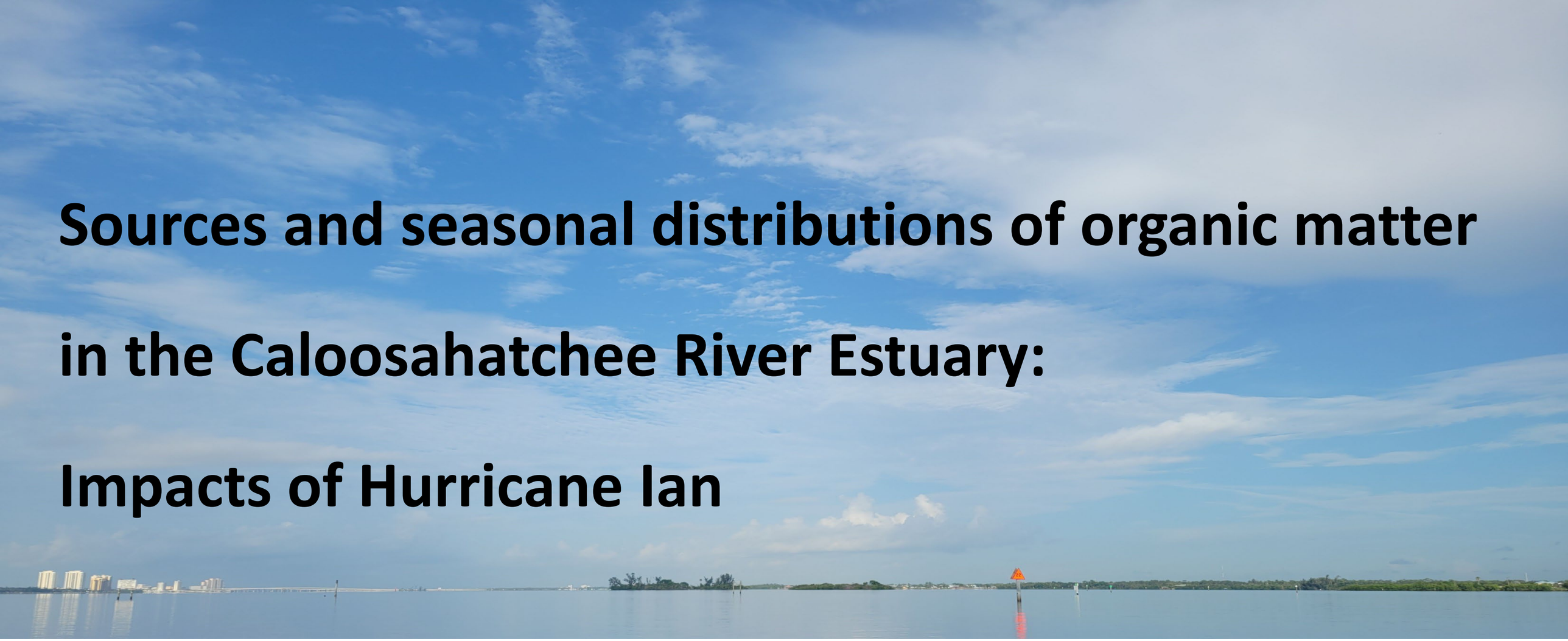


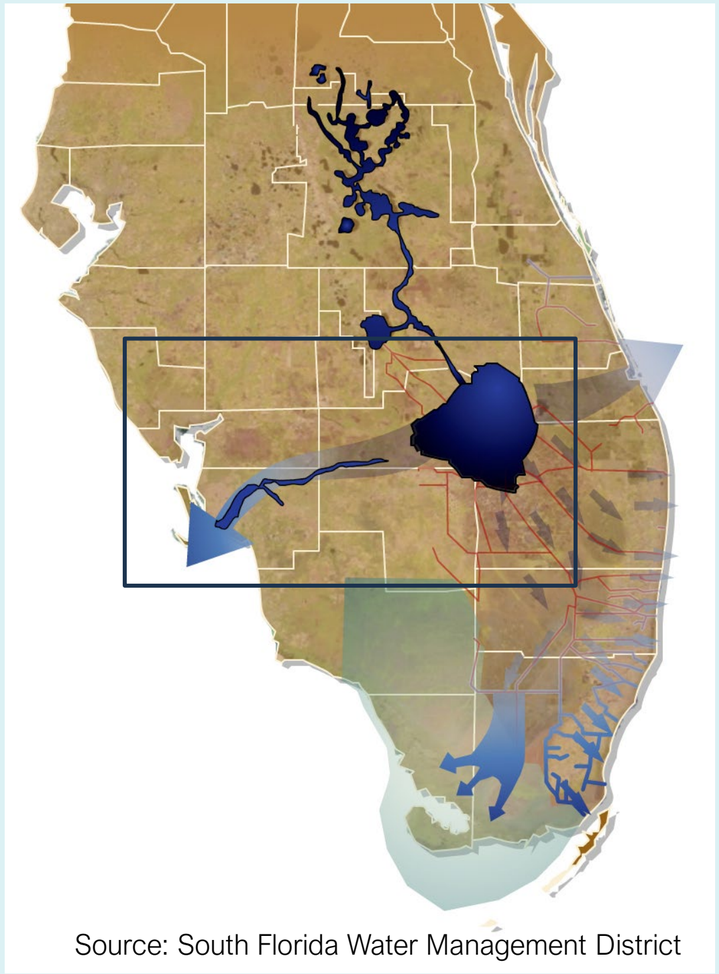
Sources and seasonal distributions of organic matter in the Caloosahatchee River Estuary: Impacts of Hurricane Ian

***Shin-Ah Lee*[1]**, *Eric Milbrandt*[2], *David Kaplan*[1], *Edward Phlips*[3], *and Elise Morrison*[1]

[1] Environmental Engineering Sciences, University of Florida, Gainesville, FL.,
[2] Marine Laboratory, Sanibel Captiva conservation Foundation, Sanibel, FL.,
[3] School of Forest, Fisheries, & Geomatics Sciences, University of Florida, Gainesville, FL.

UF Herbert Wertheim College of Engineering
Center for Coastal Solutions
UNIVERSITY of FLORIDA

SCCF
SANIBEL-CAPTIVA CONSERVATION FOUNDATION



Source: South Florida Water Management District

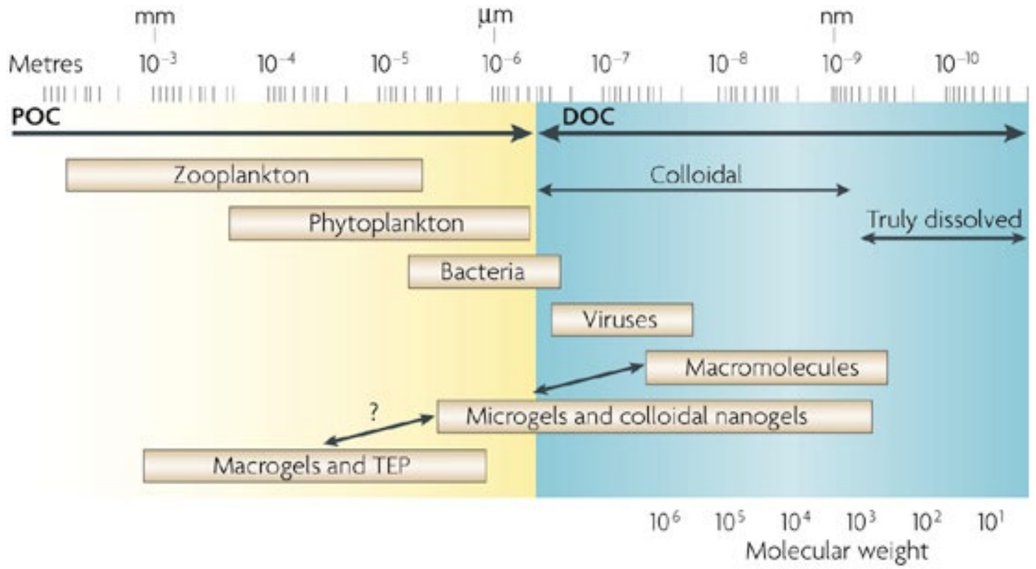
Caloosahatchee River Estuary

What are the specific sources fueling harmful algal blooms?

What is organic matter?

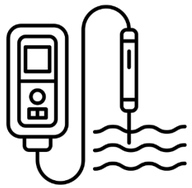
- Organic matter (OM) : organic compounds comes from decaying leaves, roots, organisms and other sources.
- Categorized based on filtering size.

  DOM < pore size 0.2 – 0.7 μm < POM



(Azam and Malfatti 2007)

Importance of organic matter in estuarine systems

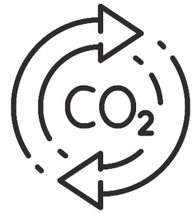


Water quality

Influences **dissolved oxygen** and **turbidity.**

Supports food webs

primary energy source for estuarine food webs.

