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Characterization of oil components from Deepwater Horizon oil spill using fluorescence EEMs and parallel factor analysis

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2010 oil spill in the Gulf of Mexico

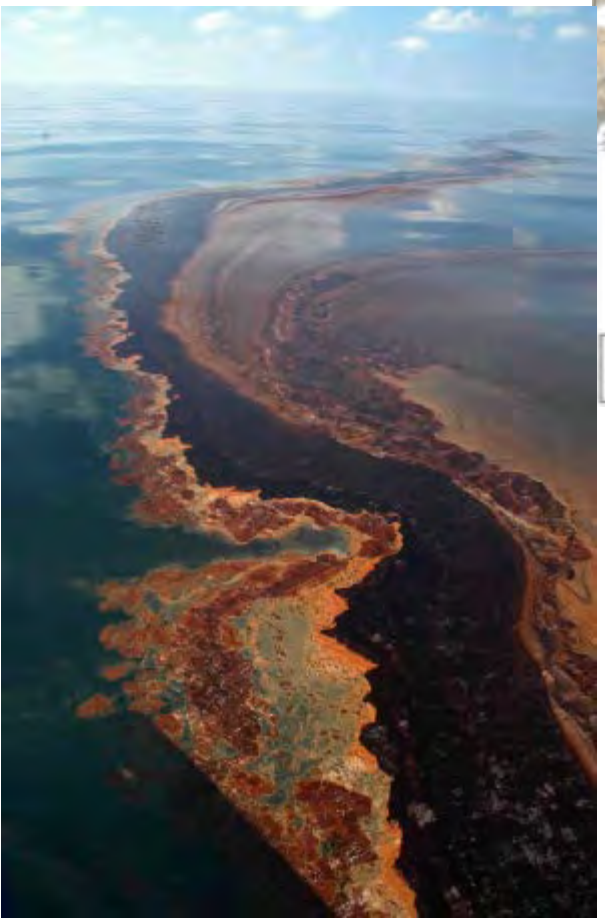


Photo credit: Dr. Vernon Asper

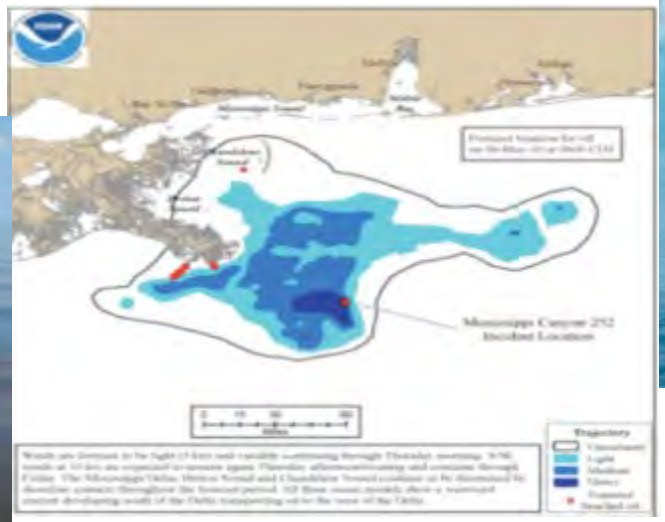
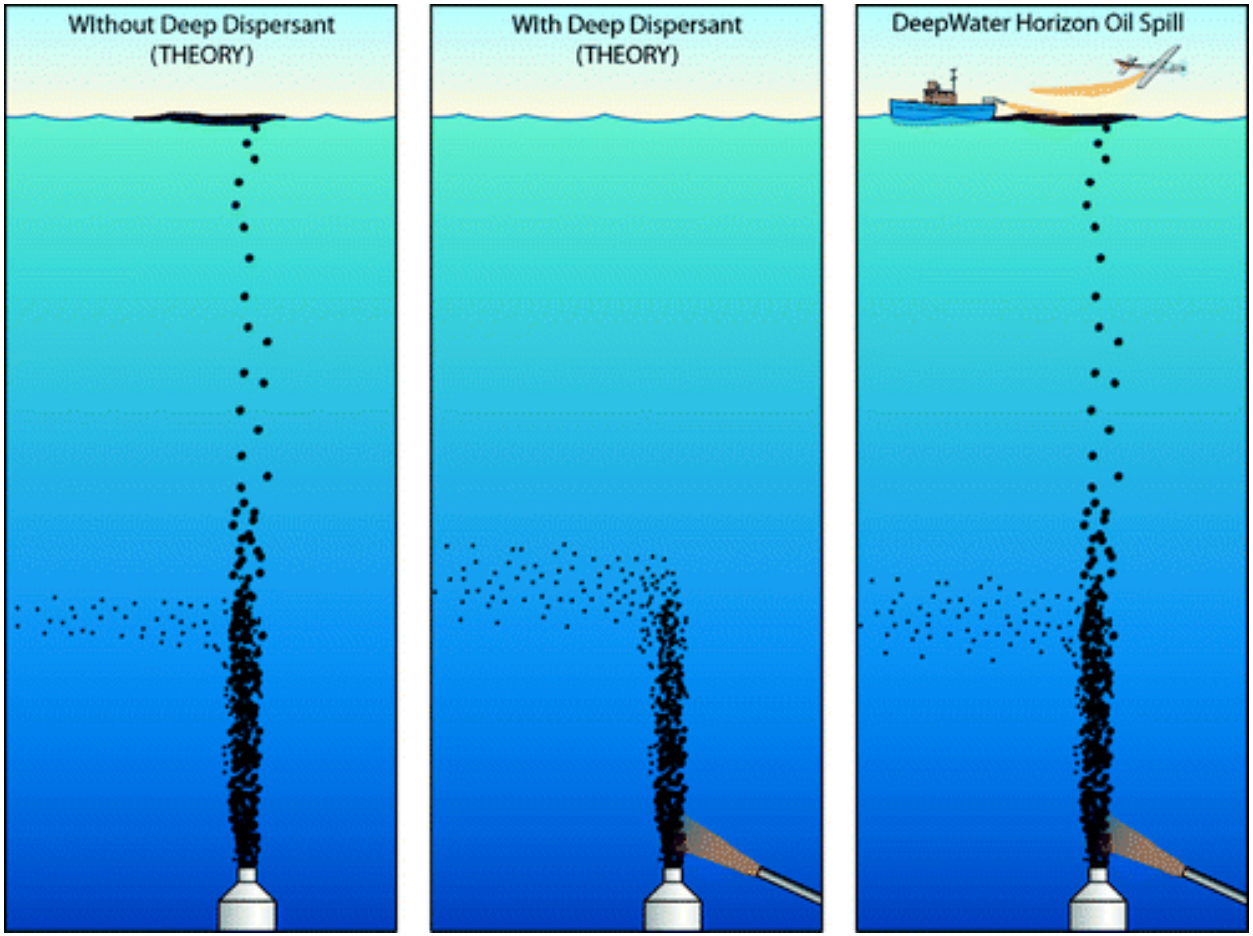


Photo credit: http://www.salon.com

- Unprecedented oil spill, last 84 days;
- Underwater spill: long transit of oil to surface
- Application of dispersants: both surface and deep water;

