

Terrestrial CDOM in the Marine Environment

Prof. Peter Croot (NUI Galway)

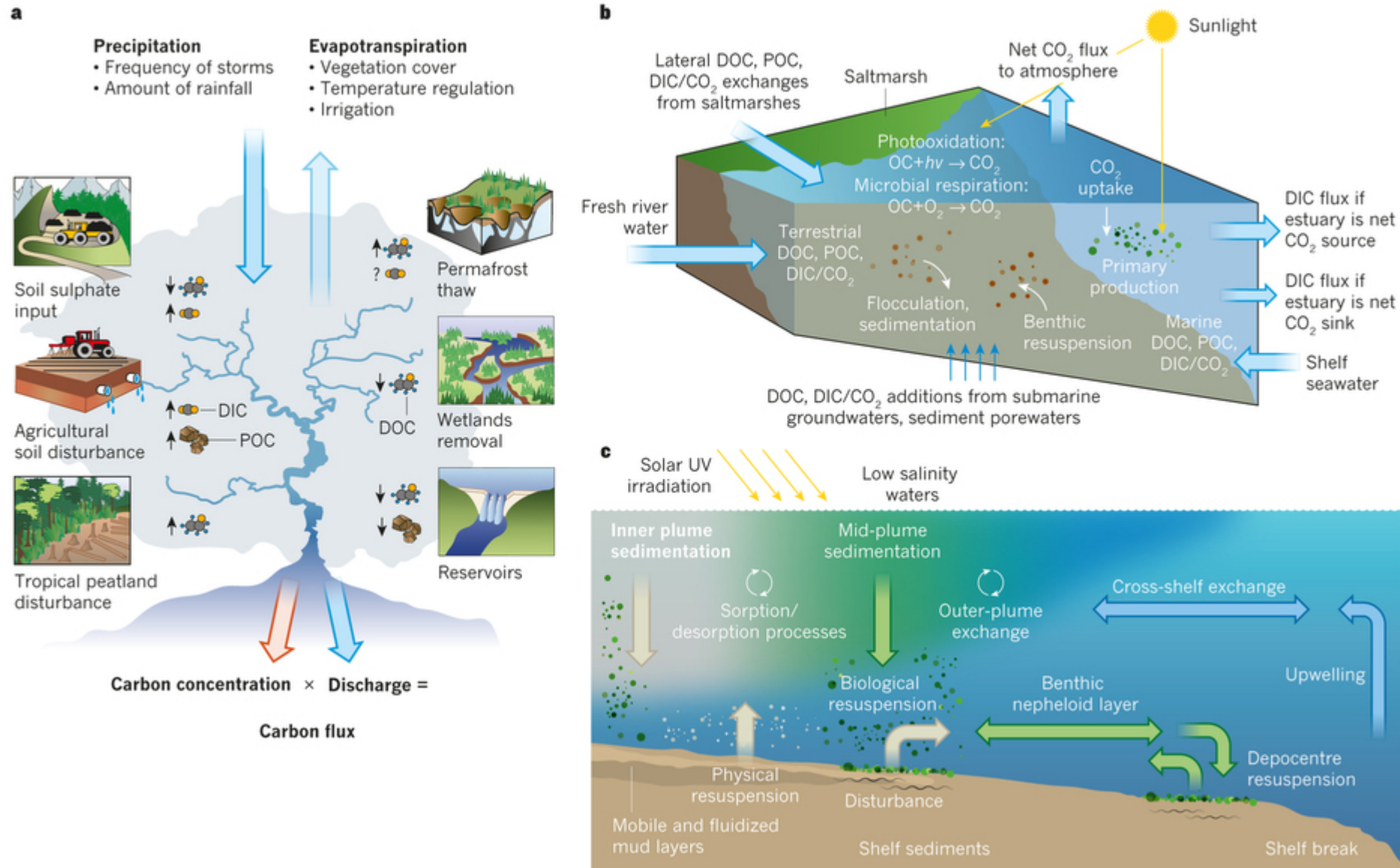
Allan Grassie (NUI Galway), Maija Heller (UCSC)



