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THE STATE UNIVERSITY OF NEW JERSEY

Insights into seasonal organic carbon cycling in the Delaware Estuary from *N*-alkane biomarkers and stable carbon isotopes

Hermes, A.L. and E.L. Sikes

9:30 AM - 20 January 2013
Session 15 – What's Mud Got to Do With It?
Delaware Estuary Science and Environmental Summit
Cape May, NJ

Overview

1. Introduction

- Estuarine organic carbon (OC) cycling
- OC cycling in the Delaware Estuary

2. Results

- Bulk measurements of surface and bottom waters:
  - suspended solid content (SSC) and
  - total organic carbon (TOC)
- Alkane biomarkers: algal vs. land-derived OC
- Alkane compound-specific isotopes: marsh vs. terrestrial sources of land-derived OC

3. Summary and Conclusions

- Land-derived OC is trapped in the estuarine turbidity maximum (ETM) and estuarine bottom waters.
- Marsh inputs from the lower estuary are substantial in Delaware Estuary bottom waters and the ETM.

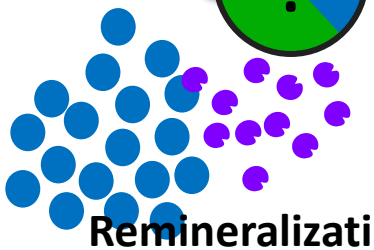
Estuarine OC cycling links land and sea.

WETLANDS

RIVER

POC

Burial



Remineralization

OCEAN

Export

Vascular plant (land) OC:

- **Terrestrial from the river**
- **Marsh from the fringing wetlands**

Algal OC:

- **Brought in by tidal pumping**
- **Seasonally produced within the estuary**

1. What are the sources of OC through the estuary?
2. How are these sources partitioned through estuarine physical, chemical, and biological gradients?
3. What are their fates?

1. The Delaware River is the primary source of freshwater, sediments, and **land-derived OC** *(e.g. Cook et al., 2007; Mannino and Harvey, 1999)*.

2. Seasonal **algal blooms** occur in Delaware Bay and the upper freshwater river *(e.g. Pennock and Sharp, 1986; Cifuentes et al., 1988)*.

1. The **ETM** is a mud trap and mixing zone for OC *(e.g. Biggs et al., 1983; Sommerfield and Wong, 2011; Mannino and Harvey, 1999)*.

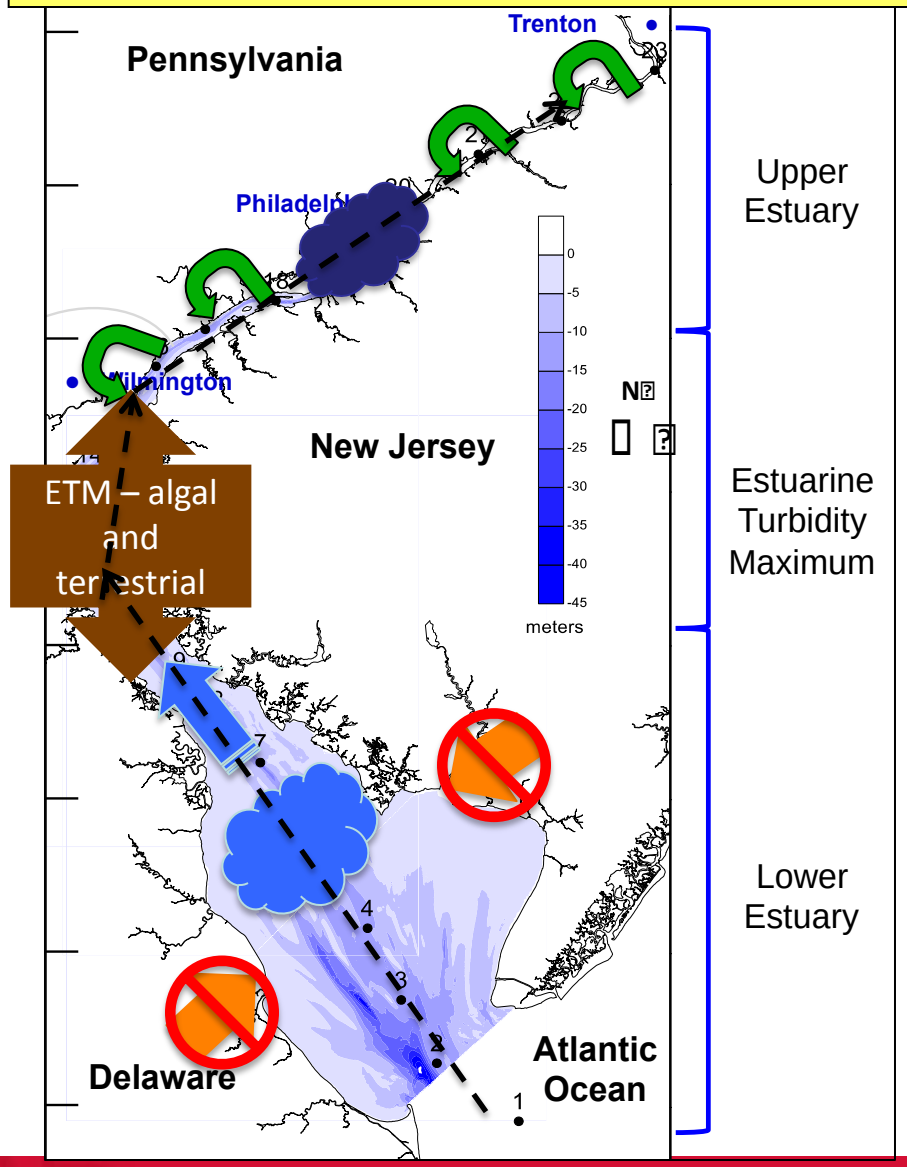
2. **Marsh OC** is not significant in the Delaware Estuary *(e.g. Cifuentes, 1991; Mannino and Harvey, 1999).*

Mismatch between observed wetland erosion and geochemical analyses?

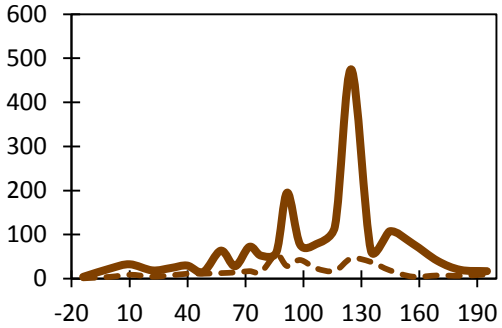
Previous work – Surface waters

This work – Surface and Bottom waters

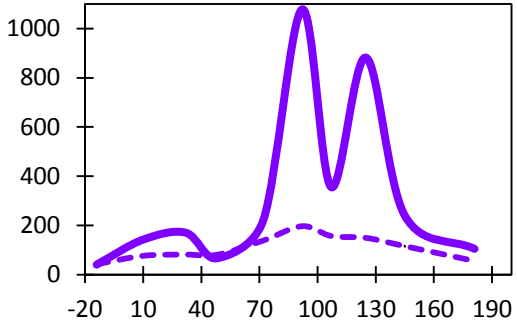
The Delaware Estuary is a model system to assess OC cycling.



More OC in bottom water than surface water!