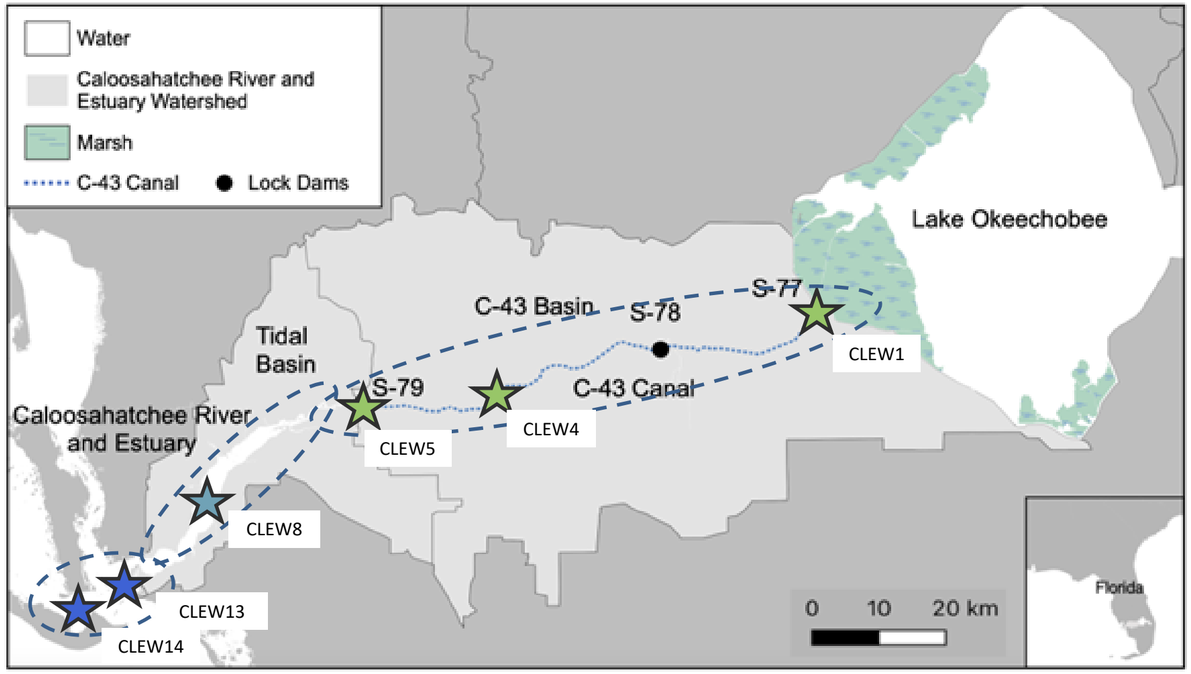


Carbon cycle

affects **photosynthesis, decomposition, and carbon sequestration**.

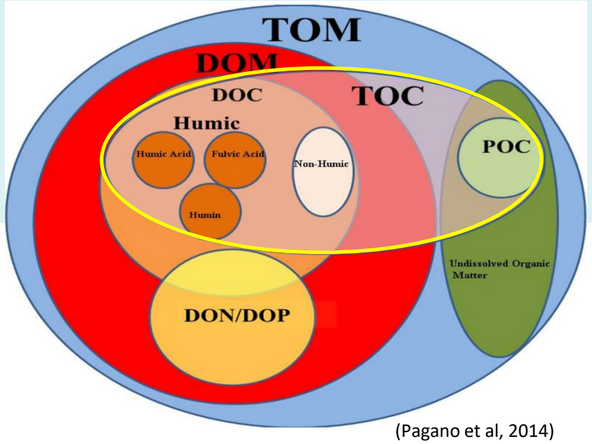
Study site

Sampling site	Caloosahatchee River Estuary, FL
Sampling periods	April 2022 – September 2023



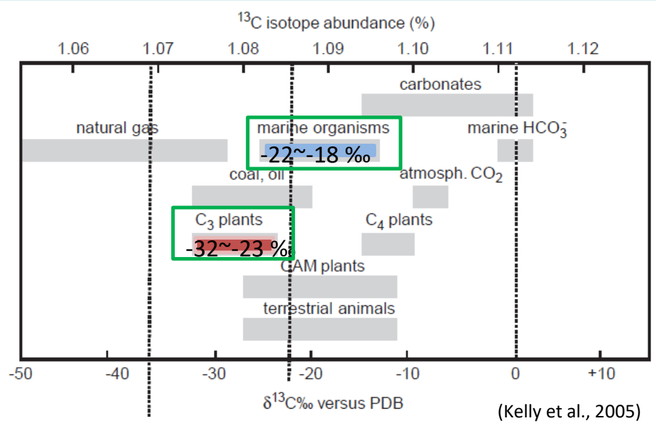
(Montefiore et al., In review)

Multiple organic matter tracers



(Pagano et al, 2014)

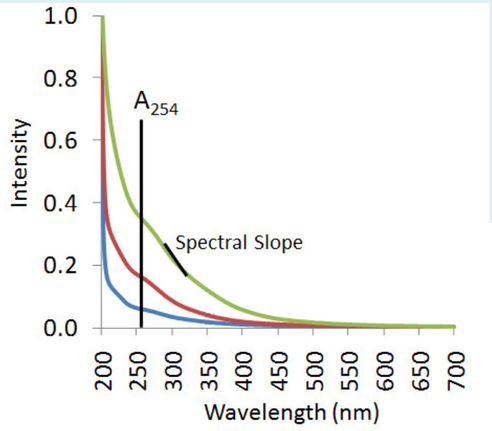
Dissolved/Particulate organic carbon (DOC, POC)



(Kelly et al., 2005)

Stable isotope of carbon & nitrogen ($\delta^{13}C$ & $\delta^{15}N$)

$$\delta X\,(‰) = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$$



(https://www.usgs.gov/media/images/response-single-wavelength-related-dom-concentration)

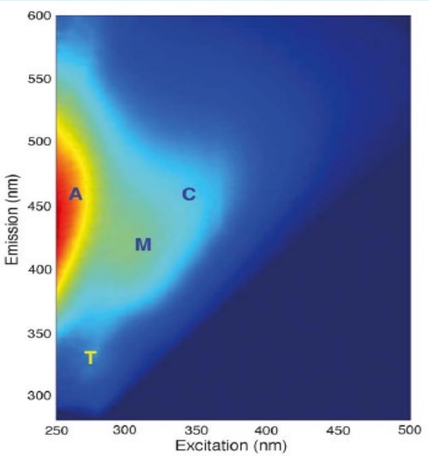
Colored DOM (CDOM)

- **Absorbance at 254nm (a_{254})**

  : indicator of the aromatic rings

- **Spectral slope at 275-295 nm ($S_{275\text{-}295}$)**

  : related to DOM molecular weight

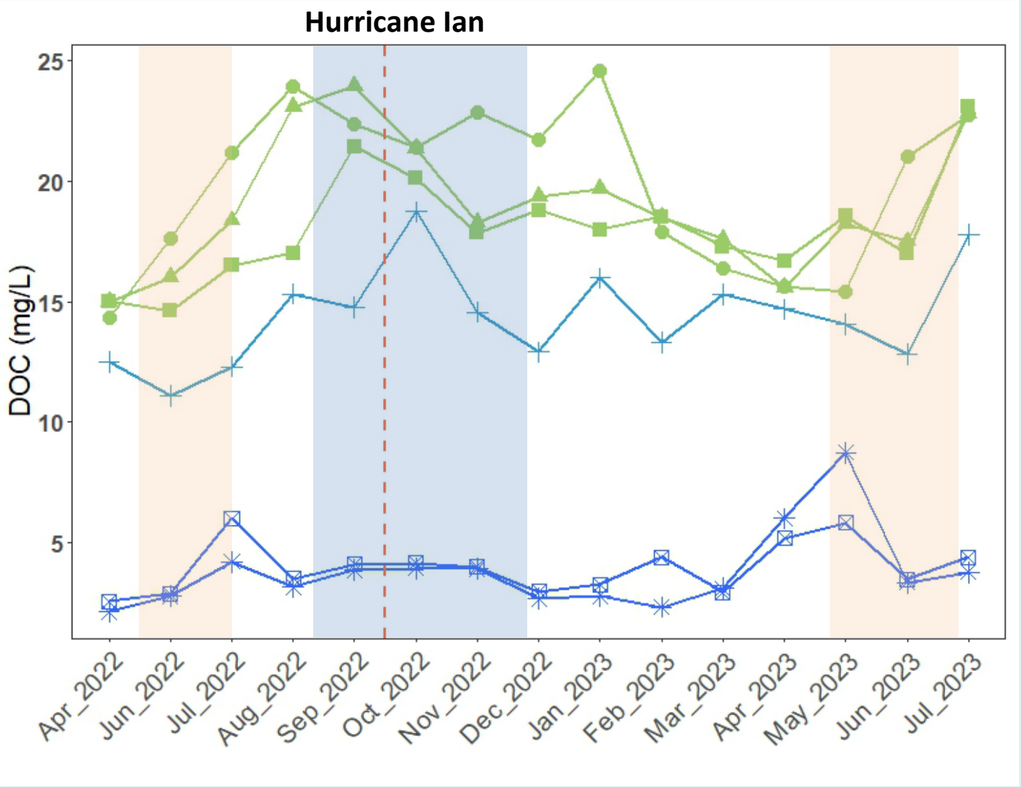


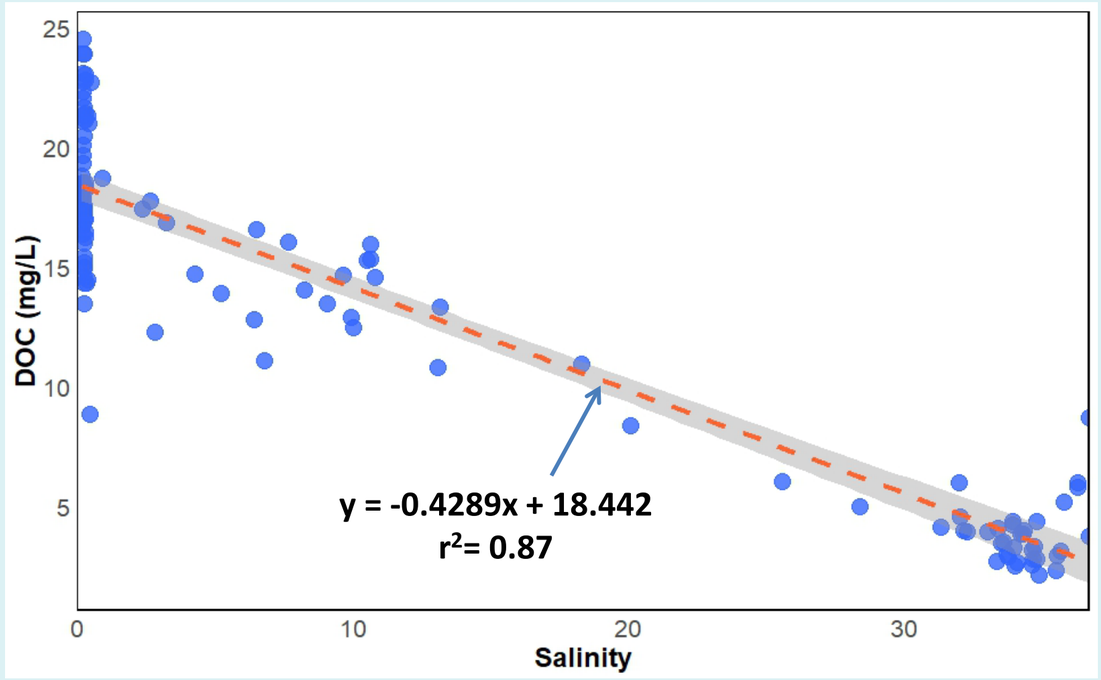
(Zepp et al, 2004)

