

Characterization of CDOM in an Organic Rich River and Surrounding Coastal Ocean

Cast of Characters

- Brooks Avery
- Mike Durako
 - Bob Kieber
- Piotr Kowalczyk
 - Steve Skrabal
 - Rob Whitehead
 - Joan Willey
- Wade Sheldon kindly provided software for the 3-D spectra analysis

Funding

- NOAA through the:
- Coastal Ocean Research and Monitoring Project at UNCW

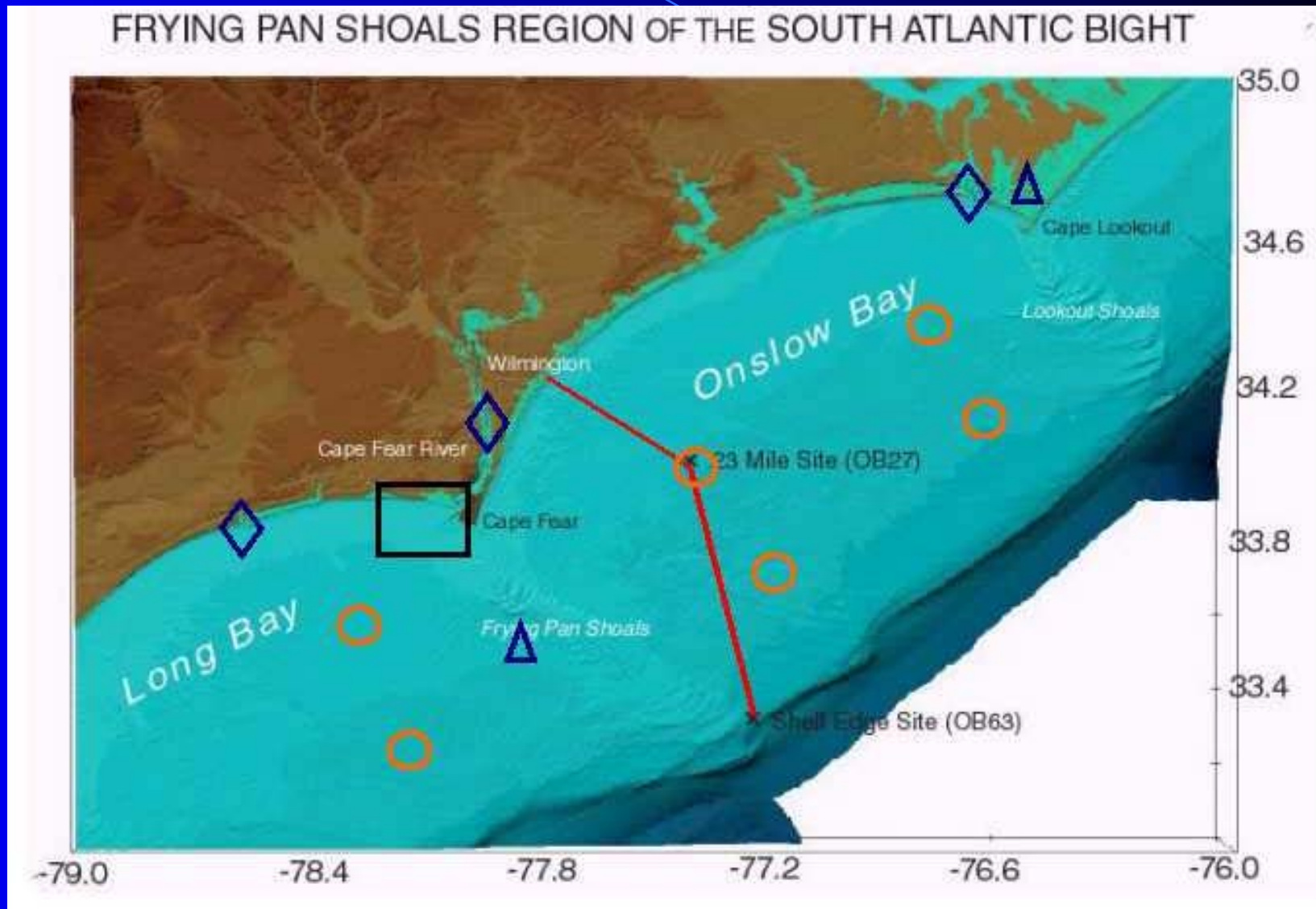
CORMP

- Overall Goal:
- To characterize and compare coastal embayments with low terrestrial input
- To those
- Estuarine-riverine dominated continental shelf ecosystems

