathlength in meters (0.05 for our samples). Measurements of pH were made using an Orion Ross 8102 combination electrode calibrated using NBS buffers.

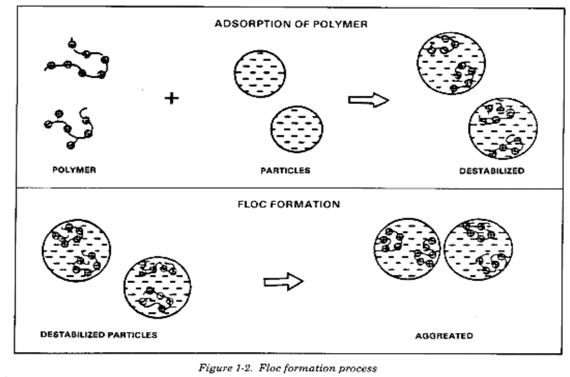
Alternating biological and photochemical degradation—DOM in the water samples was exposed to alternating cycles

Miller and Moran, 1997

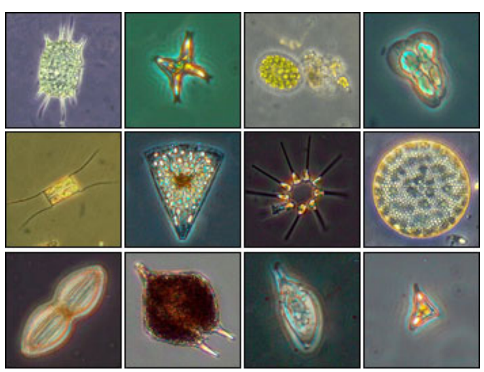
Possible Sources and Sinks

Photochemical Transformation

Bacterial Degradation



Flocculation



Phytoplankton Production

Addition from marsh, sewage et al.

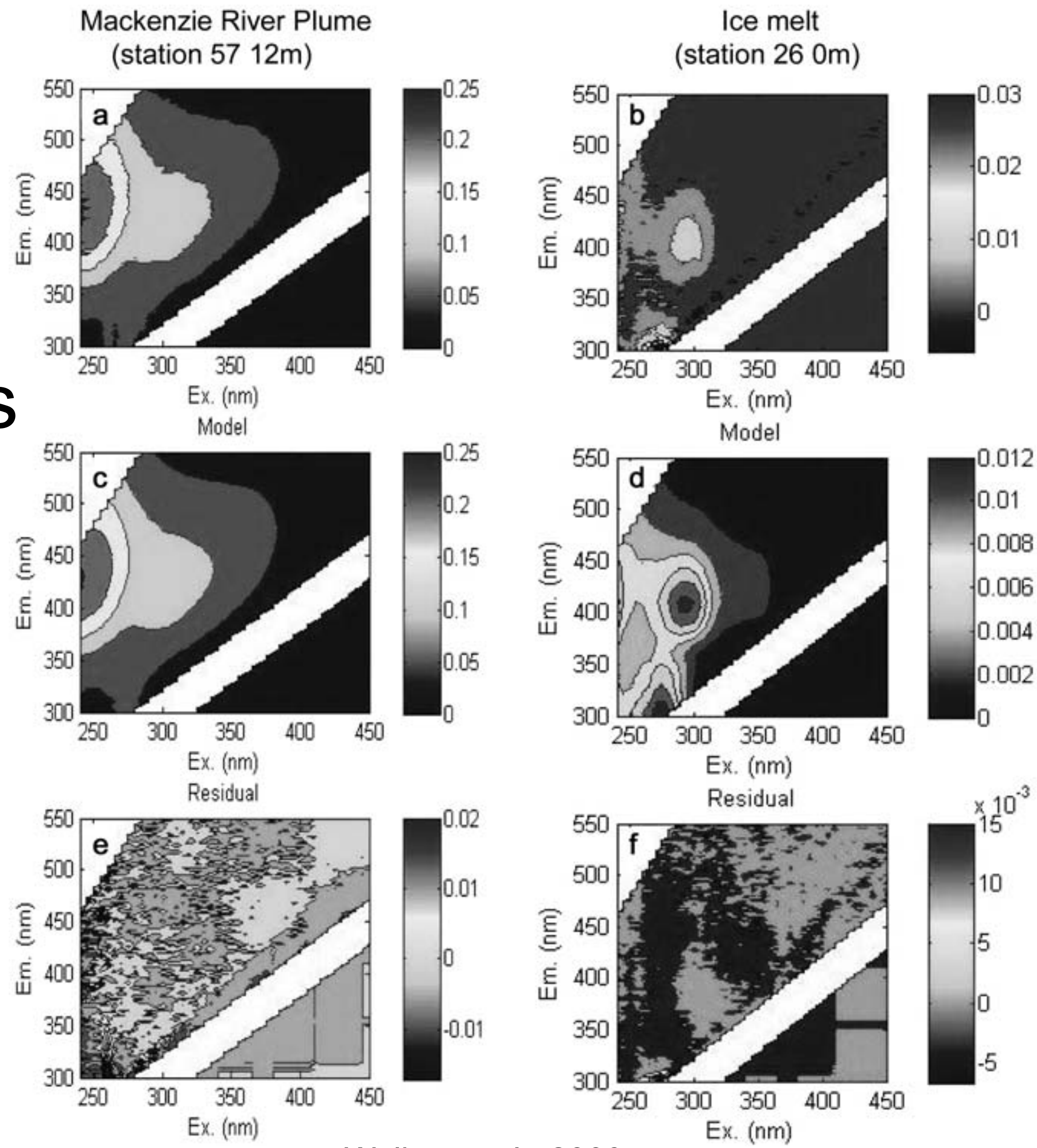
What application could you use CDOM measurements for?

- 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

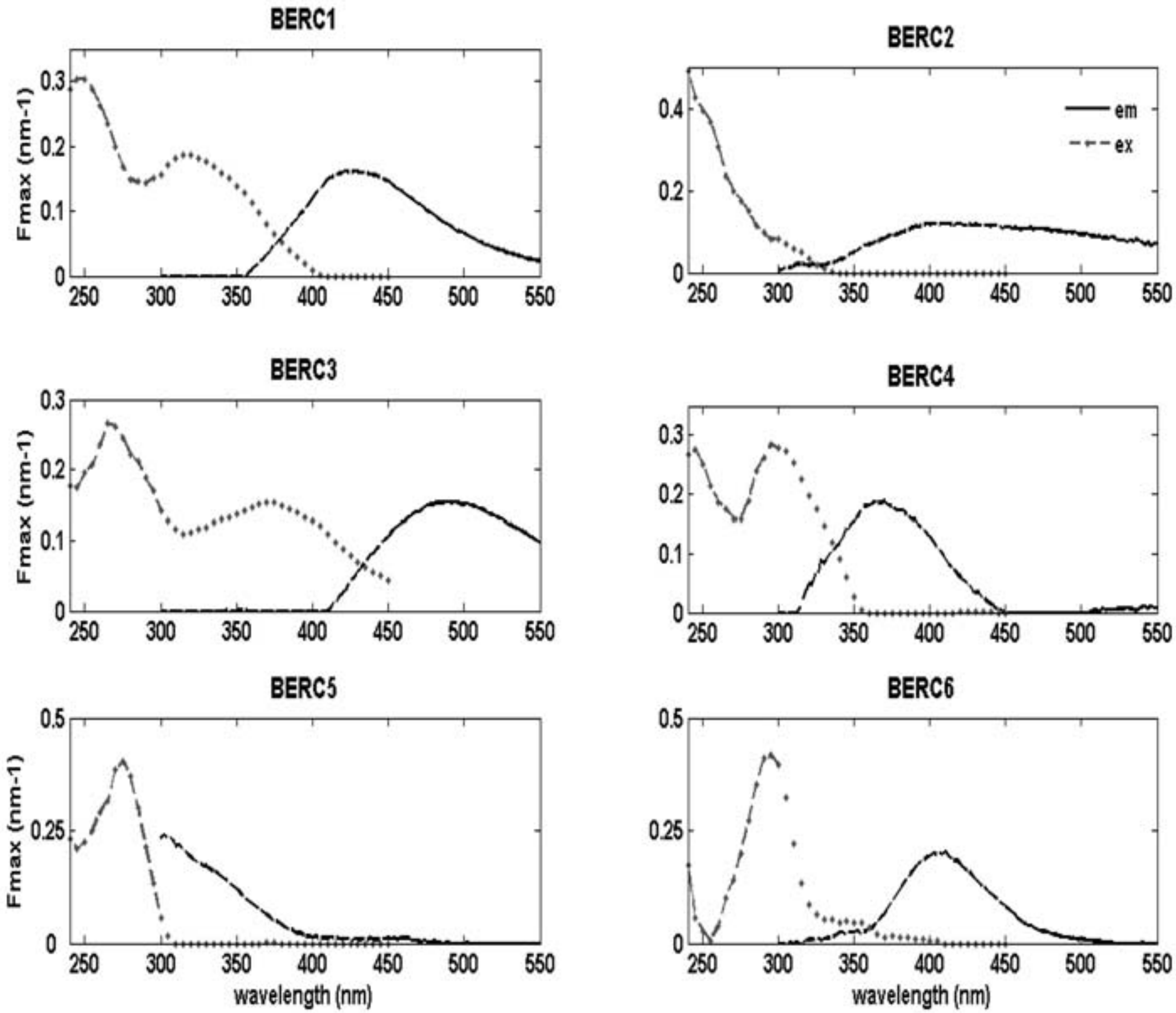
- Tracing terrestrial inputs into the ocean