Acknowledgements: Funders and International Programs

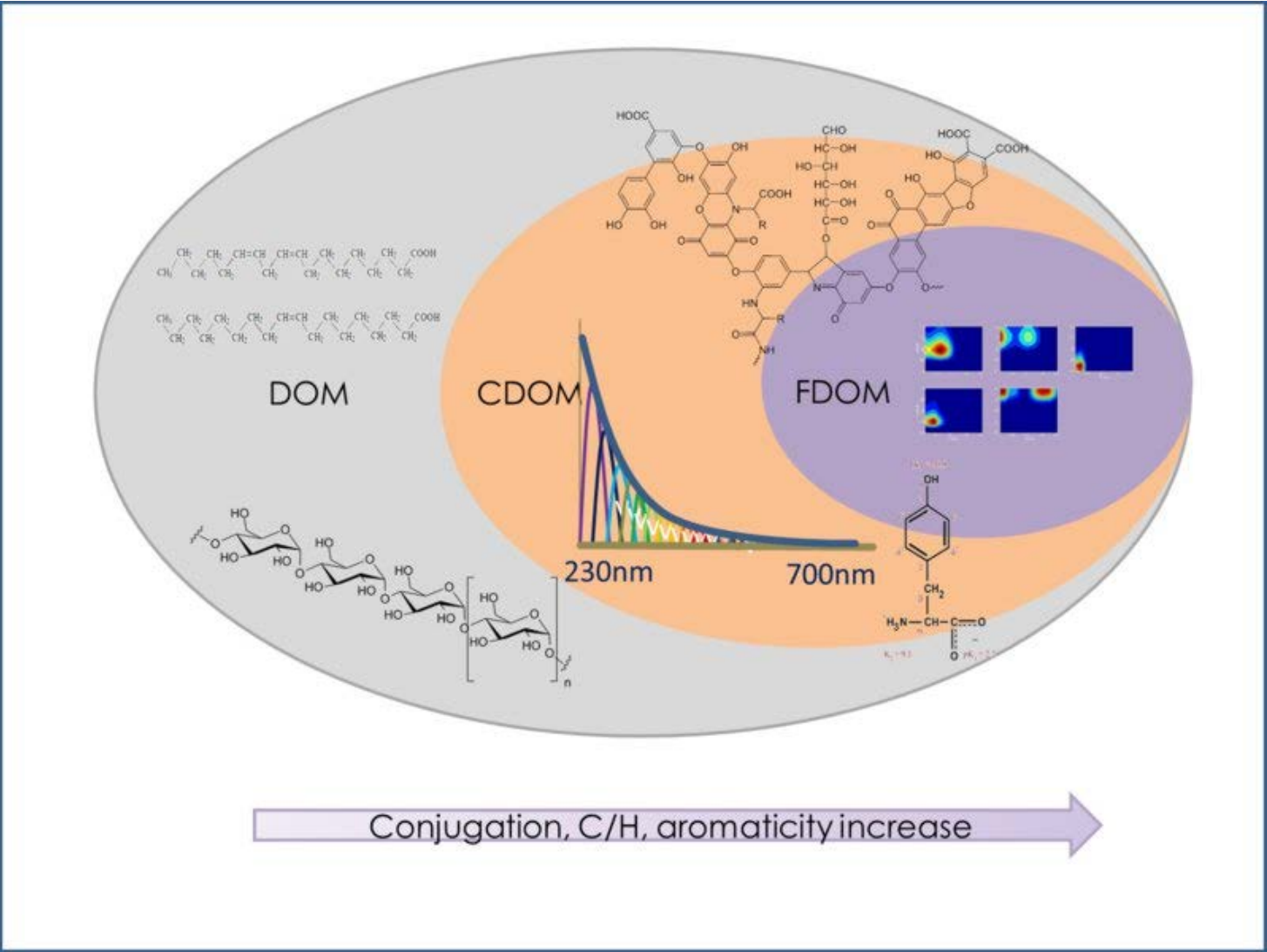


Carbon Cycling in the Coastal Ocean

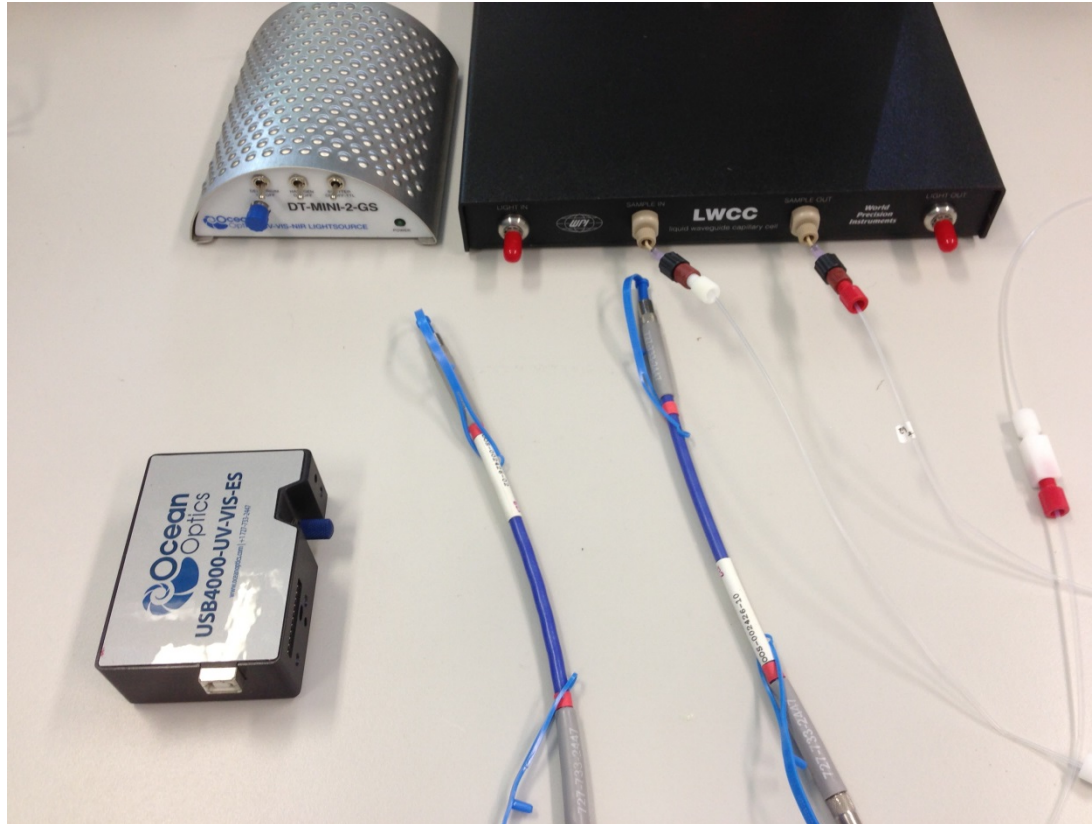


Bauer et al.
2013

CDOM and FDOM



CDOM measurement



Collect seawater

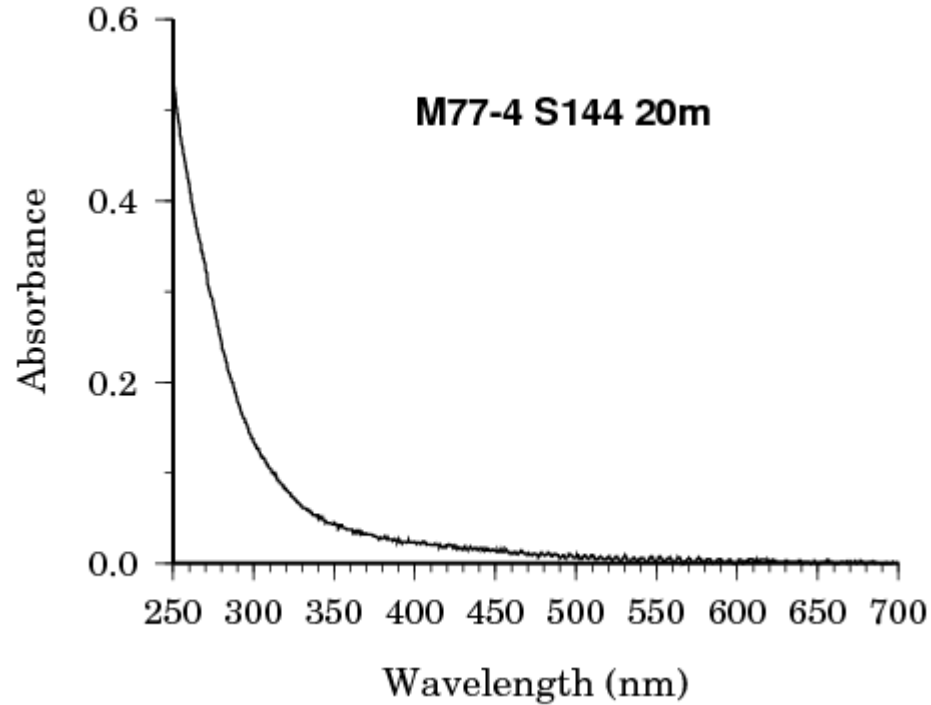
0.2 μm syringe filtration

Measure absorbance using
0.1, 1 or 2 m pathlength
LWCC connected via optical
fibres to an Ocean Optics
USB4000 and DT-mini-2-GS
light source

CDOM absorbance

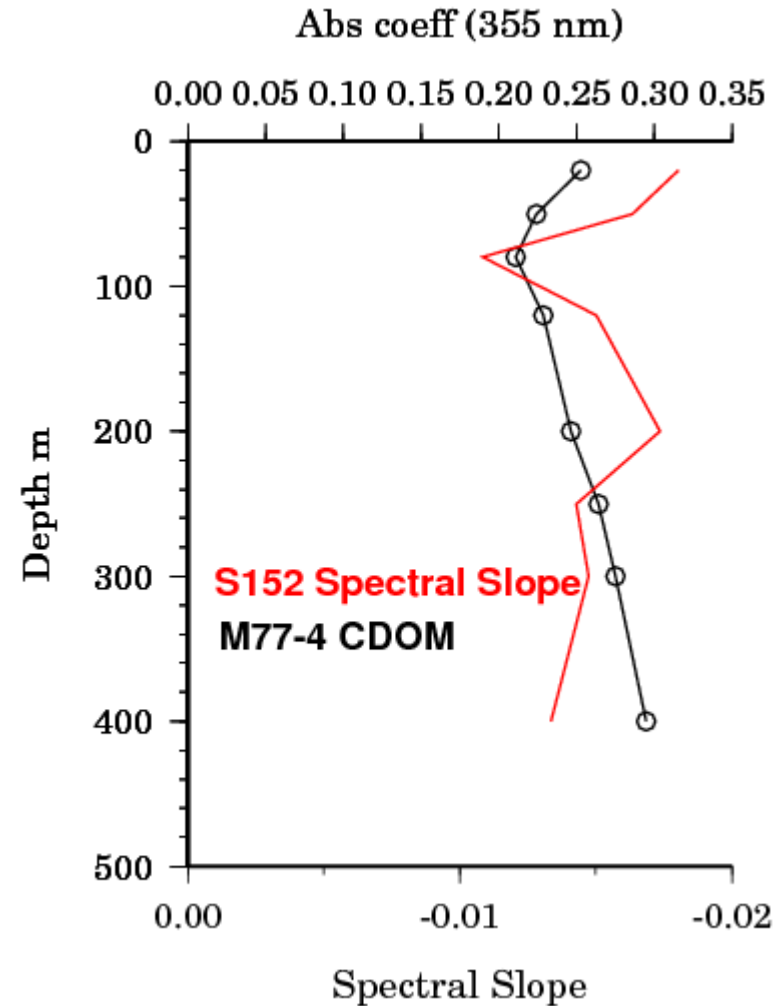
- CDOM of terrestrial origin is characterised by lower spectral slopes than CDOM of marine origin.
- Microbial degradation lowers spectral slopes
- Photodegradation rises spectral slopes
- (Del Vecchio and Blough, 2004; Nelson et al., 2007,2010)
- Inverse relationship between S and $a_{\text{CDOM}}(\lambda)$

