Role of organic nitrogen to eutrophication dynamics along the Neuse River Estuary, NC

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WRRI

Outline

- Introduction
  - Dissolved organic nitrogen (DON)
  - EEM-PARAFAC Technique
  - Study Questions
- Application of FluorMod
- Application of FluorMod PARAFAC Model
- Conclusions

Dissolved Organic Nitrogen (DON)

What we know:

1. Increase in DON in aquatic systems (Lebo et al., 2012; Pellerin et al., 2006)
2. There are ample sources of DON in watersheds (Coble et al., 2014; Pellerin et al., 2006)
3. Phytoplankton and bacterial assemblages can use DON as a nutrient source (Qin et al., 2015; Mesfioui et al., 2012; Bronk et al., 2007)

What we don't know:

1. If natural phytoplankton and bacterial assemblages use DON in-situ
2. What fraction of DON is available to phytoplankton in-situ
3. Seasonal and temporal distribution of broad classes of DON in estuarine systems

EEM-PARAFAC Technique

- Difficult to measure ON using traditional methods
  - Bulk measurements
  - Single molecule analysis
- Optical techniques
  - Fluorescence
  - Excitation emission matrices (EEMs)
  - Parallel Factor Analysis (PARAFAC)
- Differentiate between broad classes of organic matter

Stedmon et al., 2003; Ohno and Bro, 2006; Osburn et al., 2012

Introduction FluorMod PARAFAC Model Conclusions

Study Questions

1. What is the extent of transport and fate of DON sources in the Neuse River Estuary (NRE)?
2. What is the bio-reactivity of DON along the freshwater-estuarine continuum?

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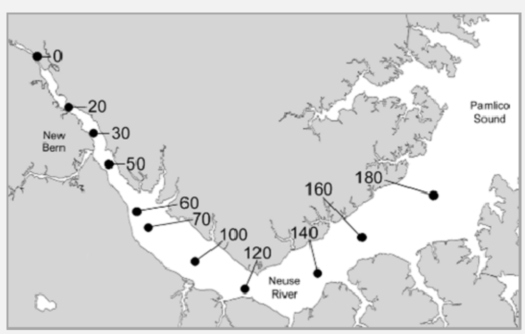
Neuse River Estuary (NRE)

- Collected EEM samples from Station 0 to 180
- July 20, 2015 to July 18, 2016
  - Collected monthly to twice weekly
- Collected both surface and bottom samples
- Coordinated with ModMon

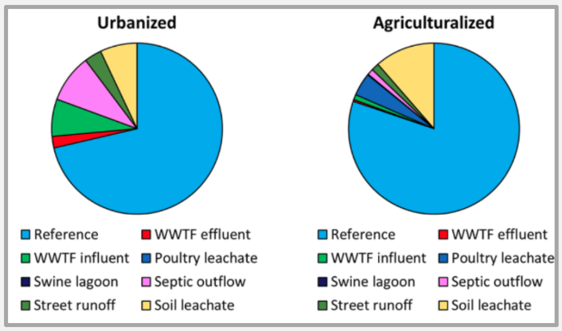


Paerl et al., 2014

Introduction FluorMod PARAFAC Model Conclusions

FluorMod

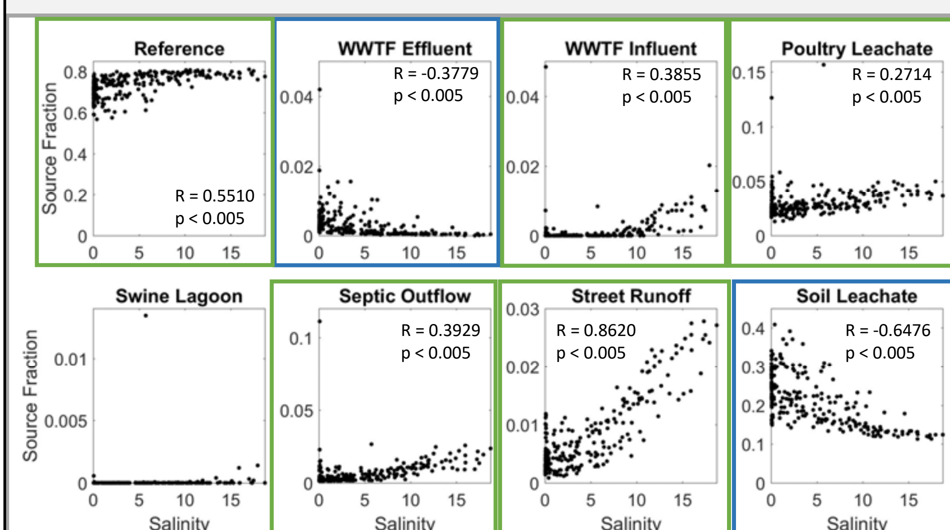
- Osburn et al., 2016 developed an additive mixing model of watershed DON sources
  - Does not include autochthonous sources
- Use to identify and track the fate of terrestrial DON in the NRE