Walker et al., 2009

PARAFAC

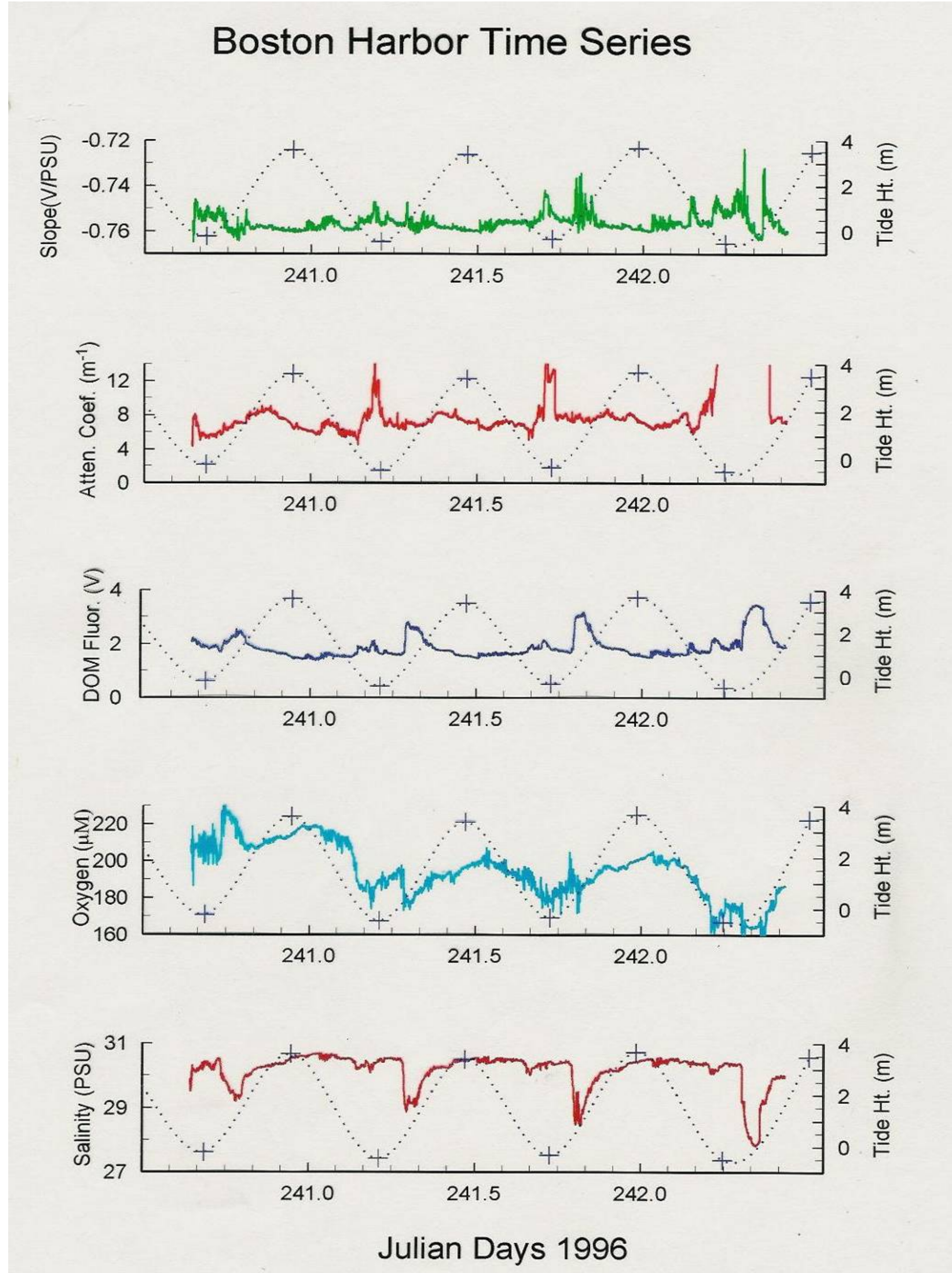
- Principle Components
- 3-9 components
- Excitation and Emission (Contours)
- >60 samples



