Optical properties of DOM from the Gulf of Mexico after the Deepwater Horizon oil spill

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Introduction

- Over 800 million liters of crude oil were released.

- Oil components and their degradation pathways remain poorly understood.

- Optical properties have widely been used to characterize natural DOM in aquatic environments.

- In this study, we combined measurements of bulk OC, UV-vis absorbance, fluorescence EEMs, and other optical properties for the characterization and fingerprinting of oil components.

Sampling Sites
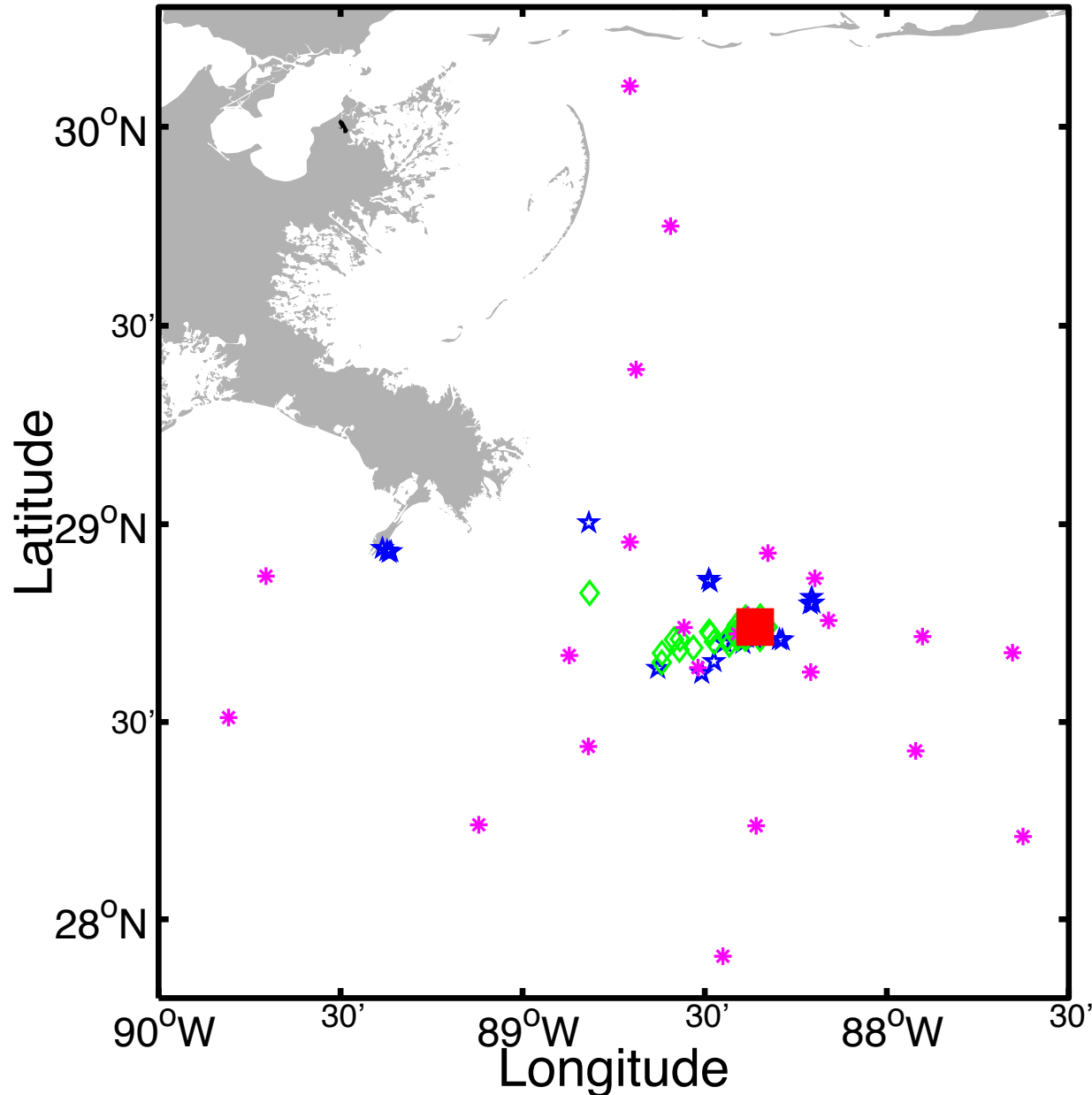
- Water samples were collected in **October 2010** after 5 months of oil spill, but will also discuss samples collected in **mid-May**, and **late-may to early-June** during the oil spill.
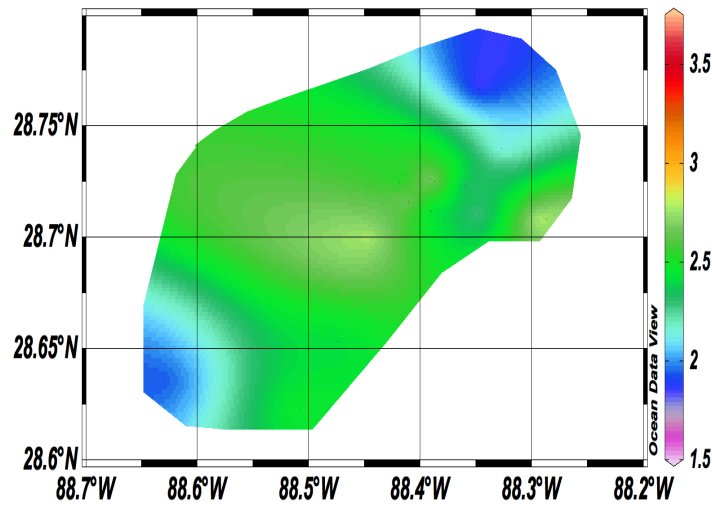
- The red square is the oil rig.