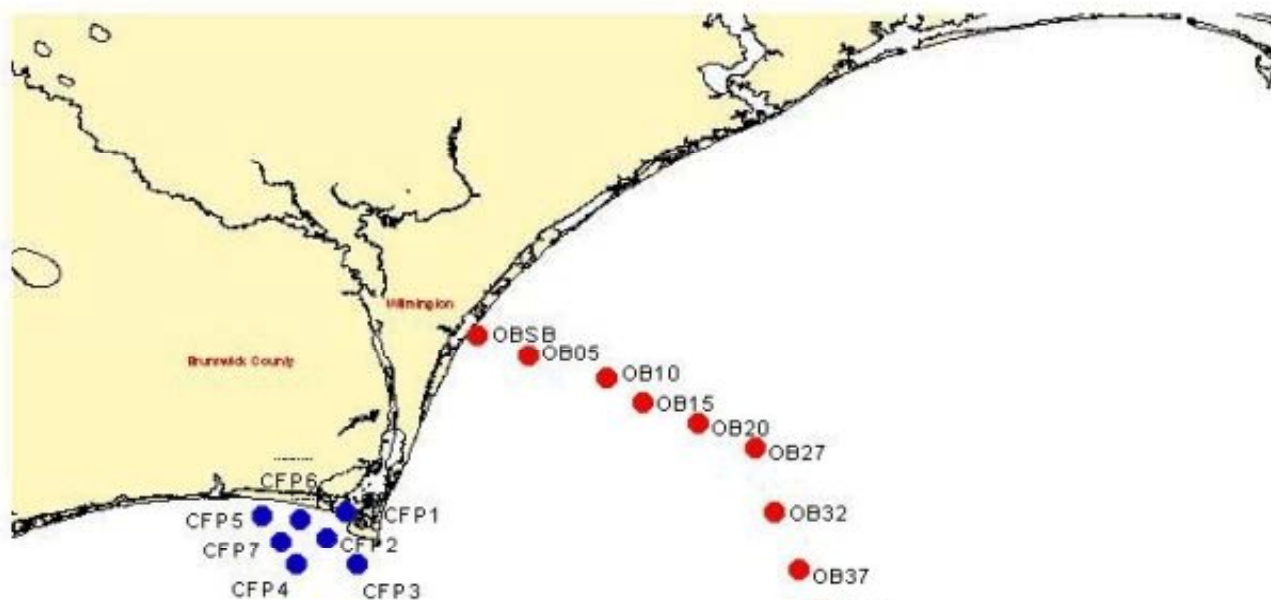
CORMP

- Where:
- Onslow Bay
- To
- Cape Fear River and Long Bay

Coastal Ocean Research and Monitoring Program sampling sites



UNCW/NOAA Coastal Monitoring Program



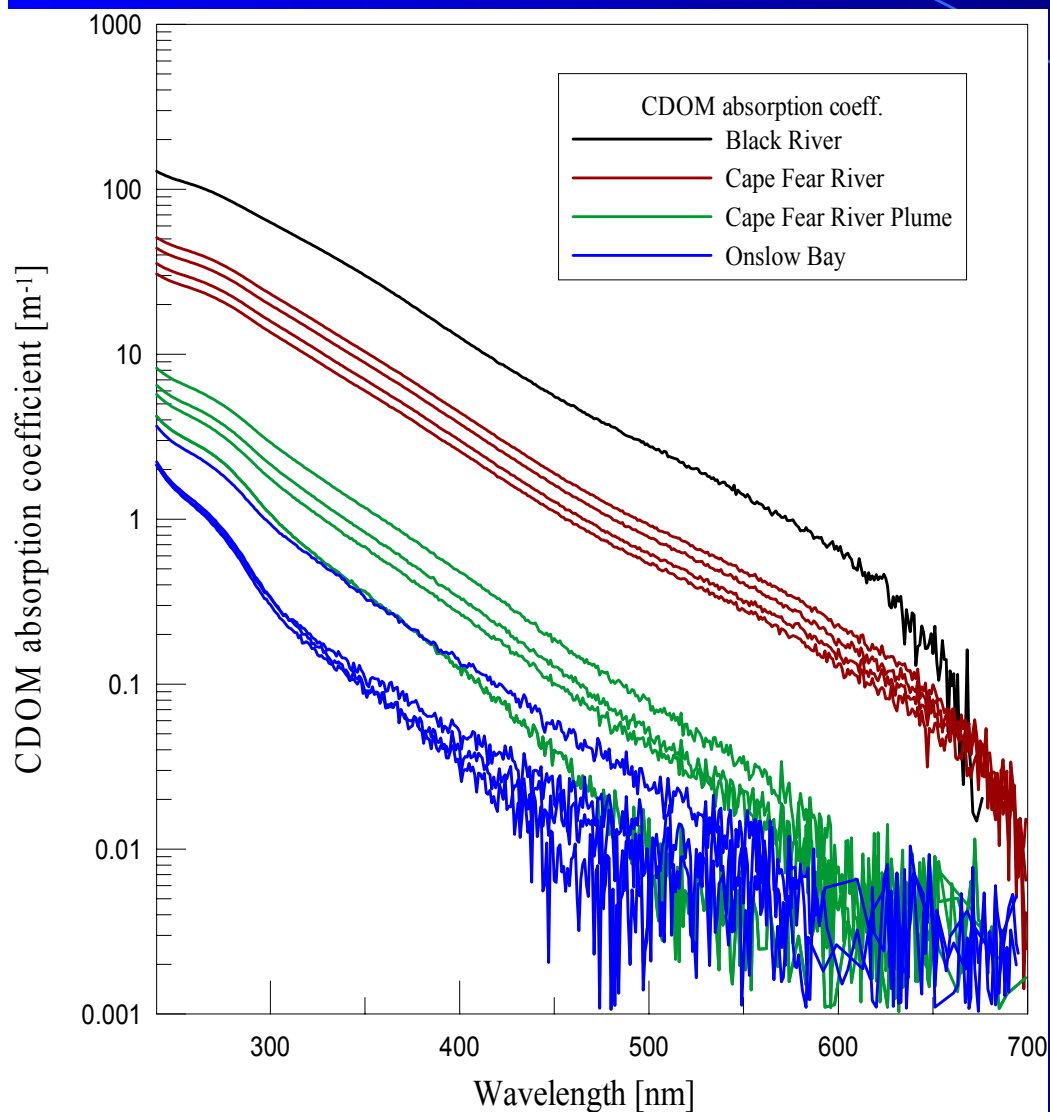
- CFP Stations
- OB Stations
- Water
- Land



CDOM Characterization

- Absorption coefficient
 - Spectrophotometric measurements on Cary 100, in UV-VIS region absorption coefficient $a_y(400)$, CDOM absorption spectrum slope coefficient S
- Excitation-Emission Matrix Spectrofluorometry
 - 3D fluorometry
 - SPEX spectrofluorometer – excitation range 250-550 nm, emission range 280-600 nm, results scaled in QSE units (quinine sulfonates equivalent)