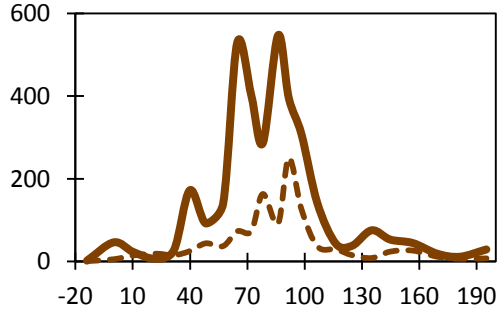


S'10-DRY

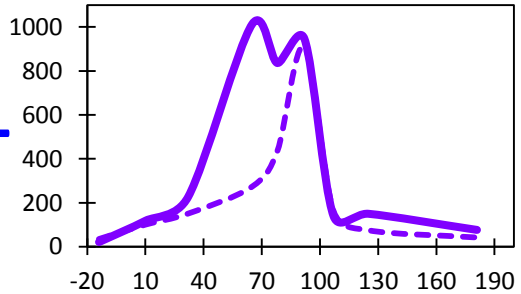


SSC (mg/L)

POC (µM)



M'11-WET



Ocean **Distance (km)** **River**

Ocean **Distance (km)** **River**

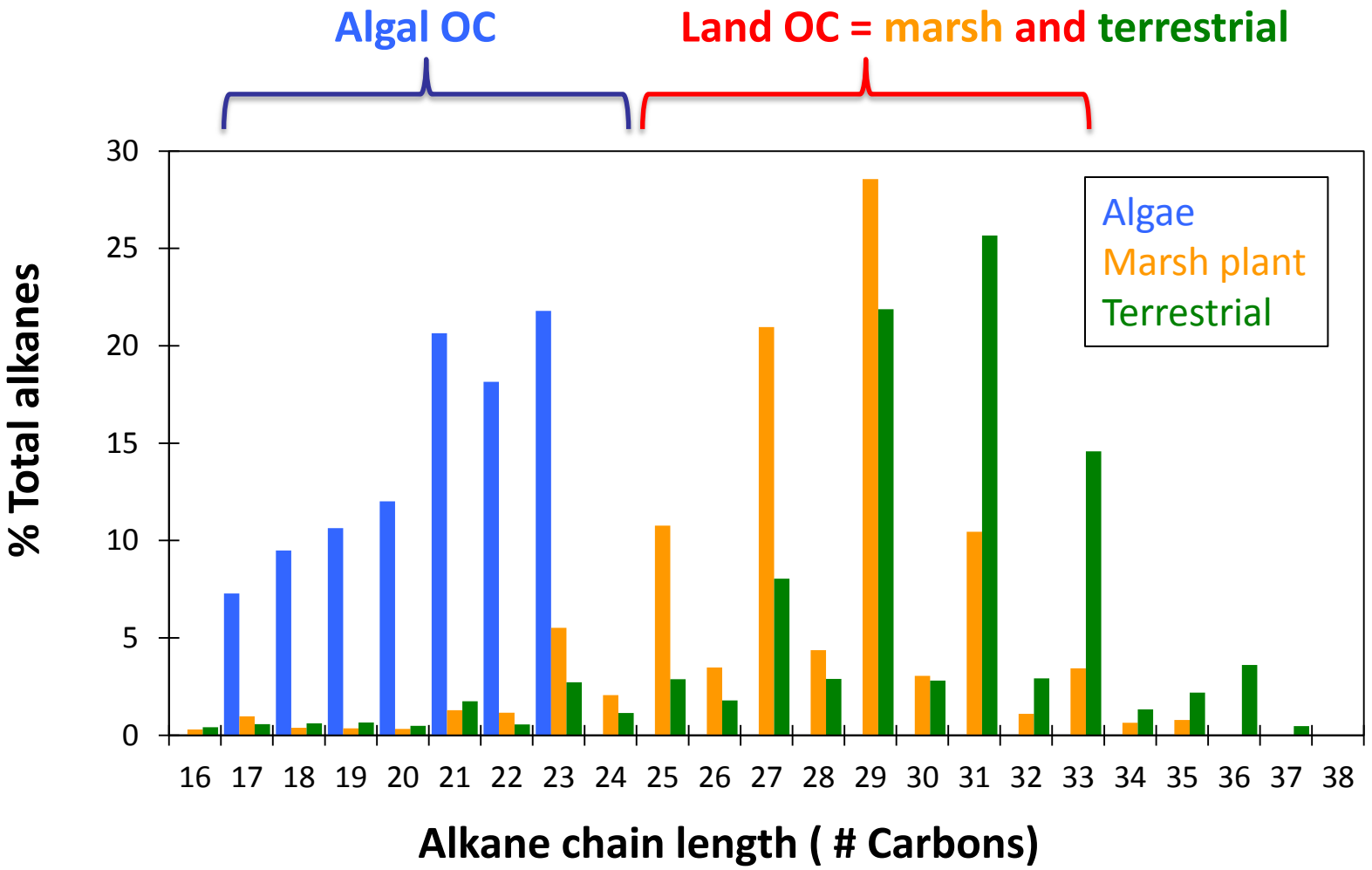
SSC data courtesy of the University of Delaware

------ **Surface water**

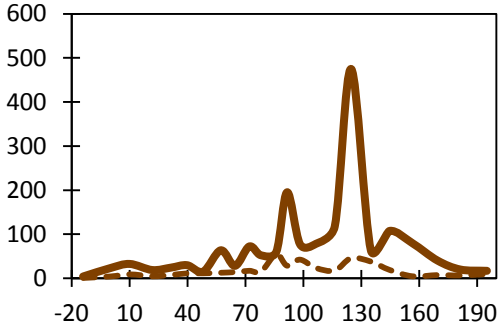
Bottom water

Alkane biomarkers trace algal vs. land plant OC.

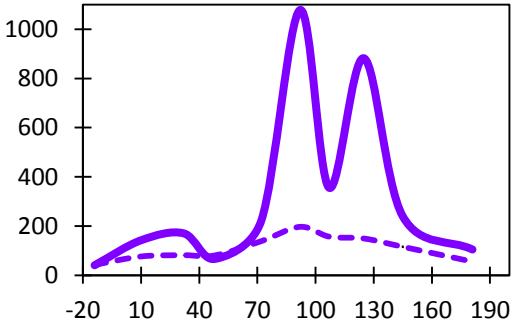
Nonacosane (C_{29}), Eglinton and Hamilton, *Science,* 1967

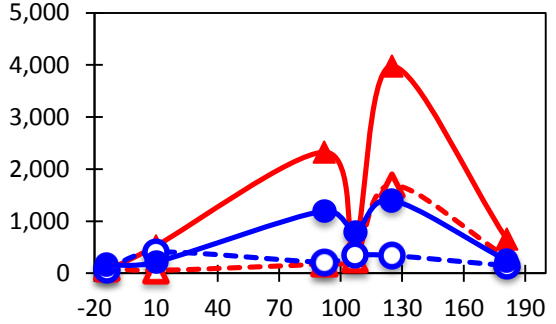


The OC in bottom waters of the ETM is primarily land-derived OC!