Methods

- DOC and DIC: Shimadzu TOC-V total organic carbon analyzer;

- Absorption spectra: UV-visible spectrophotometer;

- Fluorescence EEMs: 3D spectrofluorometer;

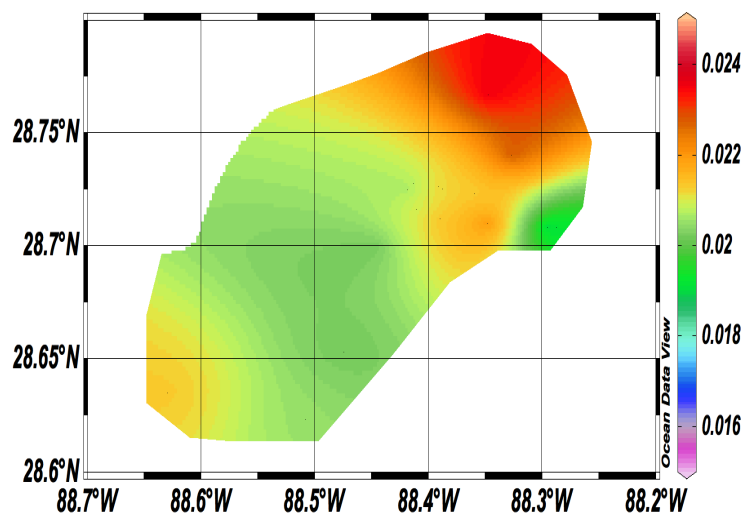- PARAFAC modeling: Matlab and the DOMFluor Toolbox.
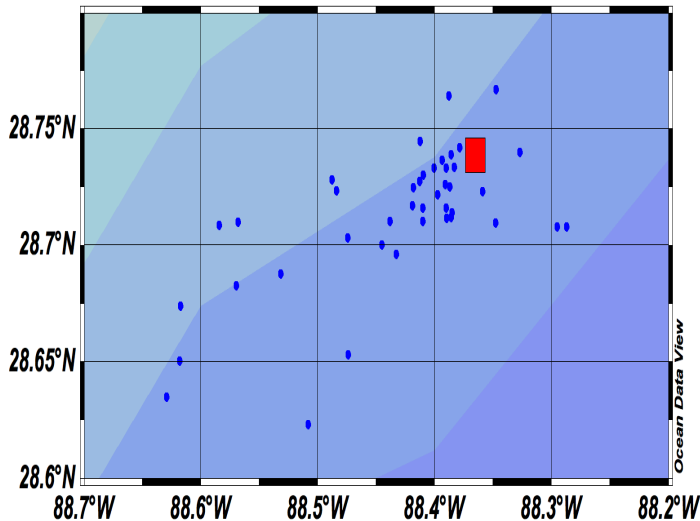
May-June 2010

DOC [mg-C/l] @ Depth [m]=3
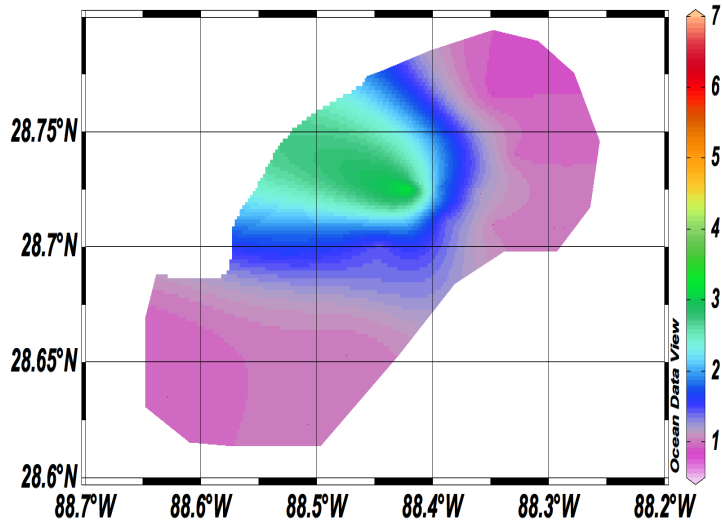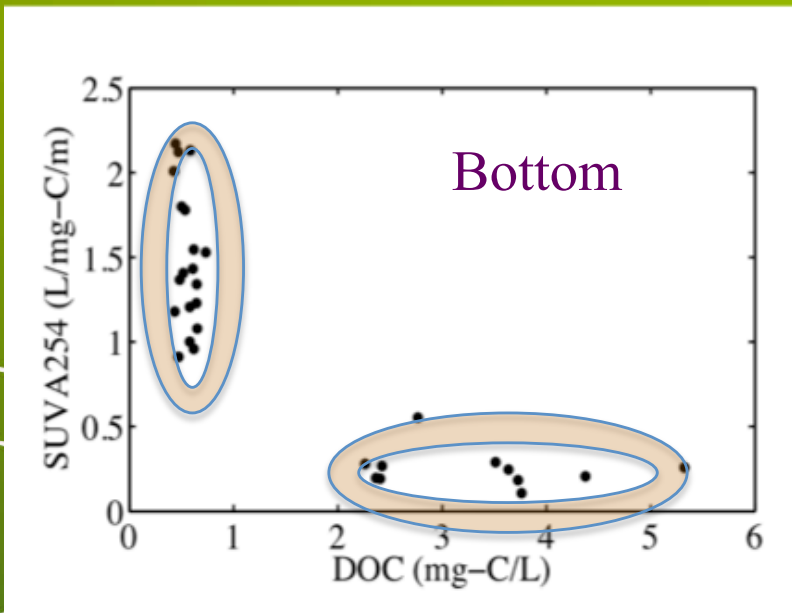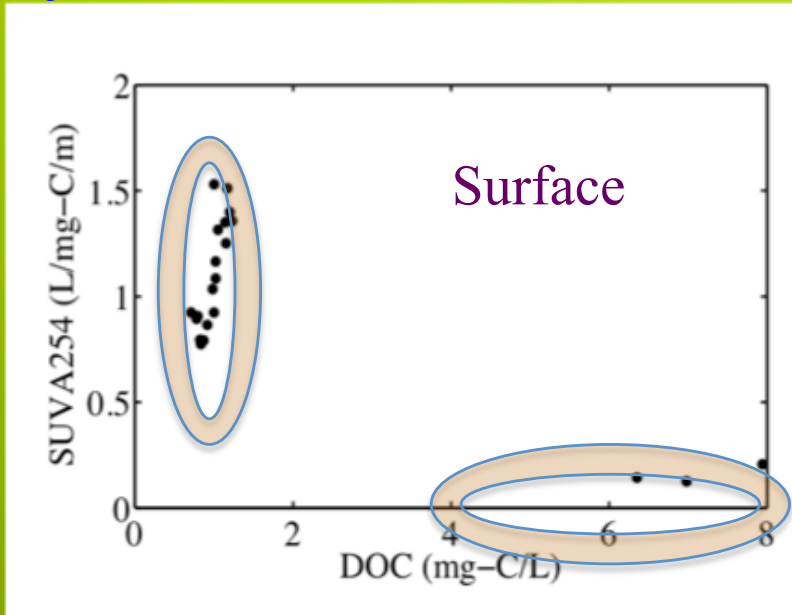