Fluorescent DOM

- Humic/fulvic acid
- Protein-like materials

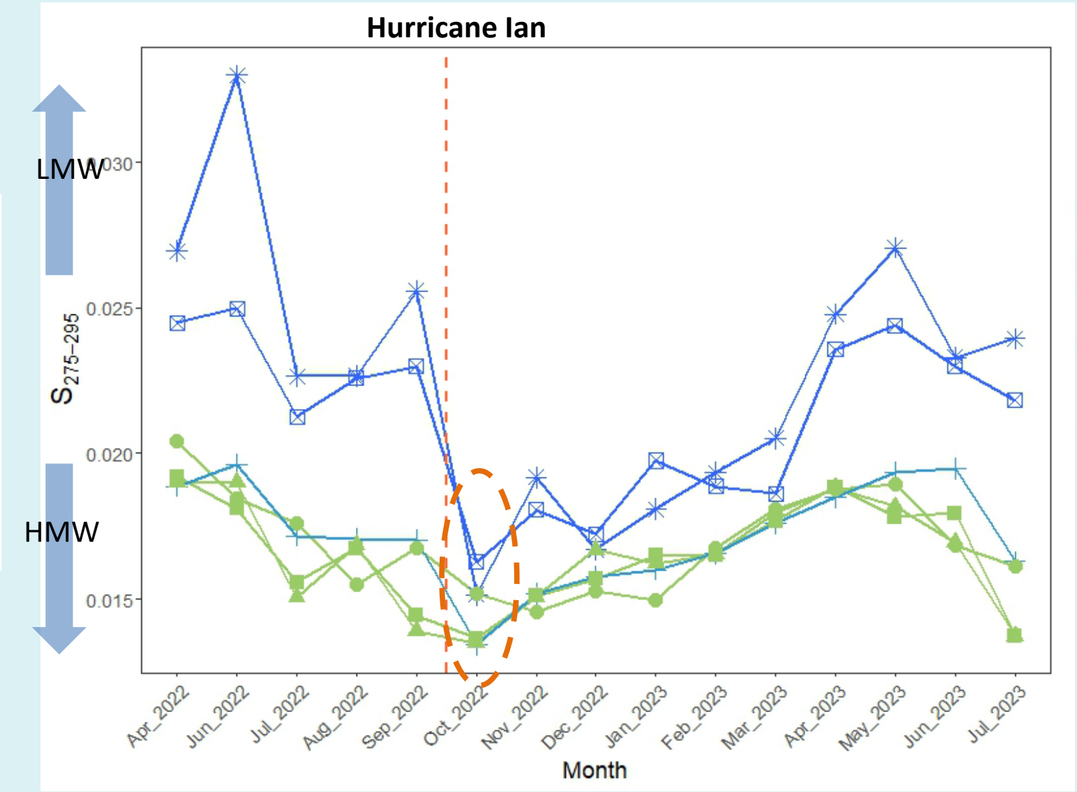
Seasonal variation and source in DOC





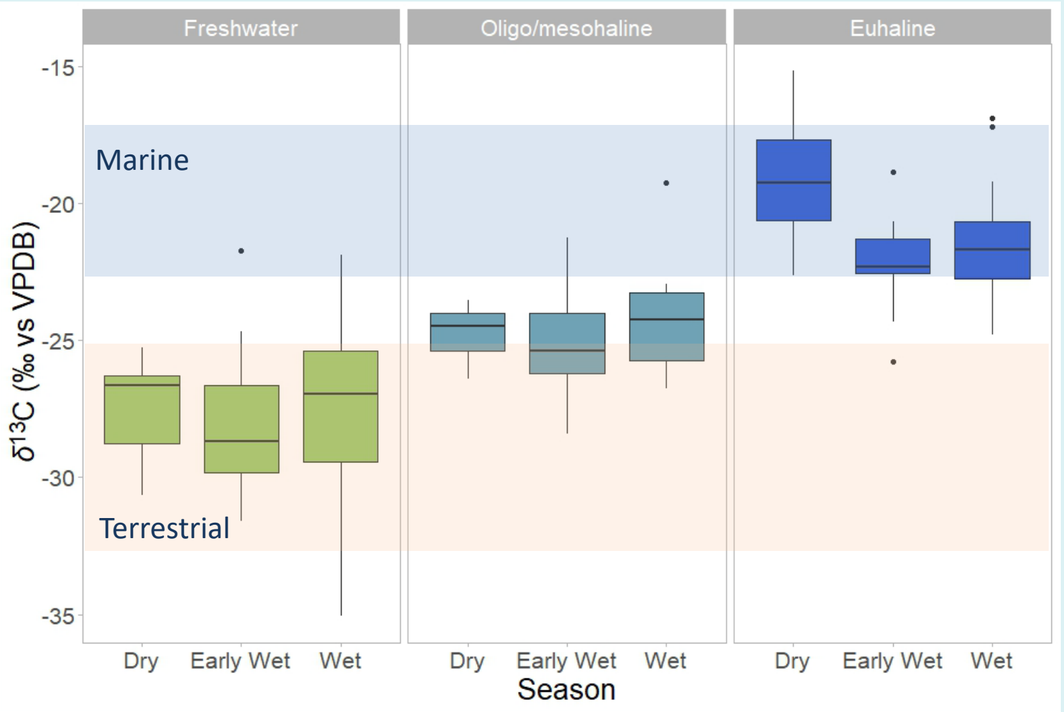
- DOC shows an increase in the early wet season (May-Jul) and a decrease in the wet season (Aug-Dec).
- The source of DOC is mainly from freshwater sources (Lake O and C-43 canals) and behave conservatively throughout the estuary.

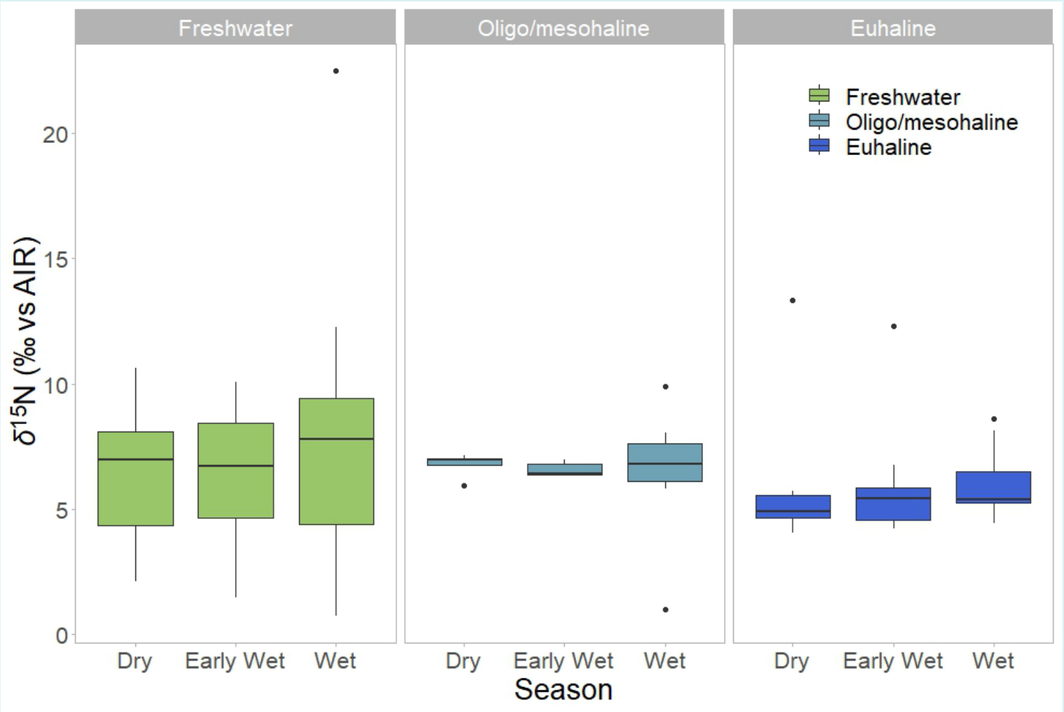
Impact of Hurricane Ian



- After Hurricane Ian, there were elevated DOC and a_{254} at mesohaline (CLEW8).
- The pattern in $S_{275-295}$ are likely opposite patterns with DOC /a_{254}, indicating that high-molecular-weight organic matter was intensively introduced to the watershed area after the hurricane event.

Source of POM using stable isotopes

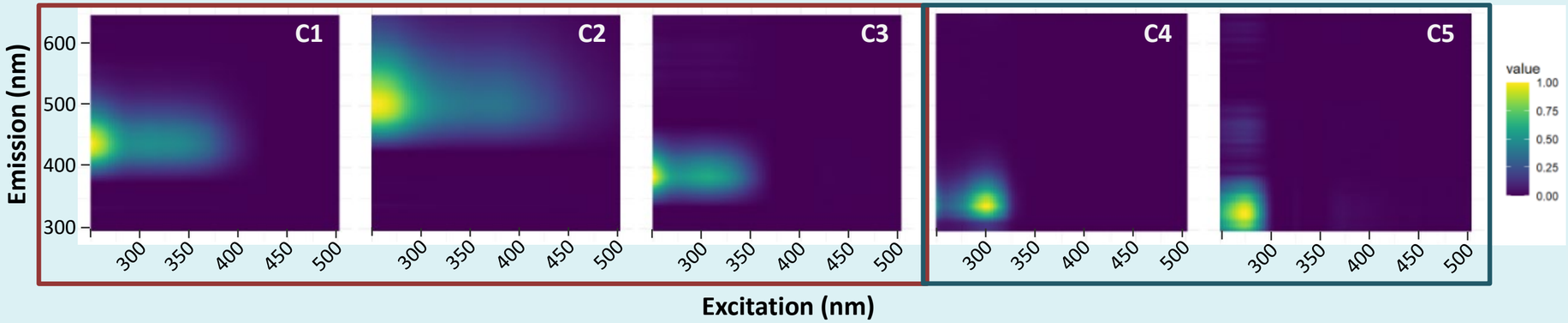




- POC is also mainly driven by terrestrial sources, with high variability in source during the wet season.
- Particulate nitrogen (PN) exhibit a similar range throughout the estuary.