CDOM absorption

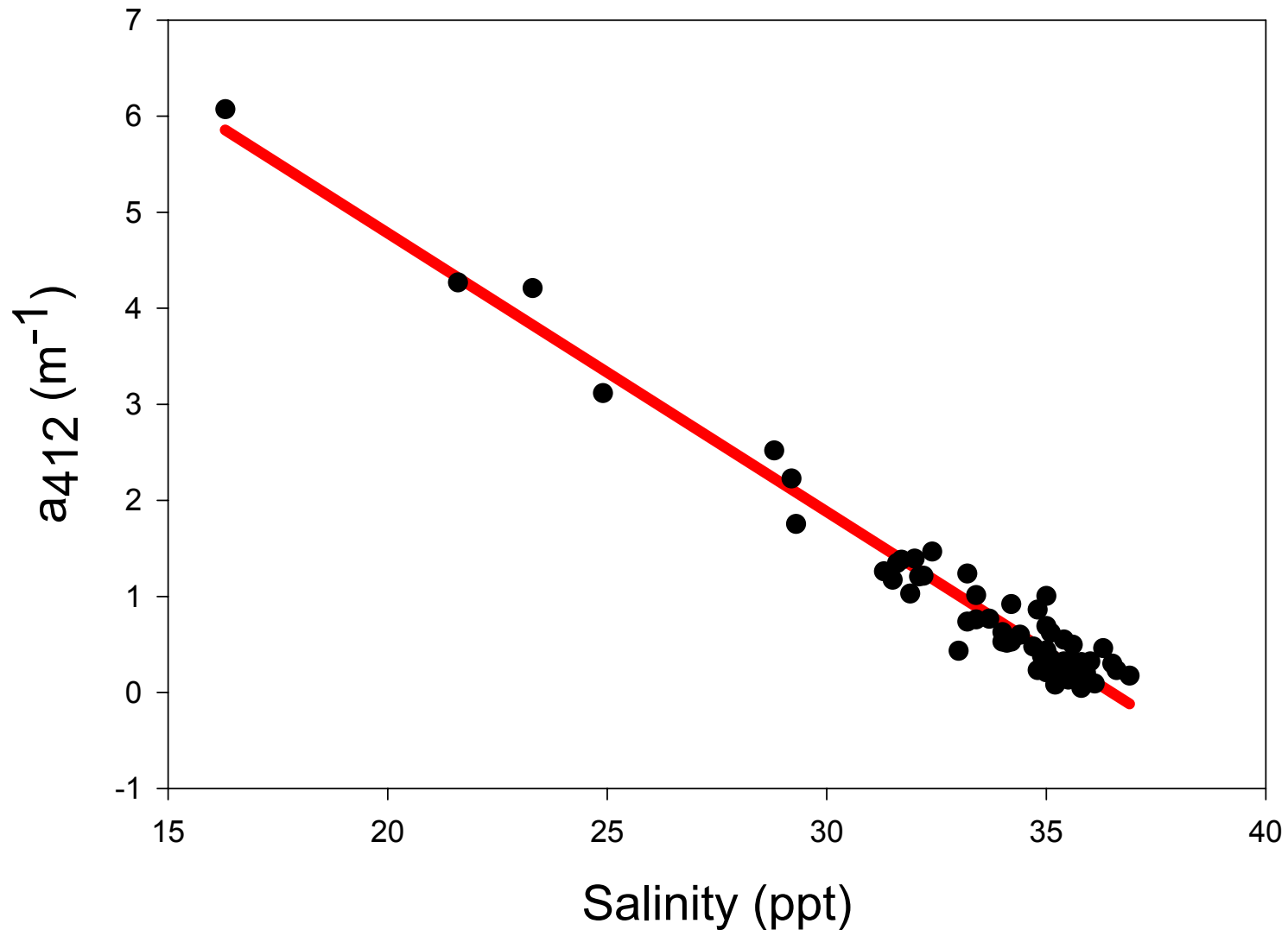


CDOM absorption characteristics

	$a_y(400)$ [m^{-1}]	S [nm^{-1}]
Black River	12.7	0.015
Cape Fear River (mean, n=4)	3.46	0.015
Cape Fear River Plume (mean, n=21)	0.71	0.018
Onslow Bay (mean, n=27)	0.088	0.024

CDOM Conservative Mixing?

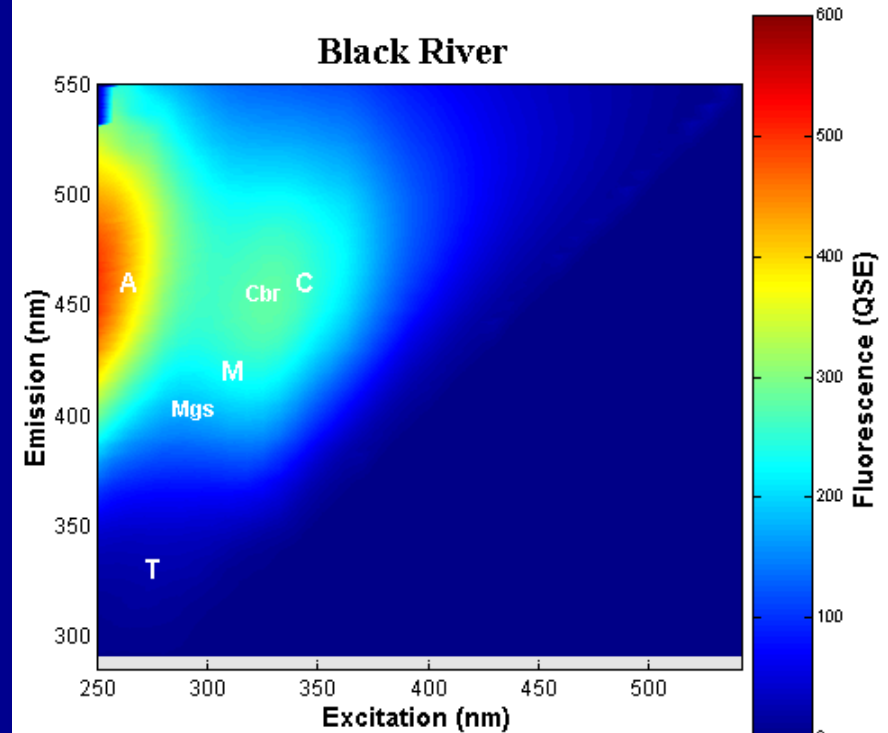
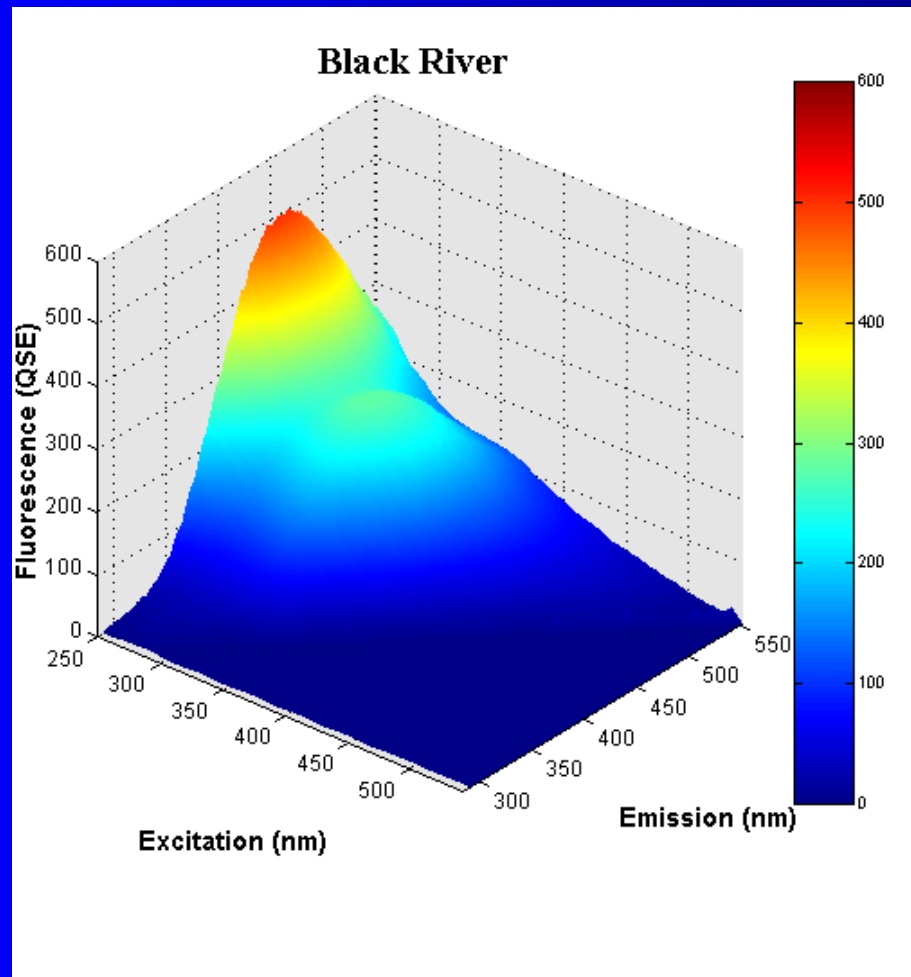
Cape Fear River Plume 2001