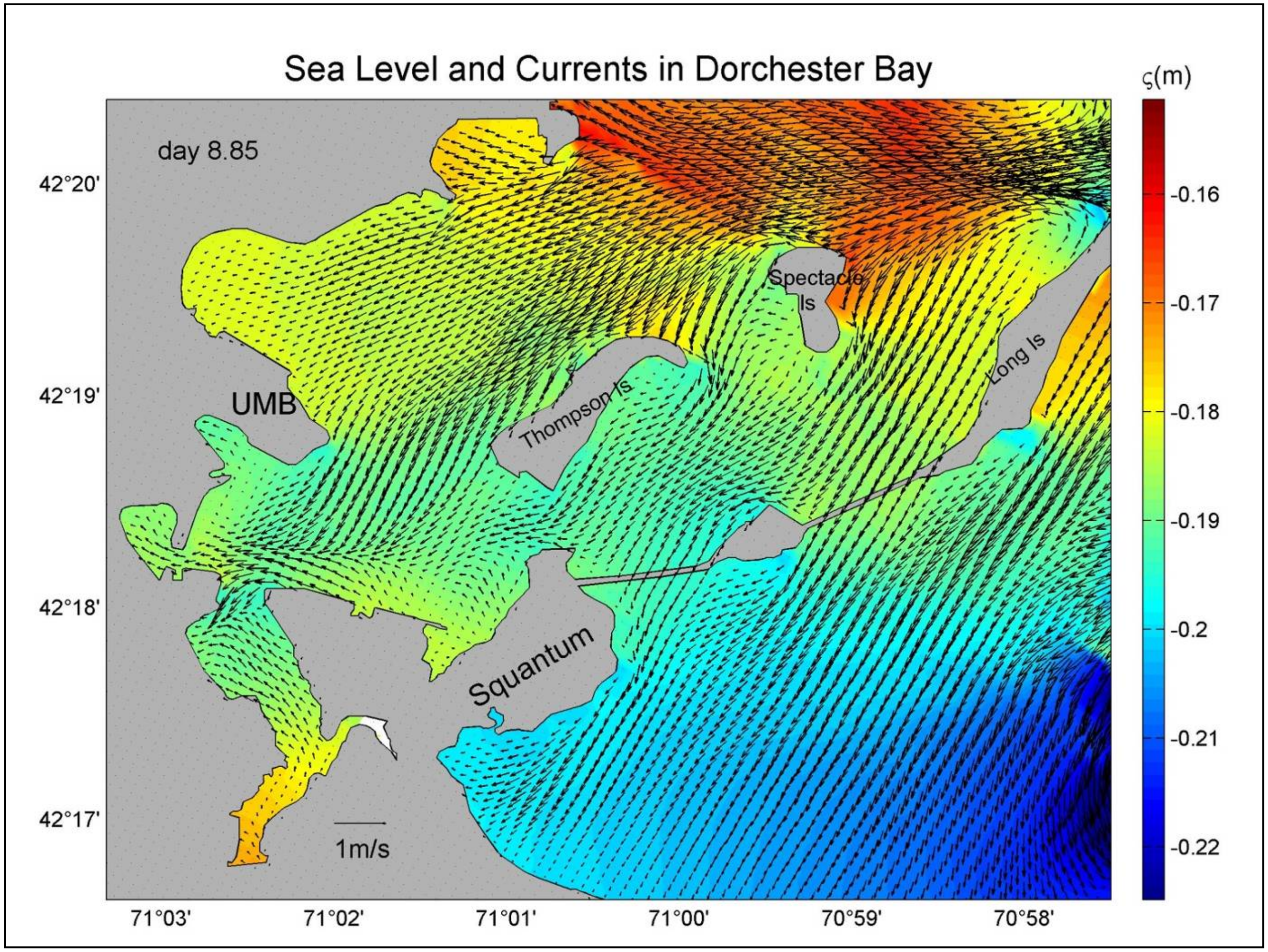
Walker et al., 2009

Coastal Dynamics

- Time Series
- Sensor Networks
- Models

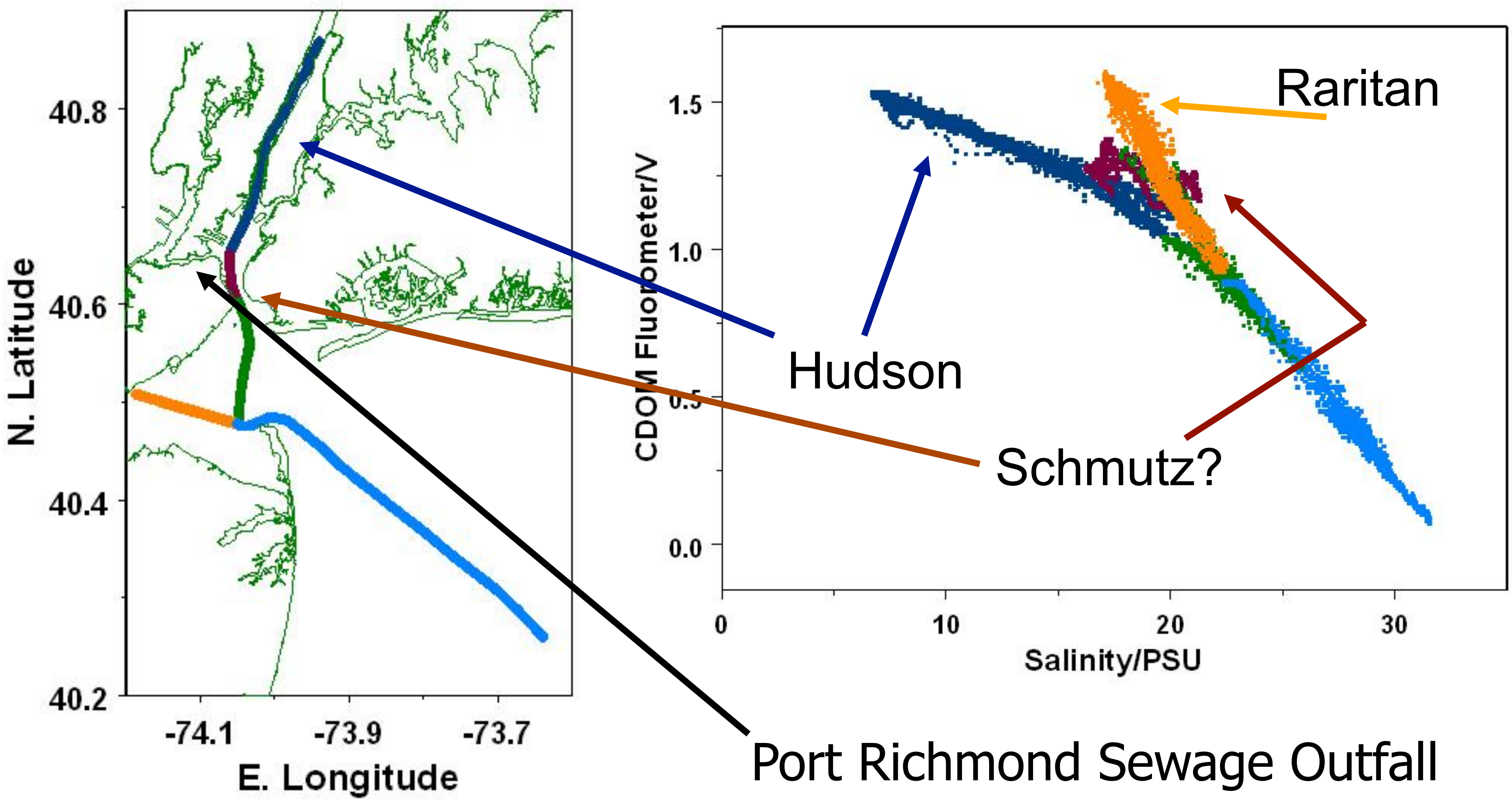


Boston Harbor



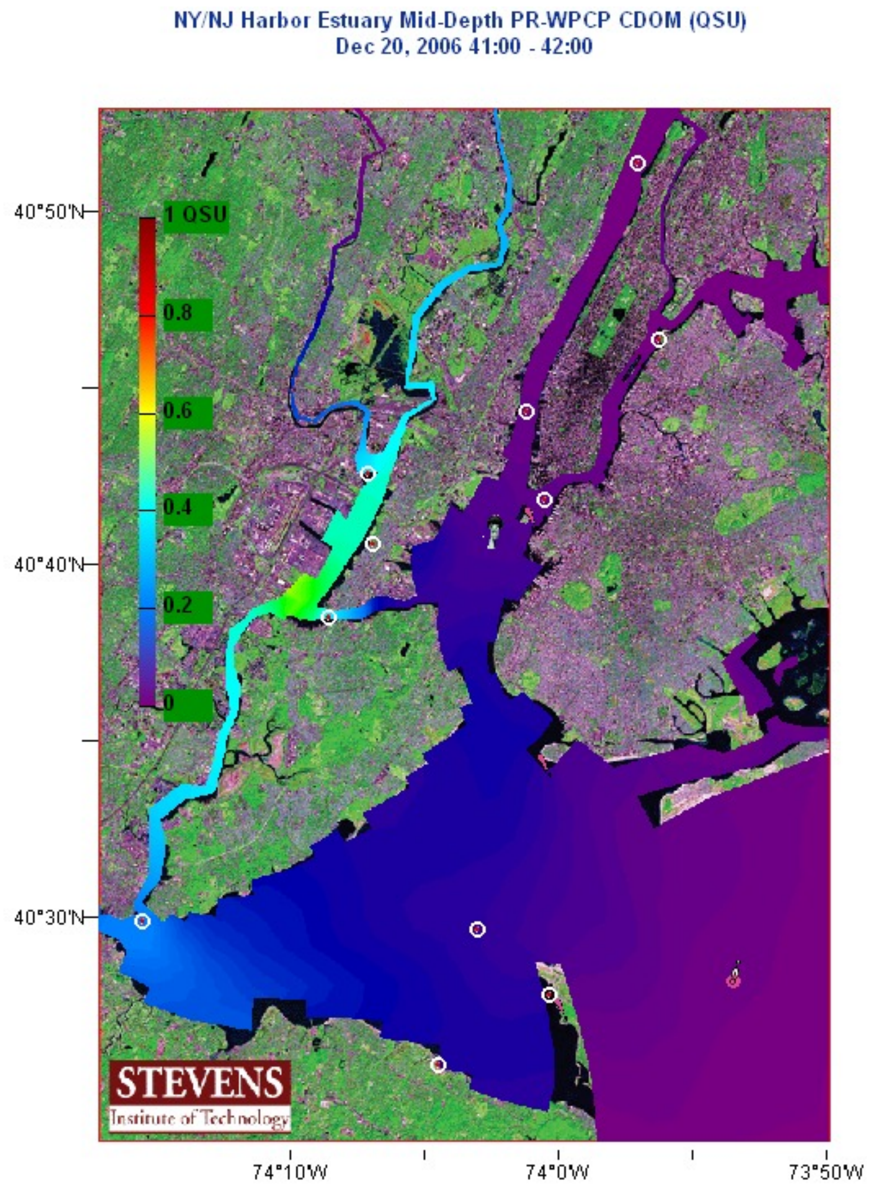