S'10

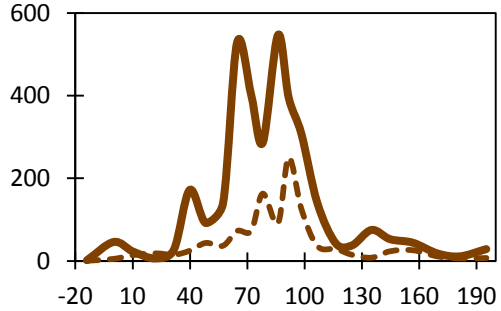




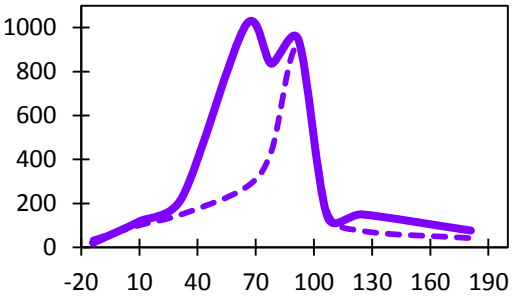
SSC (mg/L)

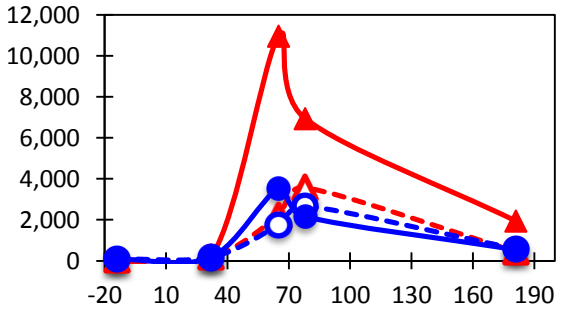
POC (µM)

Alkane abundance (ng/L)



M'11





Ocean **Distance (km)** **River**

Ocean **Distance (km)** **River**

Ocean **Distance (km)** **River**

SSC data courtesy of the University of Delaware

------ **Surface water**

____ **Bottom water**

Algal OC

Land OC = marsh & terrestrial

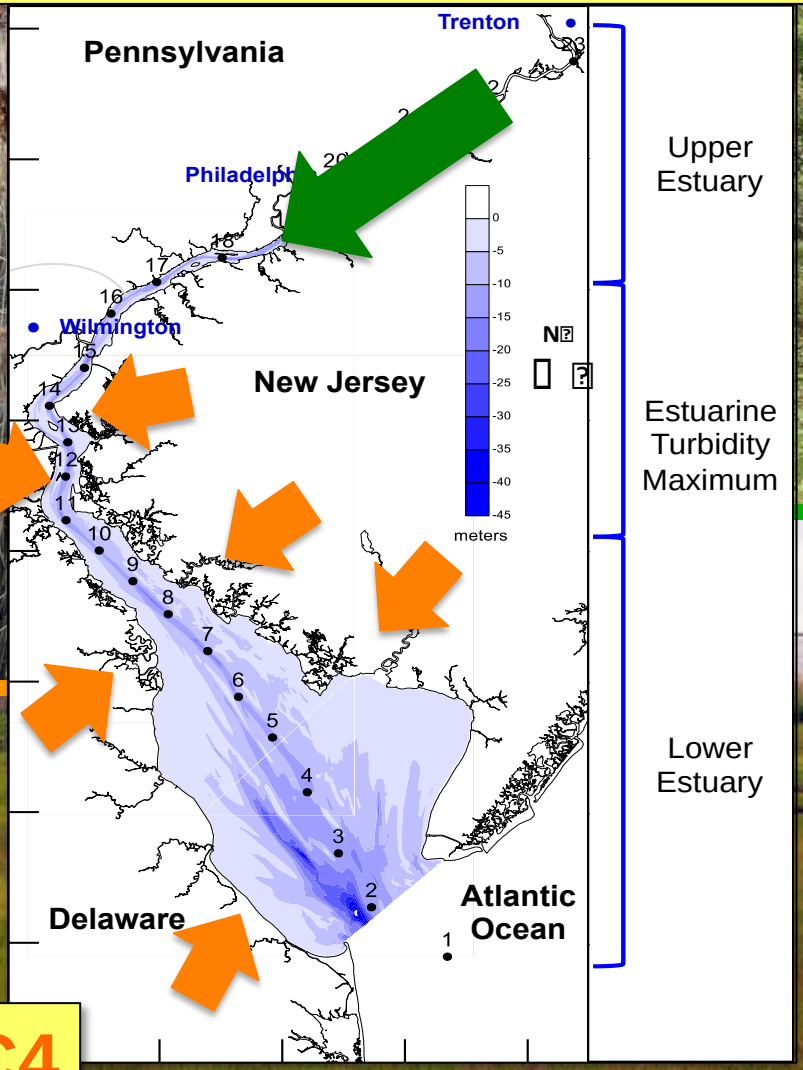
Marsh and terrestrial land OC have different delivery pathways.