a$_{254}$ [1/m] @ Depth [m]=3

SS(NLF 300-400) [1/nm] @ Depth [m]=3

- Elevated DOC concentrations,
- Higher UV-vis absorbance and
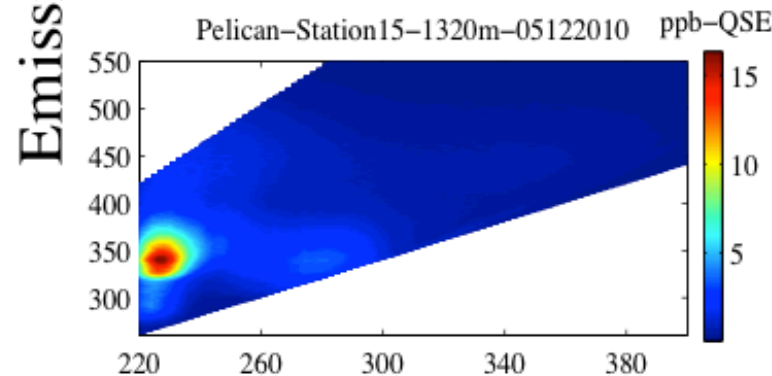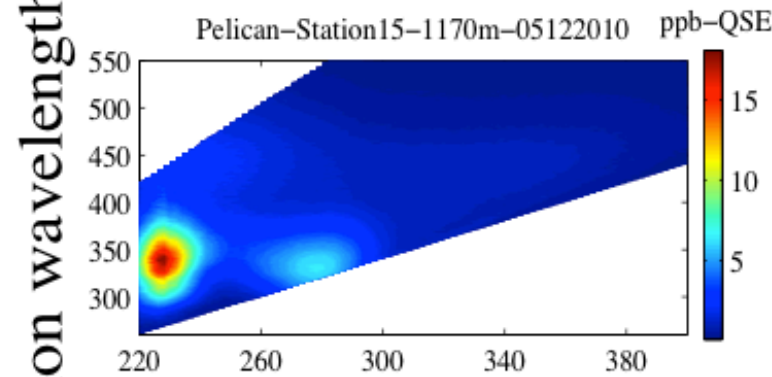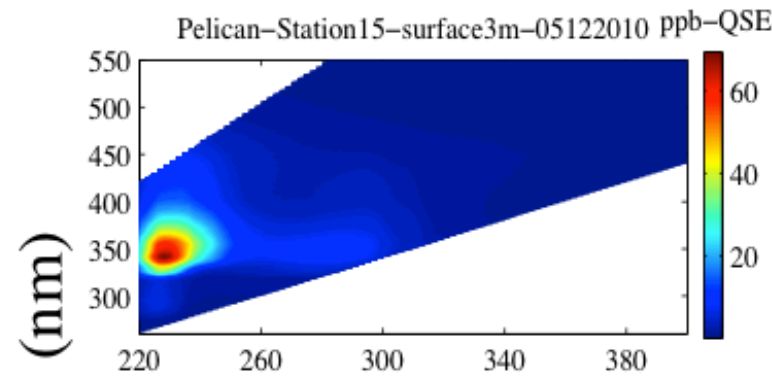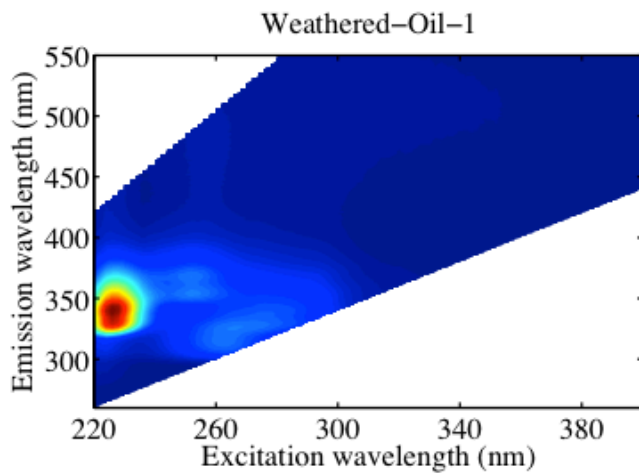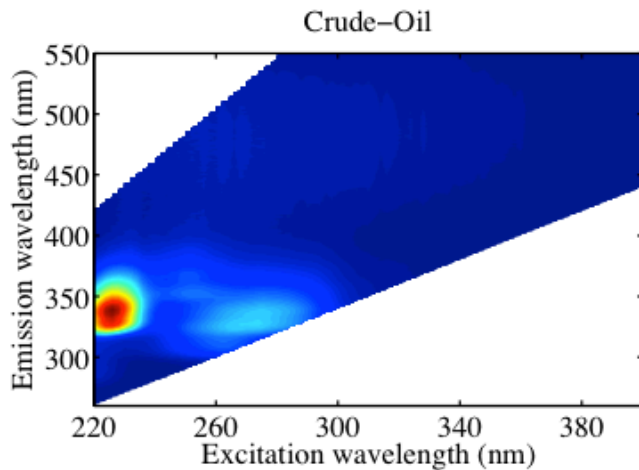- Higher inferred molecular weight DOM were found in the water column.