60 m resolution
72 hour prediction

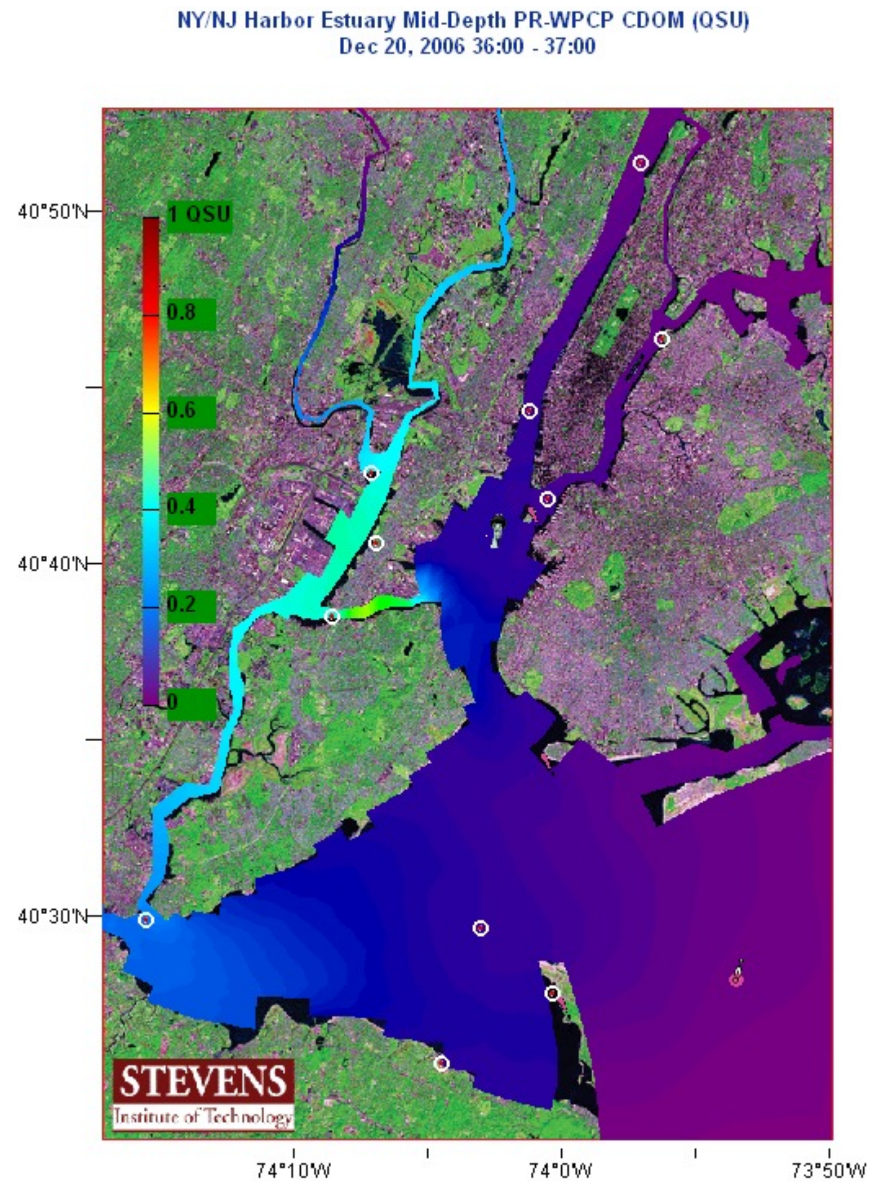
Hudson River Estuary June, 2004 (Sewage)



Model with ‘schmutz’:

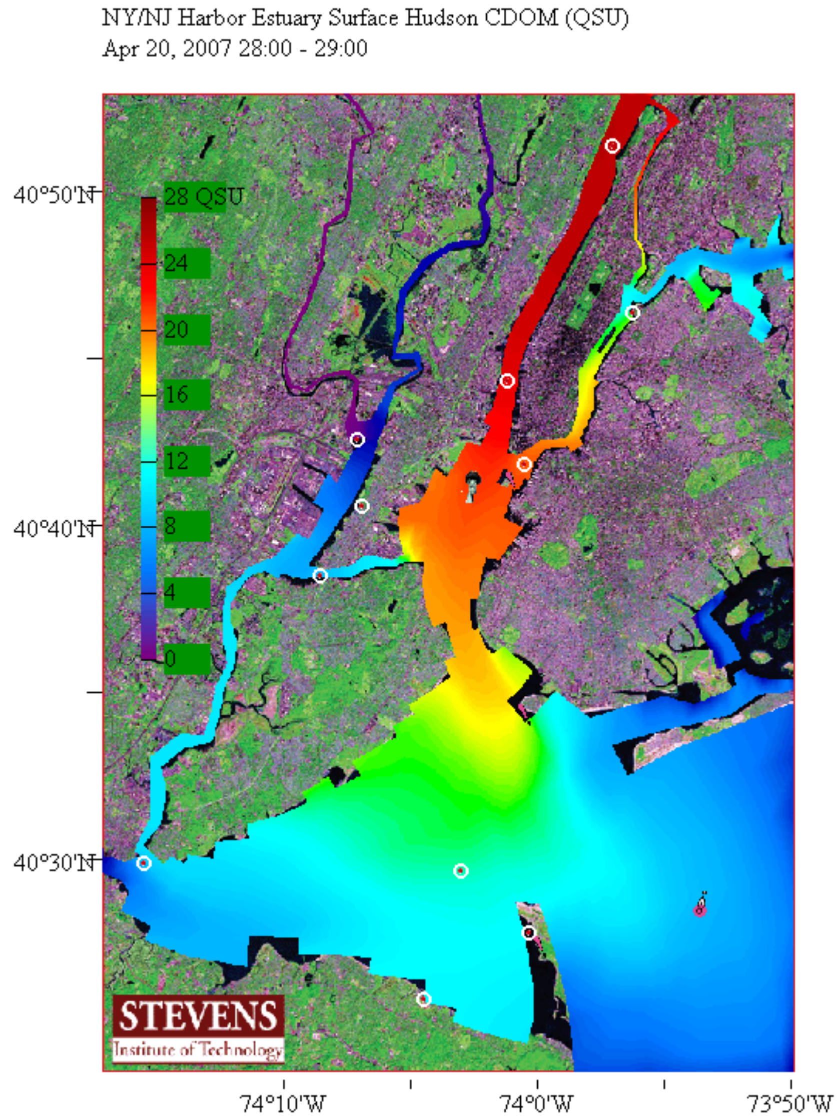
Possibly associated with Port Richmond POTW