C3

C3

Terrestrial

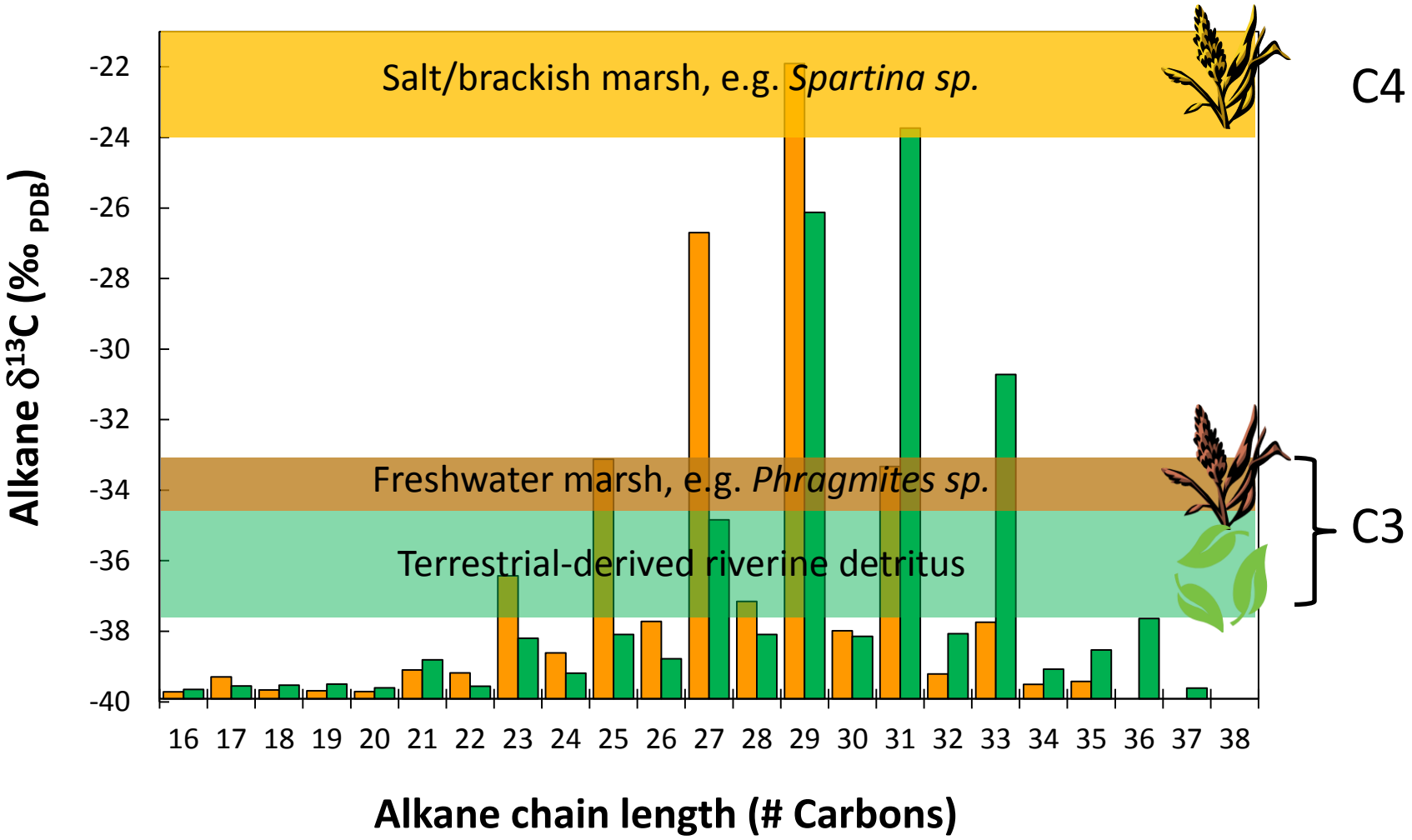
Marsh



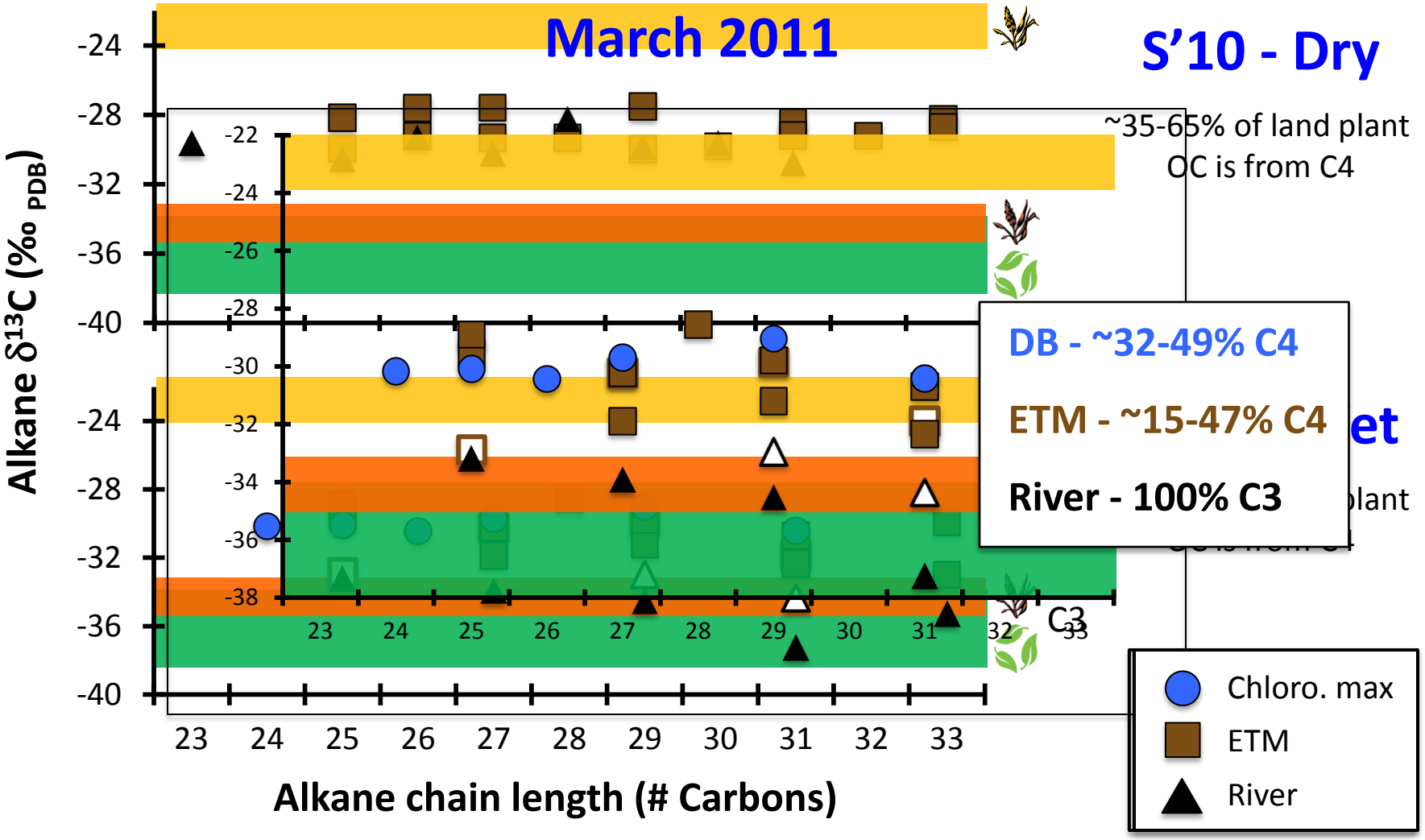
C4

http://ian.umces.edu/imagelibrary/displayimage-3283.html

The compound-specific stable carbon isotopic composition of alkanes differentiates C3 and C4 land-derived OC.

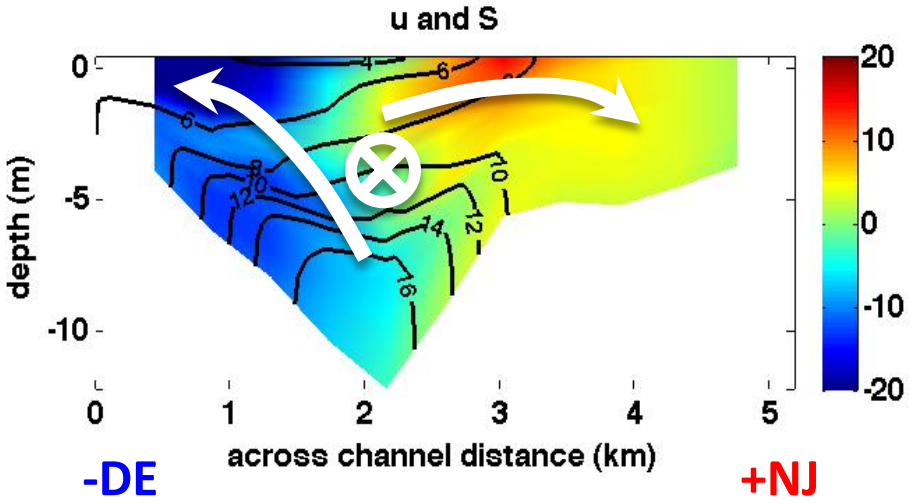


C4 inputs increase down-estuary:
C4 marsh inputs are important in the Delaware Estuary!

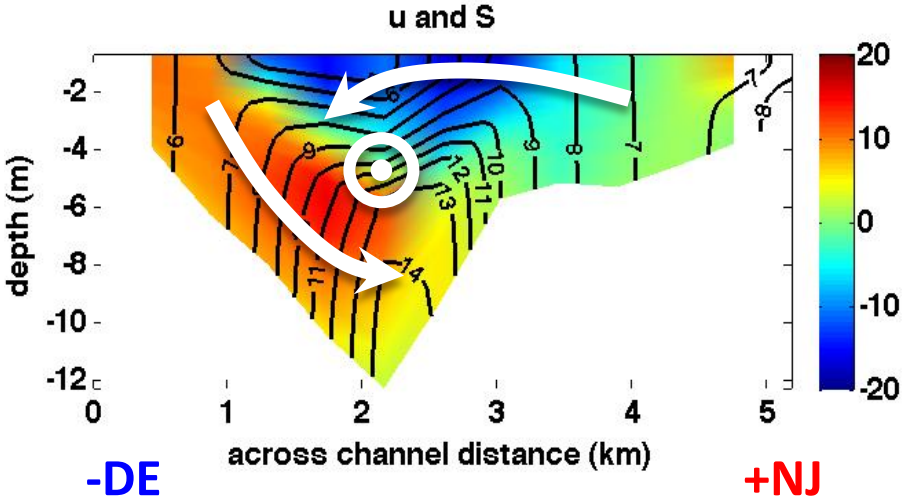


Lateral circulation demonstrated by numerical model output provides a mechanism for C4 marsh inputs.