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May-June 2010

Surface

Bottom

- Two major types of DOM were found:
- 1. low abundance but high optical activity and
- 2. high mass concentration yet low optical activity

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May to June 2010- fluorescence signatures

Crude-Oil

Weathered-Oil-1

Pelican-Station15-surface3m-05122010 ppb-QSE

Pelican-Station15-1170m-05122010 ppb-QSE

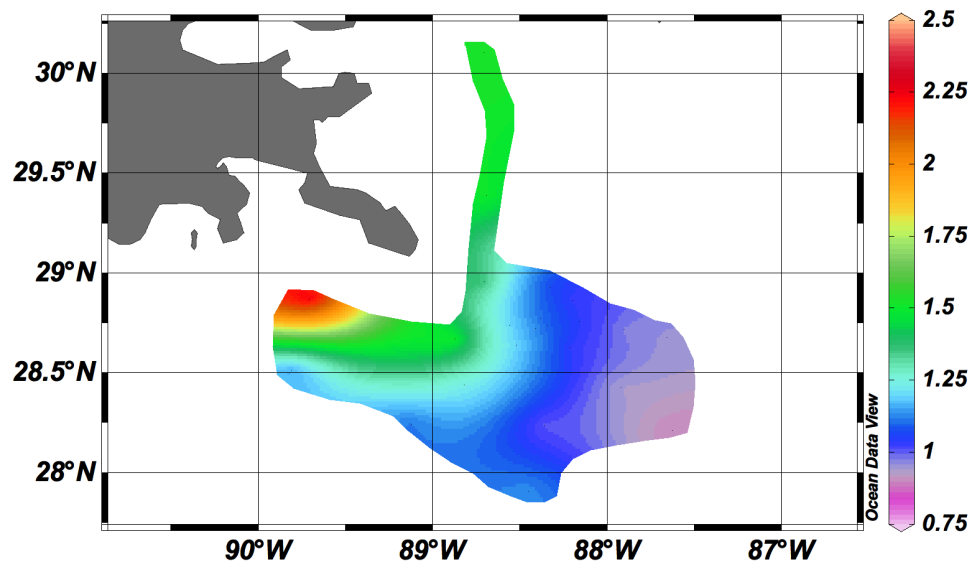Pelican-Station15-1320m-05122010 ppb-QSE
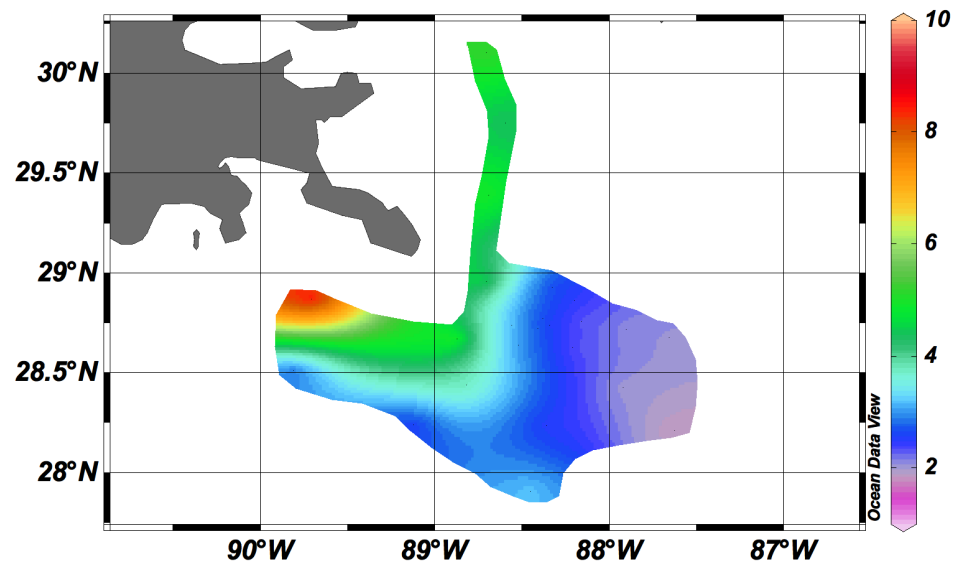
Excitation wavelength (nm)

Emission wavelength (nm)

- Fluorescence EEM spectra of seawater samples strongly resembled those of crude oil and weathered oil.