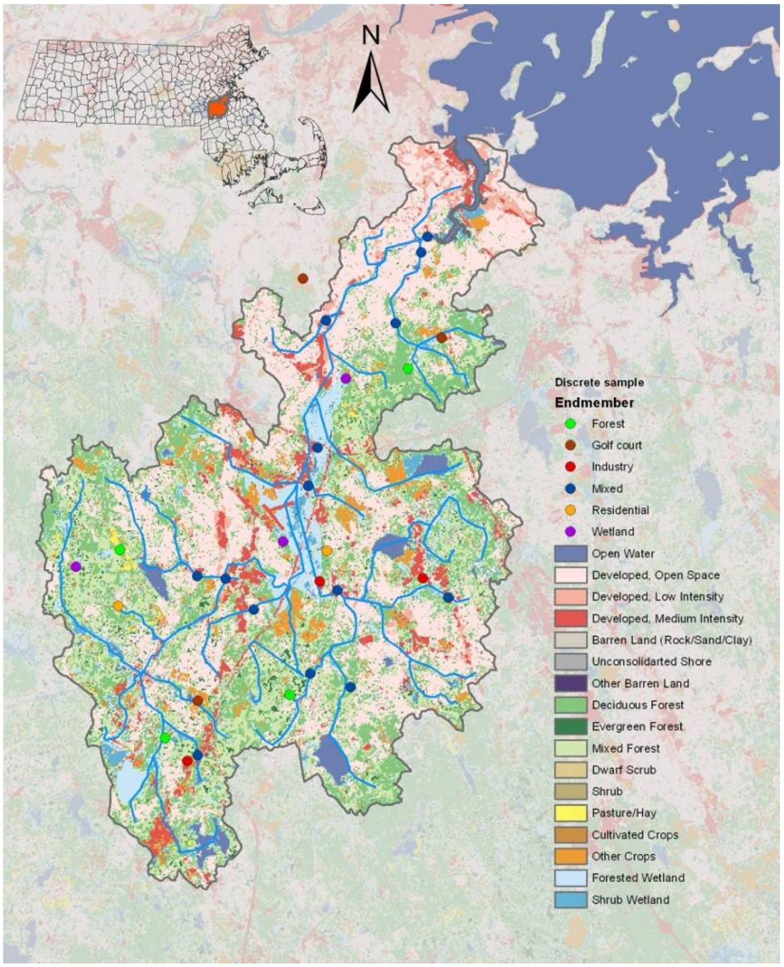
Modeling-Summary

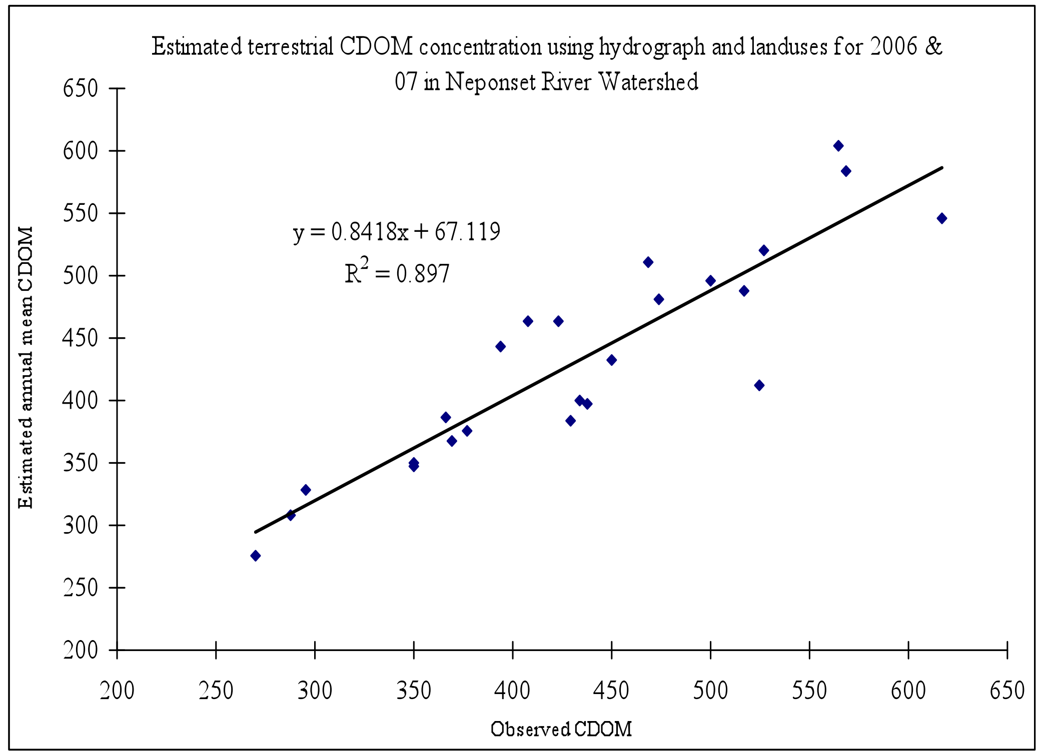
- CDOM added to existing observatory/predictive physical model
- High resolution measurements ground-truth model
- New sources and source strengths can be discovered
- Boston Harbor is being modeled as well



Blumberg and Geogas, unpubl.

Estimating CDOM concentration with hydrograph and landuse variables at Neponset River Watershed





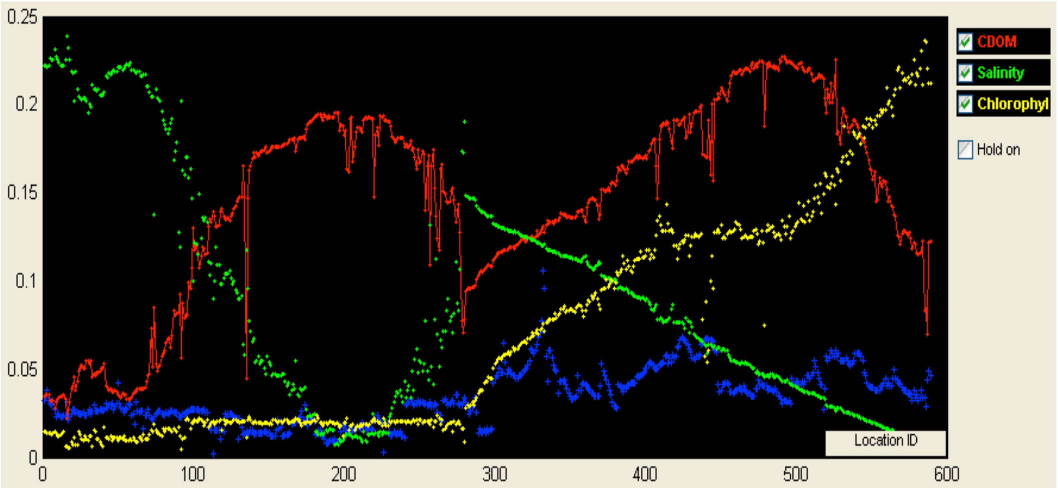
$$y = 0.306\ln(Q) - 0.226\ln(S) + 0.043w$$
$$+0.06d + 0.06f + 0.15a + 0.085wet + 0.725$$

Remote Sensing:
Field Measurements--CDOM and Spectra

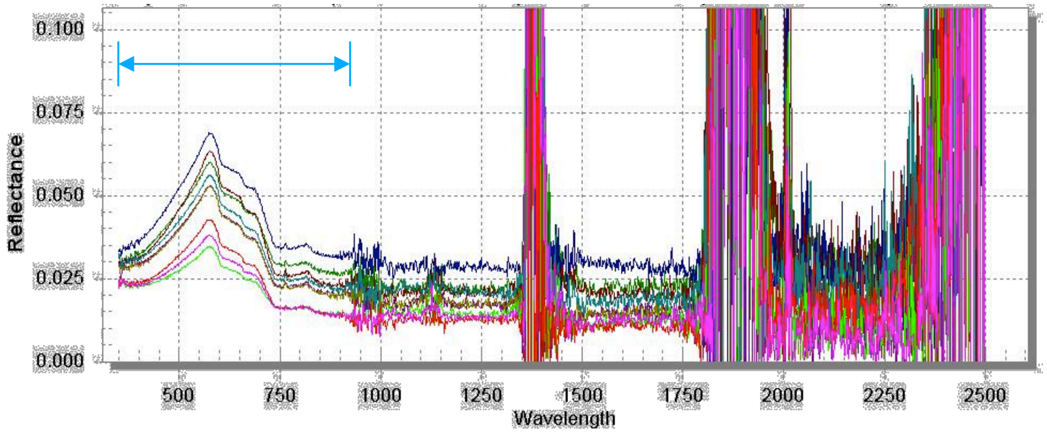
Mini-shuttle

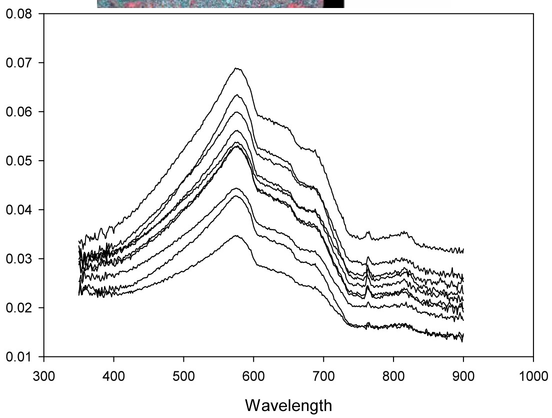
Applied Spectral Devices Spectro-Radiometer