CDOM 3D Fluorescence

- A peak – terrestrial humic acids, Ex./Em. 265/460
- 1. C peak – terrestrial fulvic acids, Ex./Em. 345/460
- 2. M peak – marine fulvic acids, Ex./Em. 312/420
- 3. T peak – Protein - tryptophan, Ex./Em. 275/330
- Peak Excitation/Emission characteristics may be different for specific locations
- For quantitative analysis we have chosen specific peak integral of 3D fluorescence spectrum
- Coble et al., 1996, Marine Chemistry 51:325-346.

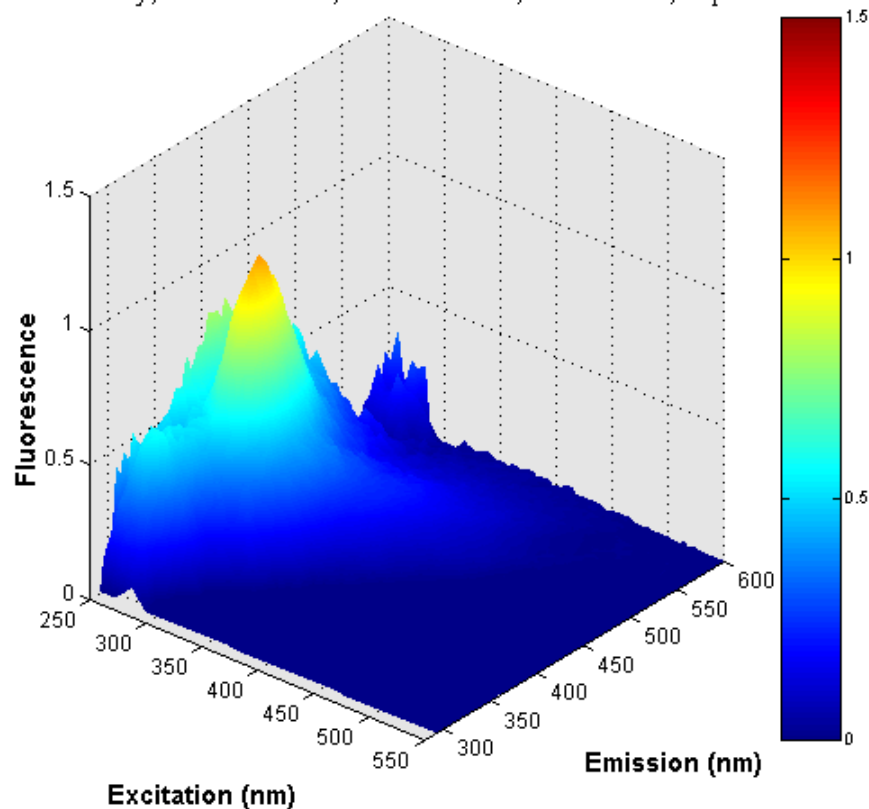
3 D fluorometry end members



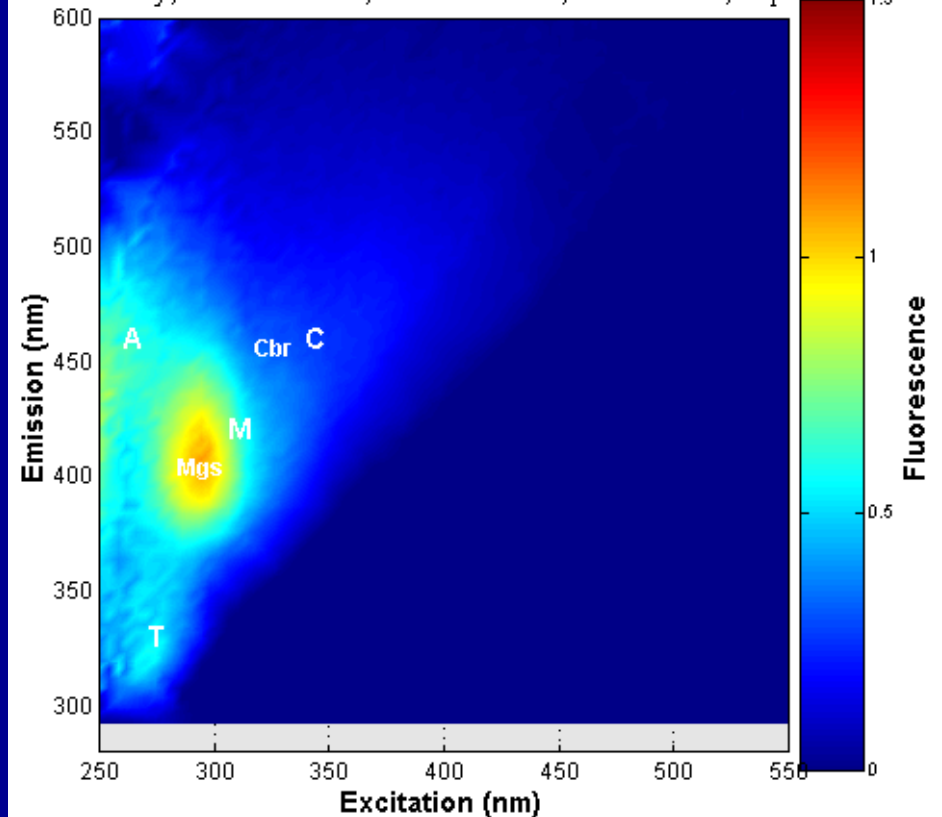
Black River - Cbr peak, $\lambda_{ex} = 326 \text{ nm}$, $\lambda_{em} = 426 \text{ nm}$, $a_y(400) = 12.7 \text{ m}^{-1}$,
 $S = 0.0152 \text{ nm}^{-1}$, Salinity = 0 psu