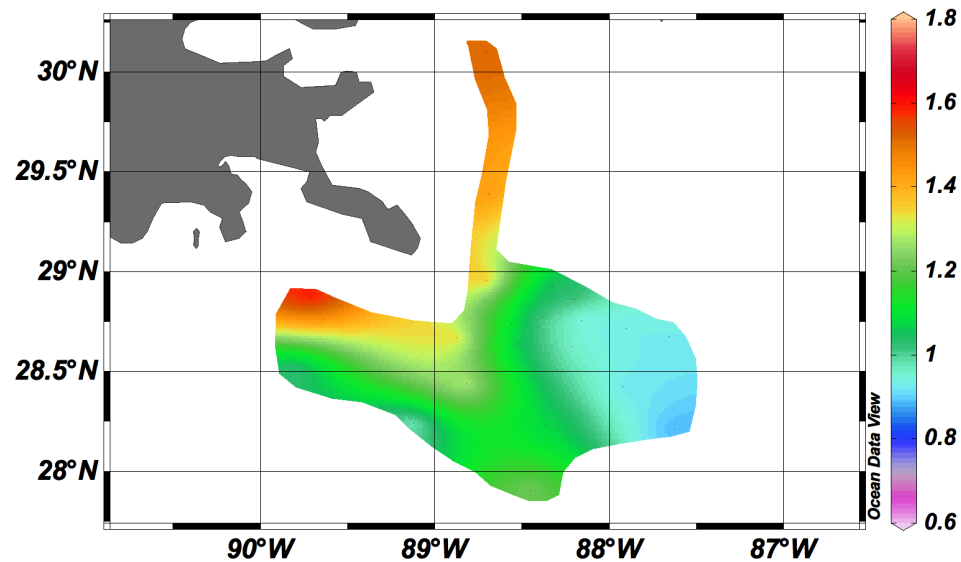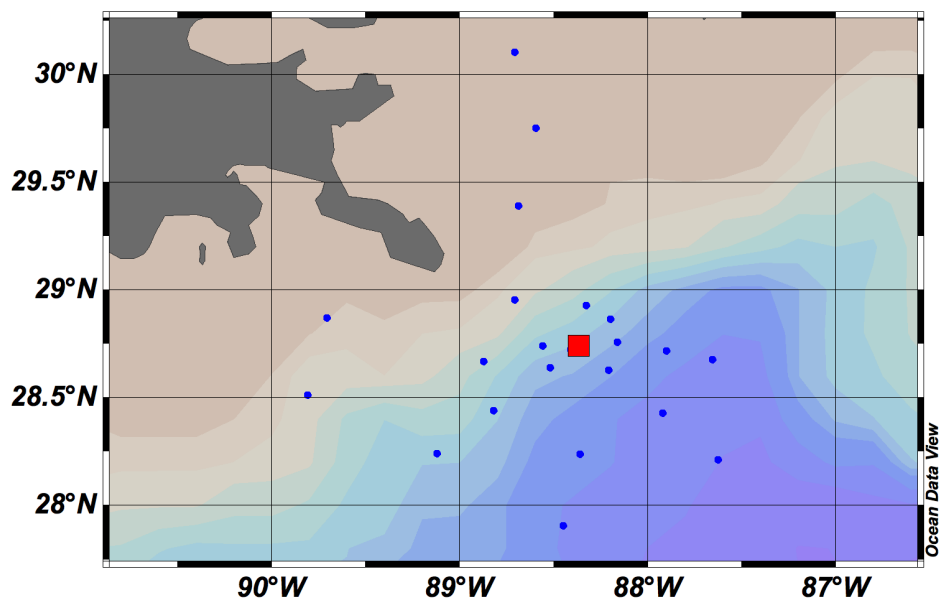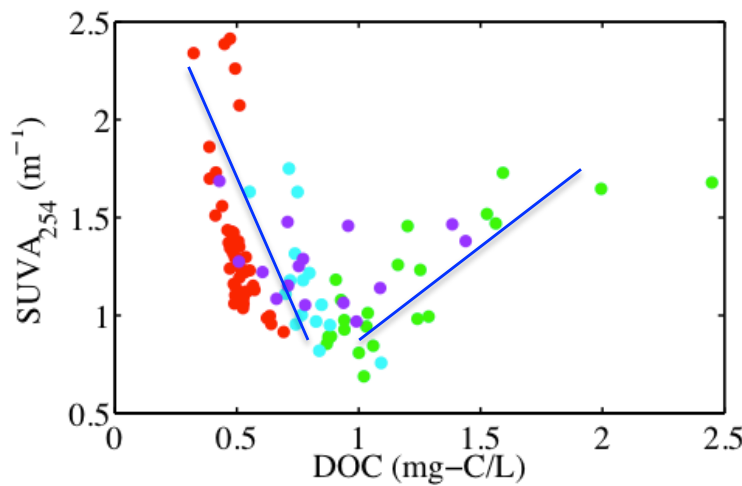- Fluorescence intensity varied with depth in the water column

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October 2010

October 2010 - CDOM

• Two major types of DOM were found in the water column

1) Positive correlation between DOC concentration and SUVA$_{254}$ values showing natural DOM characteristics for upper water column samples;