Field Data: Spectra, CDOM contents

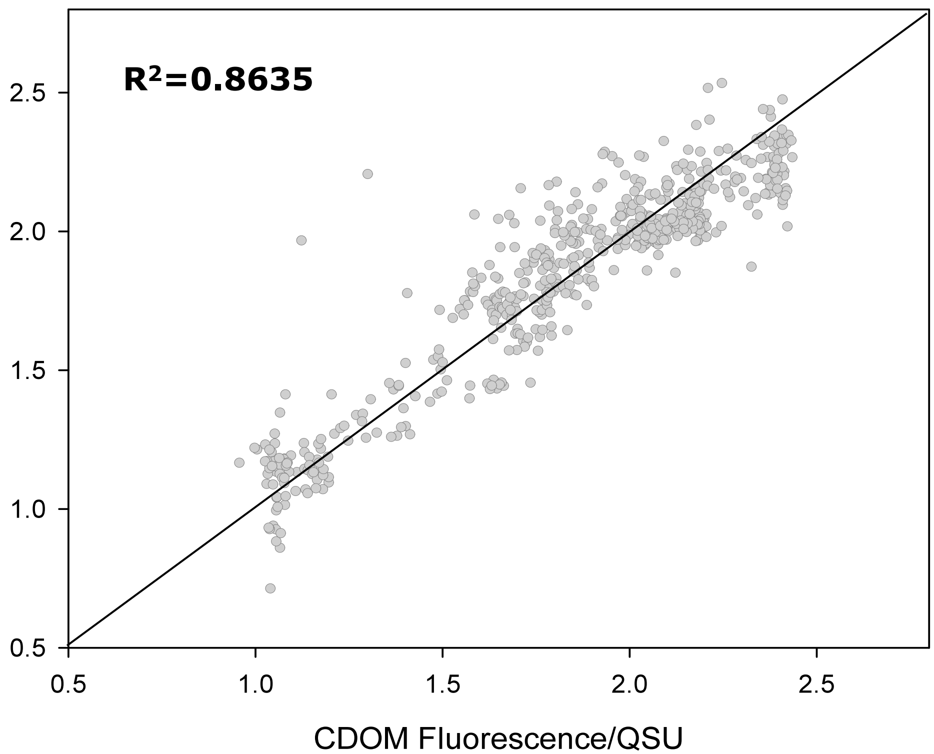


Along cruise route





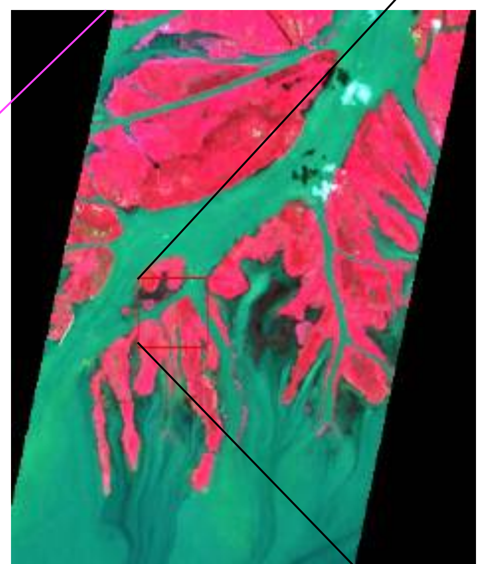
Results: model evaluation



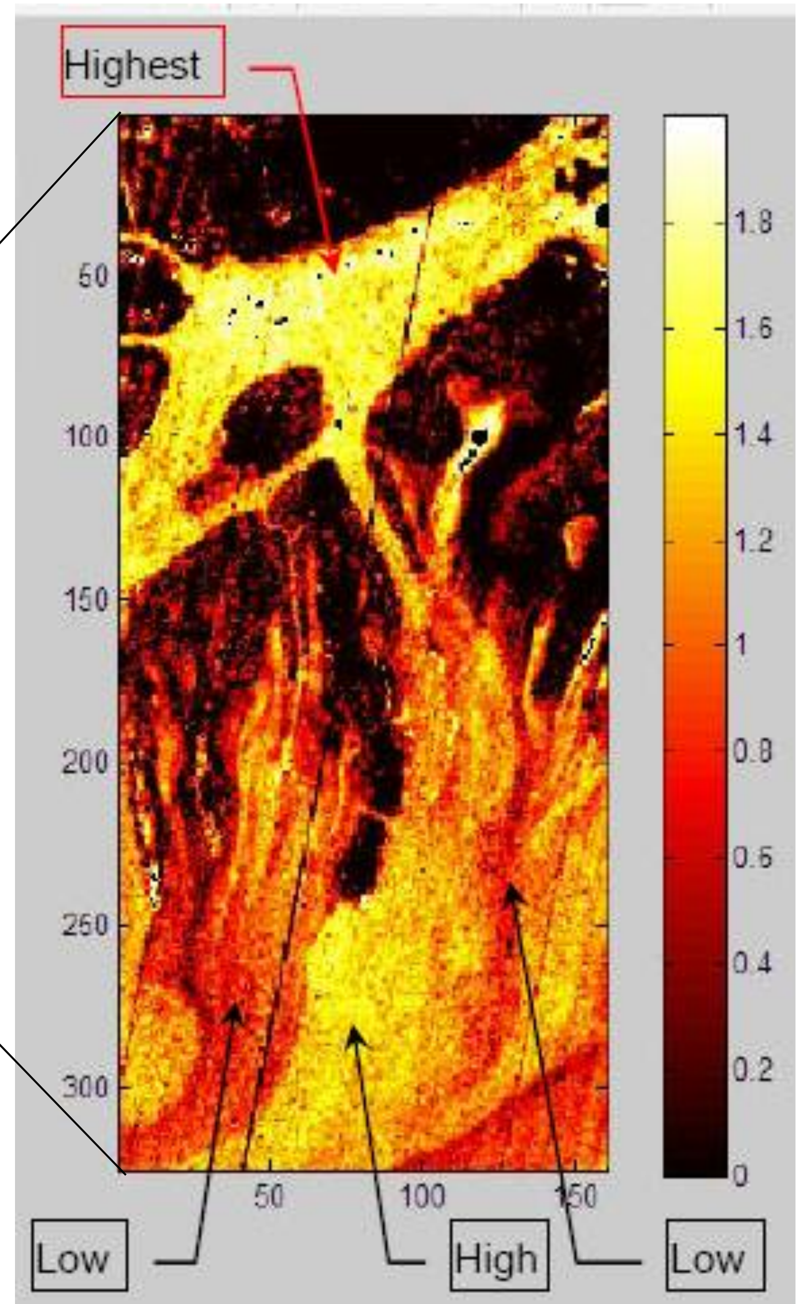
- Functional Linear Analysis
- With str1 and str2 as dummy variables, R^2=0.8635
- Without dummy variables, R^2=0.8415