CDOM Absorbance data

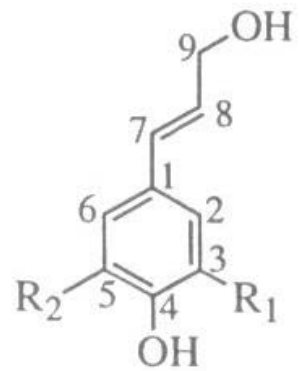


Outputs: Absorbance as function of wavelength
Can fit for spectral slope parameter
(exponential fit)

$$a_g(\lambda) = a_g(\lambda_0) \exp\{-s(\lambda - \lambda_0)\},$$

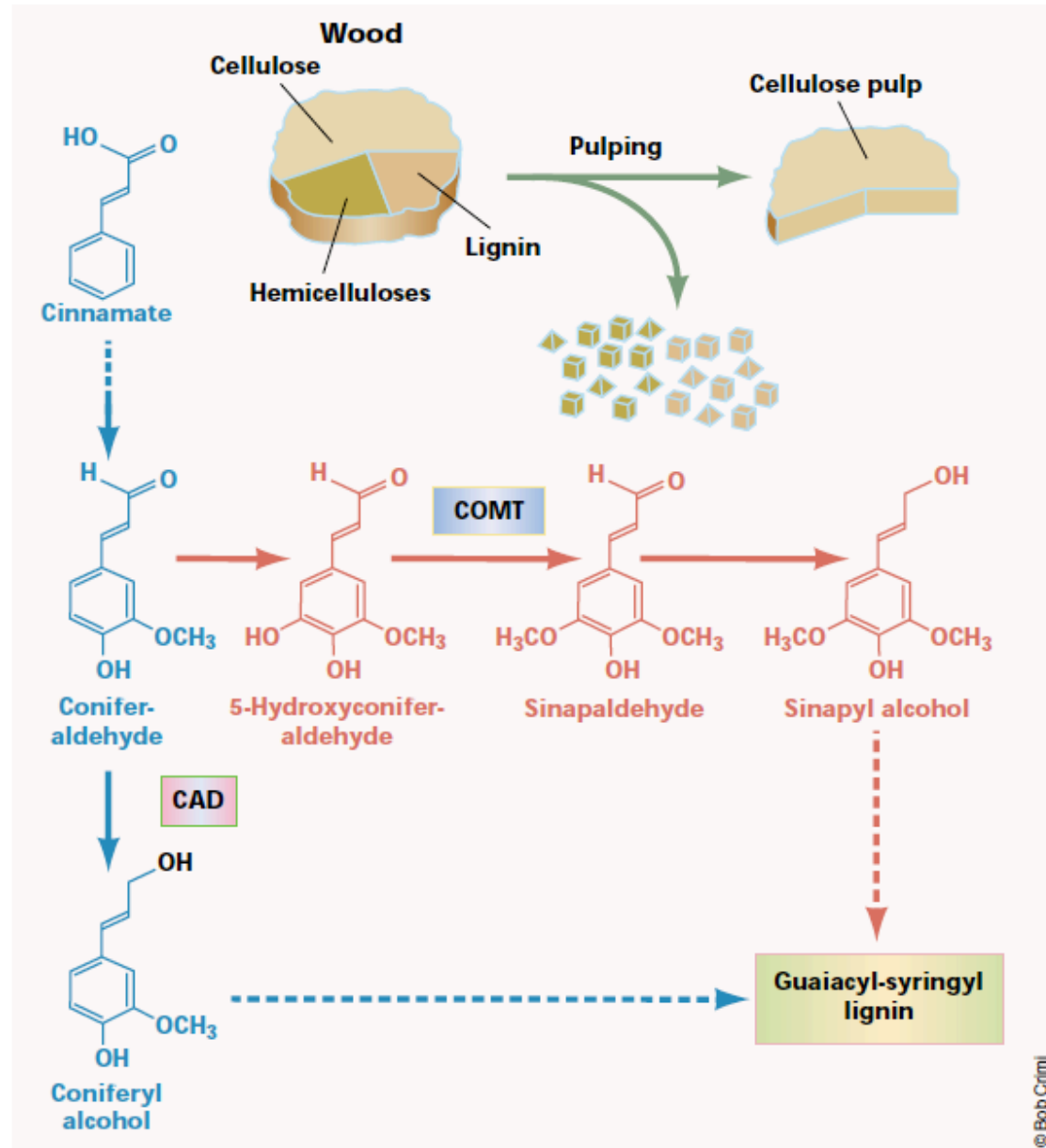


Monomers of Lignin: Tracers of Terrestrial CDOM

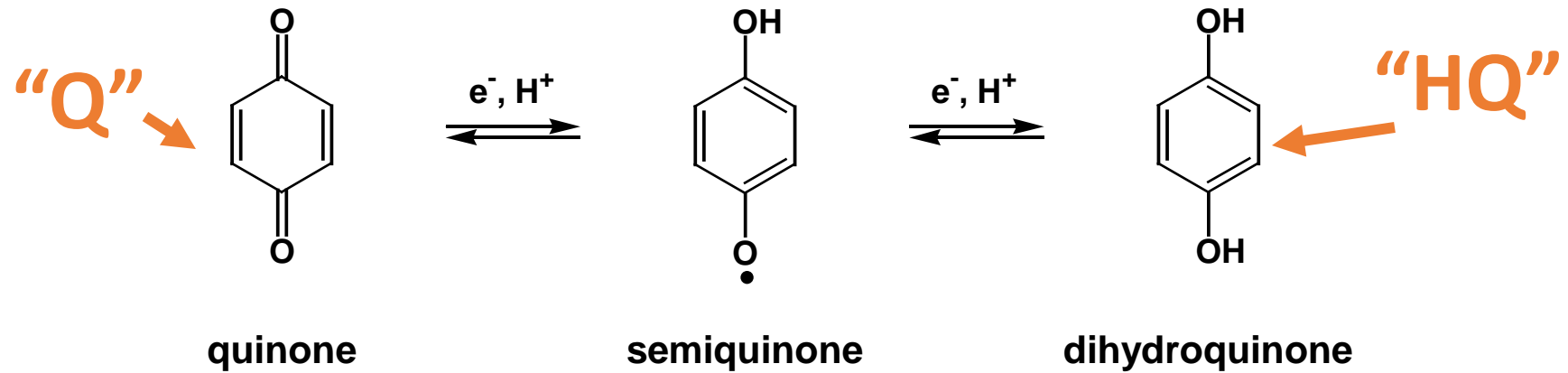


$R_1, R_2 = H$, *p*-coumaryl alcohol
 $R_1 = H, R_2 = OCH_3$,
 coniferyl alcohol
 $R_1, R_2 = OCH_3$, sinapyl alcohol

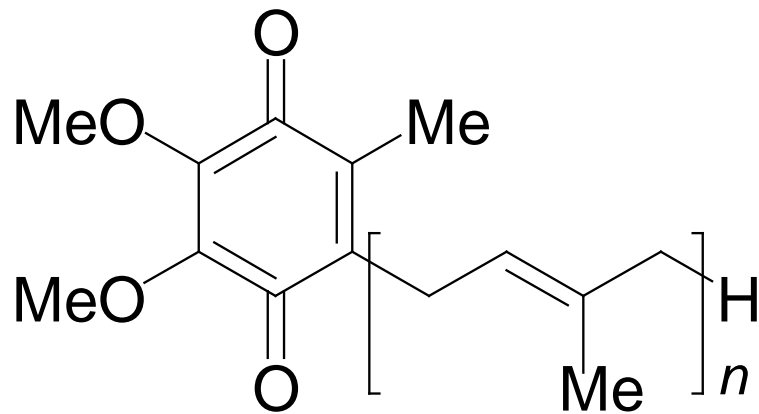
	Vanillyl Phenols	Syringyl Phenols	Cinnamyl Phenols
Aldehydes	<p>Vanillin</p>	<p>Syringaldehyde</p>	<p><i>p</i>-Coumaric Acid</p>
Ketones	<p>Vanillone</p>	<p>Acetosyringone</p>	<p>Ferulic Acid</p>
Acids	<p>Vanillic Acid</p>	<p>Syringic Acid</p>	