Spectral fingerprints of FDOM

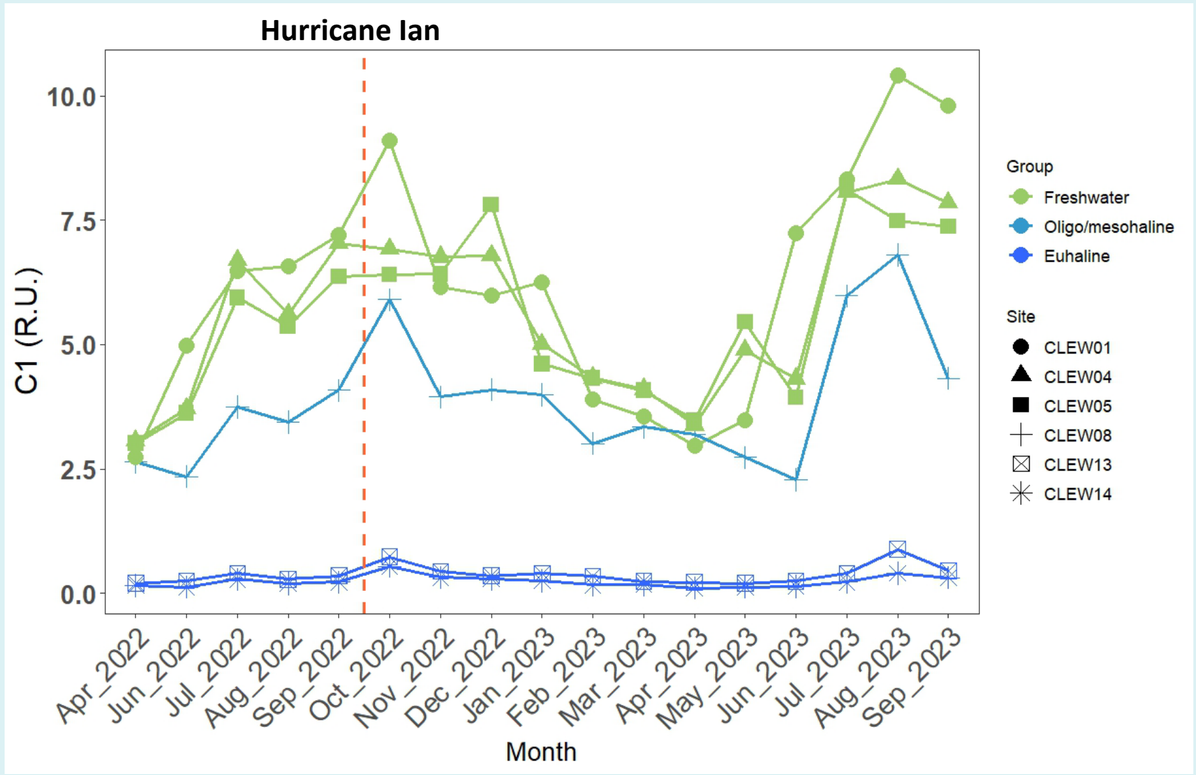
Results from the Parallel factor analysis (PARAFAC)



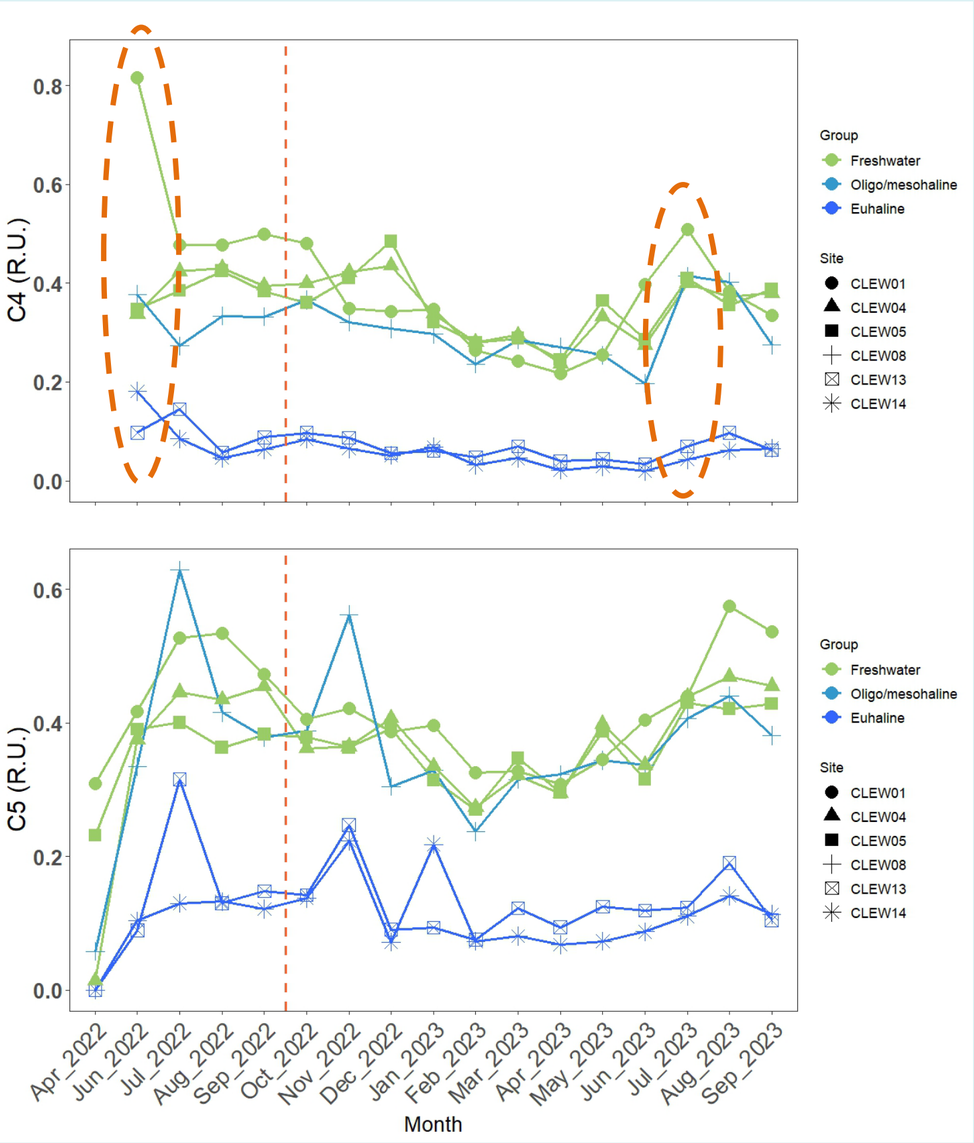
Component 1 (C1)	Ex: 333 / Em: 440 nm	Terrestrial humic-like, high organic matter loading
Component 2 (C2)	Ex: 337 / Em: 500 nm	Terrestrial humic-like
Component 3 (C3)	Ex: 305 / Em: 386 nm	Microbial humic-like
Component 4 (C4)	Ex: 300 / Em: 338 nm	Protein-like generated by microbial communities
Component 5 (C5)	Ex: 275 / Em: 326 nm	Protein-like (tryptophan-like)

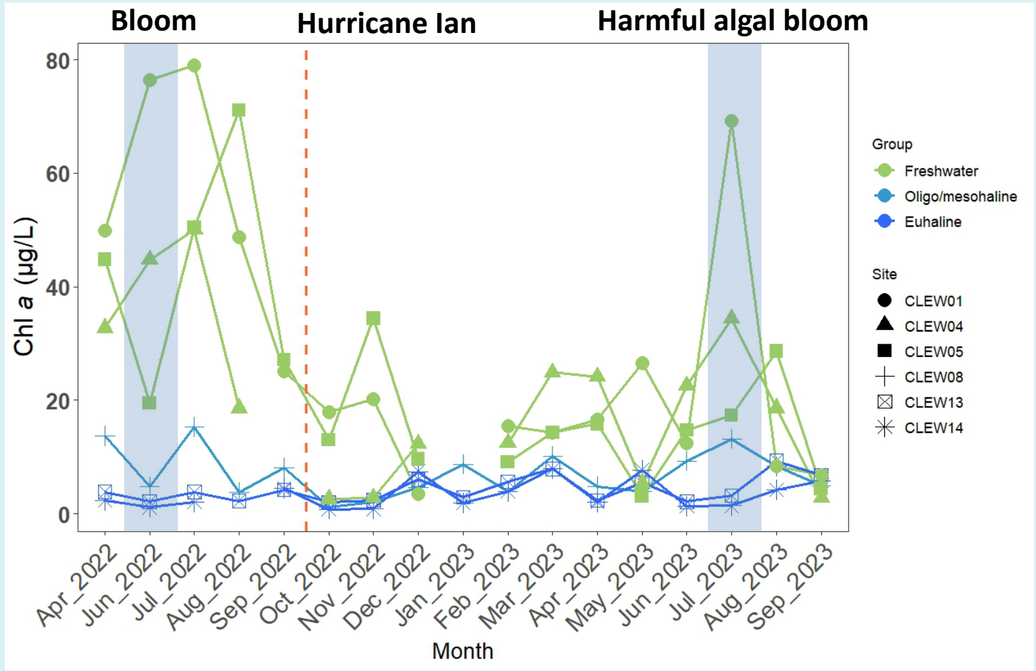
Seasonal variations in FDOM

- C1 (humic-like component) shows similar pattern with DOC and CDOM.
- CLEW1 shows a peak after Hurricane Ian, indicating the introduction of humic substances to the watershed from upper freshwater area.