Oil spill and dispersant



From Kujawinski et al (2011) ES&T

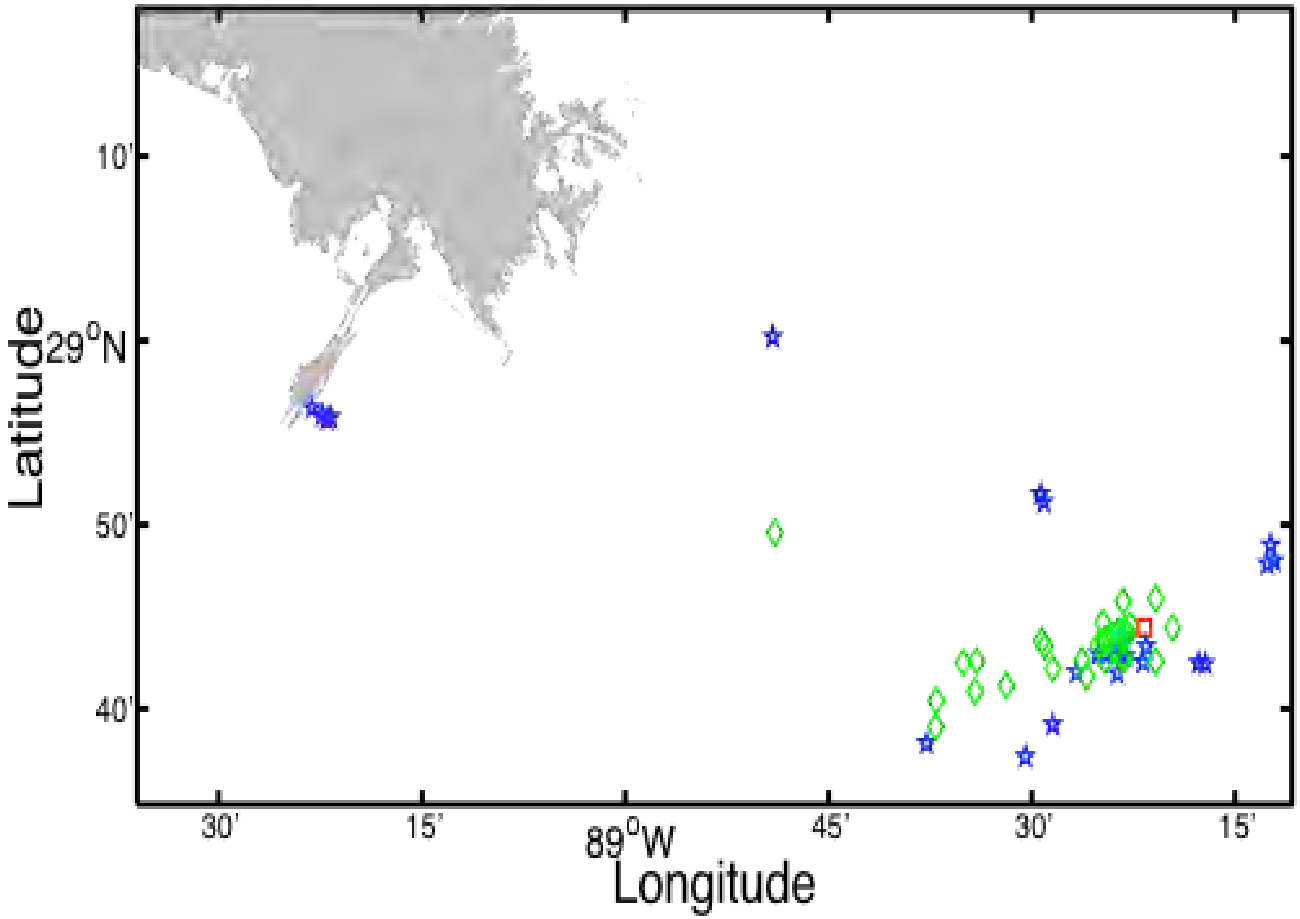
Questions

- What are the degradation pathways, fate and transport oil and dispersant?
- Can the fluorescence and other optical properties be used to track the fate and transport of oil and dispersants in the water column?
- How oil/dispersant interacts with natural dissolved organic matter in marine environments?

Methods

- Crude oil from the Macondo well, weathered oil from surface waters, dispersant from BP, and seawater samples from the Gulf of Mexico
- UV-vis spectroscopy: for the characterization of CDOM and other optical properties
- 3D fluorescence spectroscopy: for measurements of fluorescence excitation-emission matrices (EEMs)
- Parallel factor (PARAFAC) analysis: to identify oil and natural DOM components in water samples

Sampling locations in the n-GoM

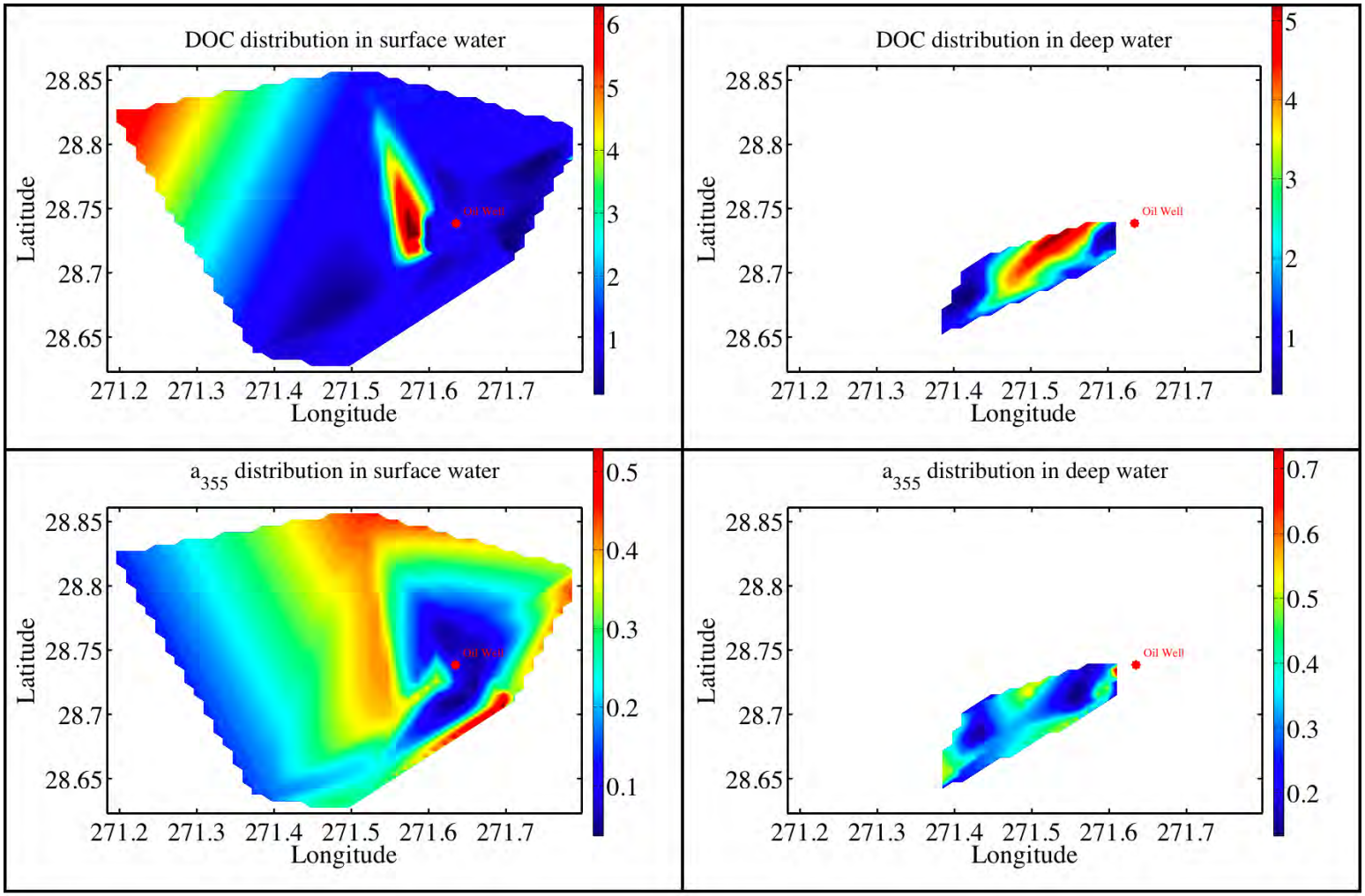


Blue stations: R/V Pelican (May 2010)