Chiang, 2002 Nature
Biotech 20:557

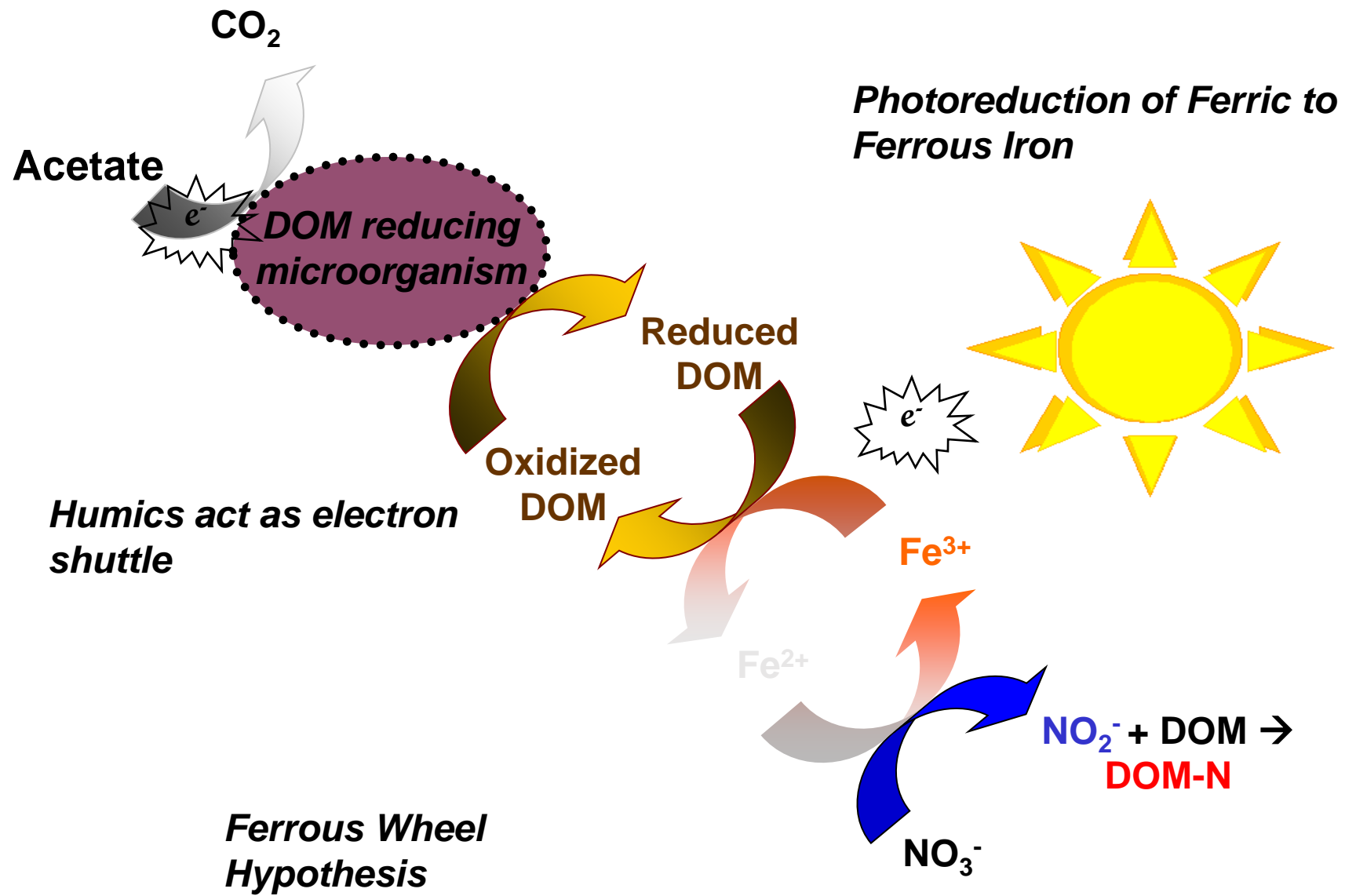


Quinones found in enzymes, e.g ubiquinone, and formed by lignin oxidation.

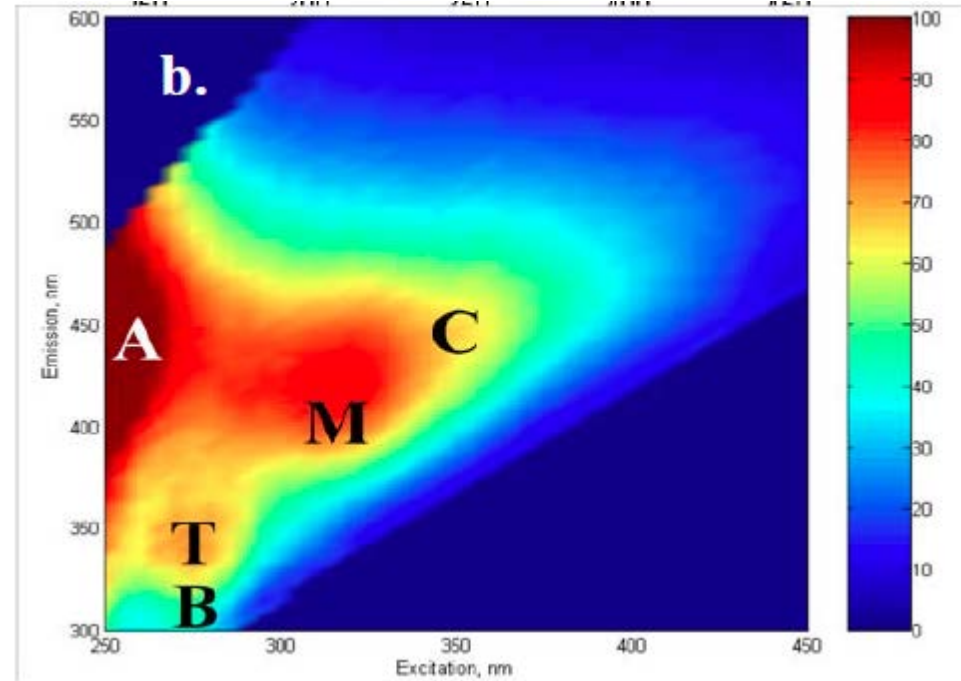
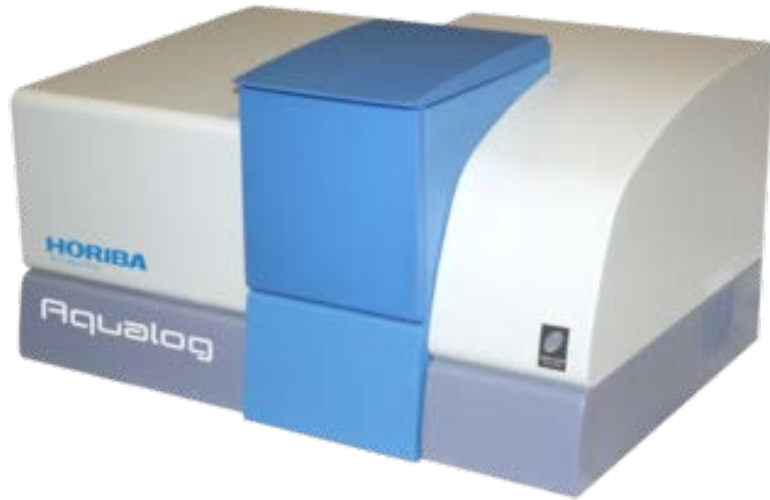


Ubiquinone

- Forms of this complex are found throughout cells
- Important in electron transfer reactions, such as the oxidation of NADH
- Also known as coenzyme Q



Marine CDOM fluorescence



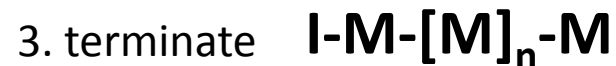
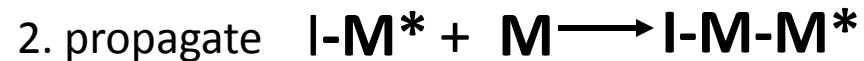
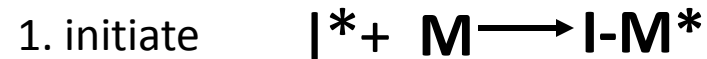
Compare data to 3D EEM measured by Horiba Aqualog (analysis via PARAFAC)

Major component identified typically Humic substances (320 ex/420 em).

260	400-460	A	UVC humic-like	Humic, terrestrial, autochthonous
320-360	420-460	C	UVA humic-like	Terrestrial, anthropogenic, agriculture
290-310	370-410	M	UVA marine humic-like	Microbial/biological in origin
250(385)	504		UVA humic-like	Fulvic, terrestrial autochthonous
275	305	B	Tyrosine-like, protein-like	Autochthonous
275	340	T	Tryptophan-like, protein like	Autochthonous
398	660	P	Pigment-like	

Polymerization pathways: Free Radical Coupling

M= molecules that form covalent bonds, while propagating reactive species (*)



With lignin the radical is coupled between monomers and then the initiator must create a new radical. Step 1 and then step 3.