From: Osburn et al., 2016

Decrease with salinity

Increase with salinity



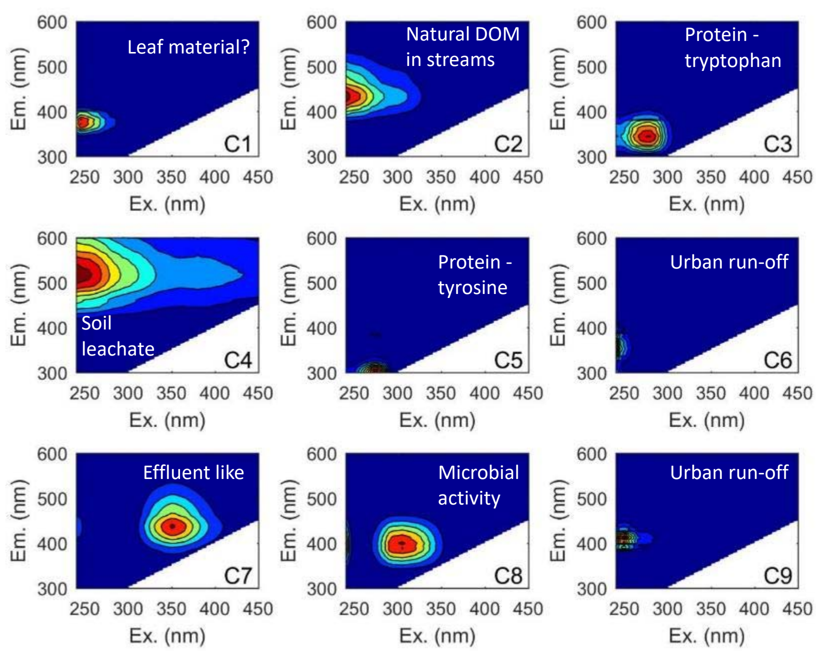
Introduction FluorMod **PARAFAC Model** Conclusions

FluorMod as a PARAFAC model

- FluorMod is a mixing model
- Use FluorMod as a PARAFAC model fitted to the NRE samples
- Track identified components through the estuary
  - Contains indentified terrestrial (allochthonous) and biological (autochthonous) components
- Are there changes in the identified 'autochthonous' sources that indicate utilization or production of DON components by phytoplankton and bacterial assemblages?

Osburn et al., 2016

c4



From: Osburn et al., 2016

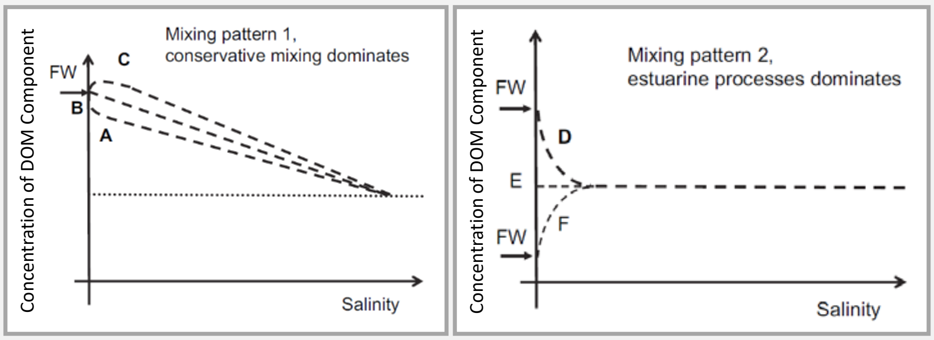
Slide 10

c2 closburn, 3/13/2017

c3 C1 is tricky no real idea yet
closburn, 3/13/2017

c4 C7 is not only an Effluent signal but was enriched. I think overall I would not try to interpret these Components as discrete source signals. Or rather show that a component like C7 is "enriched in Effluent"
closburn, 3/13/2017