2) Anomalously high optical yields, with negative correlation between SUVA and DOC, found exclusively in deep waters, showing oil influence
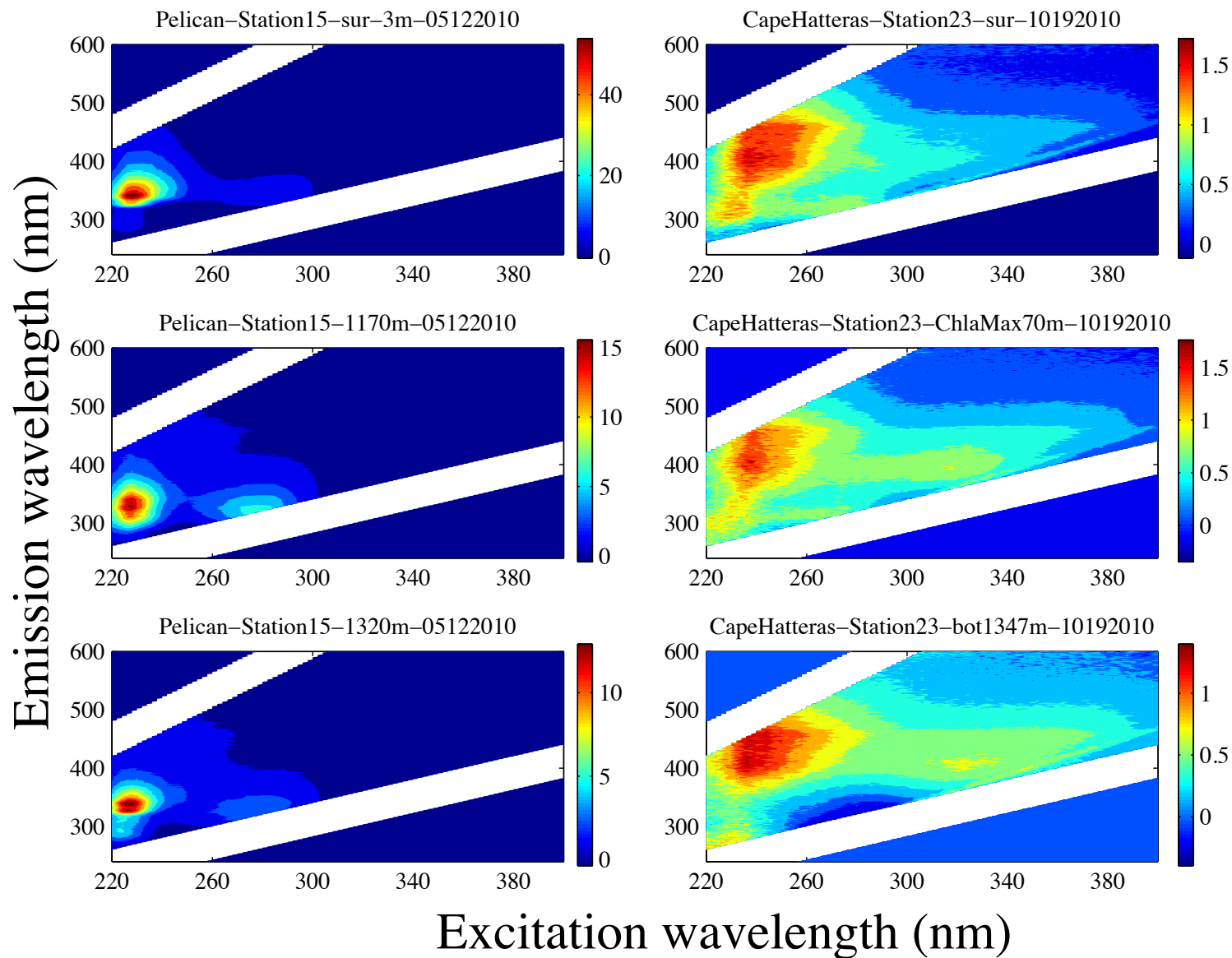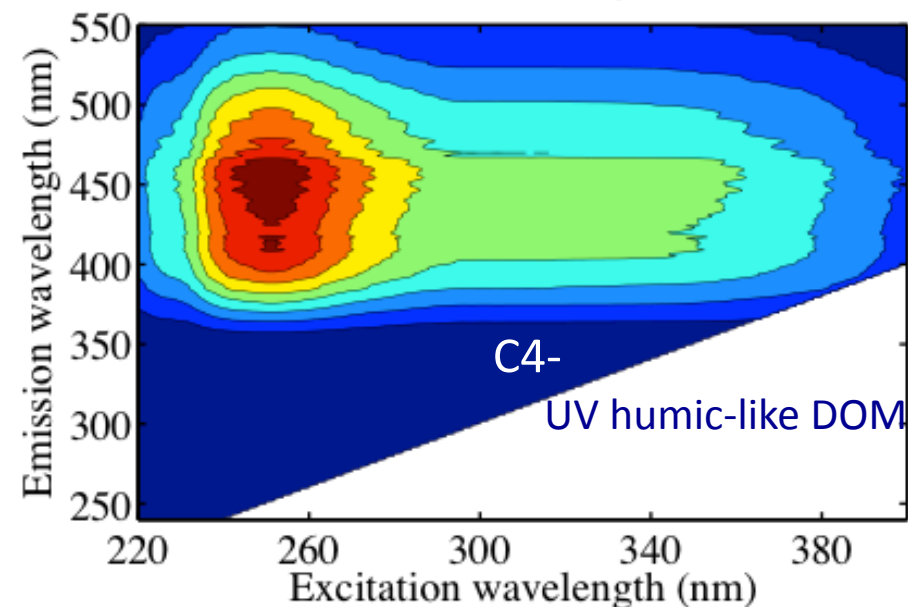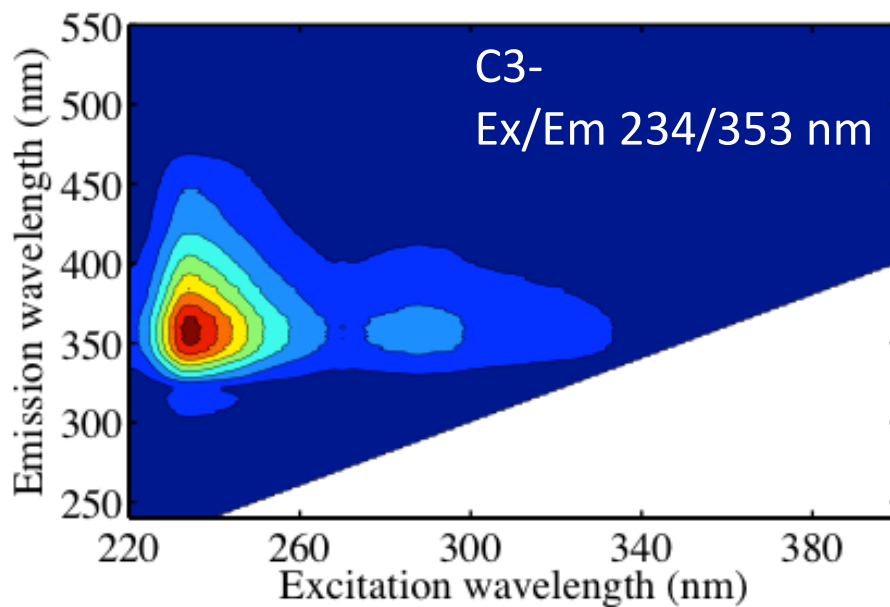
October 2010 - fluorescence signatures