Green stations: R/V Walton Smith (May/June 2010)

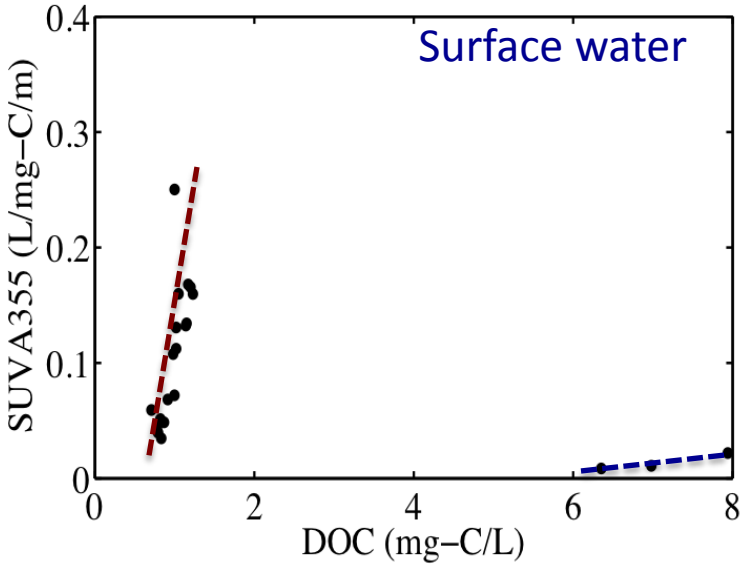
Red: Macondo well

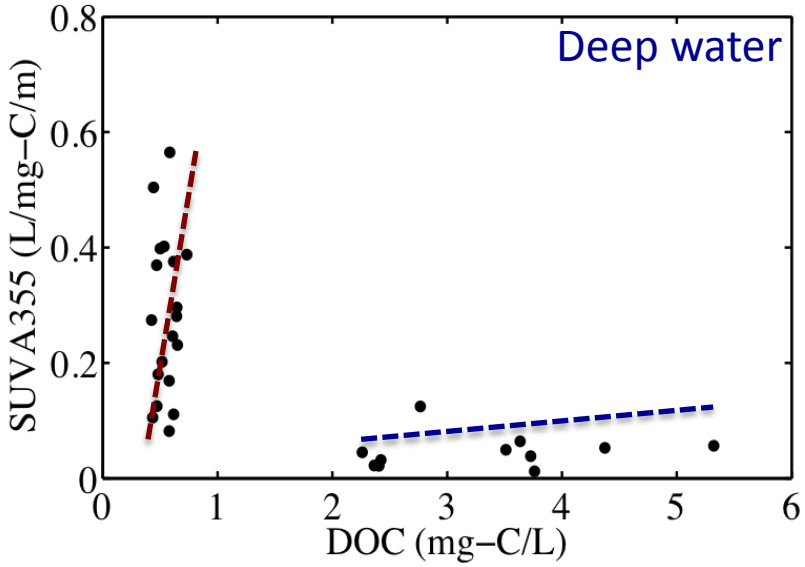
Distributions of dissolved organic carbon (DOC) and DOM absorbance in surface and deep waters in the northern Gulf of Mexico during May/June 2010



Normal DOC concentration: <1 mg-C/L

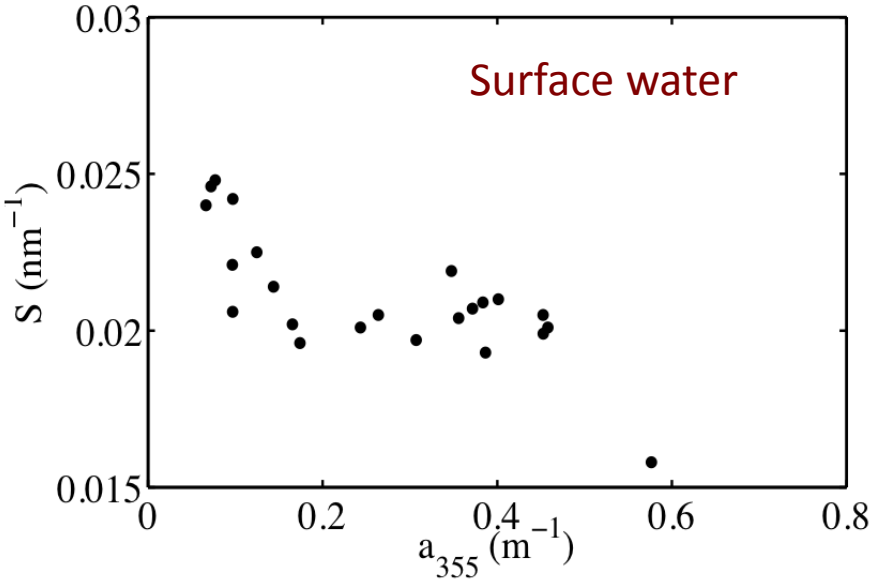
Relationship between DOC concentration and specific UV absorbance

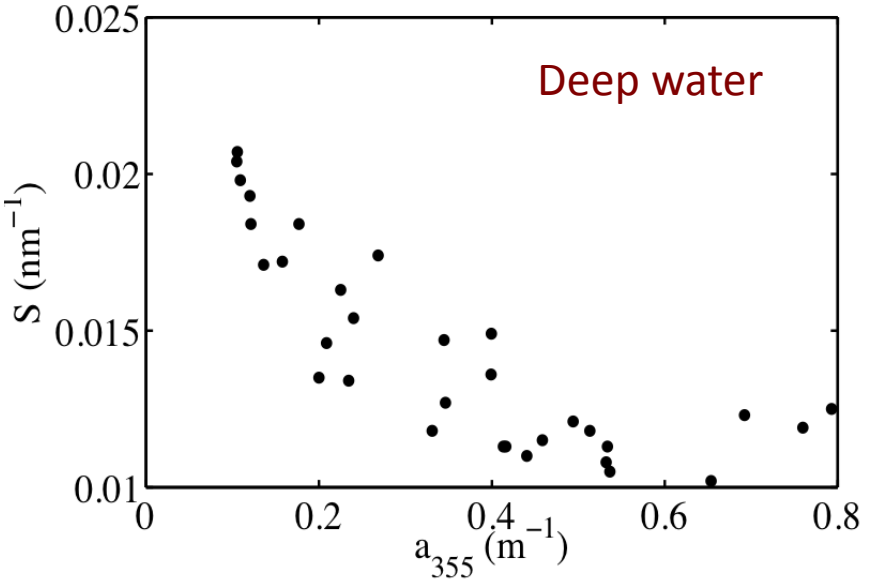




Two types of DOM were identified in the water column:
One with high optical activity but low mass concentration
The other has high mass concentration but low optical activity