3 D fluorometry end members

Onslow Bay, Station OB57, 12 Dec. 2001, 19:10 UTC, depth 0 m

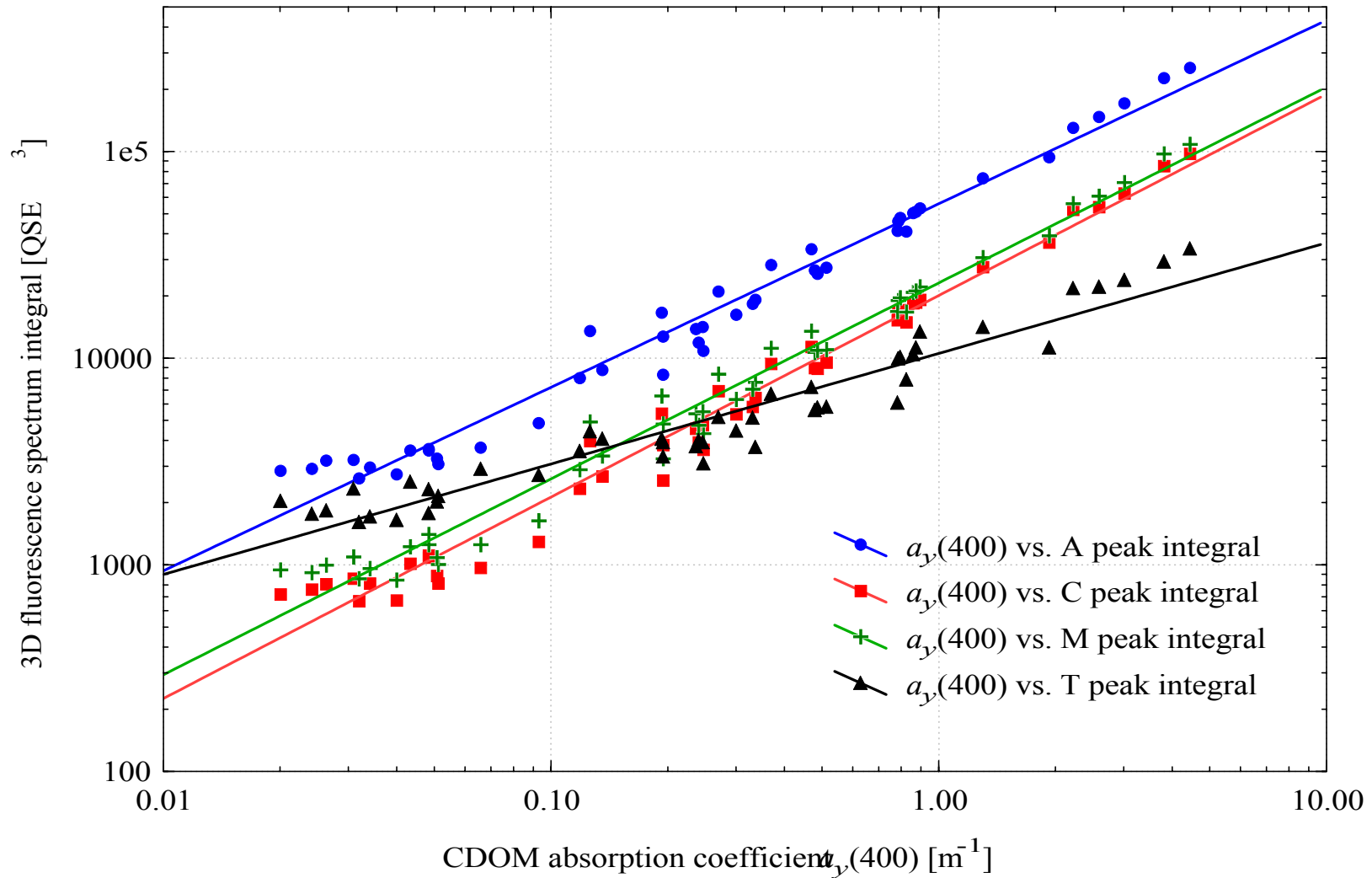


Onslow Bay, Station OB57, 12 Dec. 2001, 19:10 UTC, depth 0 m



Gulfstream, Mgs peak, $\lambda_{ex} = 294 \text{ nm}$, $\lambda_{em} = 404 \text{ nm}$, $a_y(400) \approx 0 \text{ m}^{-1}$, $S = \dots$,
Salinity = 36.3 psu