Pelican−Station15−sur−3m−05122010

CapeHatteras−Station23−sur−10192010

Pelican−Station15−1170m−05122010

CapeHatteras−Station23−ChlaMax70m−10192010

Pelican−Station15−1320m−05122010

CapeHatteras−Station23−bot1347m−10192010

Emission wavelength (nm)

Excitation wavelength (nm)

• Fluorescence EEM spectra of seawater samples taken in October has lost obvious oil signatures.

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Fluorescent oil DOM components

C1-
Ex/Em 226/340 nm

C2-
Ex/Em 226/320
and 275/320nm

C3-
Ex/Em 234/353 nm

C4-
UV humic-like DOM
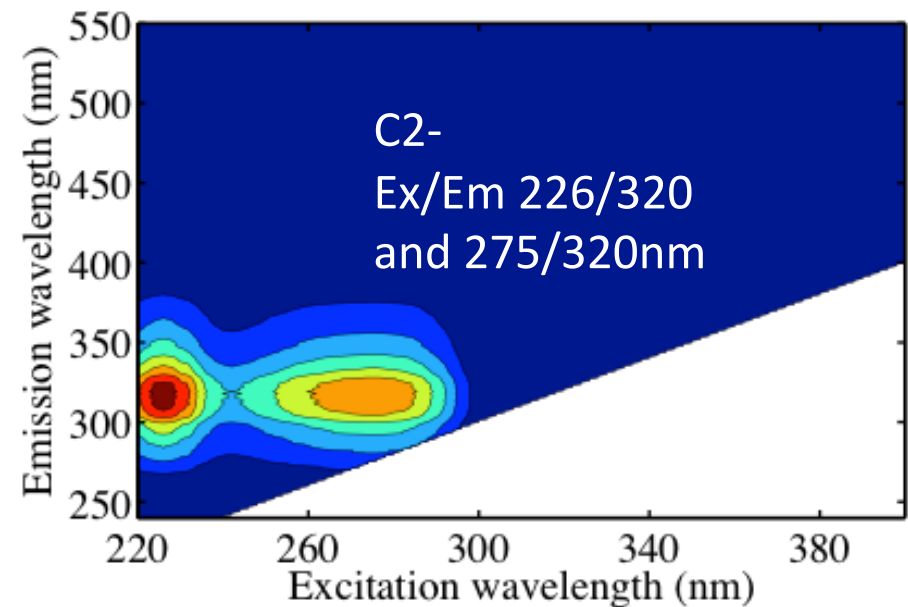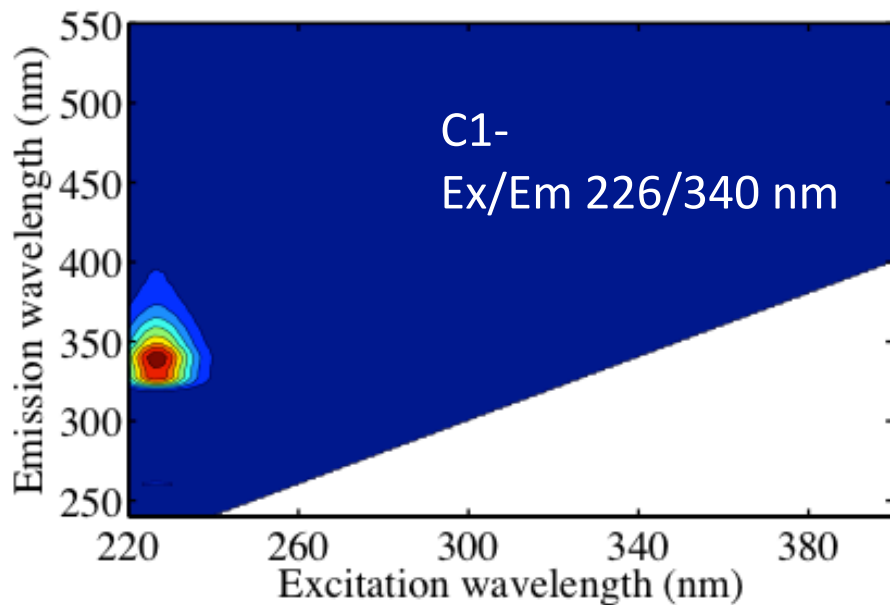
Fluorescent oil DOM components