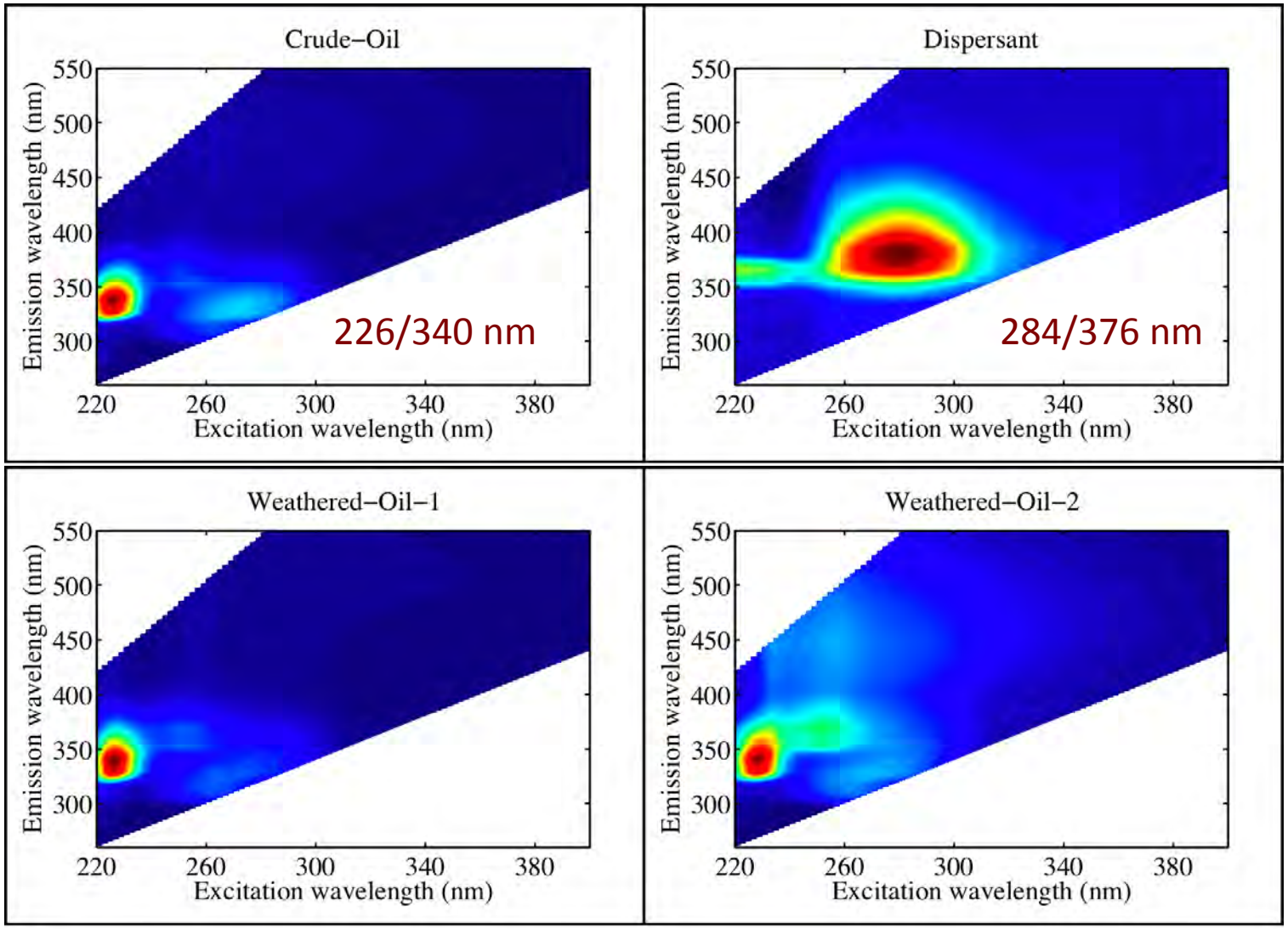
Relationship between spectral slope (S) and UV-vis absorbance (a355)



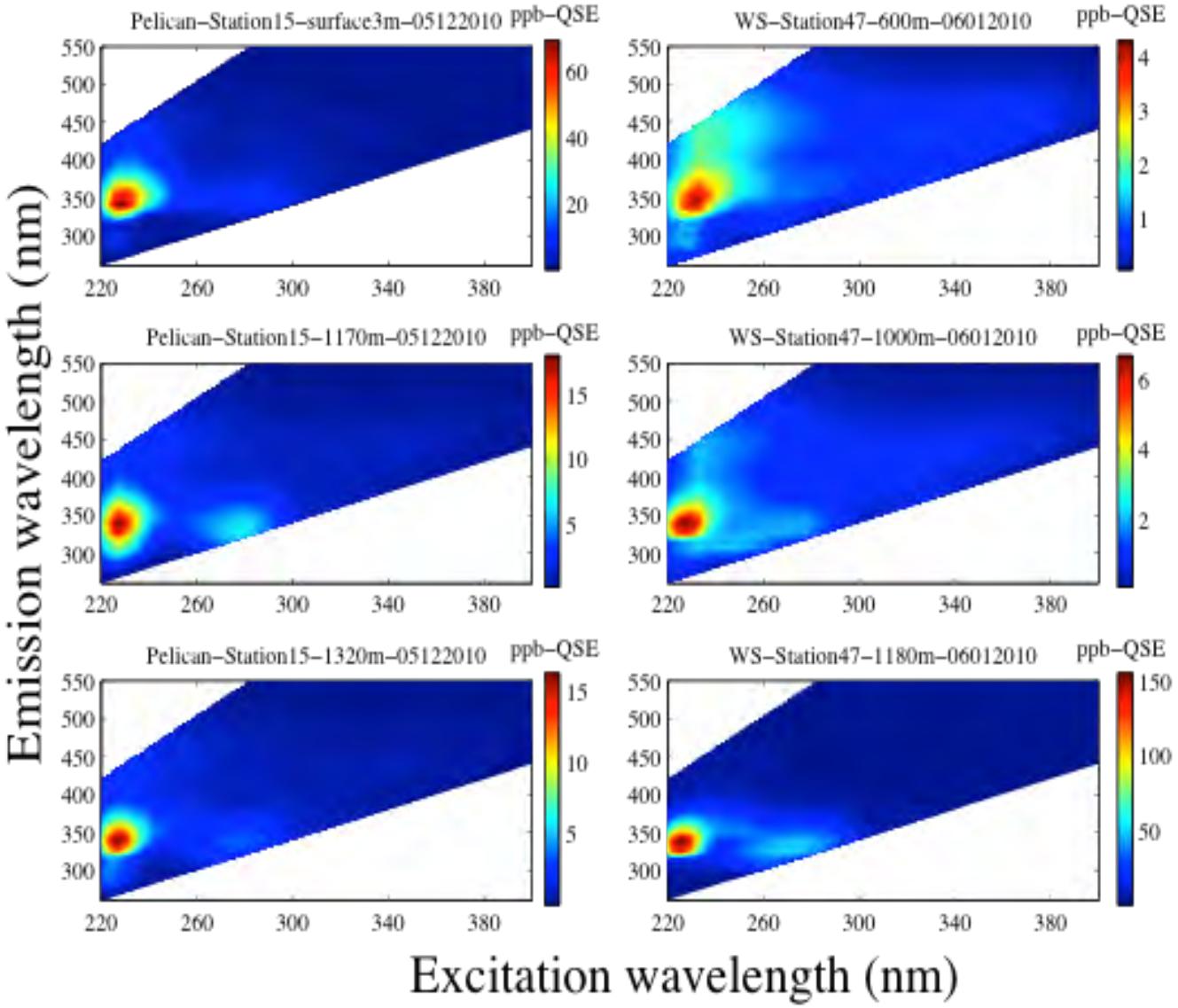


The higher DOM concentration, the lower spectral slope, the higher molecular weight