Flood



Ebb

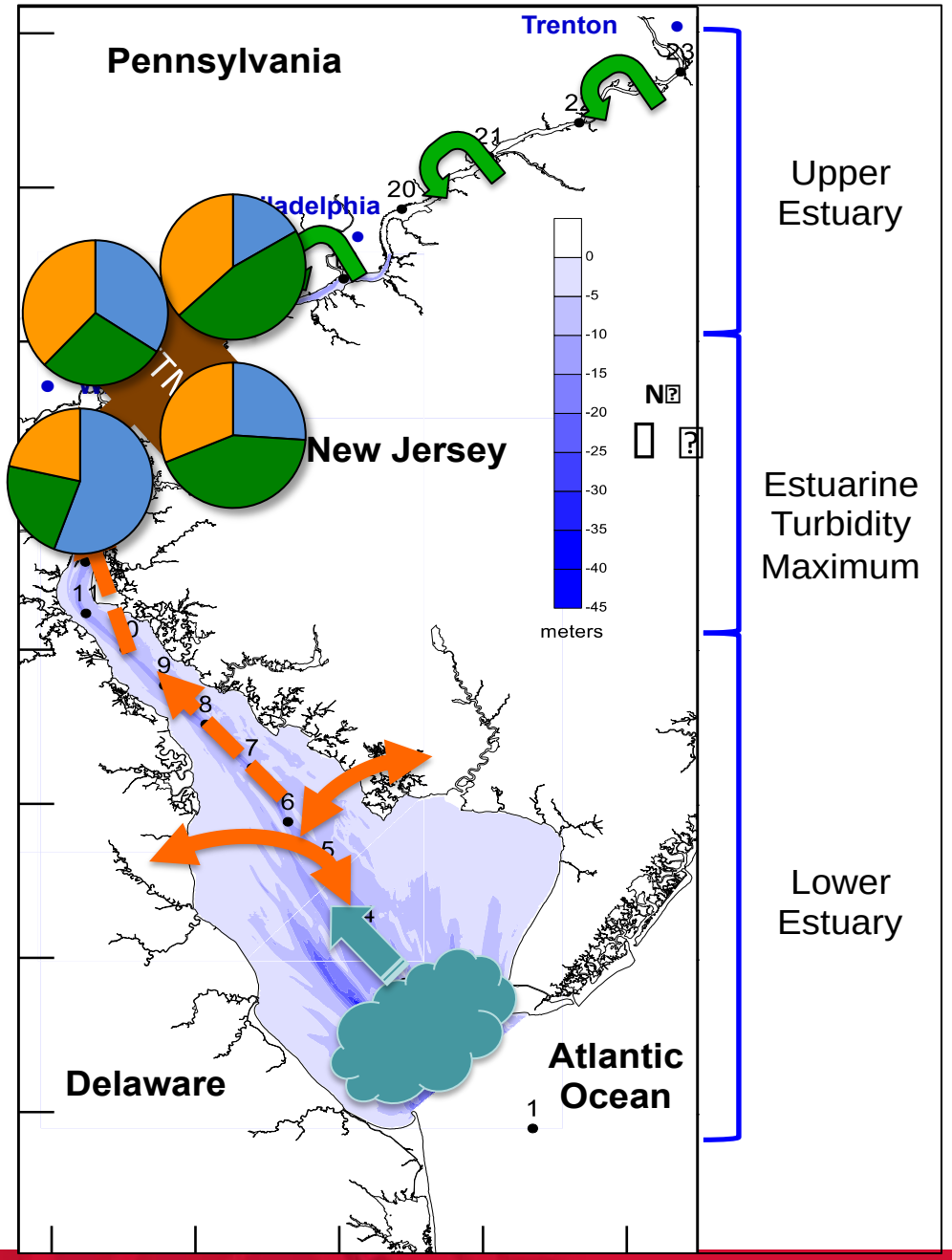


Model output courtesy of M. Aristizabal

For more, see Maria's talk during the Physical Processes Session 17 (up next!)

September 2010-

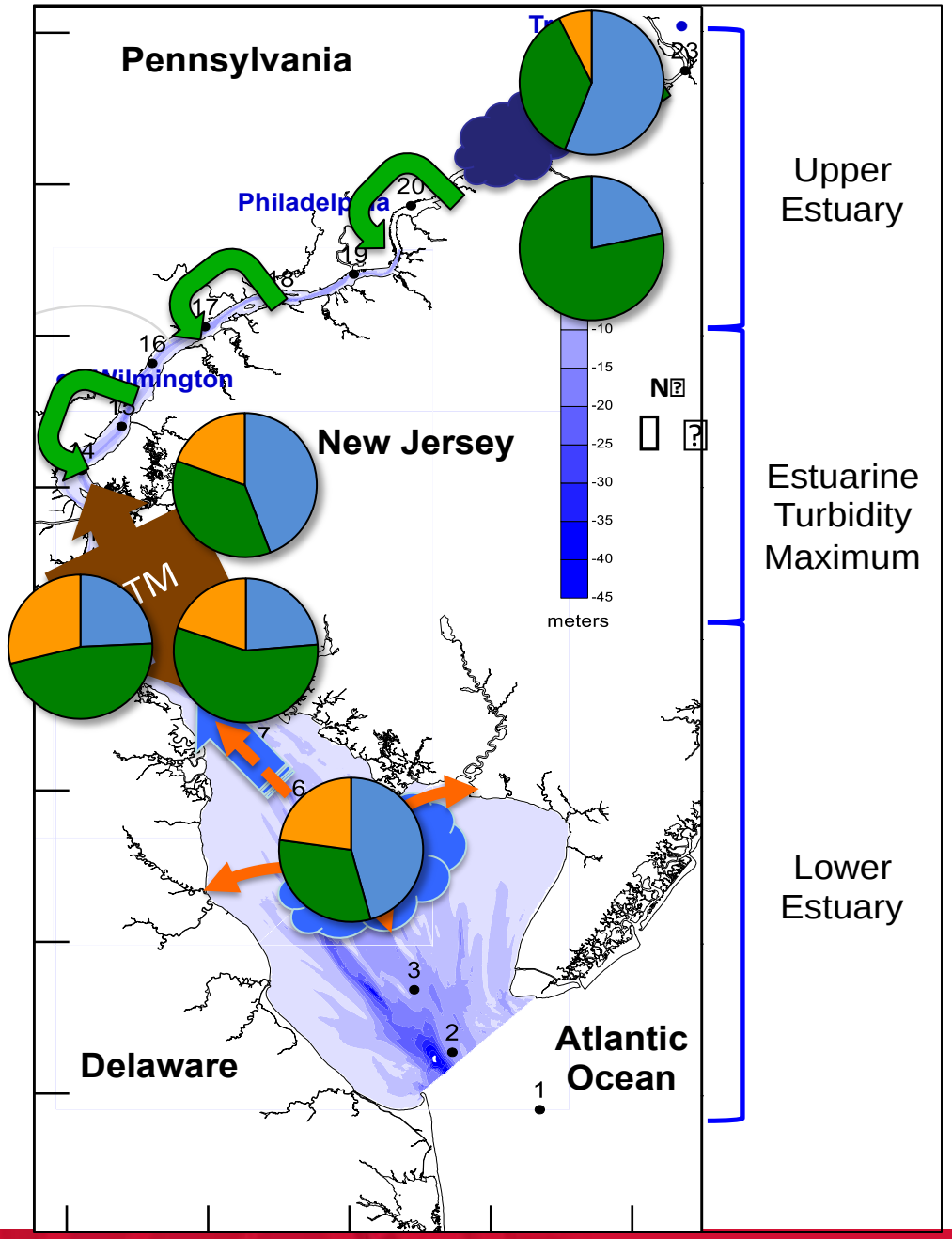
Late summer, low discharge



Marsh
Terrestrial
Algal

March 2011-

Spring bloom, after freshets



Marsh
Terrestrial
Algal

Summary and Conclusions:
A new perspective of estuarine OC cycling

- There is more carbon in bottom waters than surface waters in the Delaware Estuary.
- The composition of bottom water is different than surface waters – it's derived from the land.
- Compound-specific isotopes of biomarkers allow us to assess the role of wetlands in the Delaware Estuary.
- Wetland OC influences the geochemical signatures of OC pools in the Delaware Estuary, especially within bottom waters of the ETM.