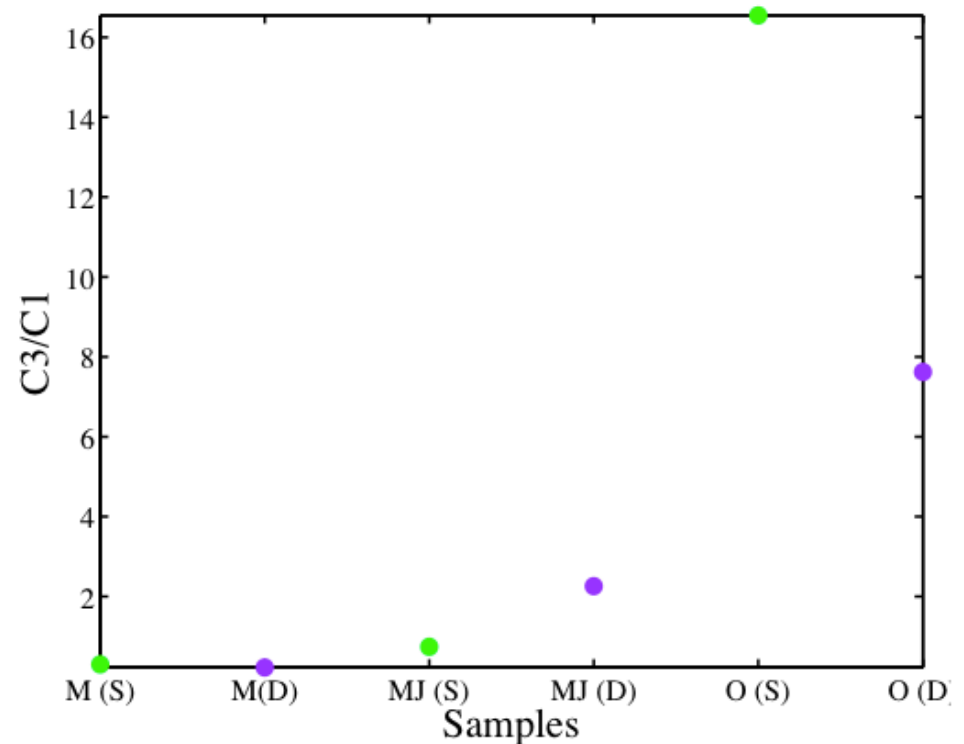- Even though the intensity/concentration of all components decreased with time from May to June to October.

- The C2/C1 and C3/C1 increased consistently with time. We hypothesize that C2 is mostly derived from photochemical degradation and C3 is a degradation product from both microbial and photochemical degradation.
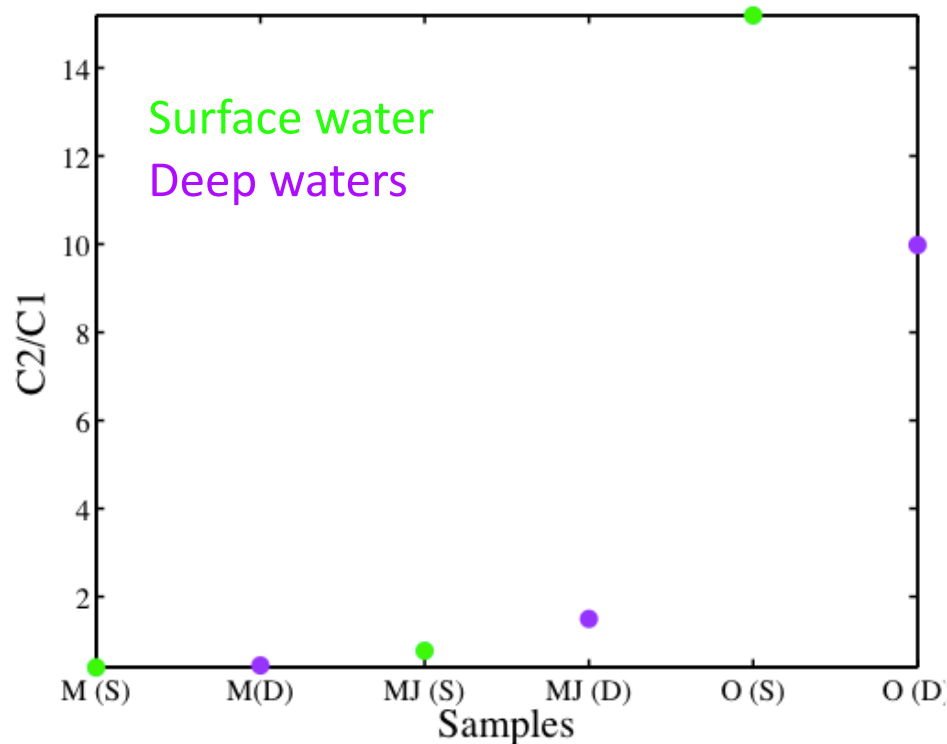
Conclusions

- The Deepwater Horizon oil spill had altered profoundly the optical characteristics of DOM in the water column.

- At the early stages (1-2 months after the spill), more fresher oil components in the water column resulted in higher DOC concentration and higher optical reactivity, with two groups of DOM throughout the entire water column.

- After 5 month of the oil spill, DOM in the upper water column seemed to contain mostly naturally occurring DOM, while anomalous DOM with high optical activity still resided in the deep water, showing the influence from oil.

- Four fluorescence components have been identified using PARAFAC analysis. Three of them are oil components and one is UV humic-like DOM.

- The fluorescence component ratios can be used to track effectively the degradation state of oil and its fate and transportation in the water column.

Acknowledgements

Thank you!

Questions?