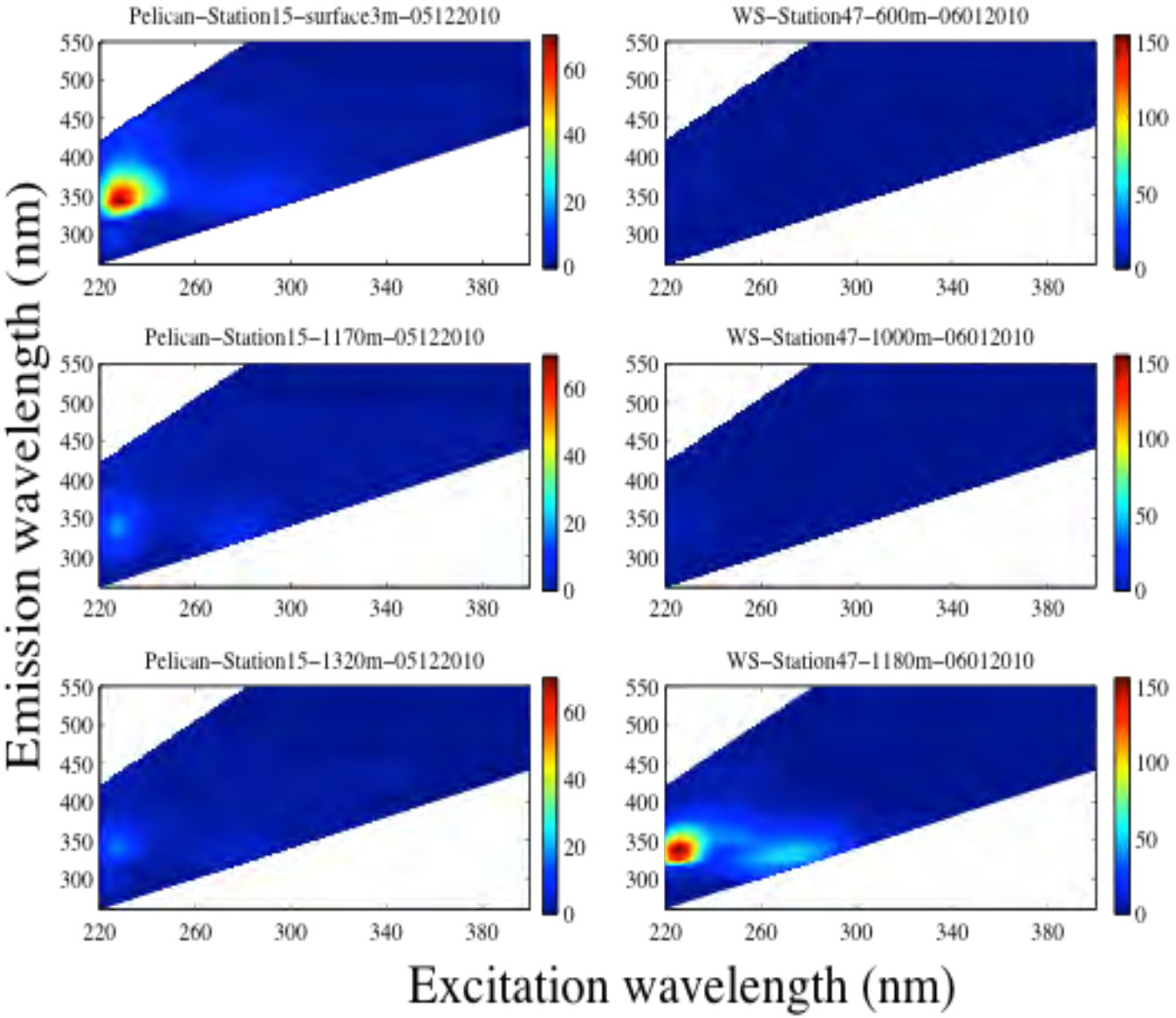
Fluorescence excitation-emission matrix spectra of crude oil, dispersant & weathered oil



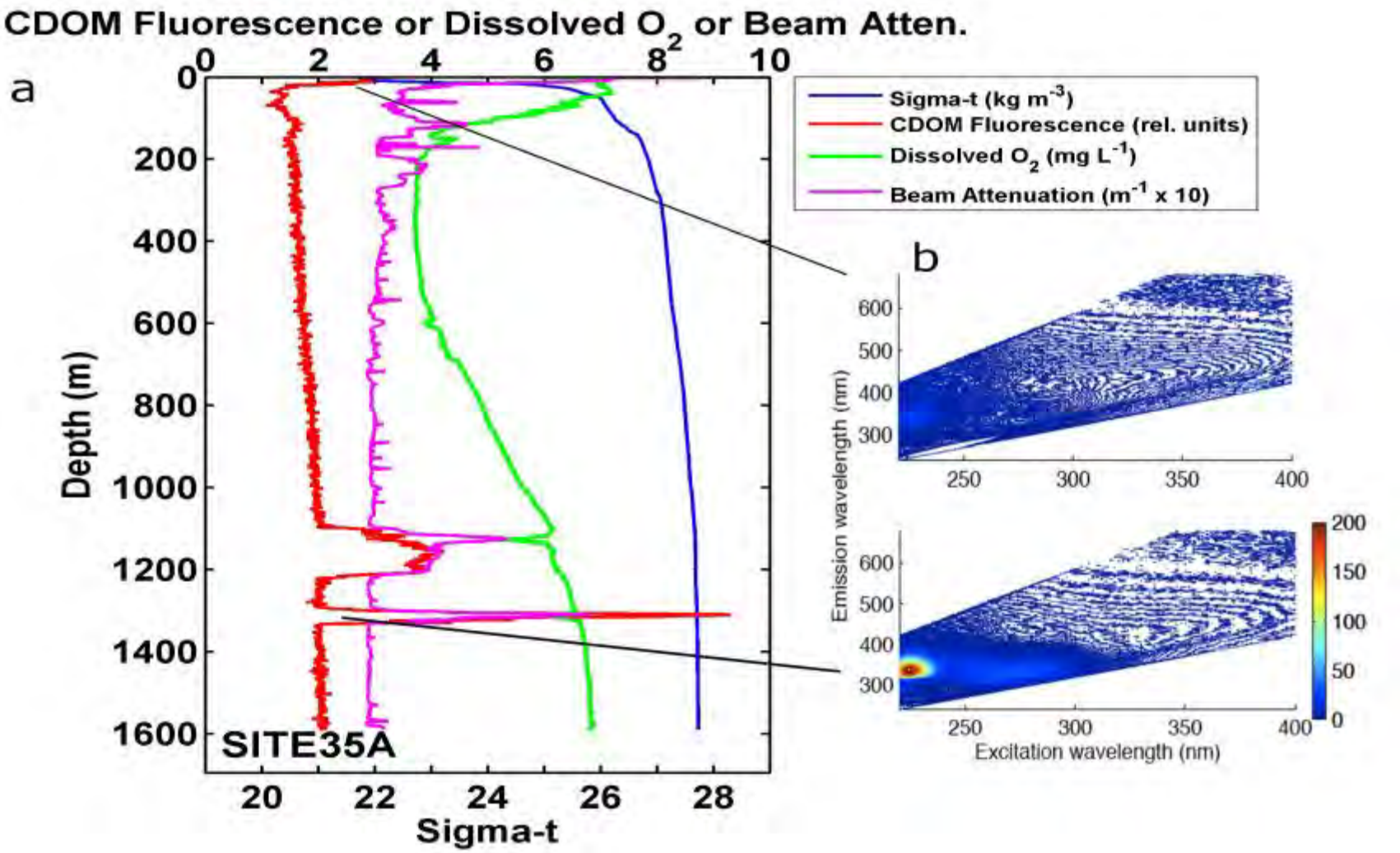
EEM spectra of seawater strongly resemble those of crude oil (226/340 nm)