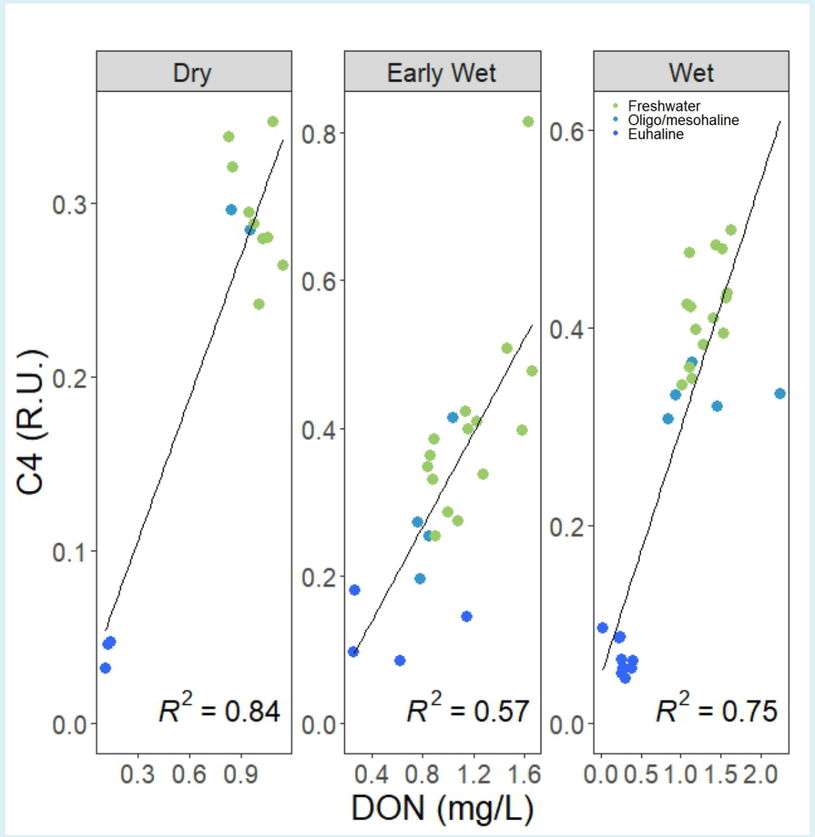
Source of FDOM

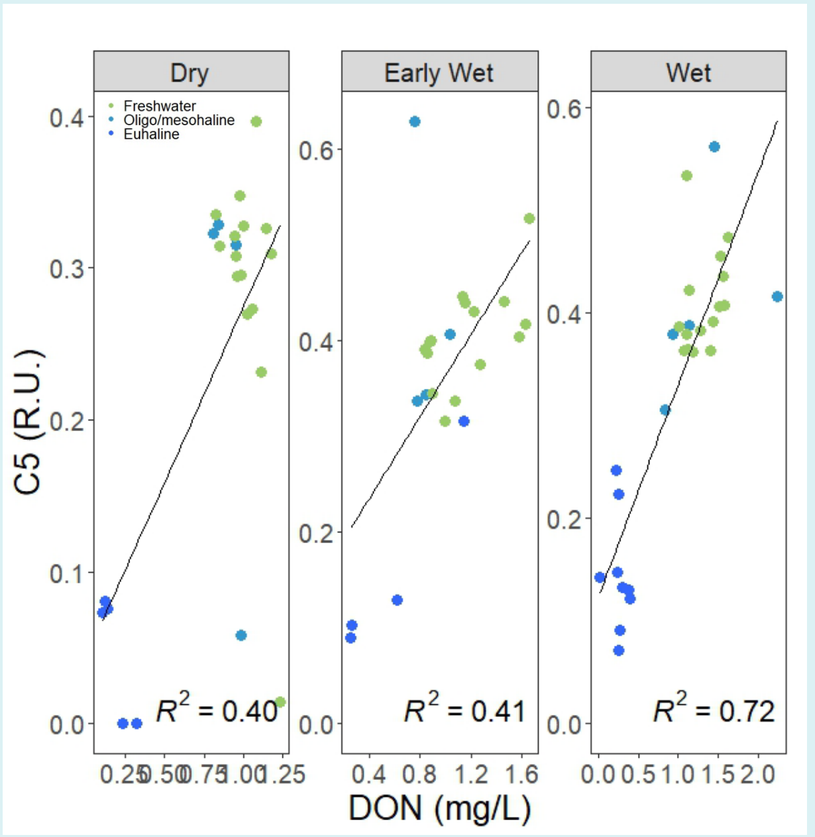




- C4 and C5 (protein-like components) varied monthly due to various sources such as biological production and non-point sources.
- C4 reflect harmful algal bloom event in July 2023.

Source of organic nitrogen





- The strong correlation between C4 (C5) and DON suggests that protein-like FDOM can be applied as a proxy for assessing DON in this system.
- Further investigation is needed to understand the role of DON in HABs in this system.

Conclusions

DOC and humic-like FDOM mostly from freshwater sources and behave conservatively.

Protein-like components reflect algal bloom event.

The influence of DON and HABs will be further investigated with isotopes of amino acids.

Studying organic matter allows us to better understand coastal biogeochemistry and phytoplankton responses to hurricanes.

THANK YOU

shinah.lee@ufl.edu

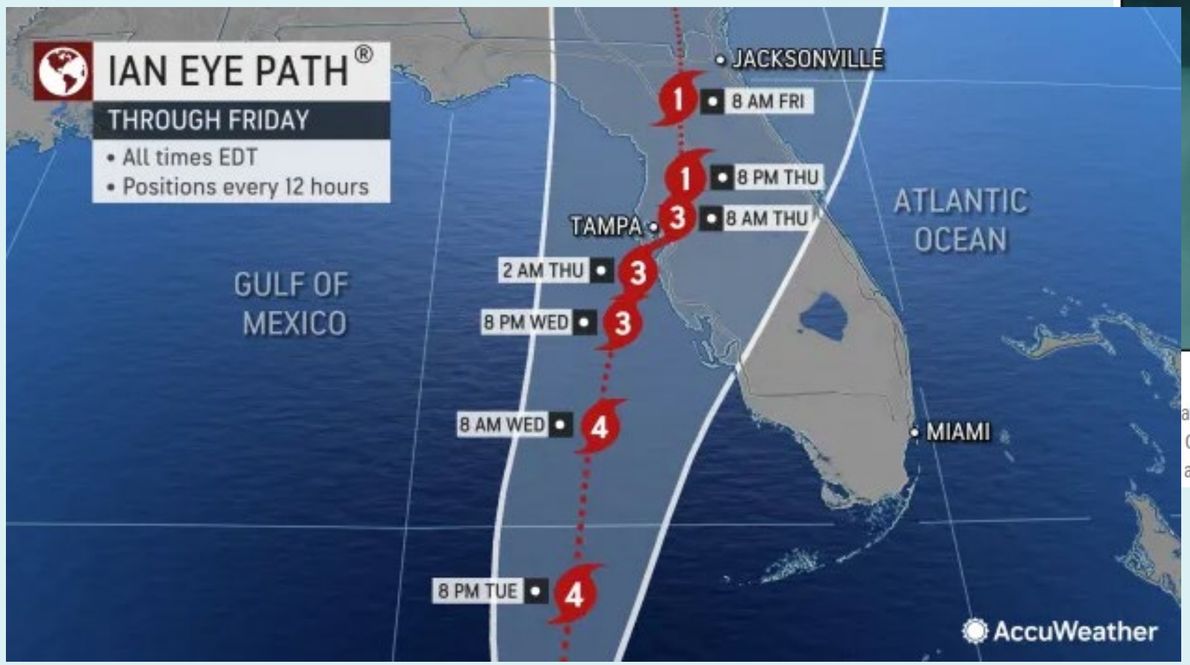
Thanks to
US Army Corps of Engineers
Joao Amaral, Bobby Scharping,
Amanda Chappel, Megan Sanford, Leanne Olson
Tom Bianchi, AJ Reisinger, Emily Taylor,
Audrey Goeckner, Jason Curtis
Sierra Greene, Benjamin Stelling
Natalie Nelson, Lise Montefiore

ERDC
ENGINEER RESEARCH & DEVELOPMENT CENTER

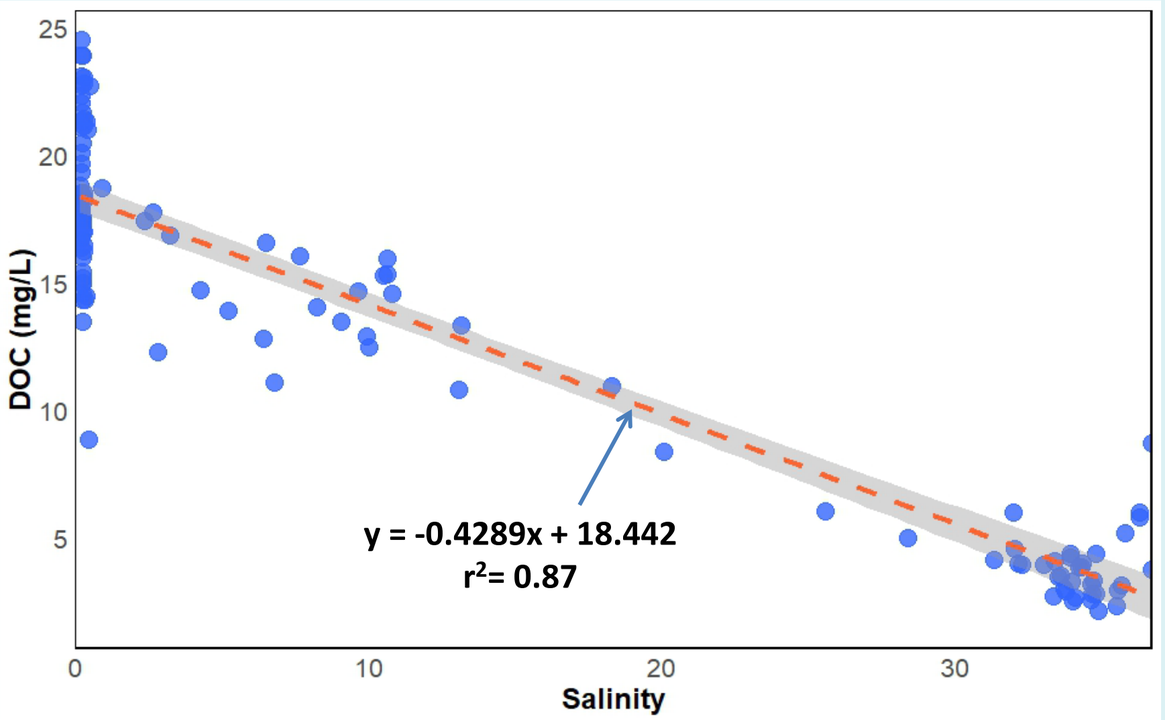
US Army Corps of Engineers®
Engineer Research and Development Center