CDOM detection from EO1-Hyperion for Atchafalaya River

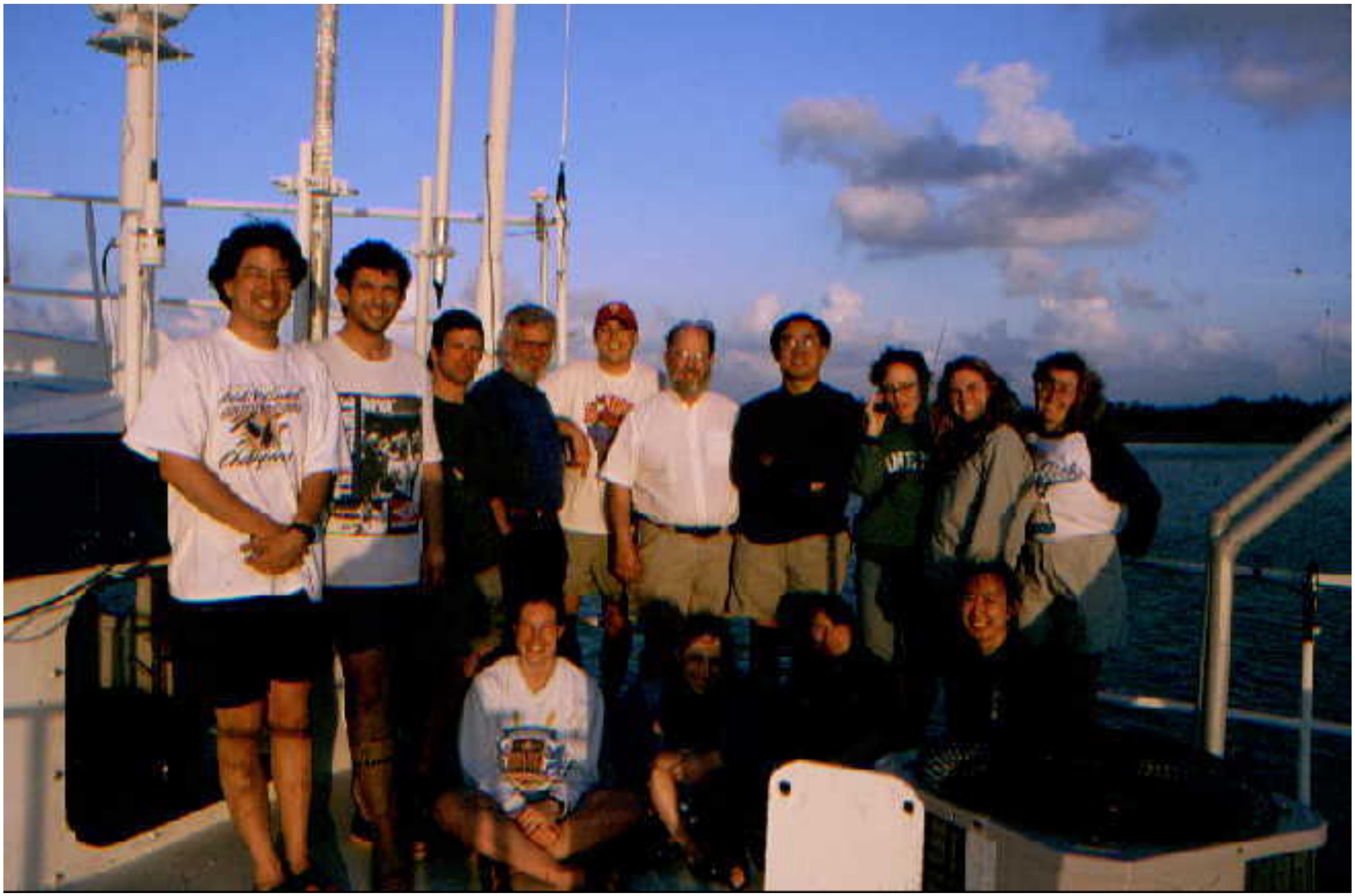
Quasi-Analytical Algorithm

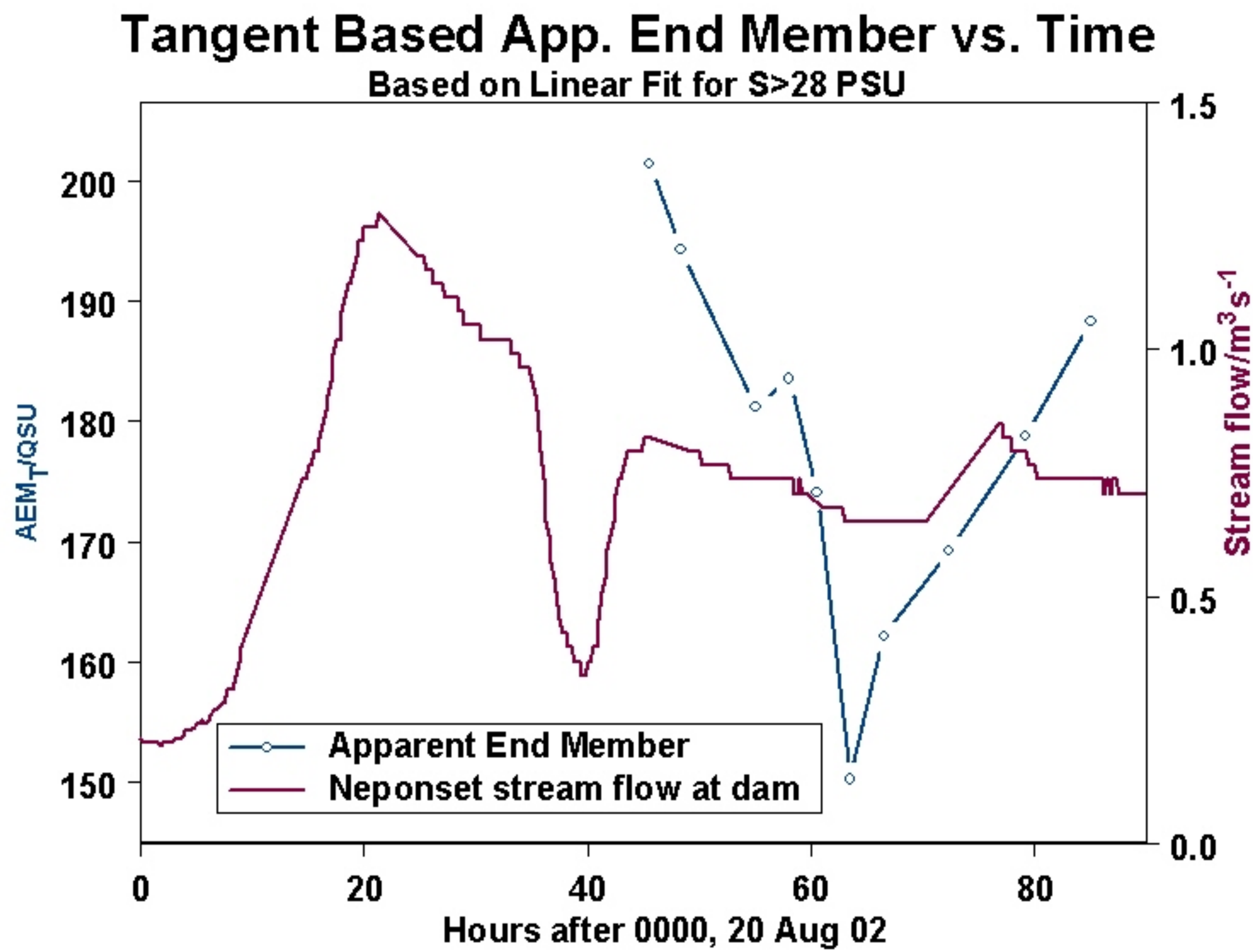


EO1-Hyperion images (220 bands,)



The CDOM "gang"