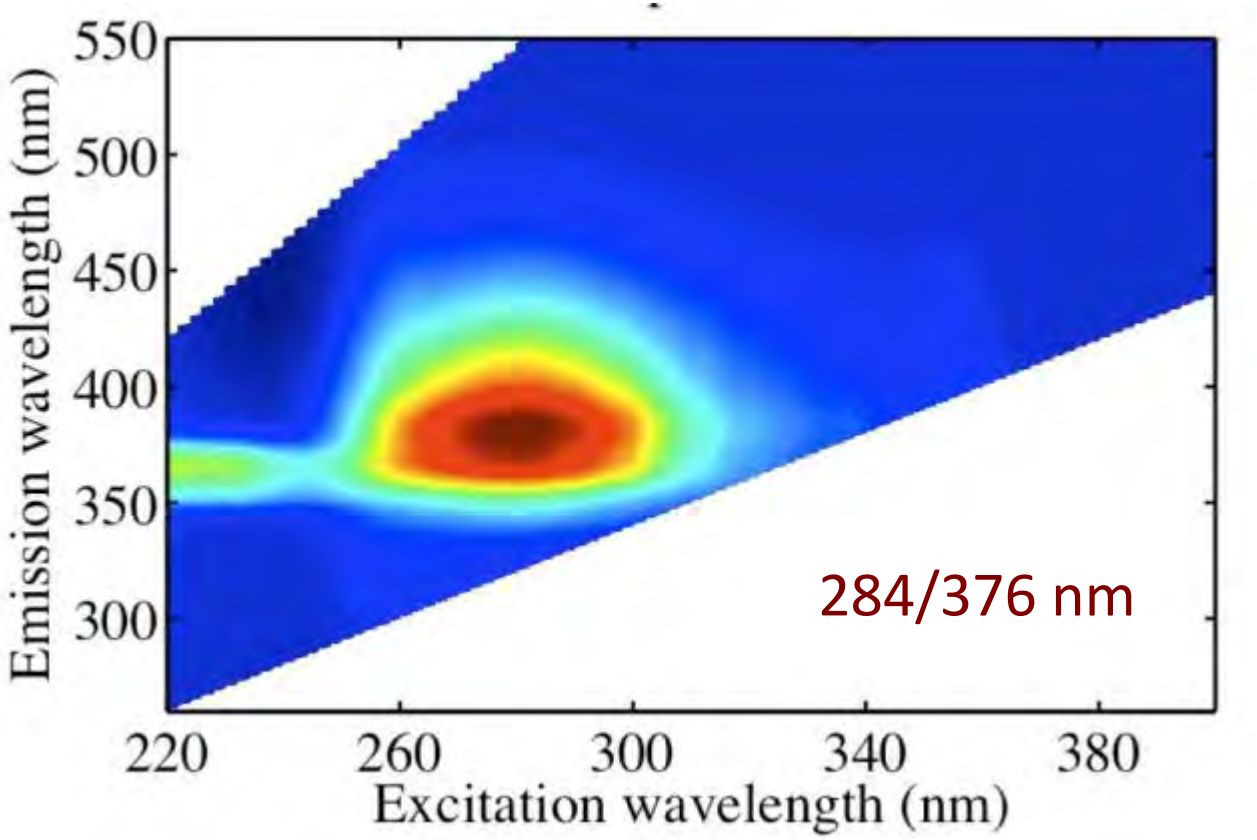
Heterogeneous distributions of oil fluorescence in the water column