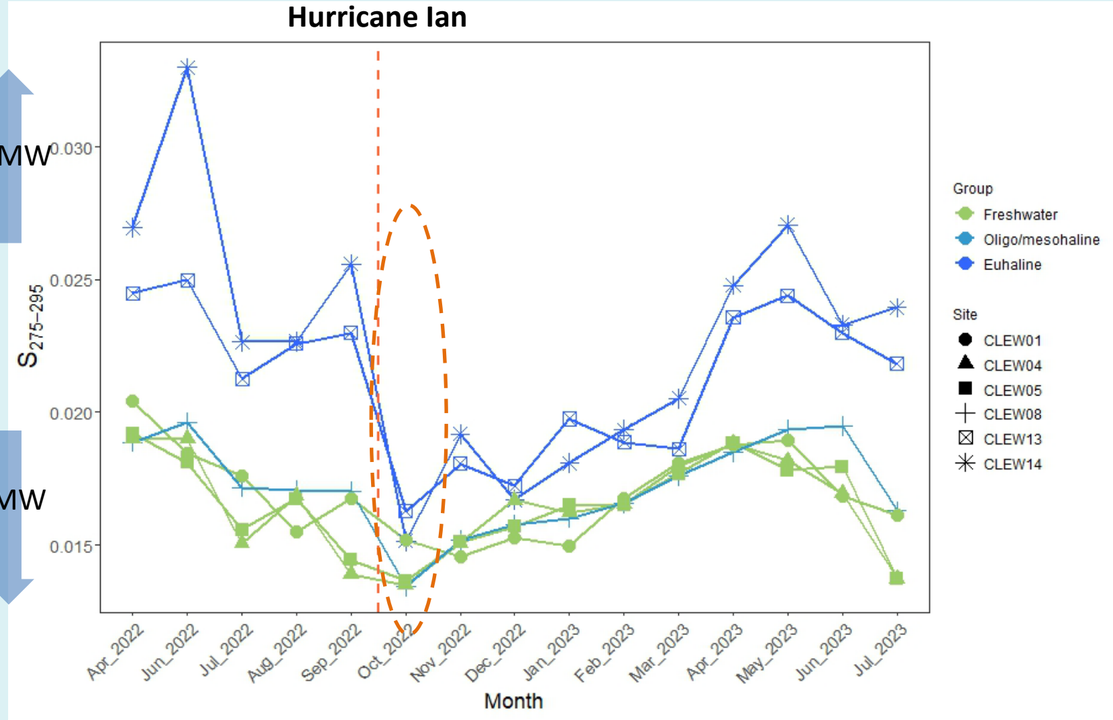
NOAA / WGCU

aters exiting back into the Gulf of Mexico carried debris, fertilizer, and other pollutants, which scientists from NOAA's National Centers for Ocean Science tracked as the blobs of nutrient pollution morphed into harmful algal blooms - red tides - in the days following Hurricane Ian's at Lee County on the Southwest Florida coast on Sept. 29, 2022