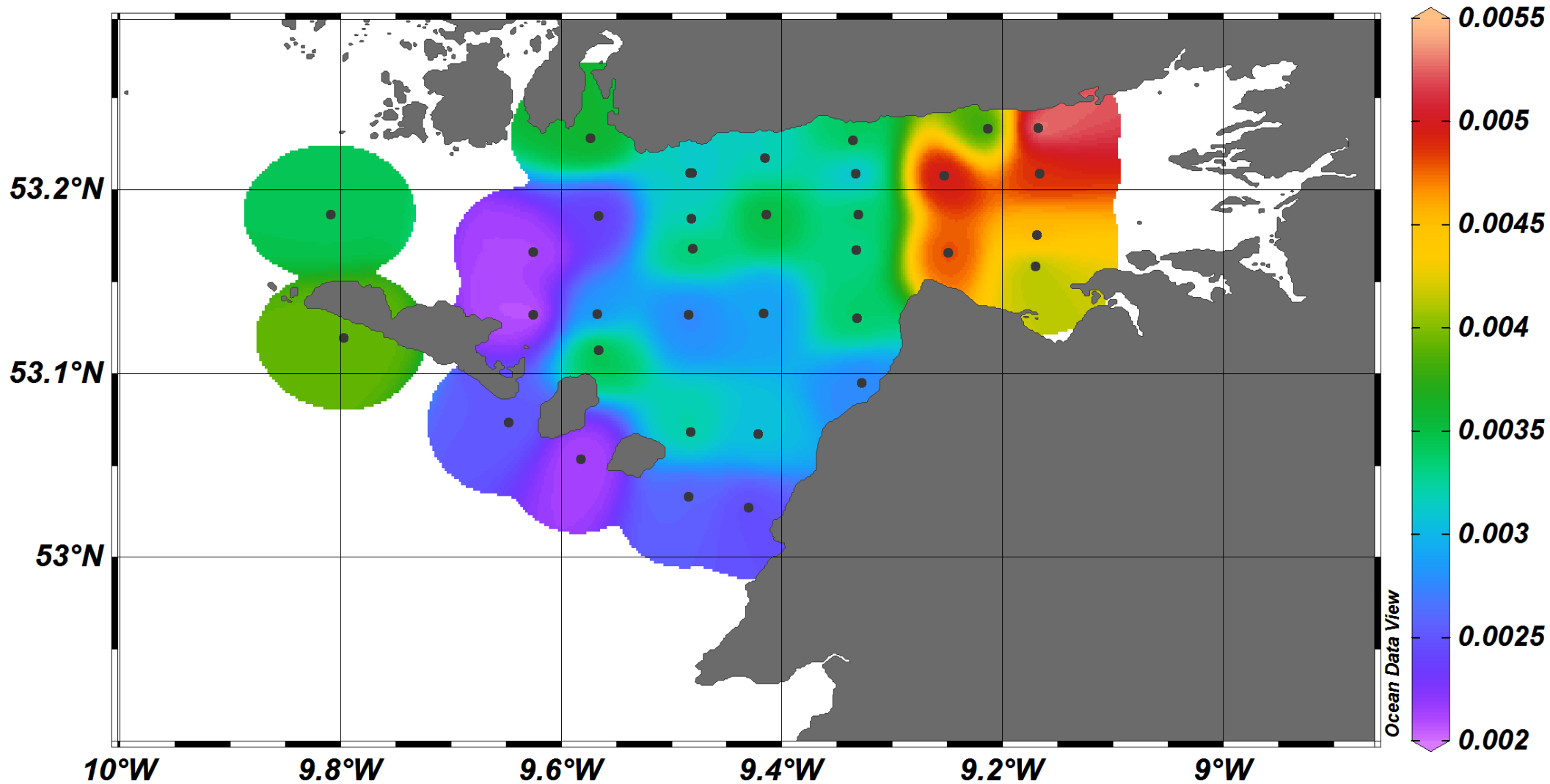
Source: www.marine.ie

Celtic Explorer CE14007
Galway Bay Survey for Radium Quartet



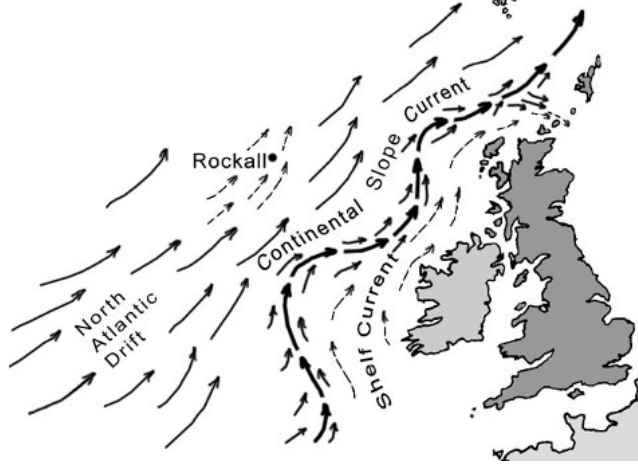
Humic Fluorescence 320ex/420em

Humic [RFU] @ Depth of sample=first



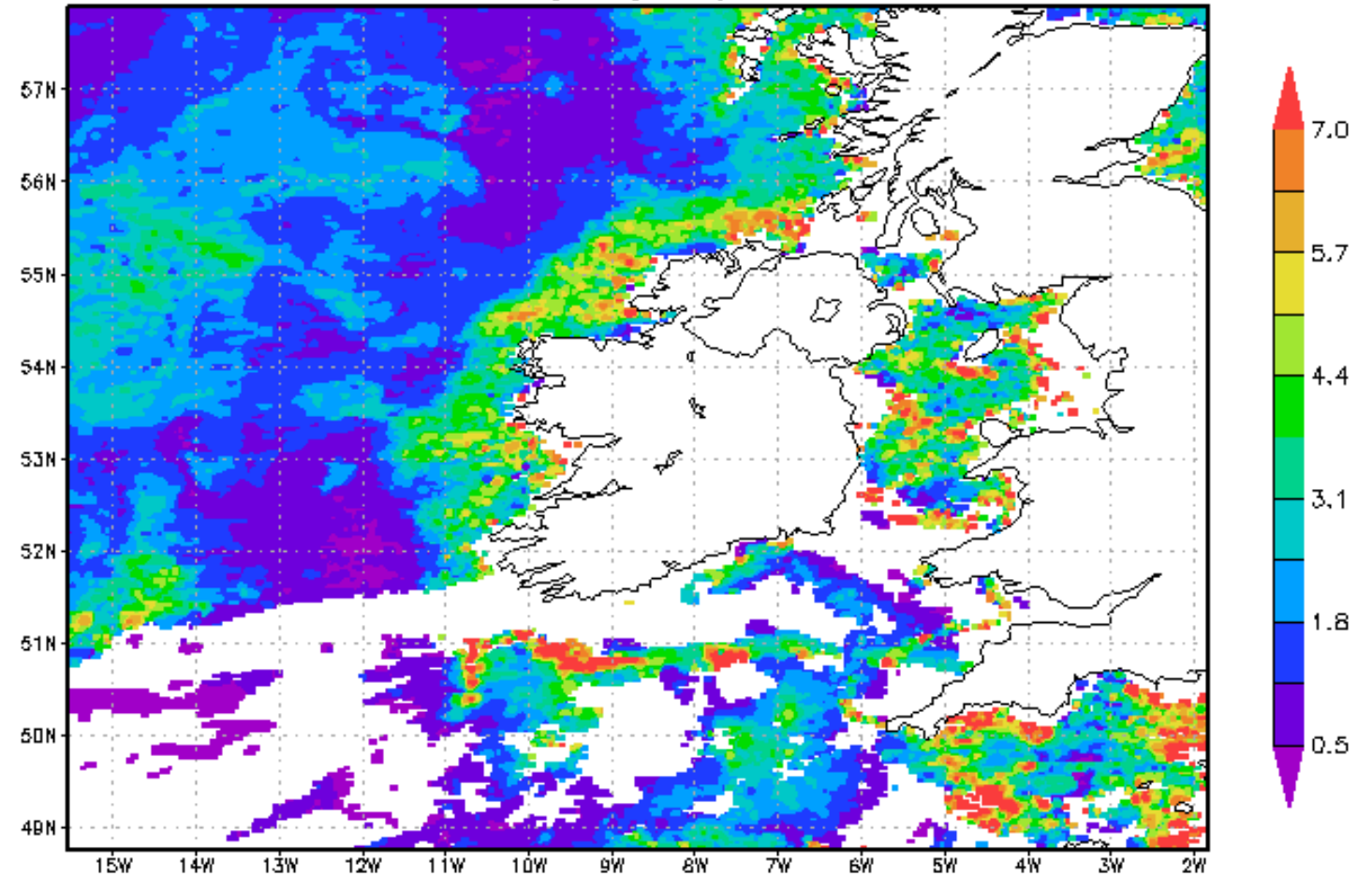
Influx from Corrib is important

Application: MODIS Satellite data – CDOM sources

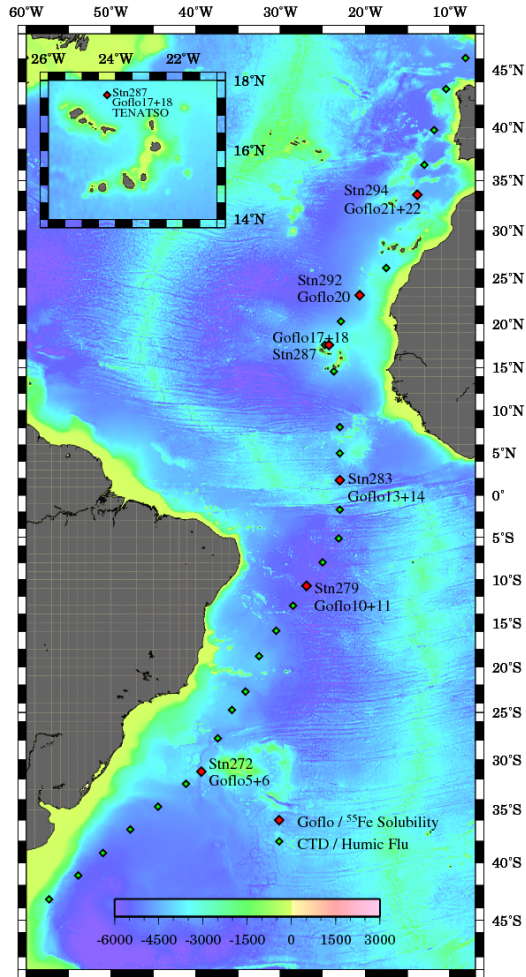


Giovanni: MODIS Aqua 412 nm

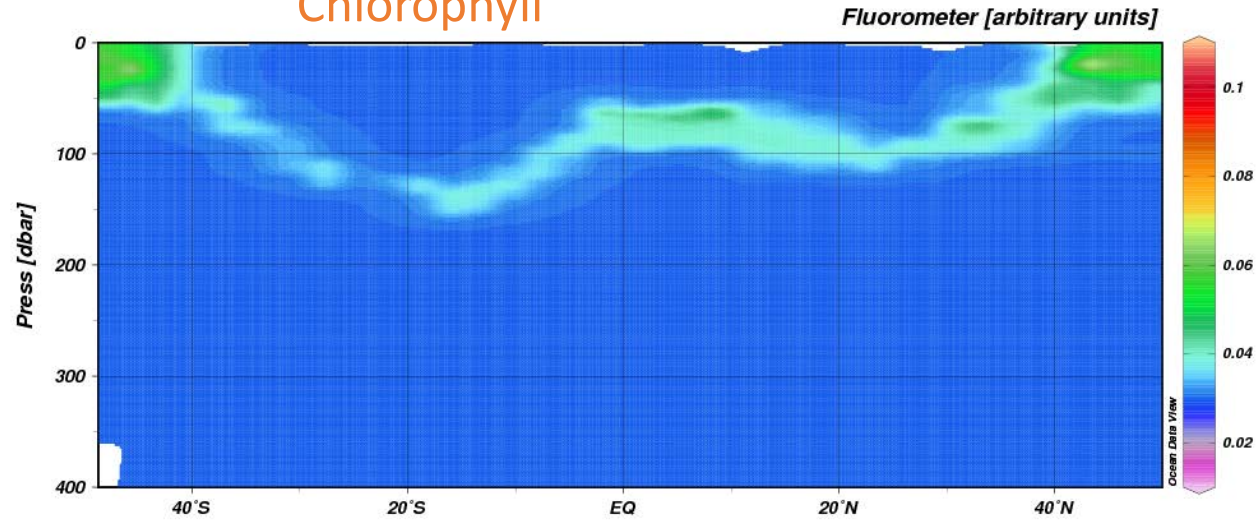