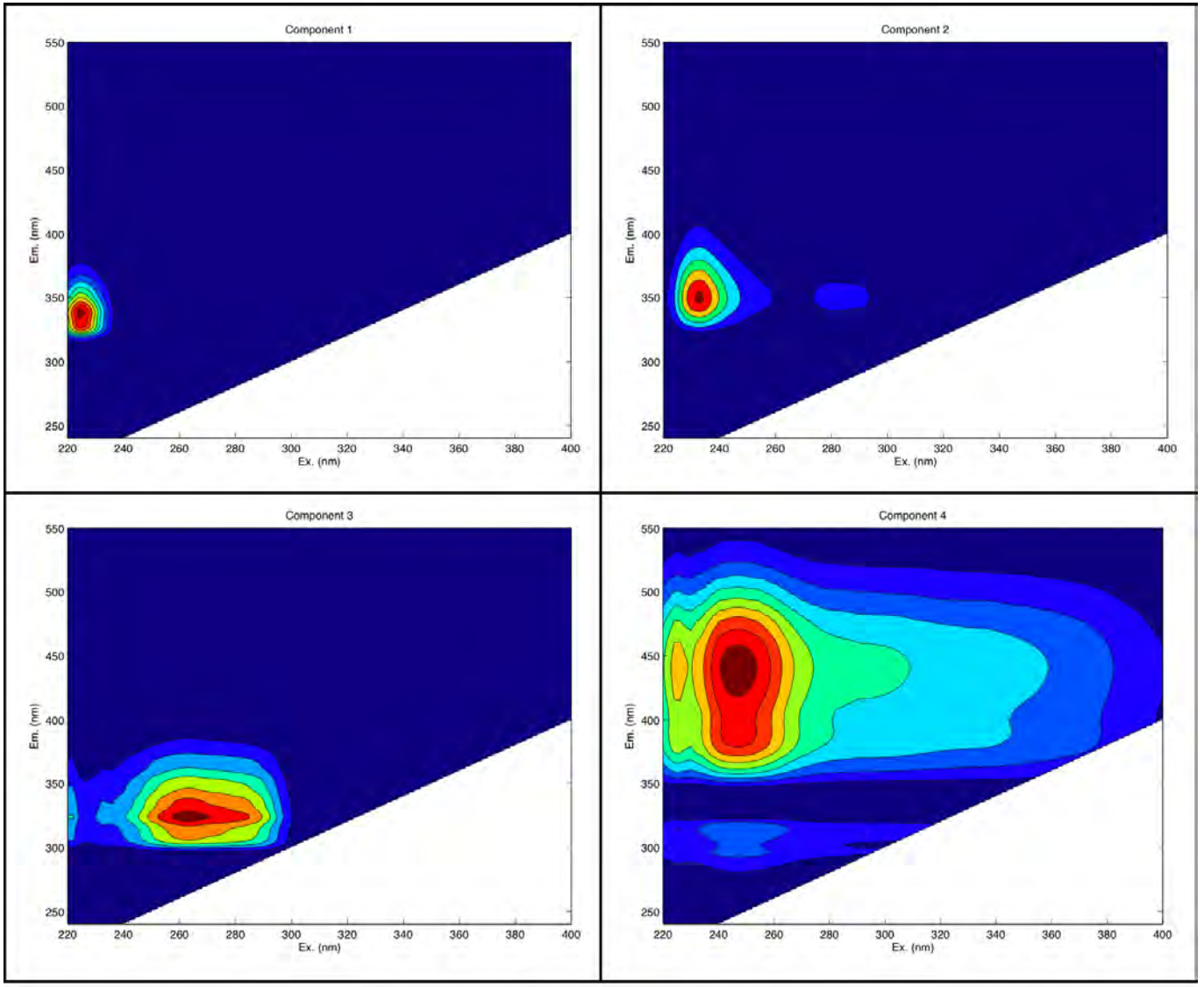
Comparisons with in situ sensor data



Unable to identify ambient dispersant in seawater based on fluorescence EEMs



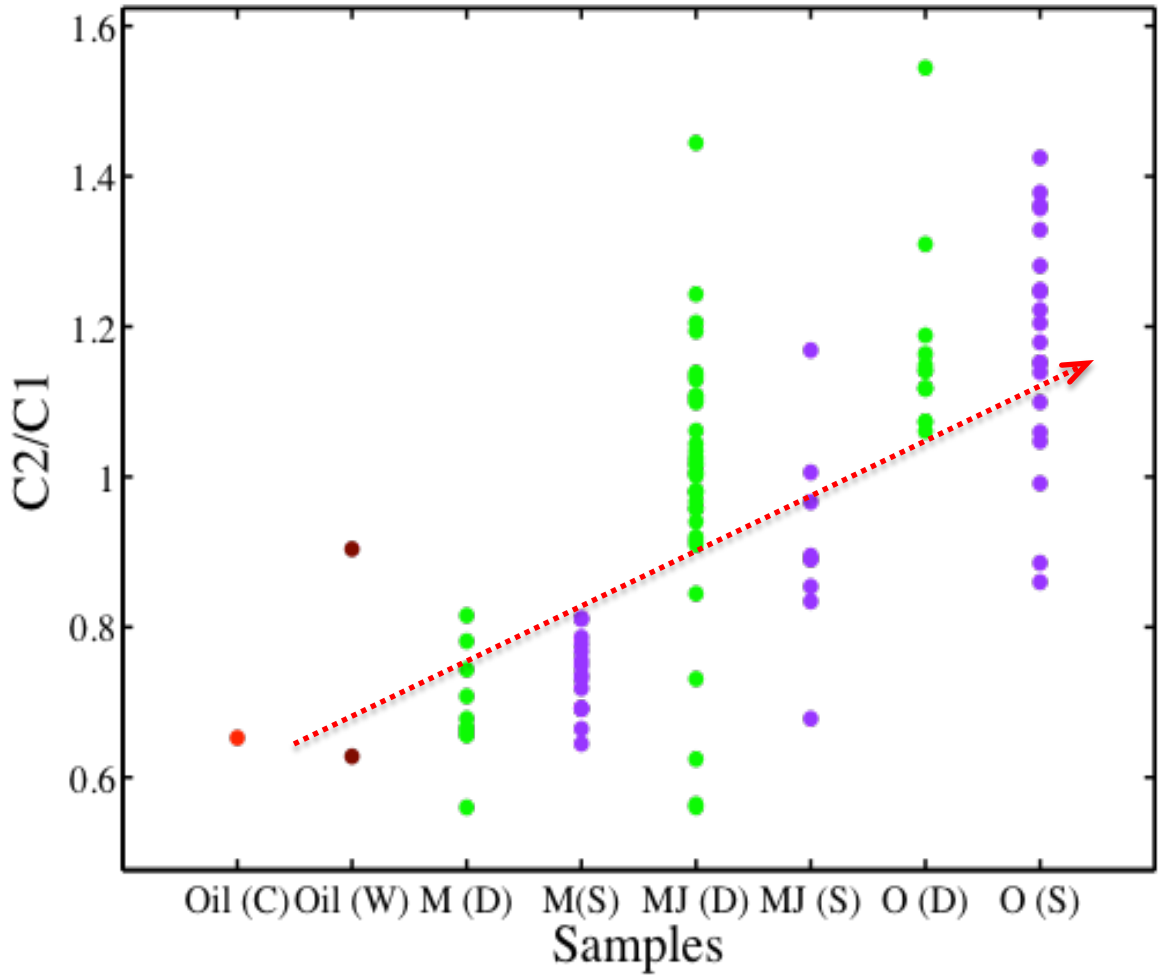
Major fluorescence DOM components identified using PARAFAC analysis



Oil and DOM components identified using parallel factor analysis

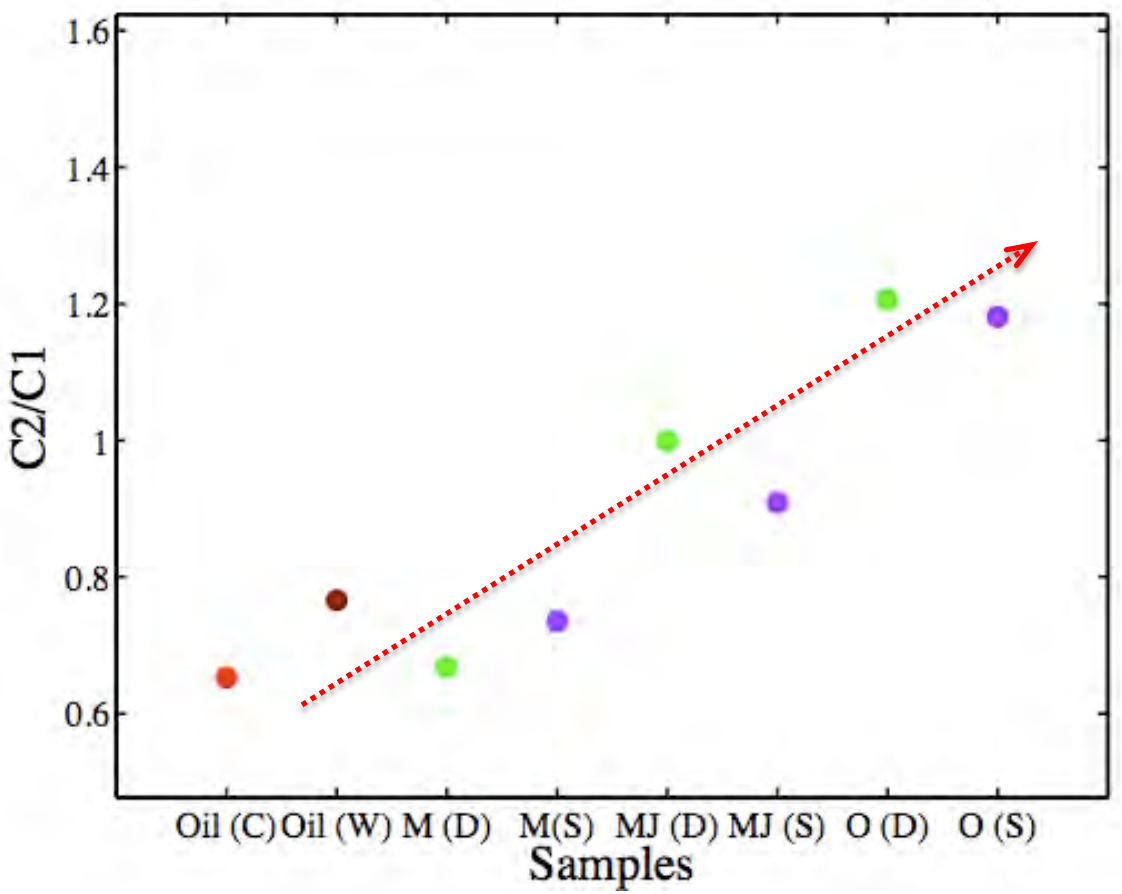
Component	Excitation Max (nm)	Emission Max (nm)	Description
1	226	340	Oil-C1
2	230	350	Oil-C2
3	260-280	322	Oil-C3
4	250	450	UV humic-like

Variations in fluorescence component ratio (C2/C1) between oil and seawater samples



- Crude oil
- Weathered oil
- Surface seawater
- Deep seawater
- Early May, May/June, and October

Variations in fluorescence component ratio (C2/C1) between oil and seawater samples