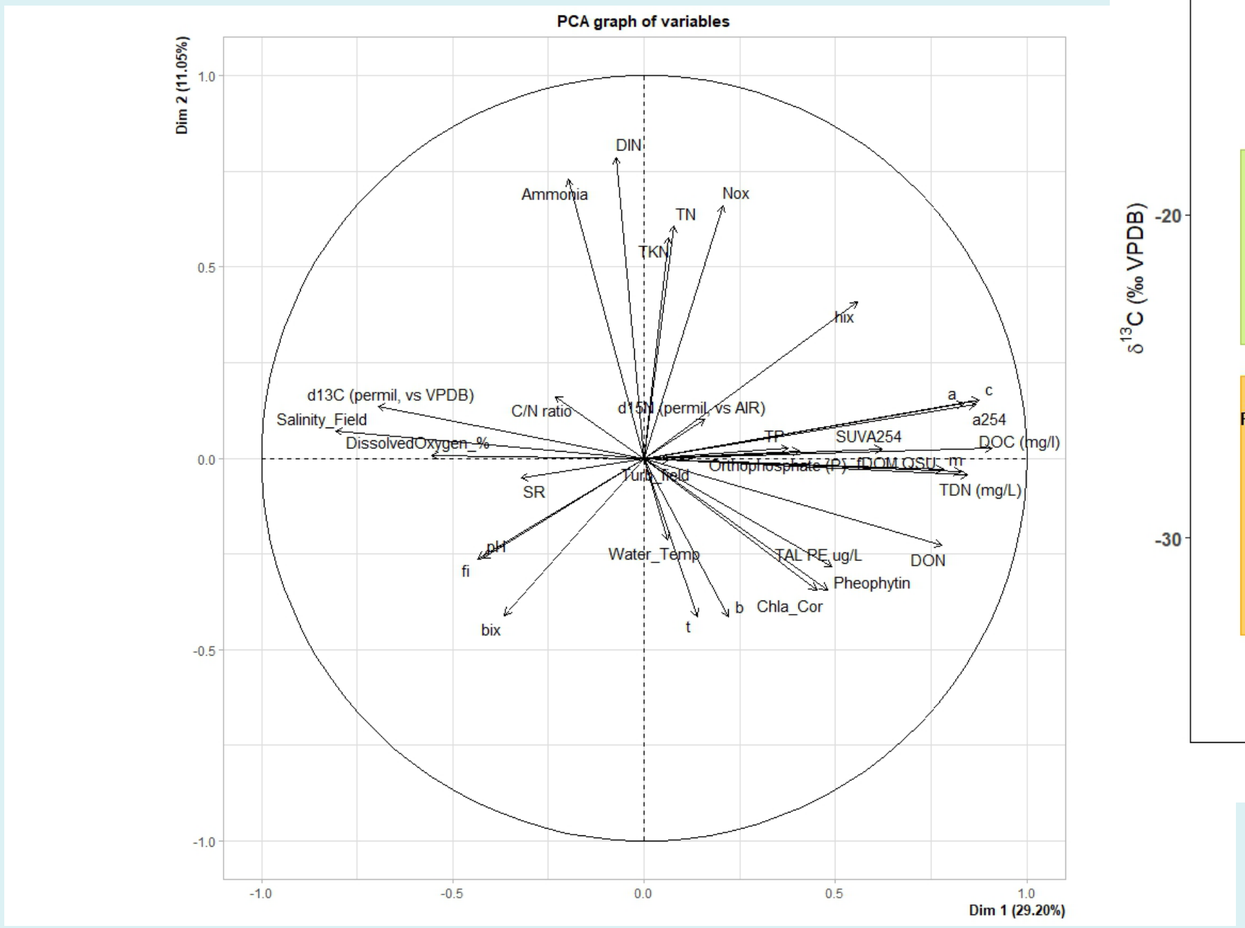


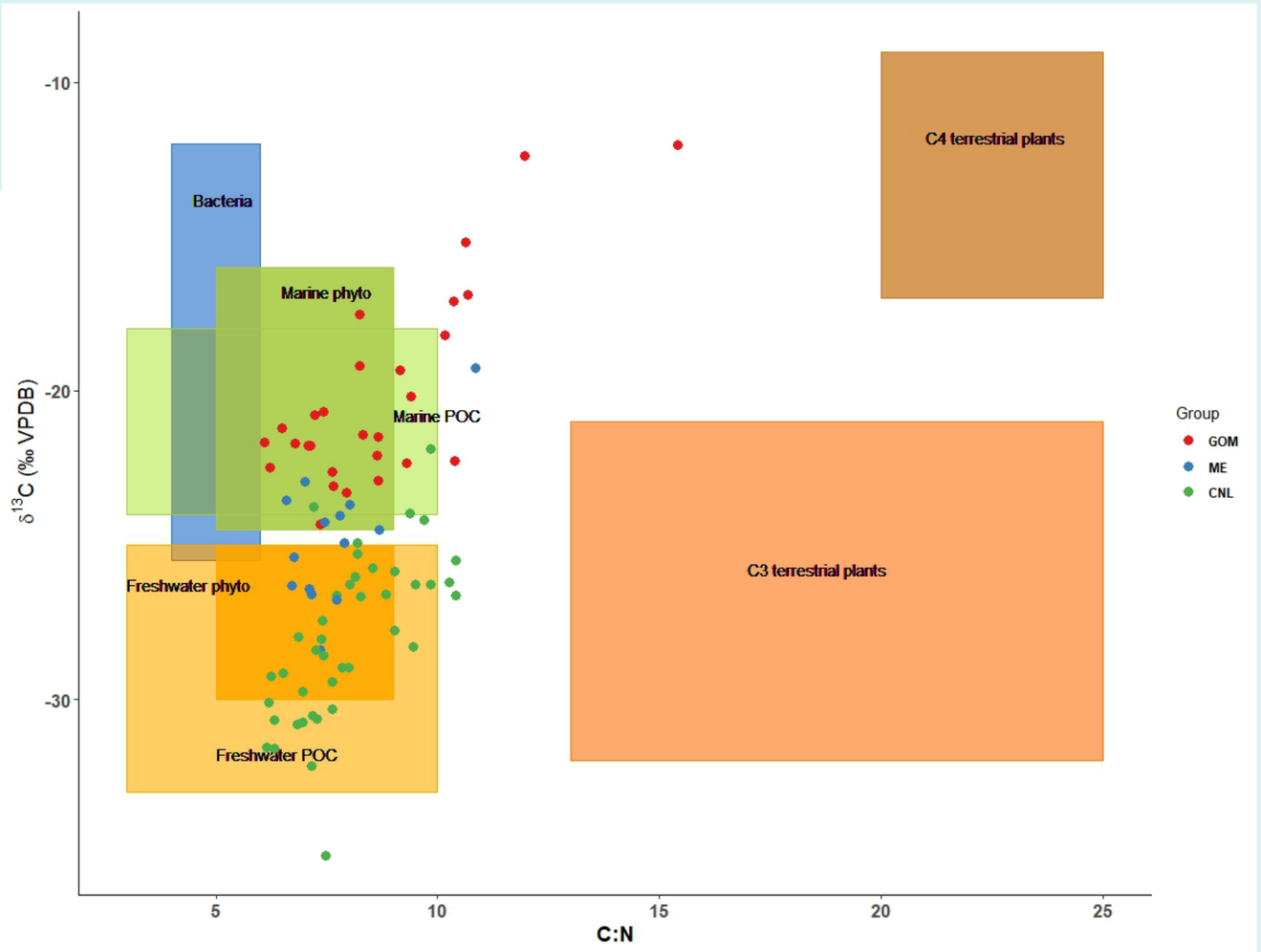
Sources of DOM



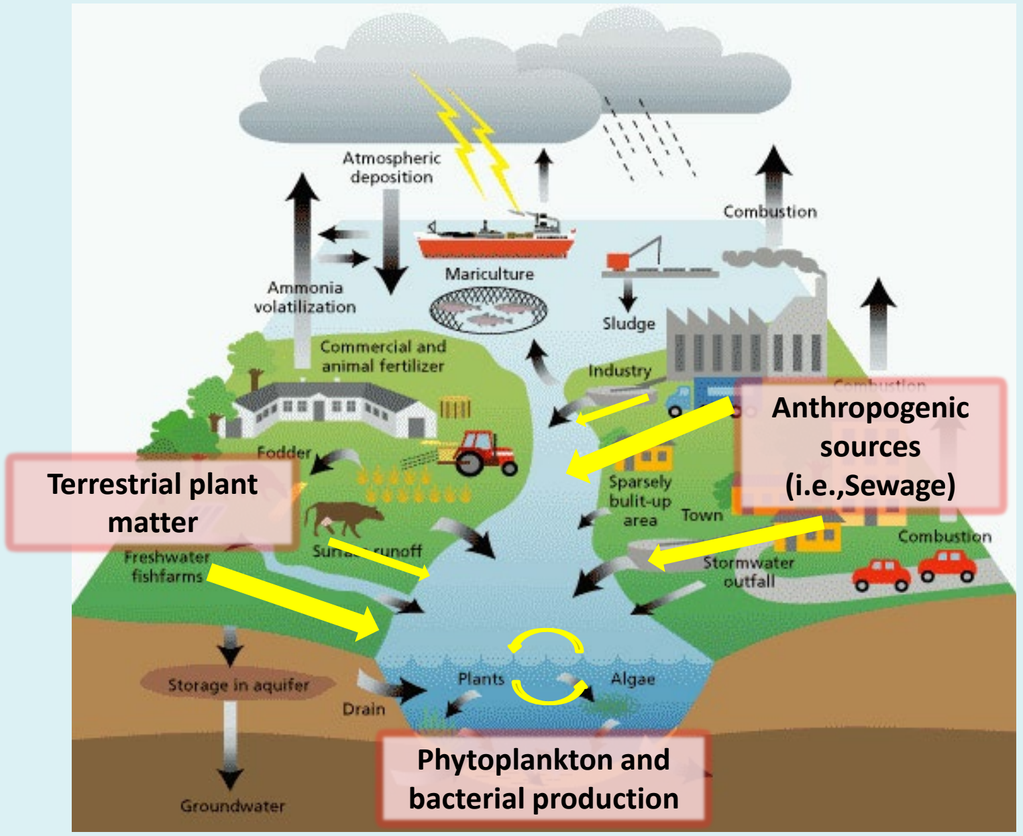


- The source of DOC is mainly from freshwater sources (Lake O and canals) and behave conservatively throughout the estuary.
- The pattern in DOC /a254 are likely opposite patterns with S275-295, indicating that high-molecular-weight organic matter was intensively introduced to the watershed area after the hurricane event.

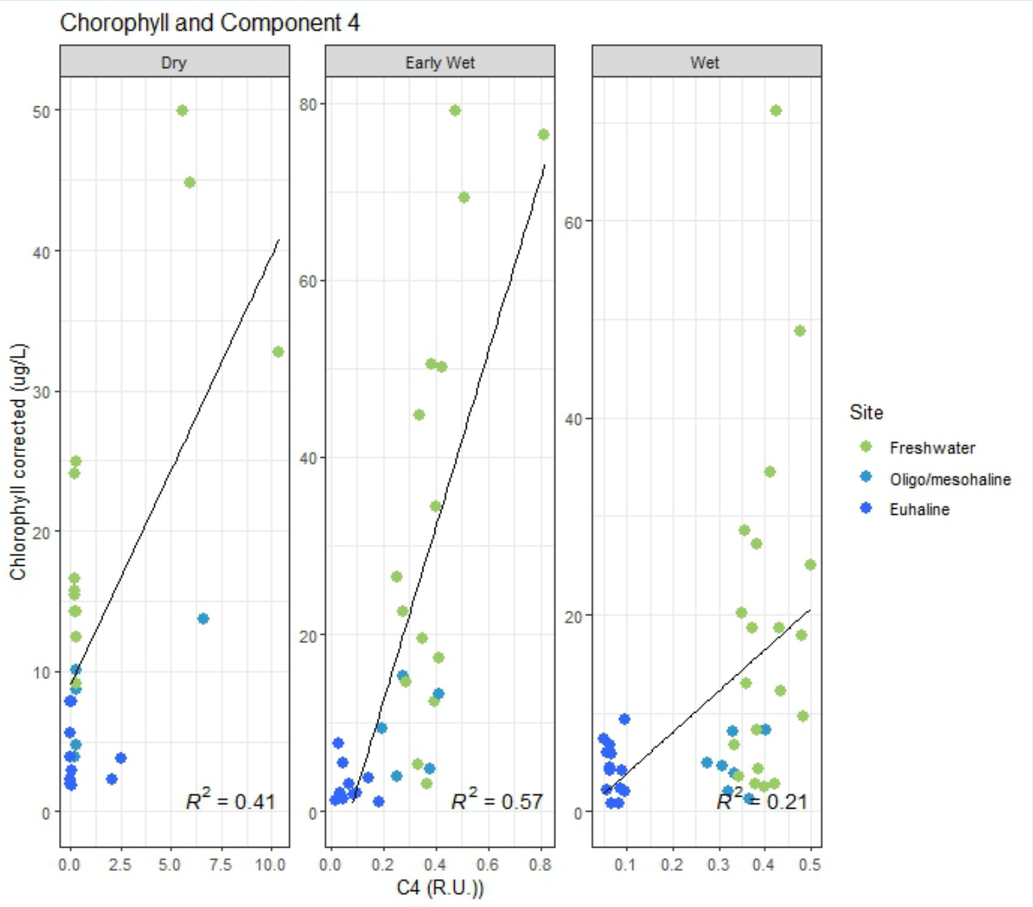

PCA graph of variables
Dim 2 (11.05%)
Dim 1 (29.20%)
1.0
0.5
0.0
-0.5
-1.0
DIN
Ammonia
Nox
TN
TKN
hix
d13C (permil, vs VPDB)
C/N ratio
d15N (permil, vs AIR)
Salinity_Field
DissolvedOxygen_%
TP
SUVA254
a
c
a254
DOC (mg/l)
Orthophosphate (PO4)
fDOM QSU
TDN (mg/L)
Turb_field
SR
pH
fi
Water_Temp
TAL PE ug/L
DON
Pheophytin
b
Chla_Cor
t
bix

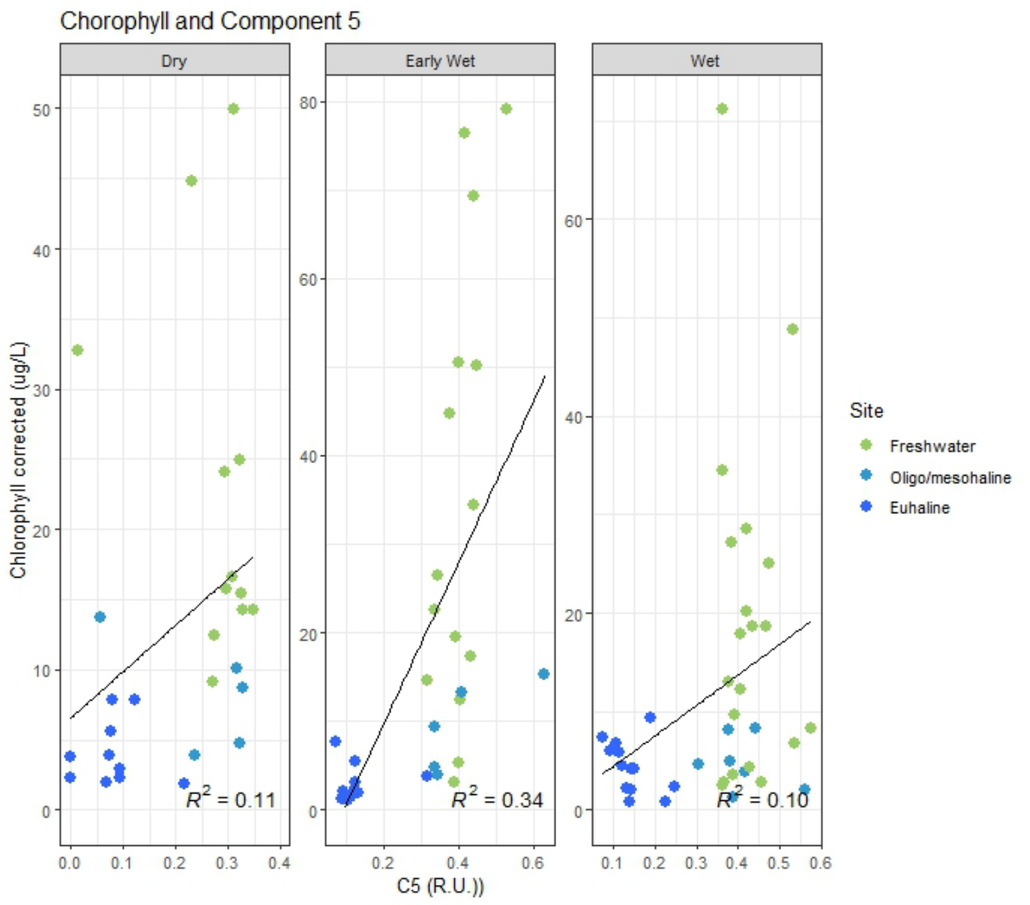

δ13C (‰ VPDB)
C:N
-10
-20
-30
5
10
15
20
25
Bacteria
Marine phyto
Marine POC
Freshwater phyto
Freshwater POC
C4 terrestrial plants
C3 terrestrial plants
Group
GOM
ME
CNL