MABD_CDOM_4km.CR Colored Dissolved Organic Matter (CDOM) Index 4km, 8-day [unitless] (24May2012)



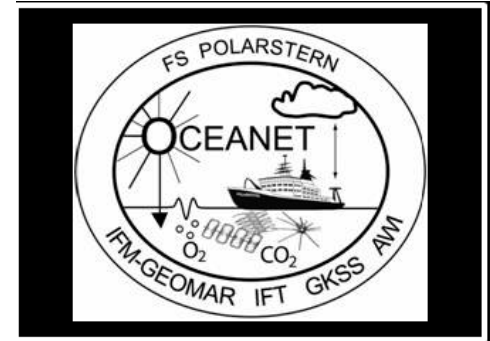
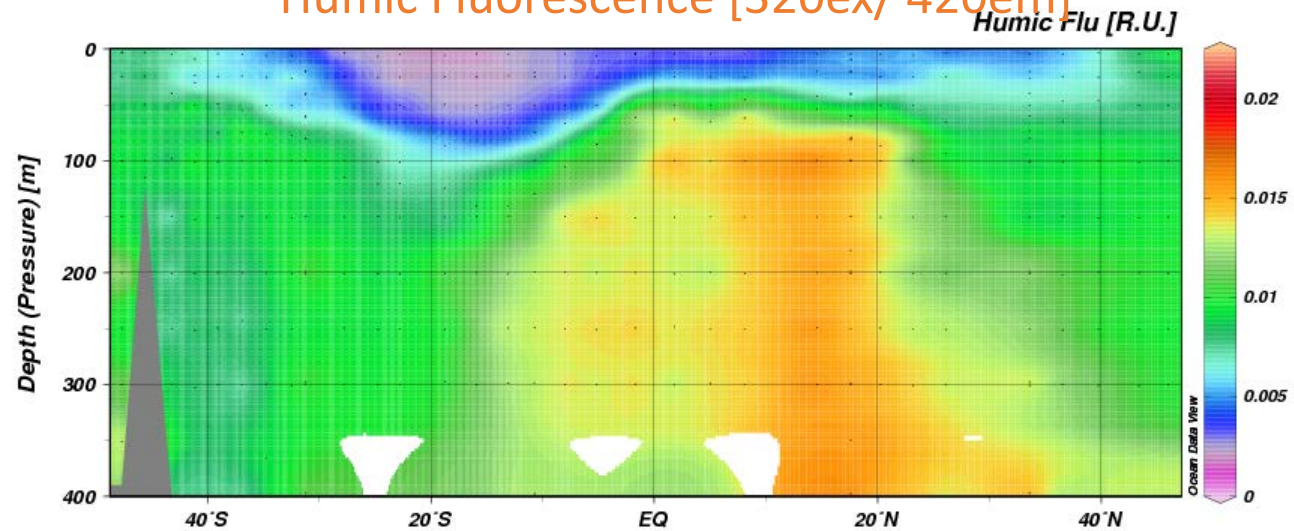
OCEANET Polarstern cruise ANTXXVI-4



Chlorophyll



Humic Fluorescence [320ex/ 420em]



Heller et al., 2013

PARAFAC

Multi-step process

Data collection and pre-processing

- Measurement
- Spectral correction
- Inner filter correction
- Calibration
- Removal of scatter

Outlier Analysis

- Identify and remove possible outliers
- Identify number of components to model the data