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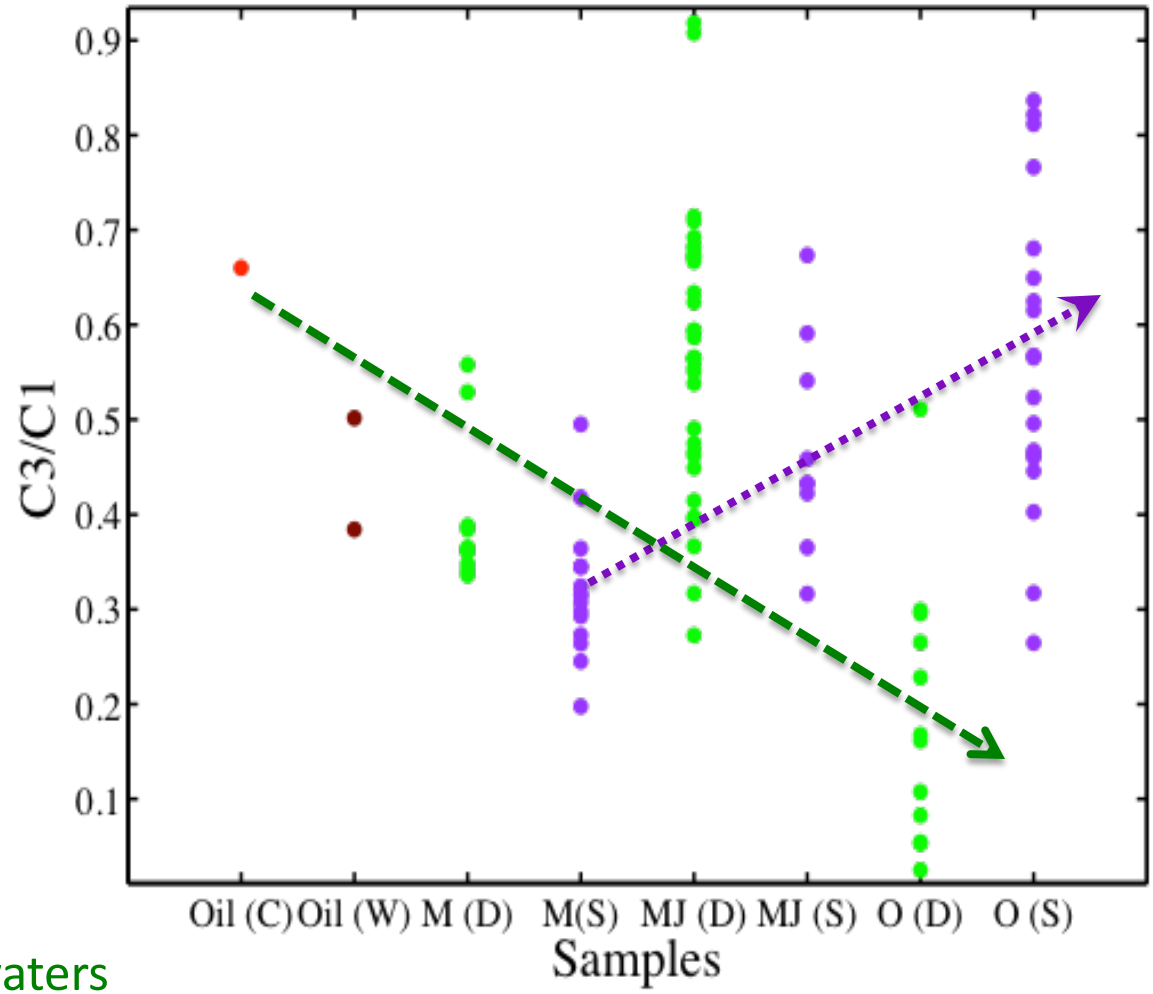
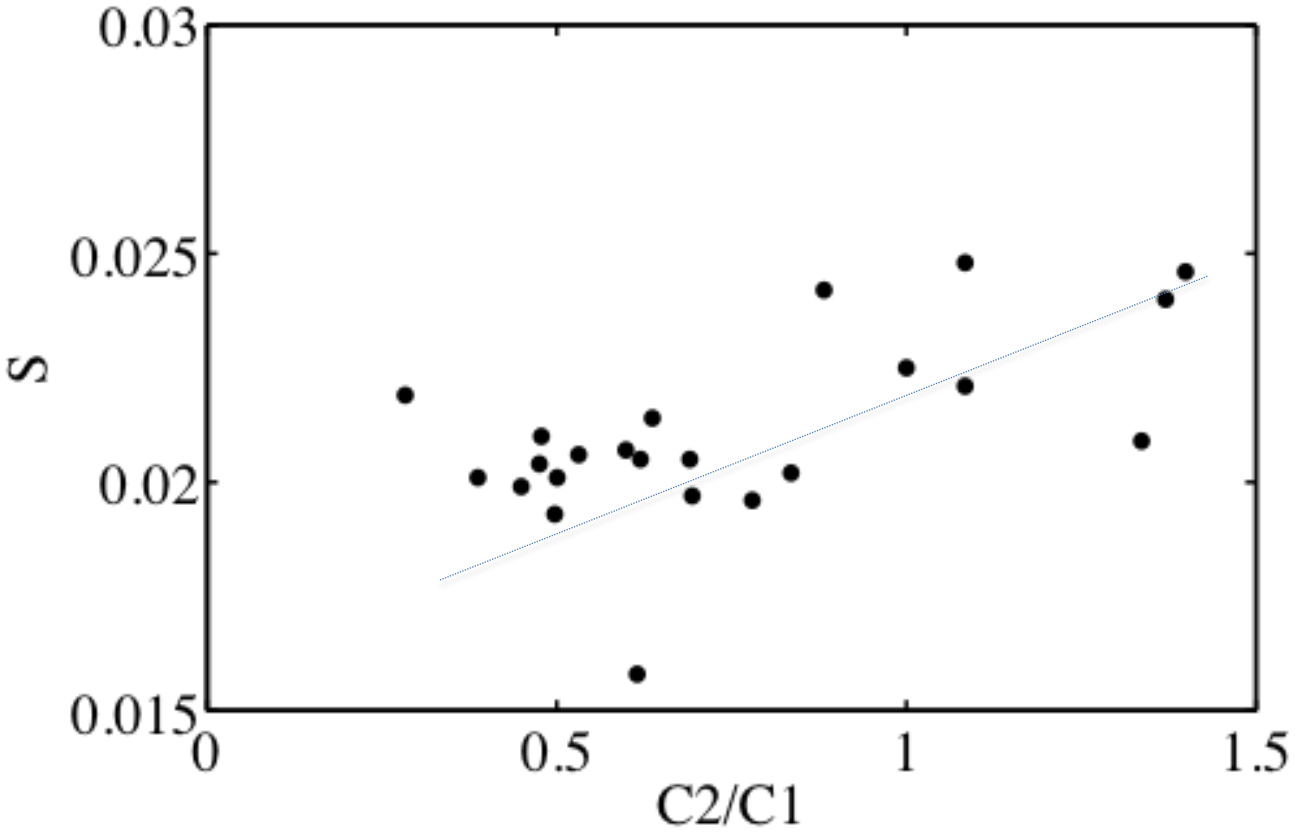
Variations in fluorescence component ratio (C3/C1) between oil and seawater samples



- Surface waters
- Deep waters

Relationship between spectral slope and C2/C1 ratio



Summary

- Fluorescence EEM techniques: very sensitive for oil fingerprinting and for measuring oil components in seawater
- EEMs + PARAFAC analysis: effective tools for identifying natural DOM and oil components
- Derived fluorescence index (e.g., component ratio): potential proxy/tracer for tracking the degradation status of oil and its fate and transport
- Controlled laboratory experiments are needed to examine the degradation pathways/mechanisms and chemical evolution of oil/dispersant systems to assist in field data interpretation