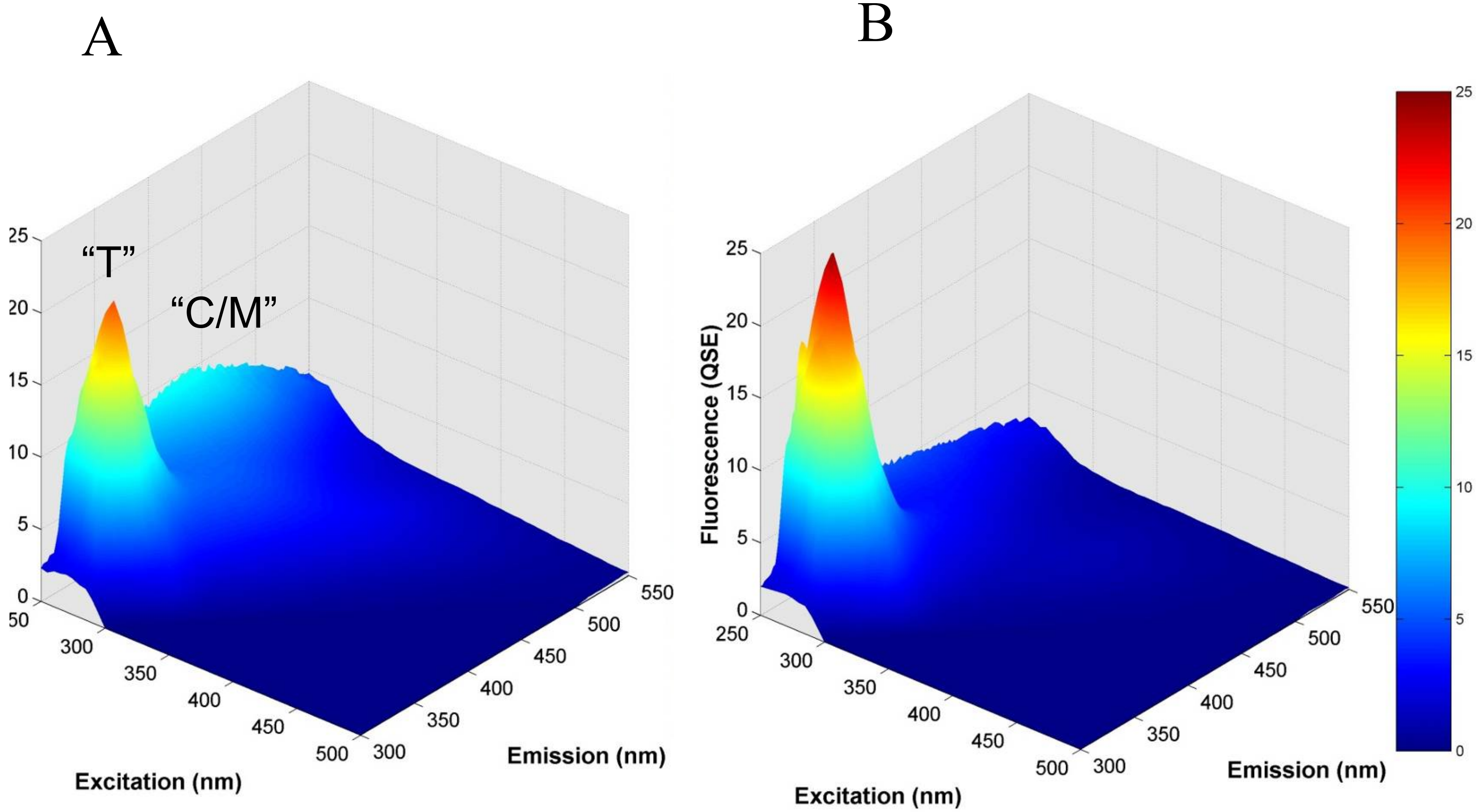




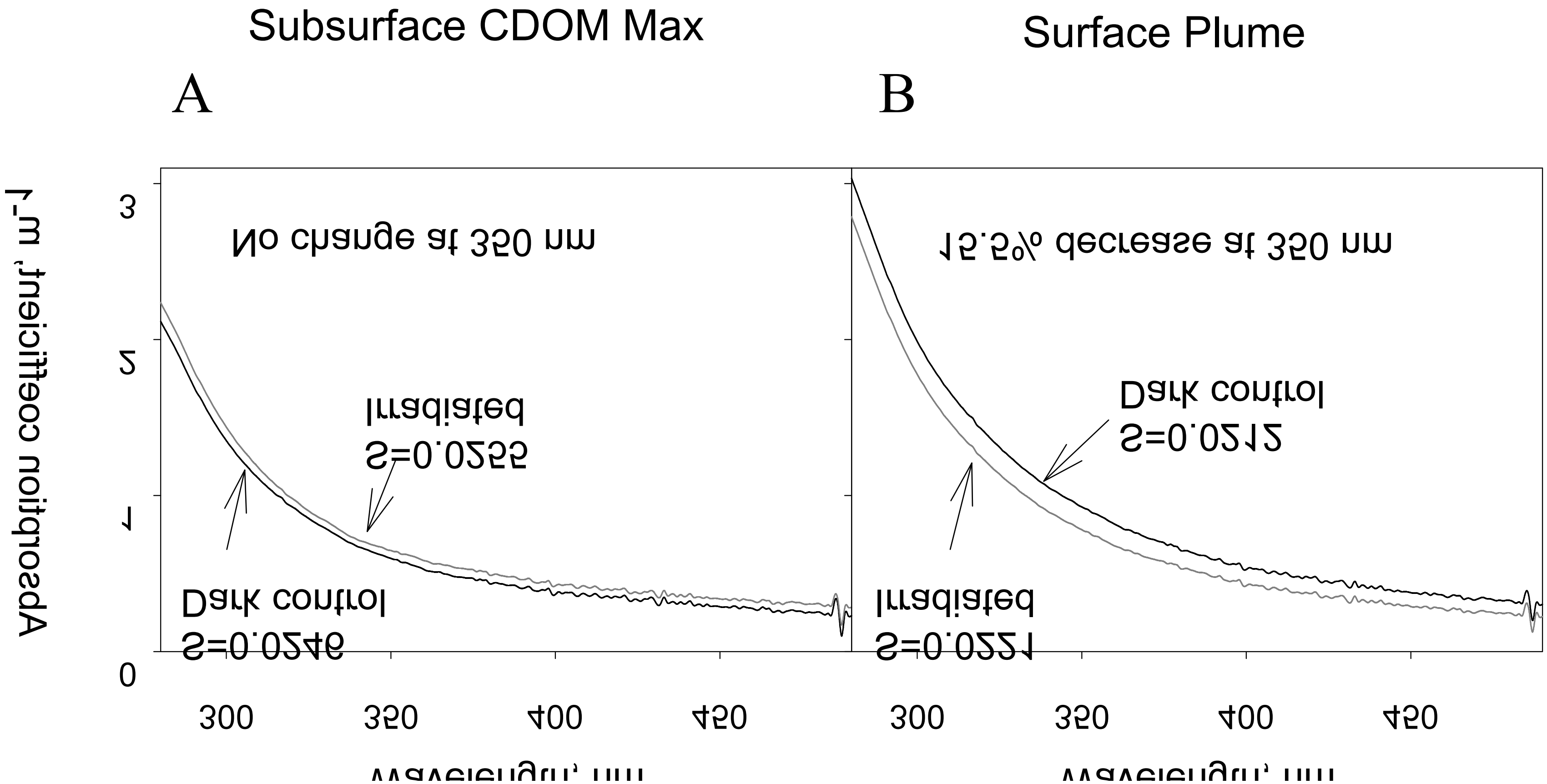
Tangent Based App. End Member vs. Time
Based on Linear Fit for S>28 PSU
AEM_T/QSU
Stream flow/m³s⁻¹
200
190
180
170
160
150
1.5
1.0
0.5
0.0
0
20
40
60
80
Hours after 0000, 20 Aug 02
Apparent End Member
Neponset stream flow at dam

Surface (River Plume)

Subsurface CDOM max

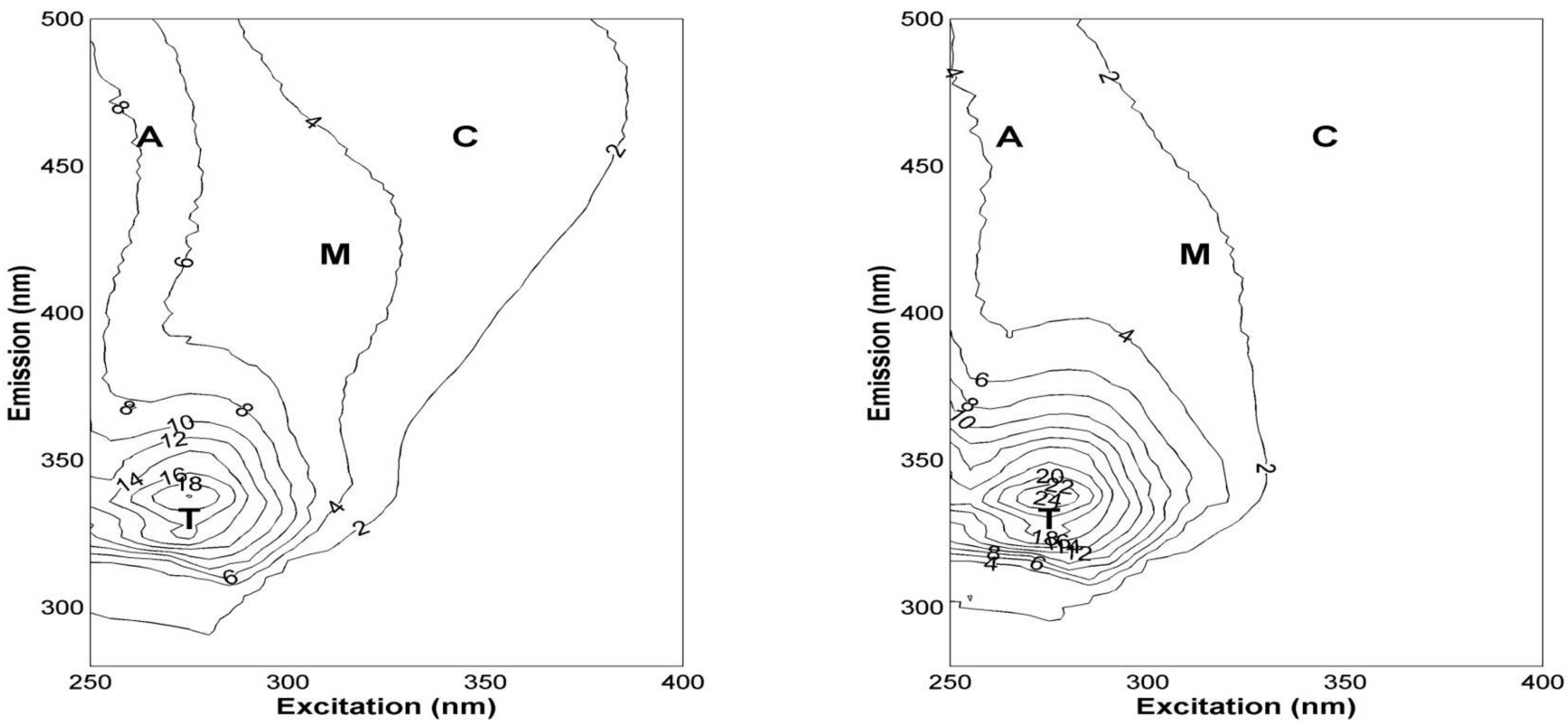


Line 20--June, 2000



Subsurface CDOM Max
Surface Plume
A
B
Absorption coefficient, m-1
No change at 350 nm
Irradiated
S=0.0255
Dark control
S=0.0246
15.5% decrease at 350 nm
Dark control
S=0.0212
Irradiated
S=0.0221
0
1
2
3
300
350
400
450

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