Model Validation

- Residual analysis
- Split-half analysis
- Random initialization

Interpret model results

Excitation (k)
Emission (j)
sample (i)

$$x_{ijk} = \sum_{f=1}^F a_{if} b_{jf} c_{kf} + e_{ijk}$$

$i = 1 \dots I; j = 1, \dots, J; k = 1, \dots, K.$

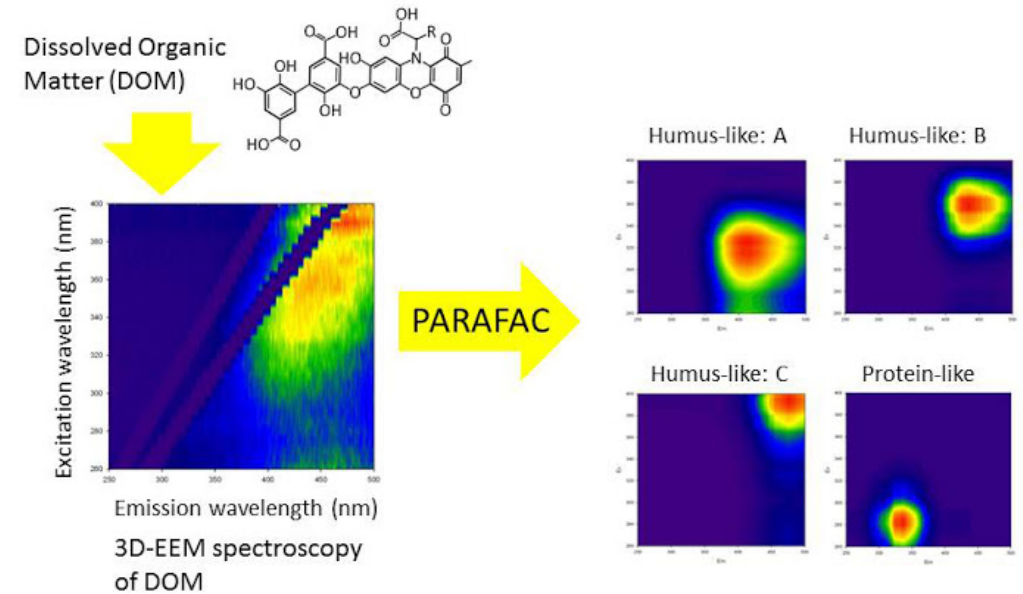
FLUOROPHORE

Fl. Intensity Z_1
 b_1
 c_1
qualitative and quantitative information

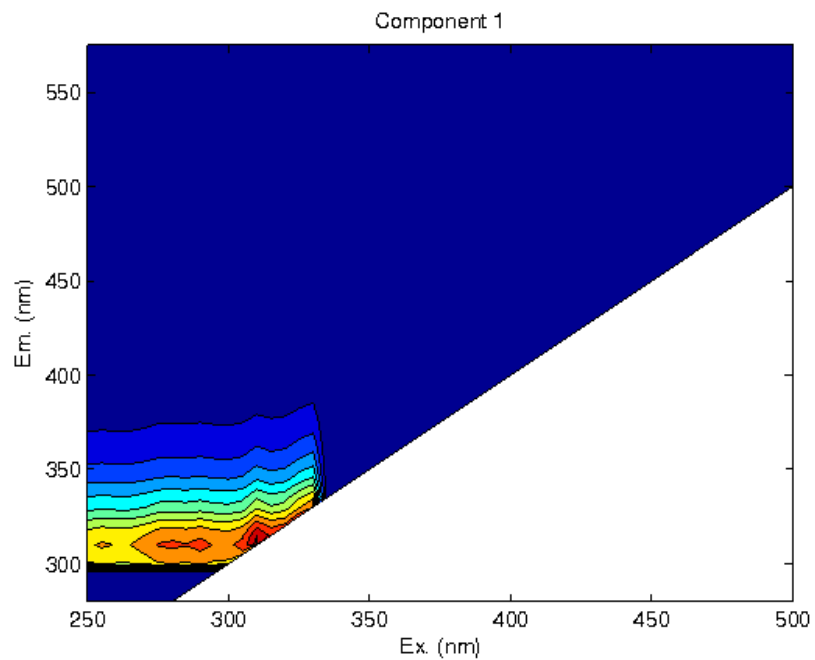
PARAFAC Parallel Factor Analysis

Identifies individual components in the fluorescence spectrum

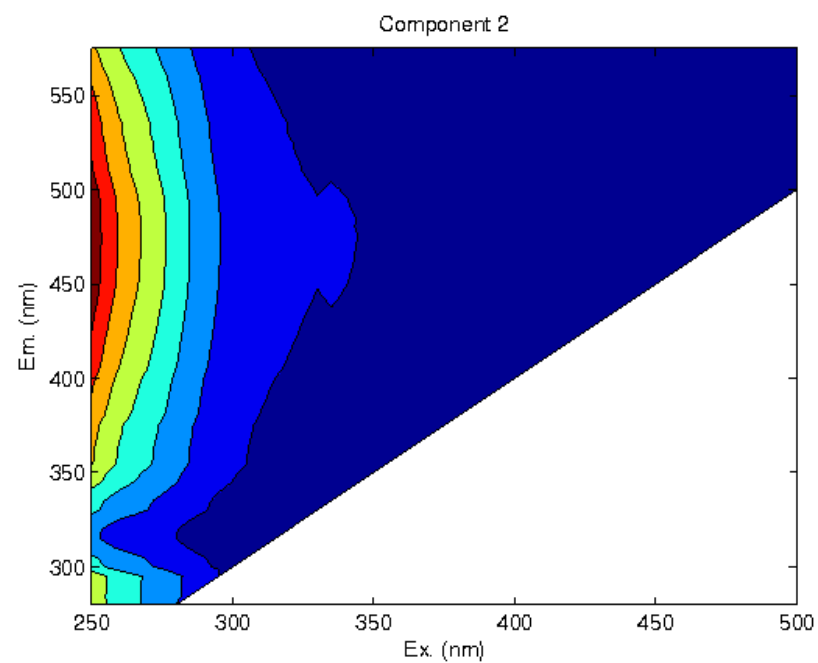
Used to follow biogeochemical processes, water masses movement or mixing in estuaries