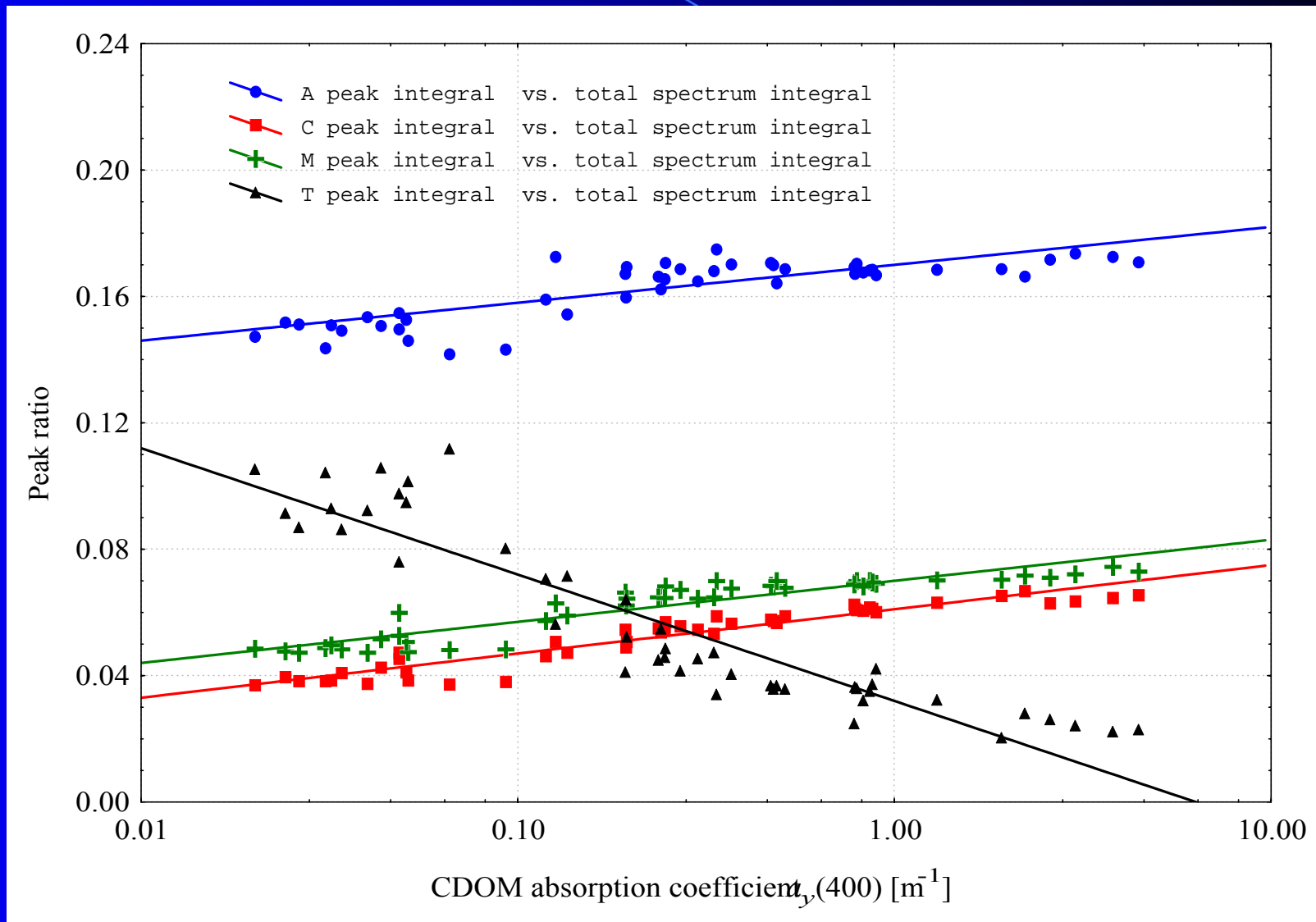
Relationship between CDOM absorption and fluorescence



Relationship between CDOM absorption and fluorescence

Variables	Equation	Correlation coeff.	Sample size
$a_y(400)$ vs. A peak integral	$A_{peak} = 10^{(4.747 + 0.888X)}$	$r = 0.99$	$n = 47$
$a_y(400)$ vs. C peak integral	$C_{peak} = 10^{(4.303 + 0.975X)}$	$r = 0.99$	$n = 47$
$a_y(400)$ vs. M peak integral	$M_{peak} = 10^{(4.364 + 0.948X)}$	$r = 0.99$	$n = 47$
$a_y(400)$ vs. T peak integral	$T_{peak} = 10^{(4.033 + 0.534X)}$	$r = 0.96$	$n = 47$