Estuarine mixing processes

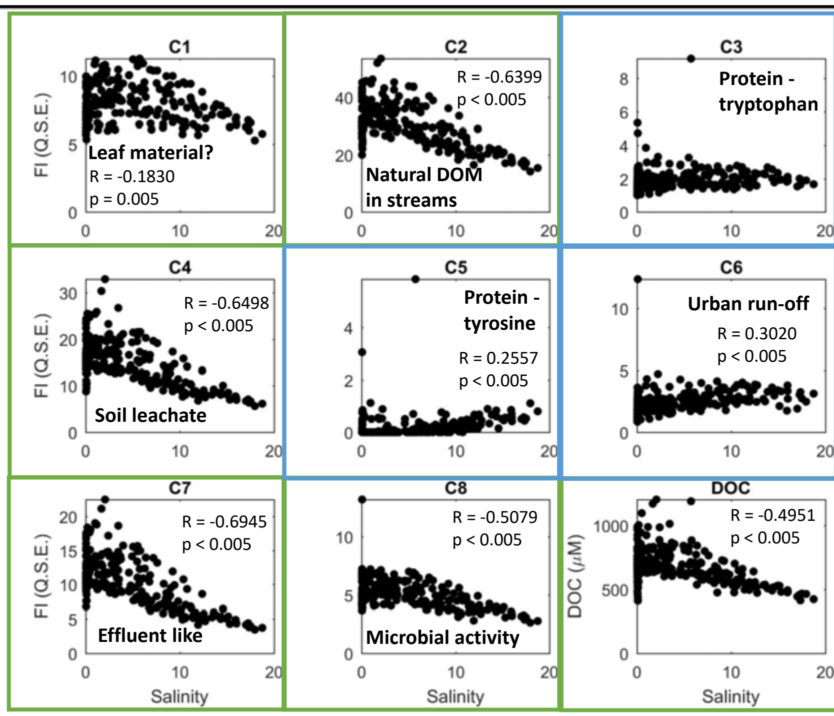


From: Margaker et al., 2011

c5
c6

Mixing processes

Estuarine processes

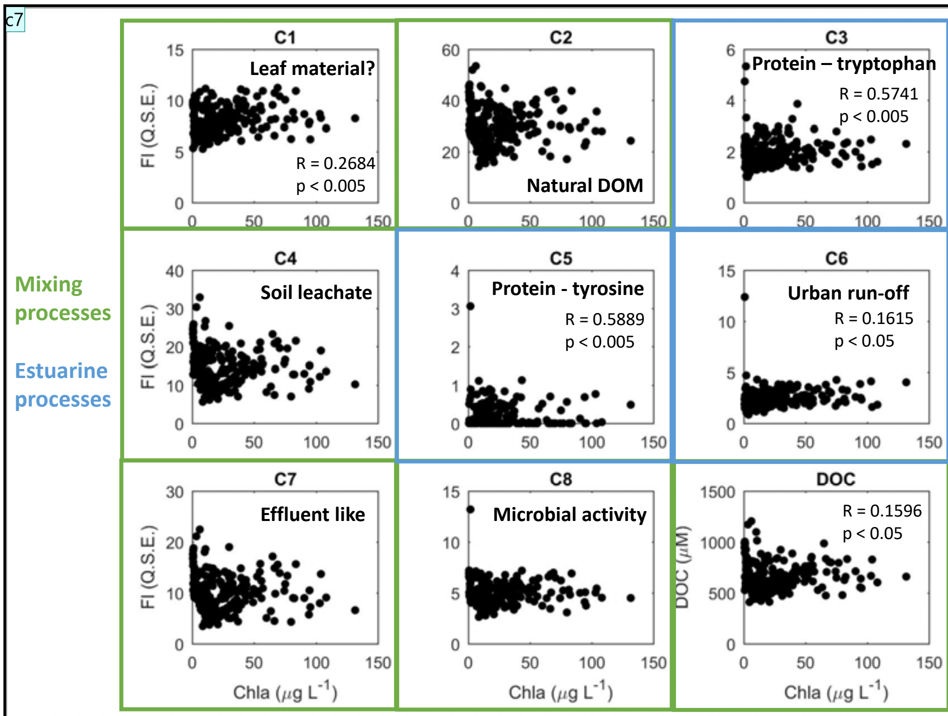


Slide 12

c5 I am unclear about your last point - you applied the FluorMod PARAFAC model to your estuarine EEMs but not applying FluorMod itself? I think you do yourself a disservice if you cannot identify specific components. Why would C1 get higher across the salinity gradient?
closburn, 3/13/2017