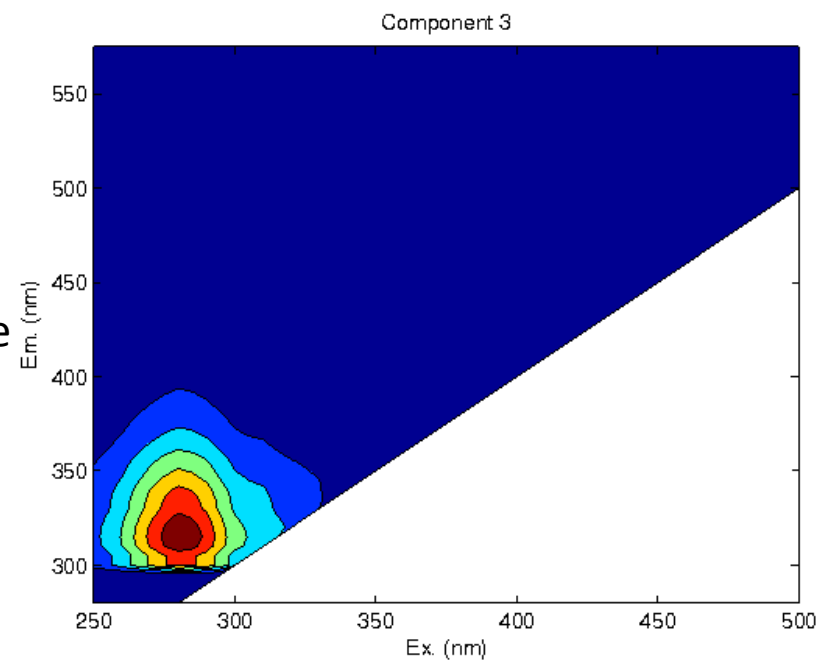
Tyrosine-like
or Polyphenol



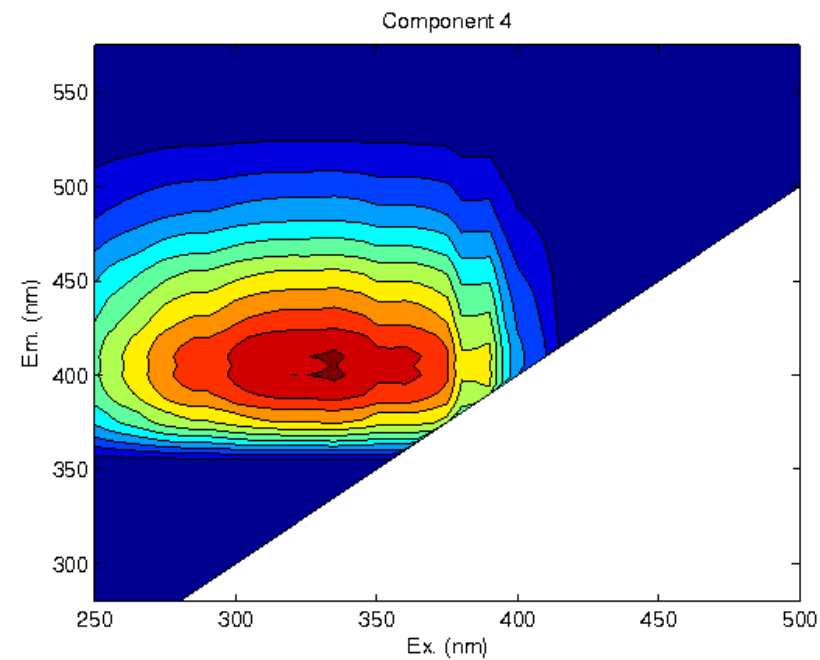
Terrestrial Humic



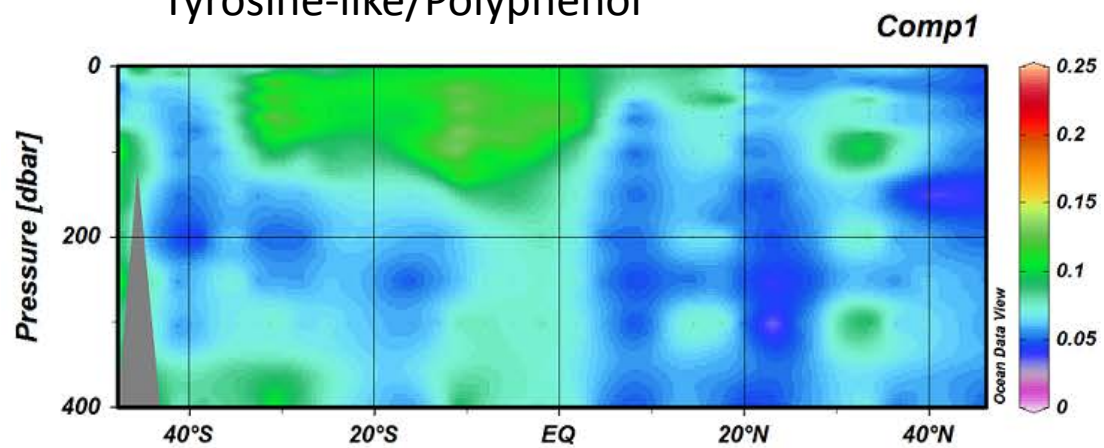
Tryptophan-like



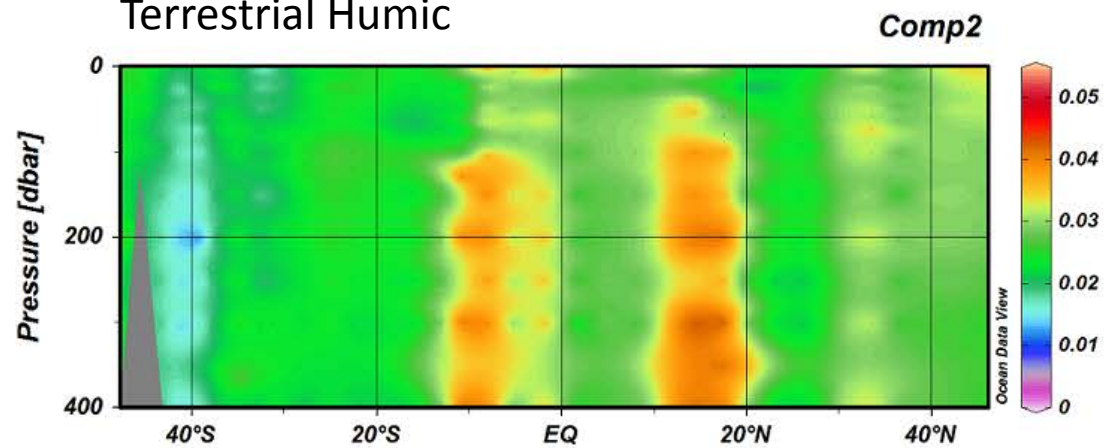
Marine Fulvic/Humic



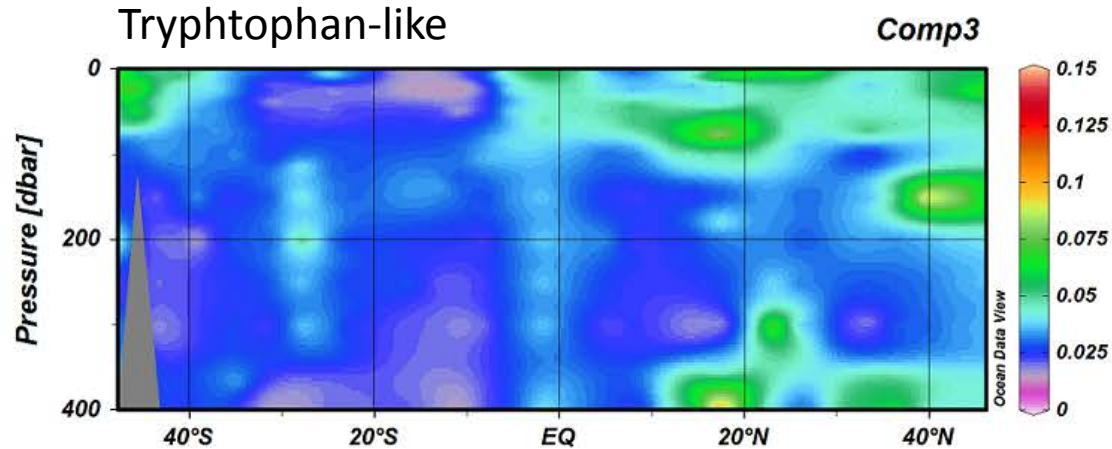
Tyrosine-like/Polyphenol



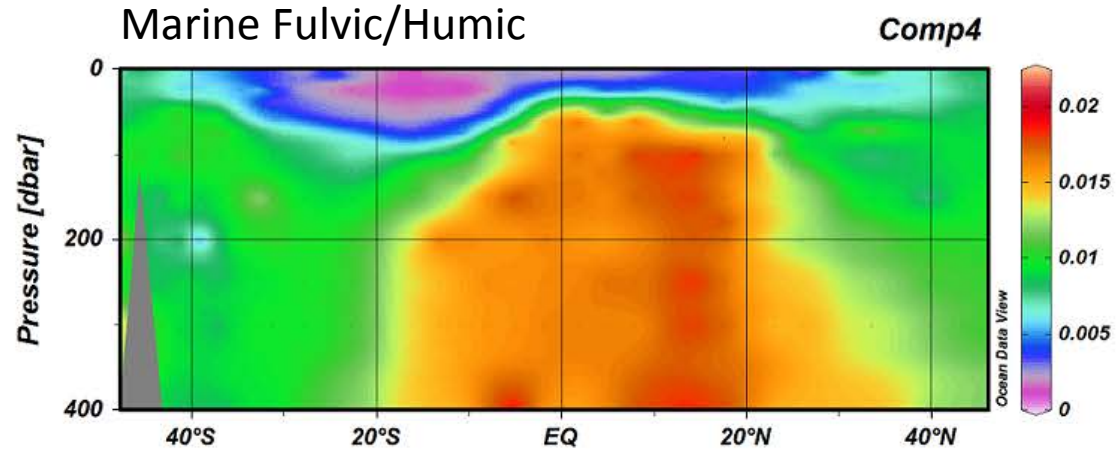
Terrestrial Humic



Tryphtophan-like



Marine Fulvic/Humic



Future Work

- Creation of a Biogeochemical Time Series in Galway Bay at the Spiddal mooring – FDOM and phycoerythrin sensors deployed
- June 16 – July 30 CE16009 Acoustic Fishing Survey Irish West Coast
- October 2016 CV16035 Western Irish Shelf



A serene sunset scene over a calm body of water. The sun is a bright orange orb on the right horizon, casting a warm glow across the sky and reflecting on the water's surface. The sky transitions from a deep orange near the horizon to a pale, hazy blue at the top. In the foreground, dark, silhouetted rocks are scattered along the shoreline. The text "THANKS FOR YOUR ATTENTION" is centered in the middle of the image in a light blue, outlined, sans-serif font, with a subtle reflection effect below it.

THANKS FOR YOUR ATTENTION