Relationship between CDOM absorption and fluorescence peak ratios



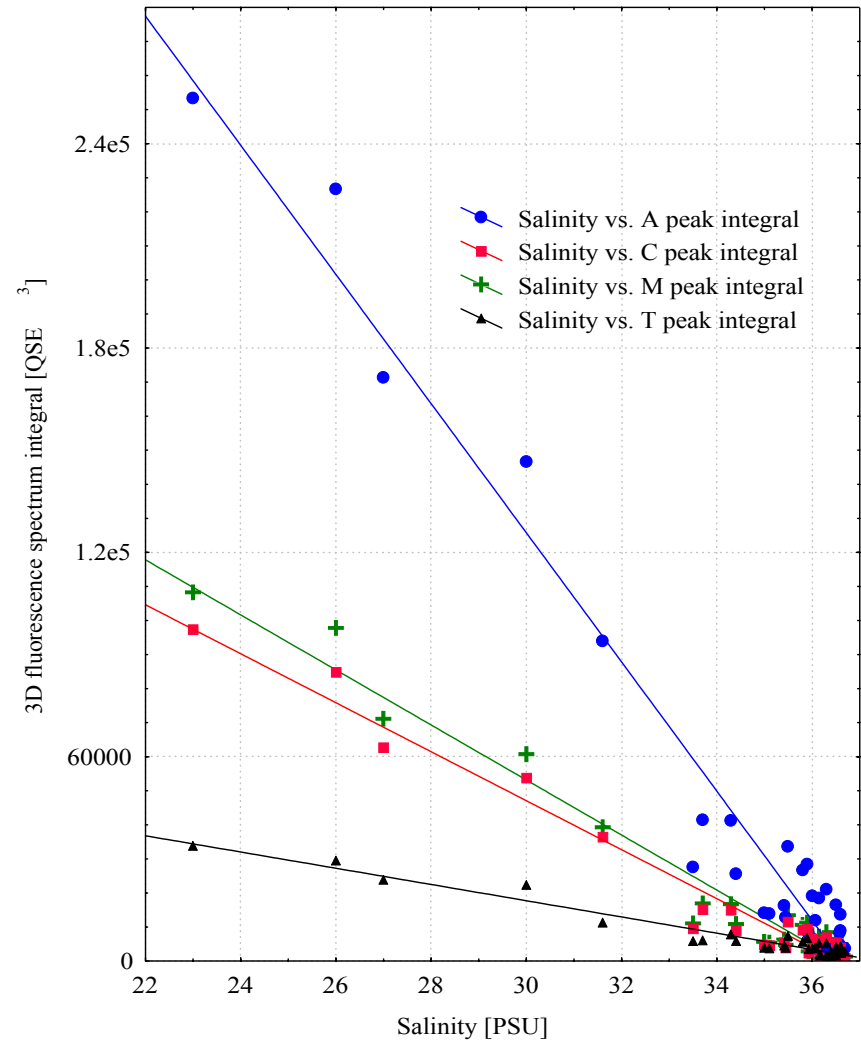
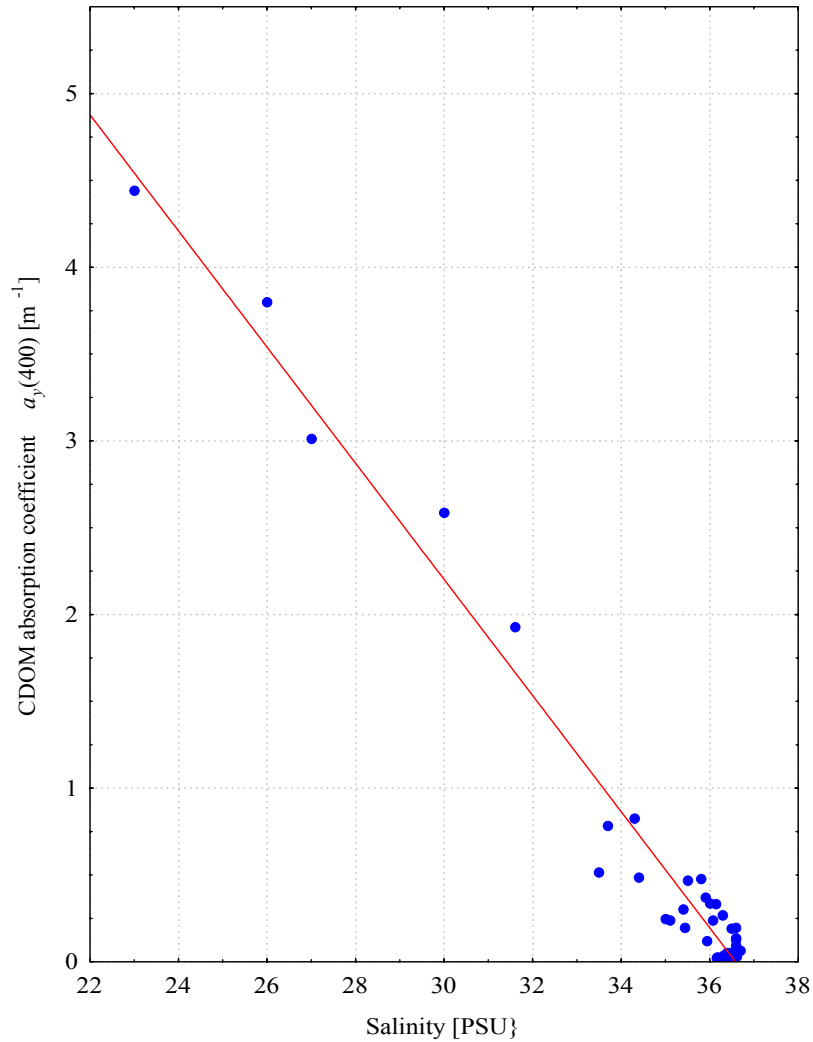
Relationship between CDOM absorption and fluorescence peak ratios

Variables	Equation	Correlation coeff.	Sample size
$a_y(400)$ vs. A/TOT integral ratio	$A/TOT = 0.017 + 0.012 * (\log_{10}(a_y(400)))$	$r = 0.82$	$n = 47$
$a_y(400)$ vs. C/TOT integral ratio	$A/TOT = 0.061 + 0.014 * (\log_{10}(a_y(400)))$	$r = 0.95$	$n = 47$
$a_y(400)$ vs. M/TOT integral ratio	$A/TOT = 0.07 + 0.013 * (\log_{10}(a_y(400)))$	$r = 0.92$	$n = 47$
$a_y(400)$ vs. T/TOT integral ratio	$A/TOT = 0.032 - 0.04 * (\log_{10}(a_y(400)))$	$r = -0.92$	$n = 47$