c6 Also it would not be surprising that FluorMod worked worse as the river signal was diluted. FluorMod had no phytoplankton source remember.
closburn, 3/13/2017

c7



c8

Preliminary Conclusions

- Fluorescence overwhelmed by terrestrial components
  - Difficult to identify and track biological components
- Patterns down estuary mainly due to mixing and dilution processes
  - But some fluorescence components are dominated by estuarine processes
- The challenge: linking these components to phytoplankton dynamics
  - Multiple processes occurring simultaneously
- Still in the process of analyzing data
  - Multivariate analyses

Slide 13

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c7 Why would C3/C6 (latter urban run off) show an incrase with Chla?
closburn, 3/13/2017

Slide 14

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c8 You must say taht FluorMod is a source model only - has no transformation component. Very reasonable that biogeochemistry has wiped out source siganls and they converge into generic humic substances.
closburn, 3/13/2017

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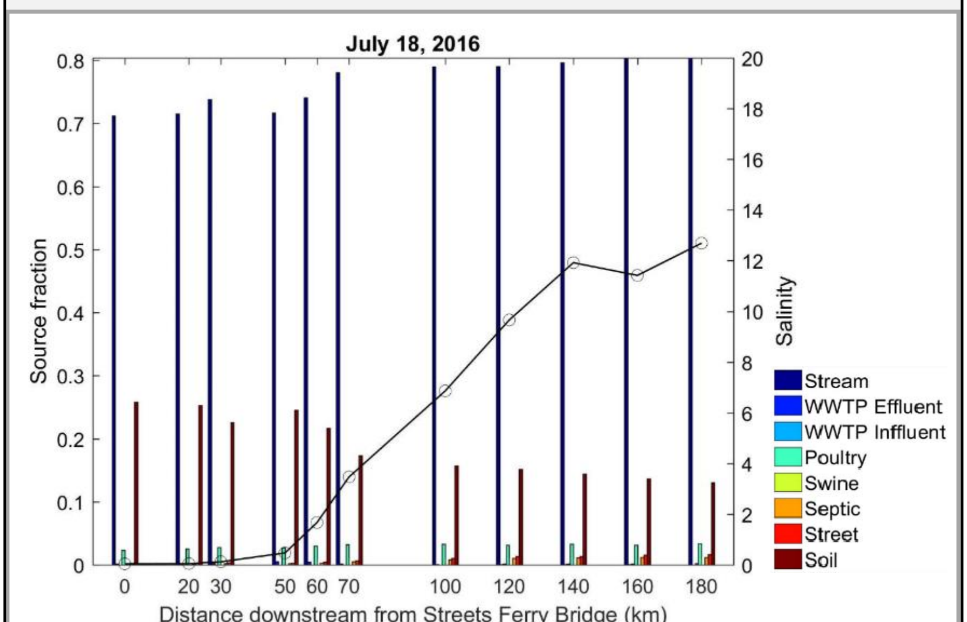
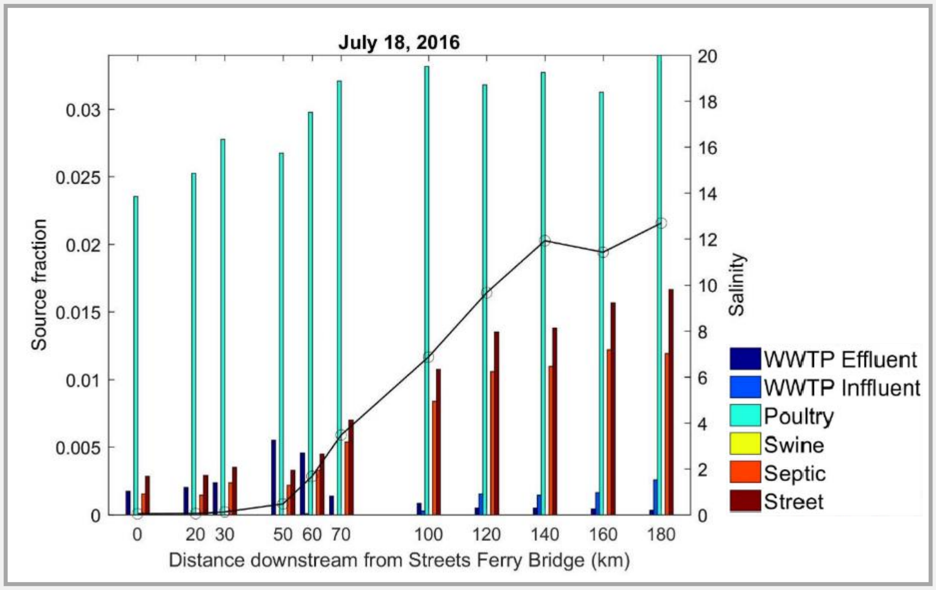
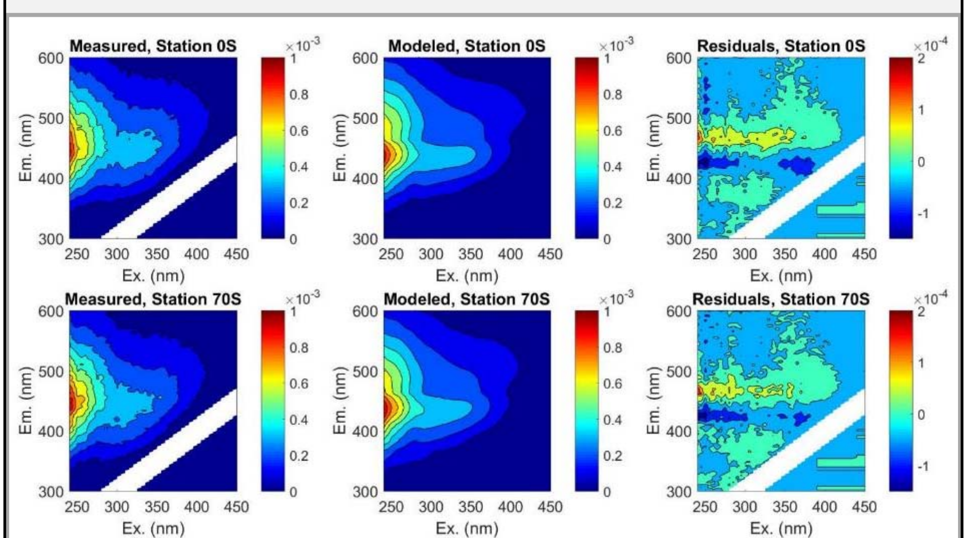
Appendix