Acknowledgements

Liz Sikes (advisor)
Chris Sommerfield and Bob Chant, Co-PIs
Liz Canuel (committee; VIMS)
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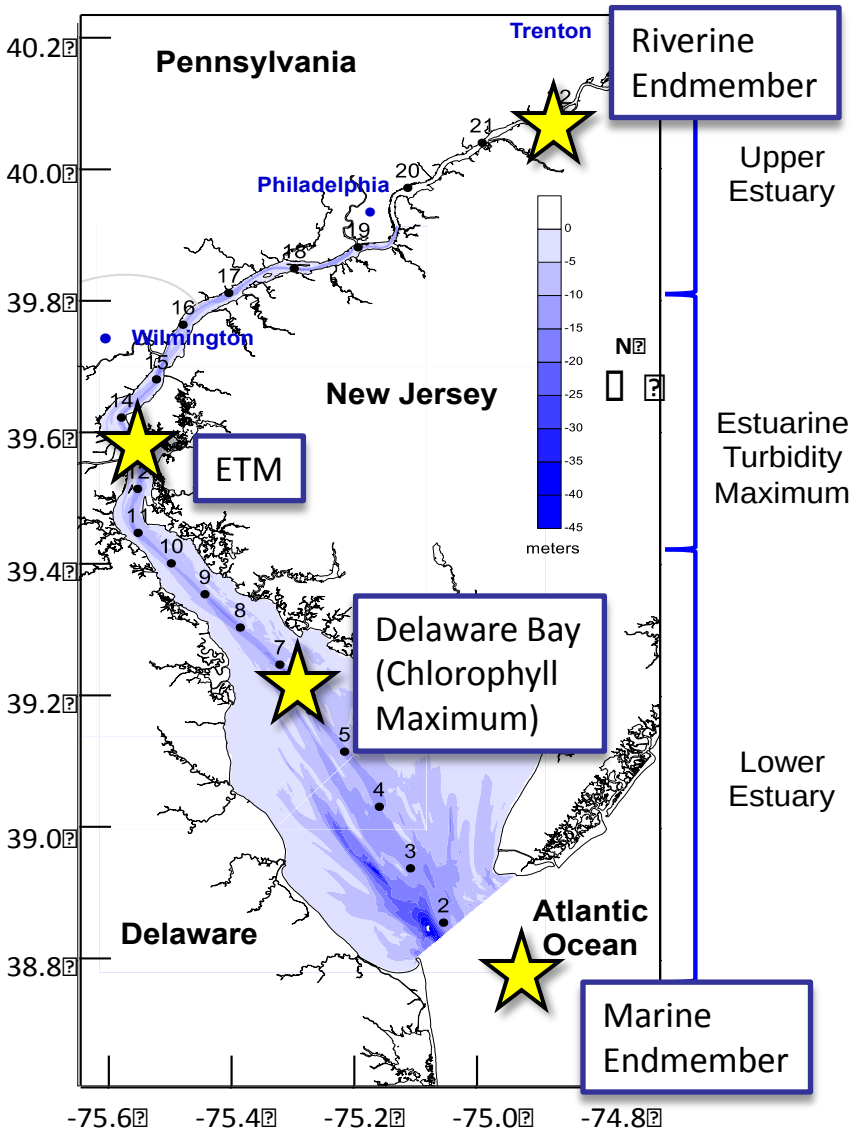
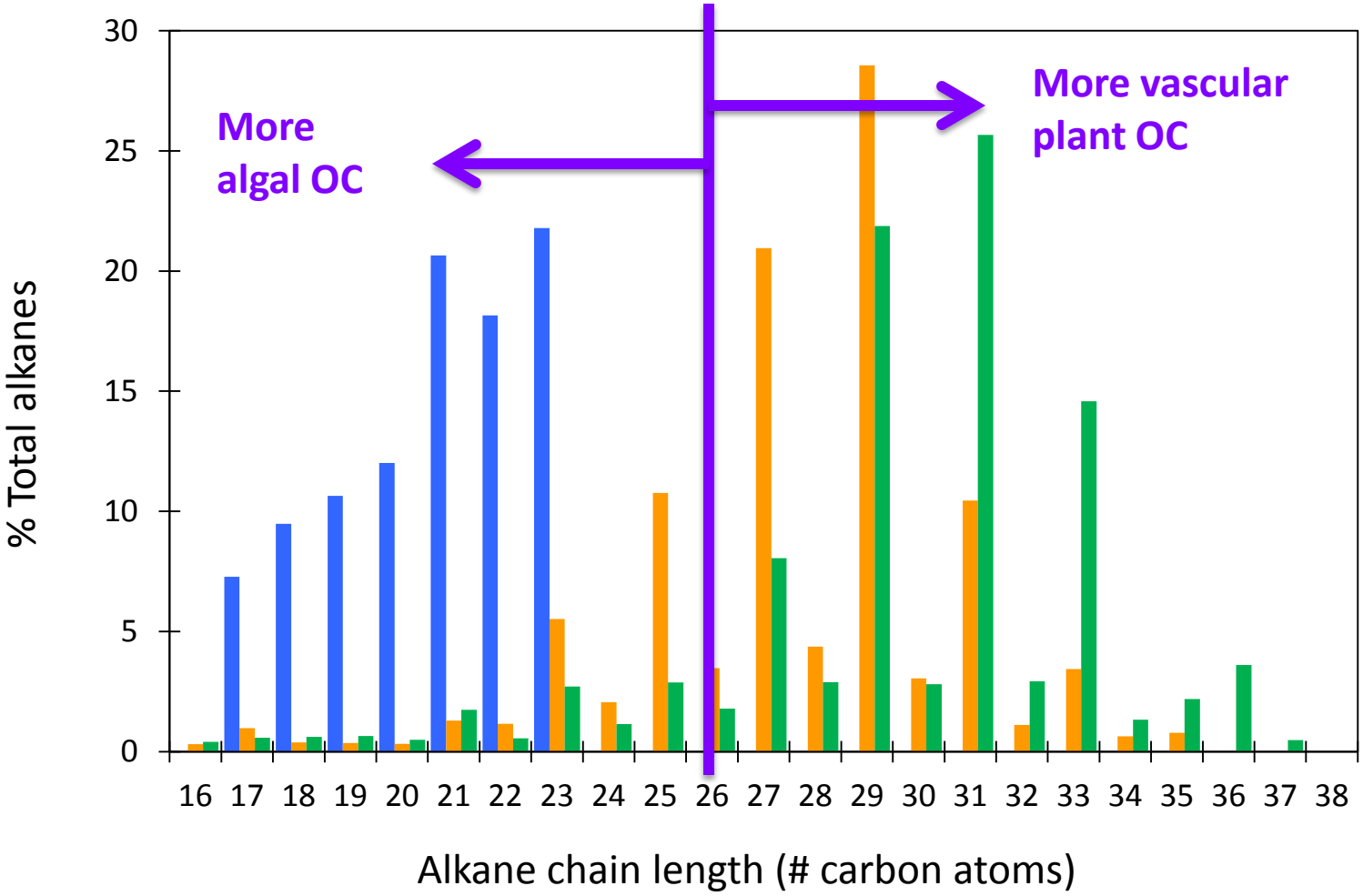
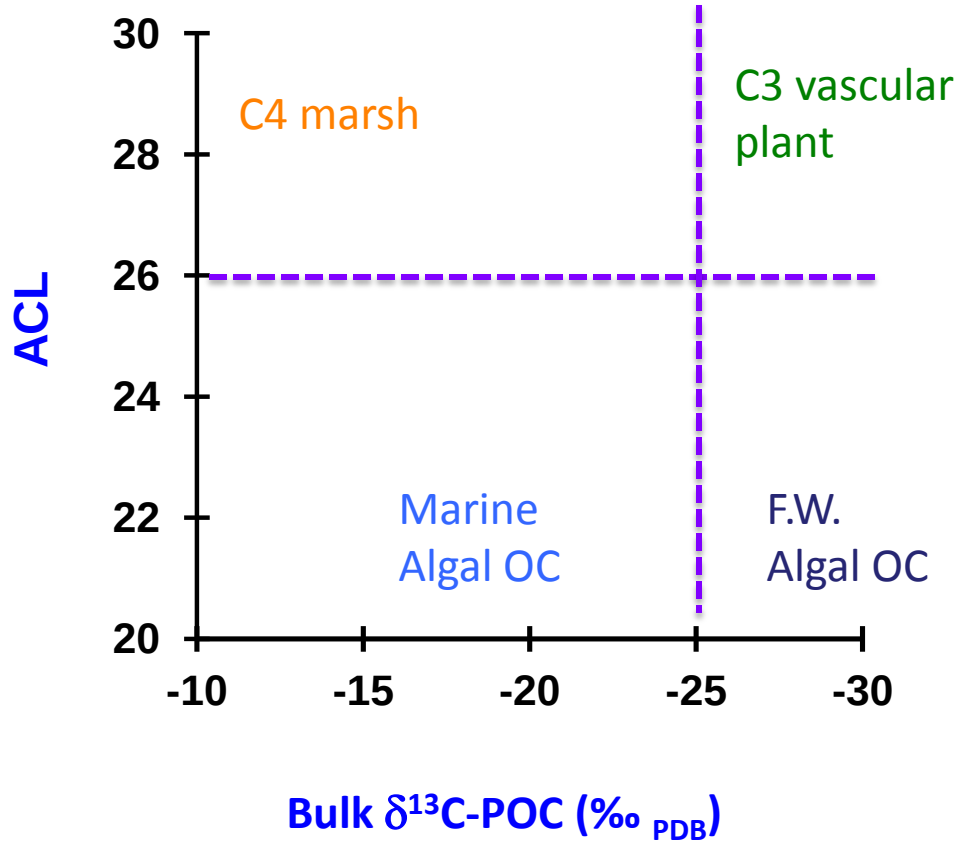
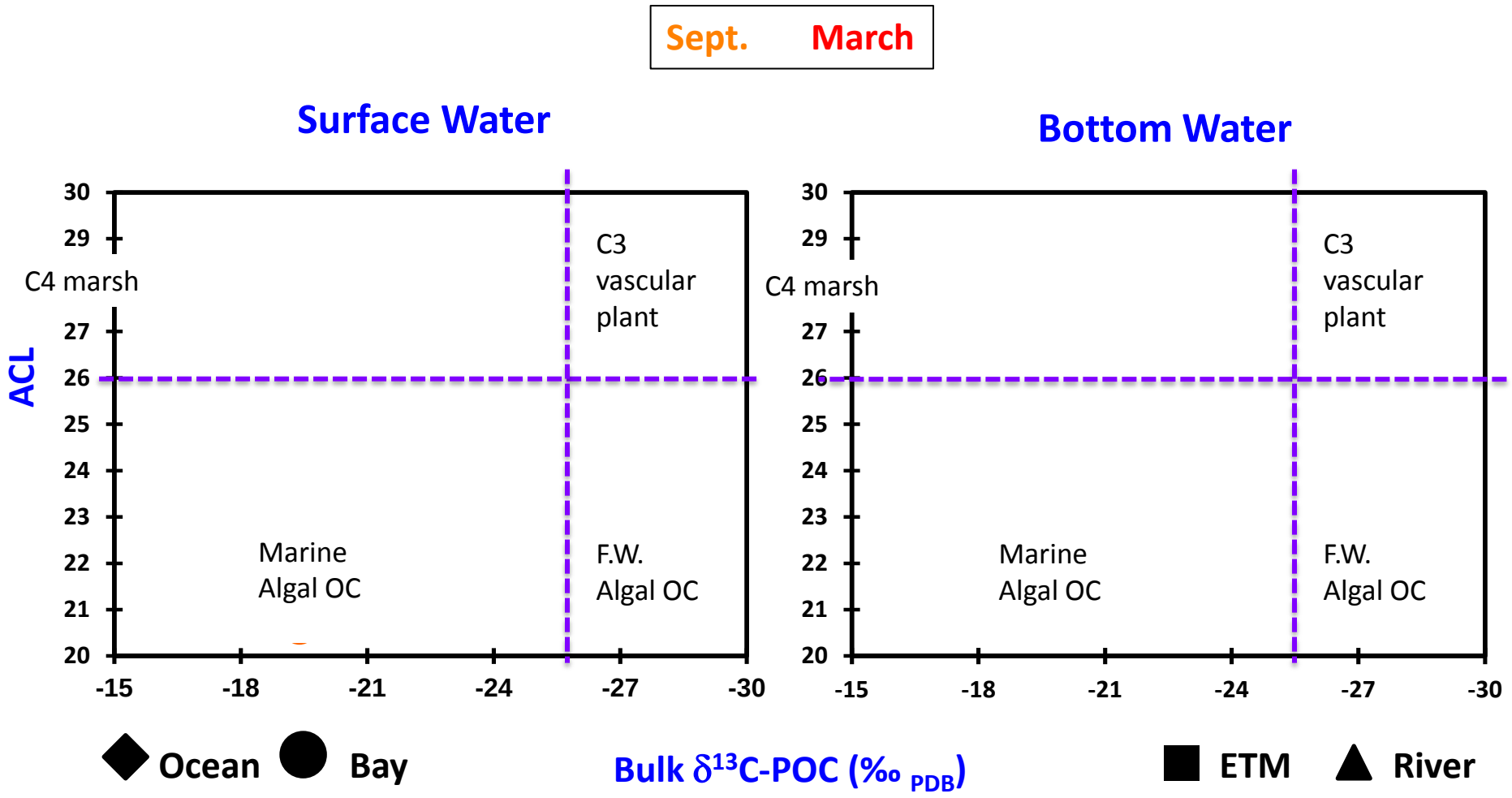