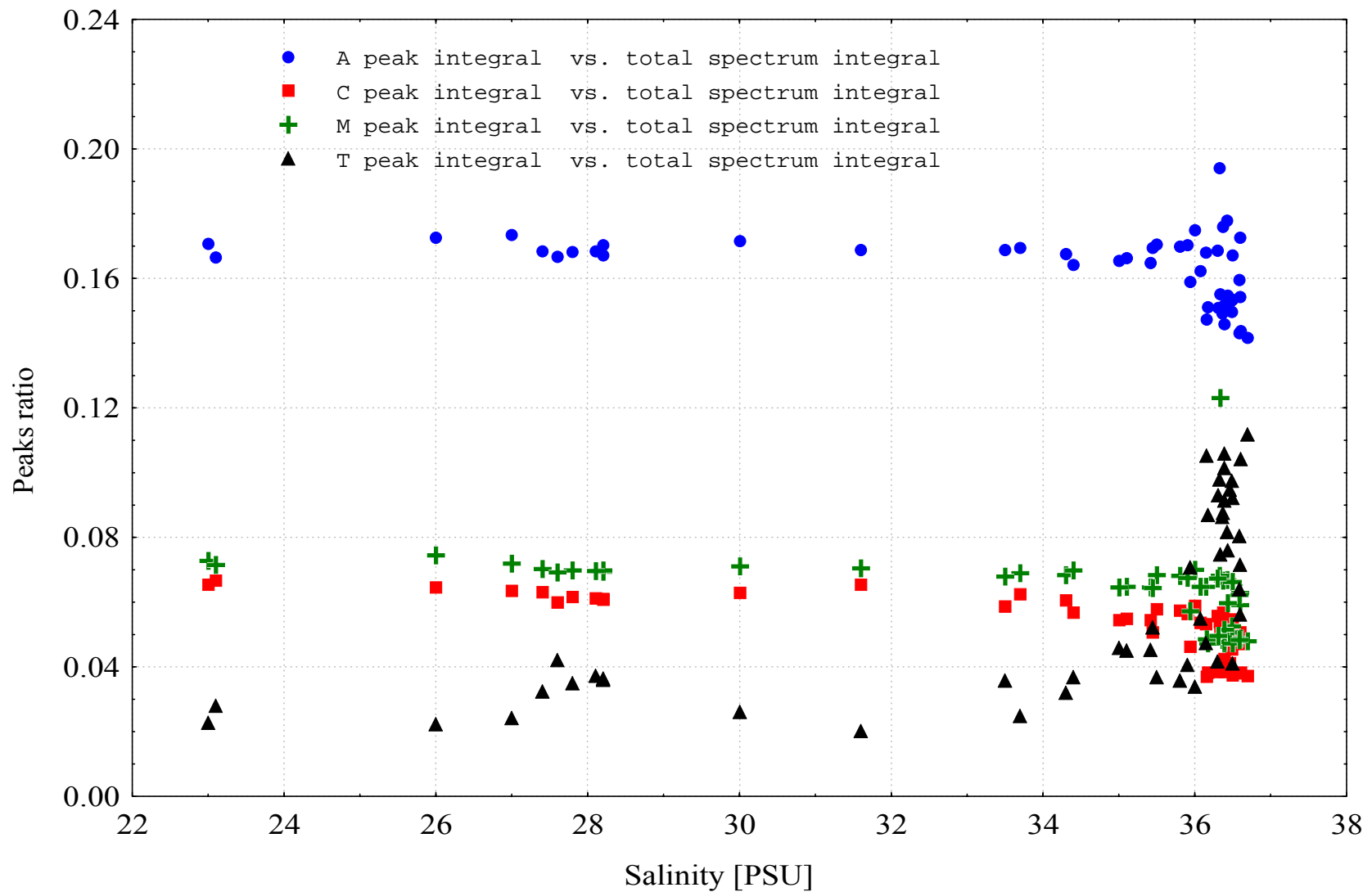
Implications

- Suggests that:
 - Protein is recalcitrant
 - Protein is a breakdown product of terrestrial CDOM
 - Protein is formed in marine environment

Relationship between CDOM absorption, fluorescence peak-integrals and salinity



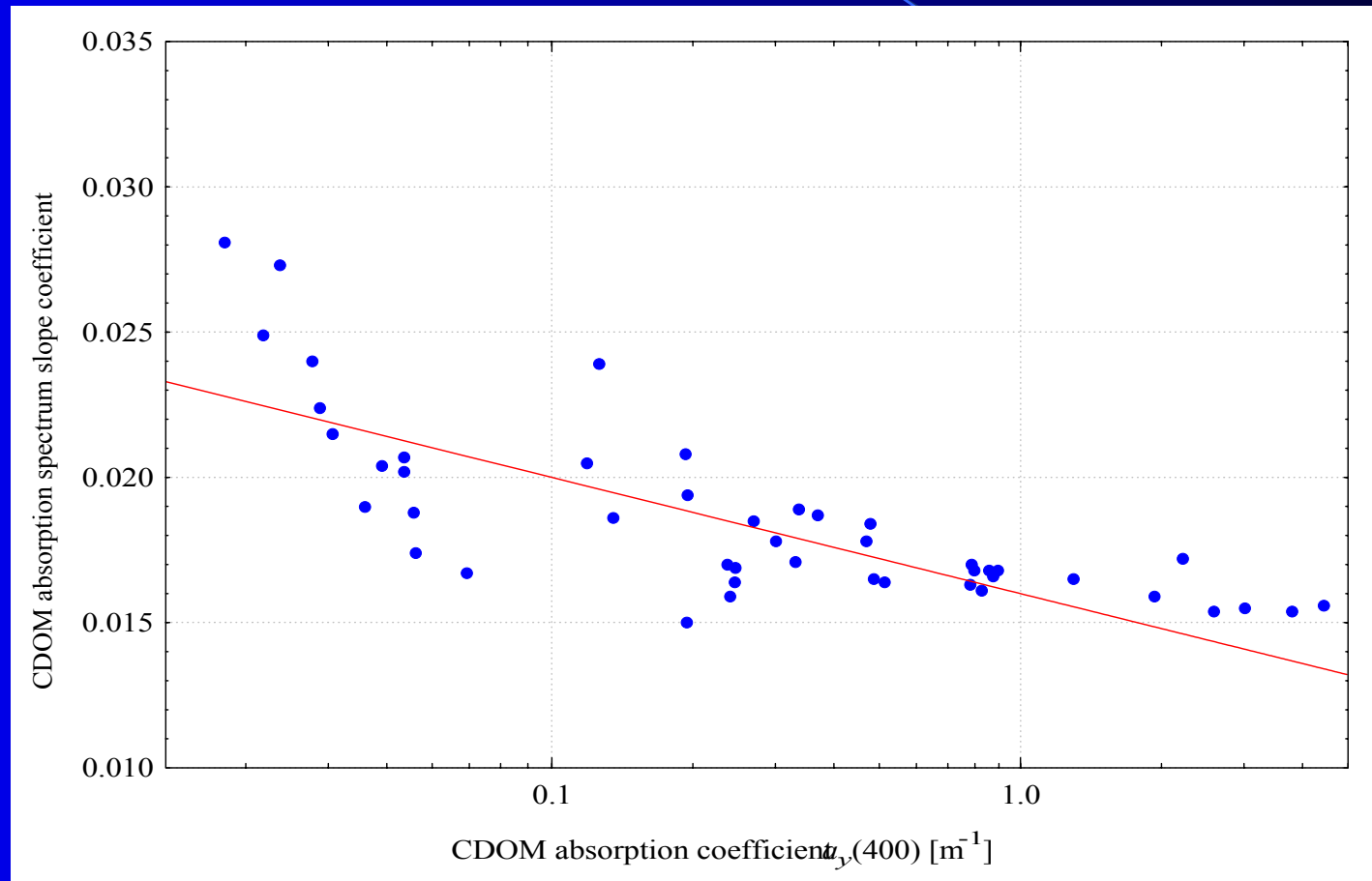
Relationship between salinity and fluorescence peak ratios



Implications

- Conservative mixing until salinity approaches 35
- WHY?
 - CDOM is so concentrated that photochemical and biological processes that result in its transformation are masked by the physical mixing process

CDOM absorption and CDOM absorption spectrum slope coefficient



$$y = 0.016 - 0.004 * \log_{10}(a_y(400)), n = 45, r = -0.76$$

Conclusions

- 3-D Fluorescence Spectroscopy enables us to study the changes in CDOM composition in the transition environment – terrestrial to marine
- This data will also be used for input to updating SeaWiFS algorithms in waters with high CDOM