July 18, 2016
Source fraction
Salinity
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
20
18
16
14
12
10
8
6
4
2
0
0
20
30
50
60
70
100
120
140
160
180
Distance downstream from Streets Ferry Bridge (km)
Stream
WWTP Effluent
WWTP Influent
Poultry
Swine
Septic
Street
Soil


July 18, 2016
Source fraction
Salinity
Distance downstream from Streets Ferry Bridge (km)
WWTP Effluent
WWTP Inffluent
Poultry
Swine
Septic
Street

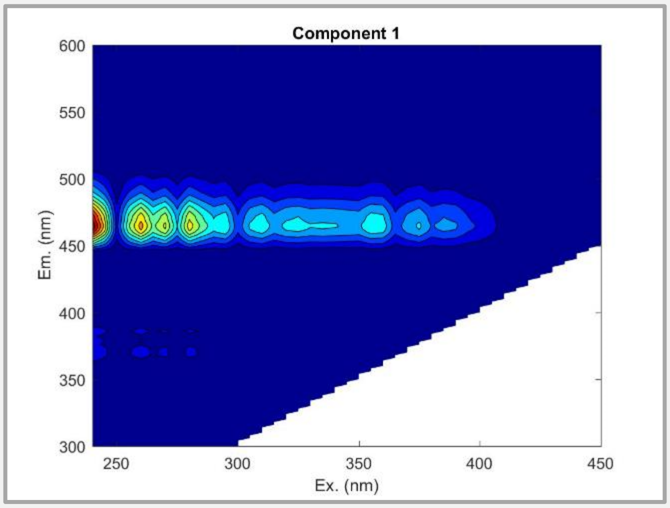
c1

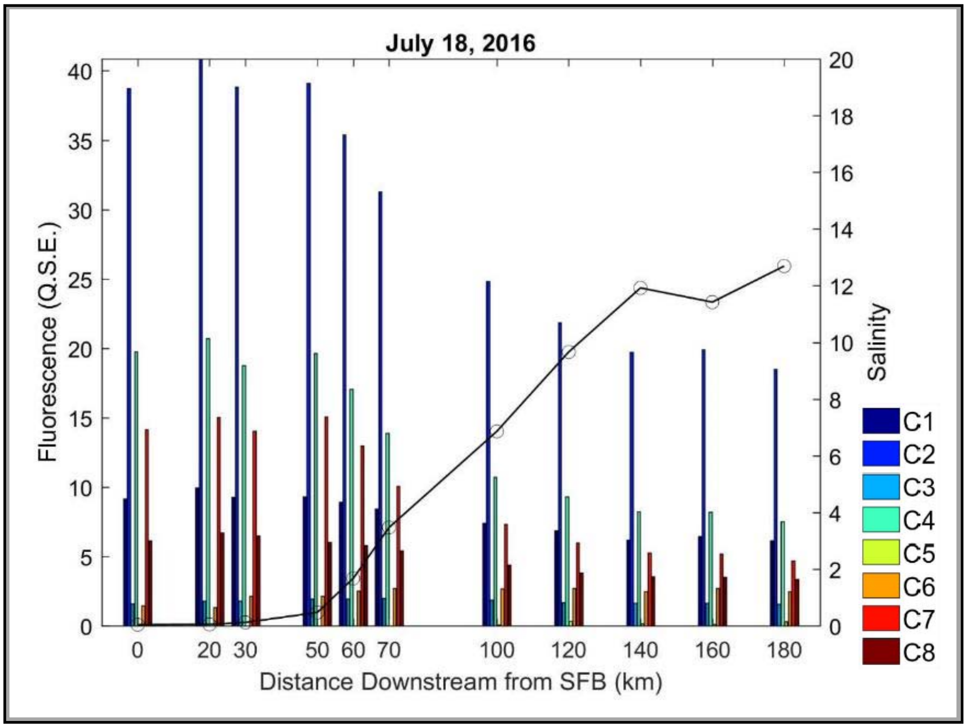

Measured, Station 0S
Modeled, Station 0S
Residuals, Station 0S
Measured, Station 70S
Modeled, Station 70S
Residuals, Station 70S
Em. (nm)
Ex. (nm)

Slide 20

c1 Have an idea for what this residual signal is...
closburn, 3/13/2017

FluorMod Residuals

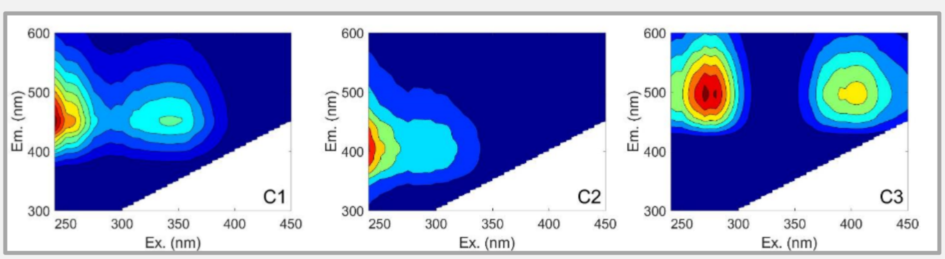




PARAFAC Model Development

- Generated a 3-component PARAFAC model
- Based on all DOM samples collected from July 2015 to July 2016
  - Included both surface and bottom samples
  - All stations from riverine to coastal end-member
  - Total of 471 samples
- Model split half validated
- 3 component model developed

PARAFAC Model: NRE-DOM



DOM Component	Λ_{ex} (nm)	Λ_{em} (nm)	Matches to OpenFluor	Assignment Corresponding to previous studies
C1	<240, 340	452	14	Humic, fulvic-acid like; terrestrially derived; combination of A and C peaks
C2	<240	406	6	Microbial, humic-like; potentially from phytoplankton exudates; eutrophic estuaries; similar to M-peak
C3	270, 205	496	4	Humic-like; terrestrially derived

Modeling Residual

- Fit a PARAFAC model to the sample residuals
- Capture what isn't being modeled in the original PARAFAC model
- Developed a 6-component model
- NOT split half validated – take results with a grain of salt…

Residual PARAFAC Model