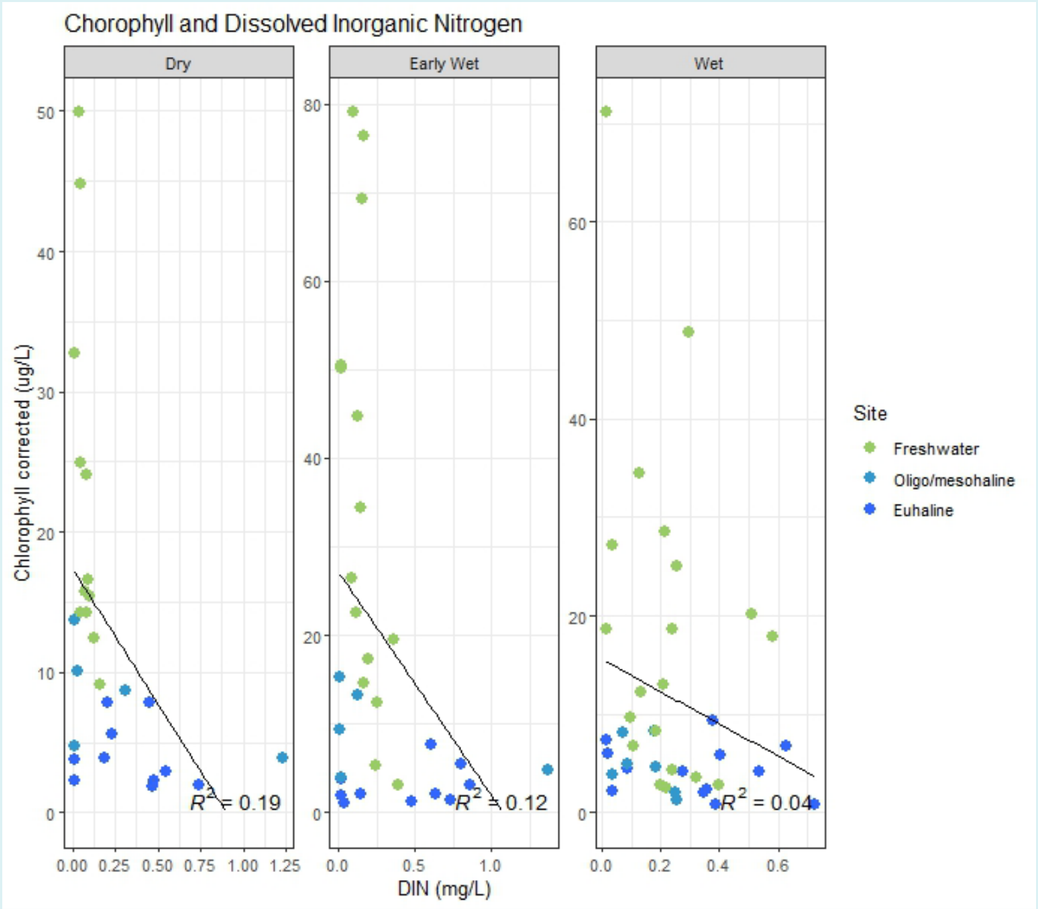
Sources of organic matter in the coastal area



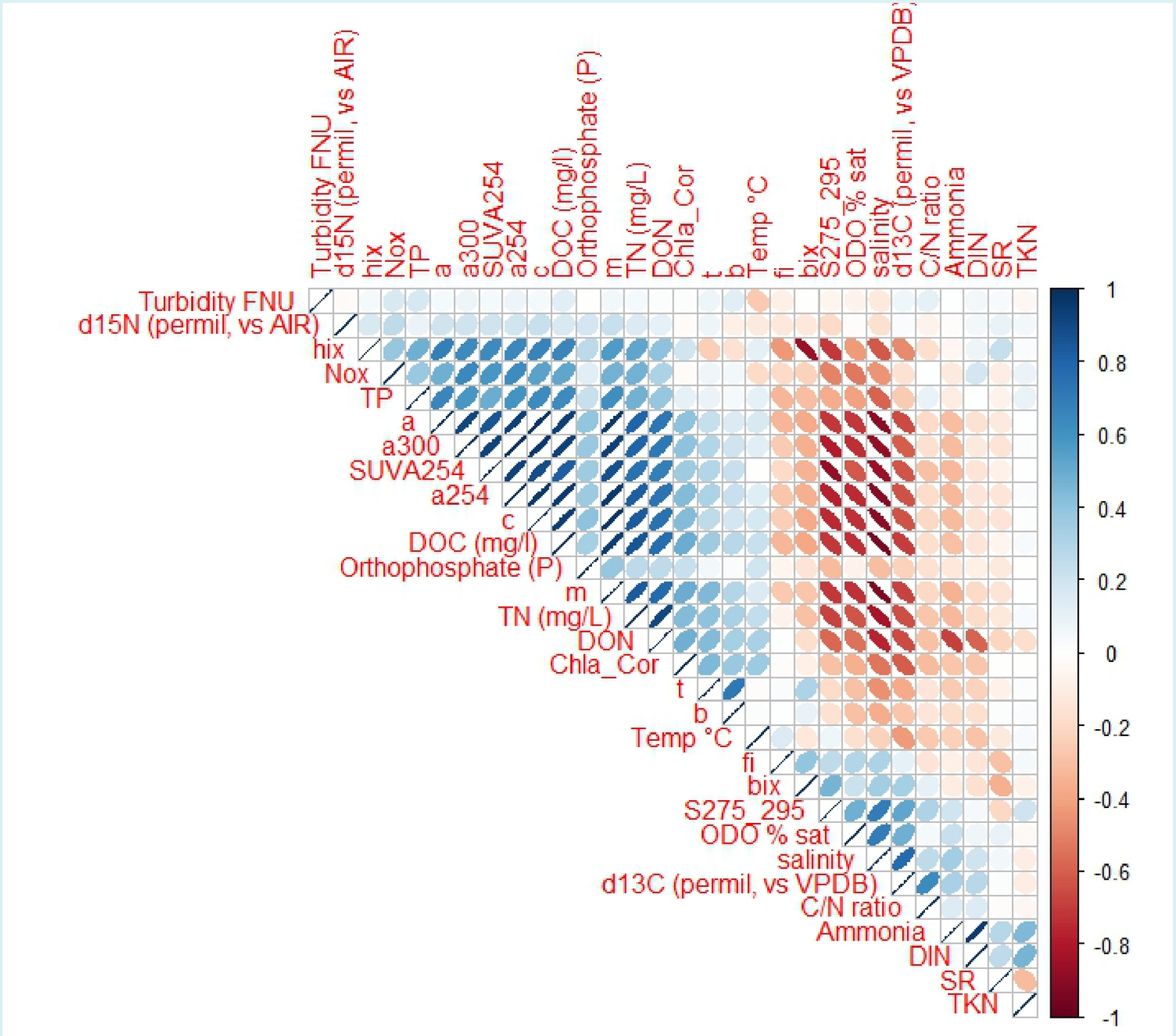
http://www.cleanwaterpartnership.co.uk/water.html


Chorophyll and Component 4
Dry
Early Wet
Wet
Chlorophyll corrected (ug/L)
C4 (R.U.))
R^2 = 0.41
R^2 = 0.57
R^2 = 0.21
Site
Freshwater
Oligo/mesohaline
Euhaline


Chorophyll and Component 5
Dry
Early Wet
Wet
Chlorophyll corrected (ug/L)
C5 (R.U.))
R^2 = 0.11
R^2 = 0.34
R^2 = 0.10
Site
Freshwater
Oligo/mesohaline
Euhaline


Chorophyll and Dissolved Inorganic Nitrogen
Dry
Early Wet
Wet
Chlorophyll corrected (ug/L)
DIN (mg/L)
R^2 = 0.19
R^2 = 0.12
R^2 = 0.04
Site
Freshwater
Oligo/mesohaline
Euhaline


Variations in C-13 by Site and Month
d13C (permil, vs VPDB)
-15
-20
-25
-30
-35
Apr_2022
Jun_2022
Jul_2022
Aug_2022
Sep_2022
Oct_2022
Nov_2022
Dec_2022
Jan_2023
Feb_2023
Mar_2023
Apr_2023
May_2023
Jun_2023
Jul_2023
Aug_2023
Sep_2023
Variations in N-15 by Site and Month
d15N (permil, vs AIR)
20
15
10
5
0
Group
Freshwater
Oligo/mesohaline
Euhaline
Site
CLEW01
CLEW04
CLEW05
CLEW08
CLEW13
CLEW14


Turbidity FNU
d15N (permil, vs AIR)
hix
Nox
TP
a
a300
SUVA254
a254
c
DOC (mg/l)
Orthophosphate (P)
m
TN (mg/L)
DON
Chla_Cor
t
b
Temp °C
fi
bix
S275_295
ODO % sat
salinity
d13C (permil, vs VPDB)
C/N ratio
Ammonia
DIN
SR
TKN
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1