Surface and bottom water sampling targeted 4 zones of geochemical interest for biomarker analyses.

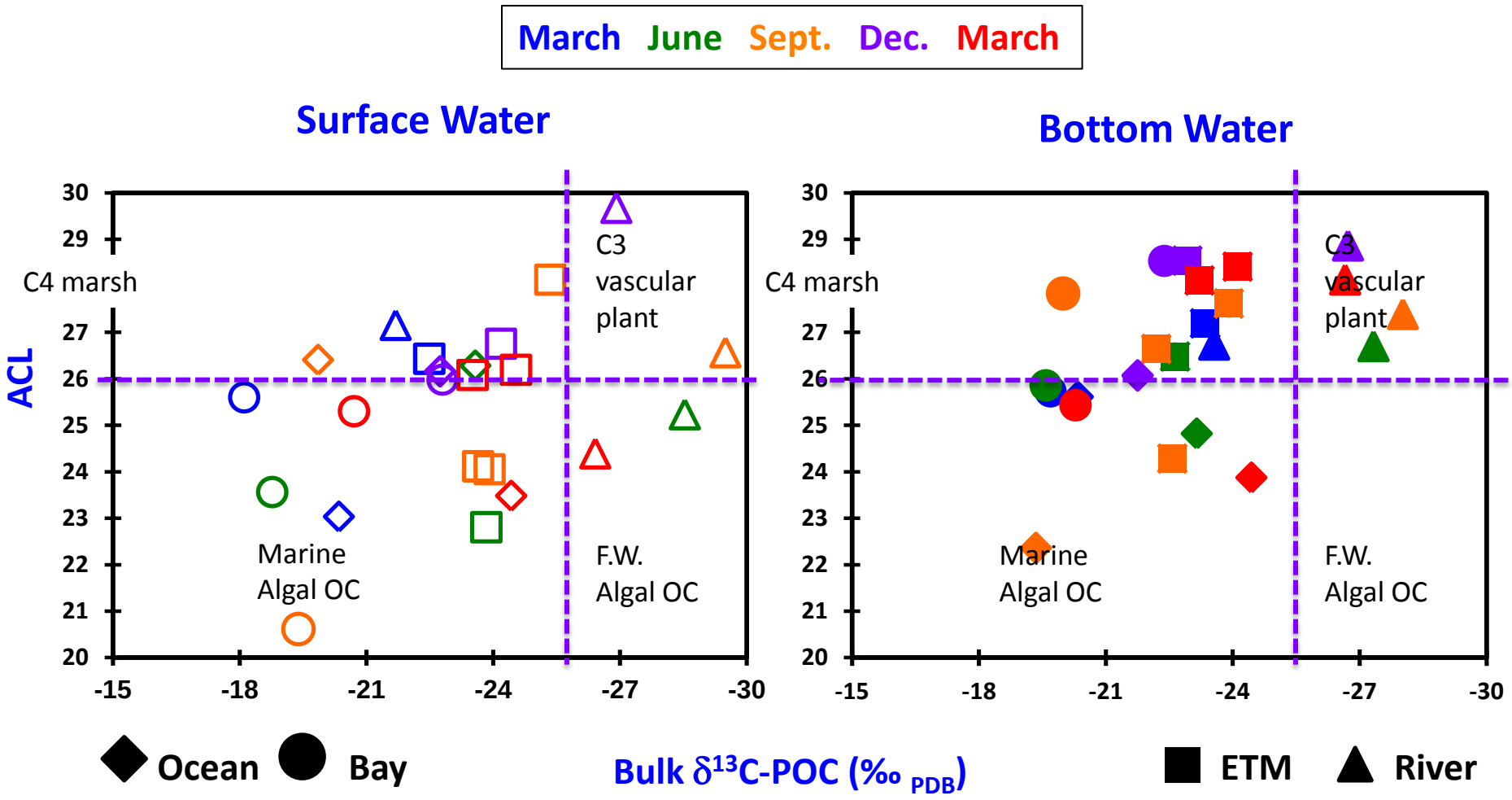


The Average Chain Length (ACL) index differentiates algal and vascular plant (land) OC.


30
28
26
24
22
20
ACL
C4 marsh
C3 vascular plant
Marine Algal OC
F.W. Algal OC
-10
-15
-20
-25
-30
Bulk δ13C-POC (‰ PDB)



Surface water is imprinted by seasonal algal OC throughout the estuary, but bottom water is consistently dominated by land OC.



Surface water is imprinted by seasonal algal OC throughout the estuary, but bottom water is consistently dominated by land OC.

Summary and Conclusions:
A new perspective of estuarine OC cycling

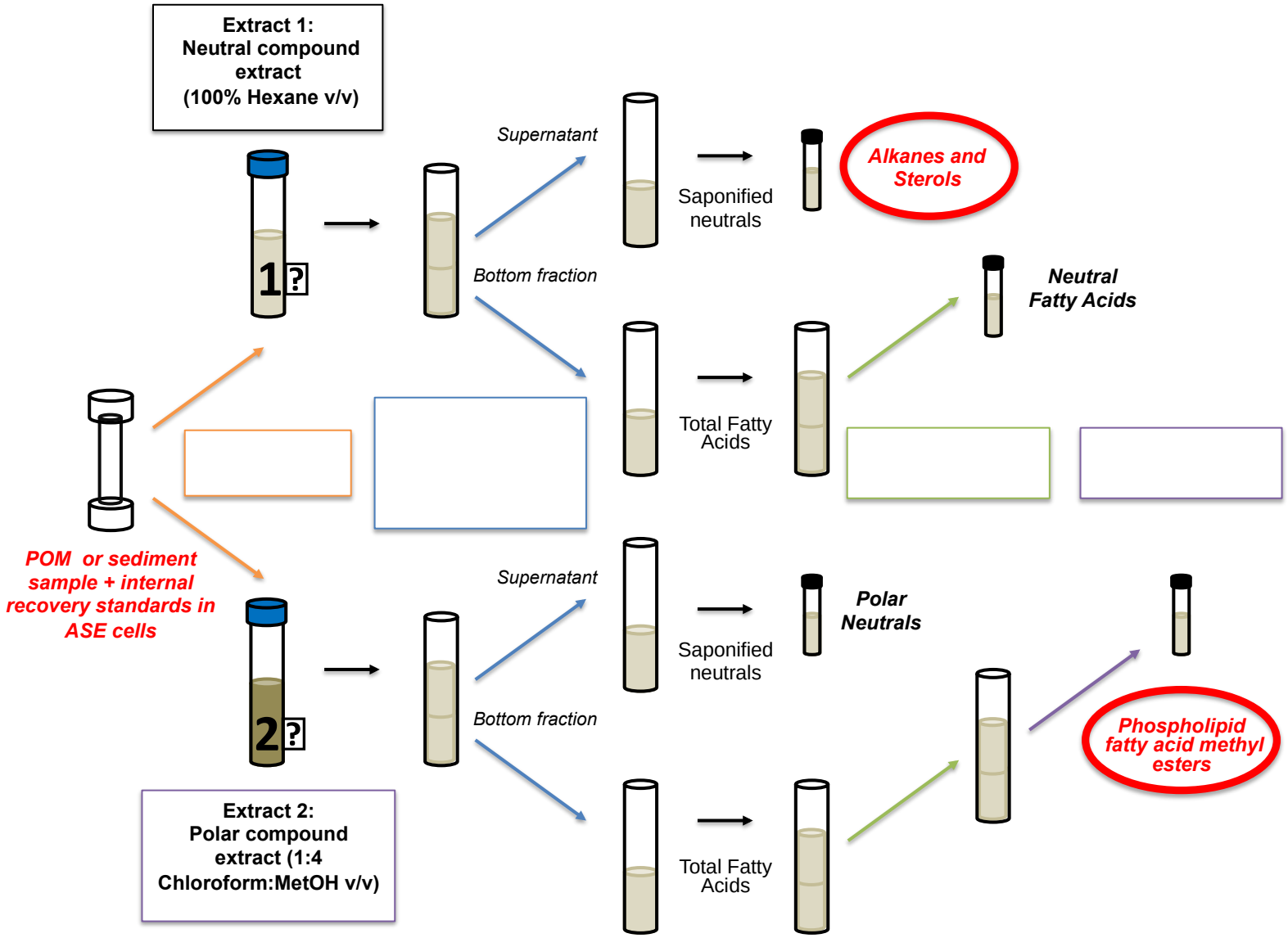
- There is more carbon in bottom waters than surface waters in the Delaware Estuary.

- The ETM traps vascular plant material, and as a reactor for OC processing, may fuel remineralization of terrestrial-derived OC, contributing to the net heterotrophy of estuaries.

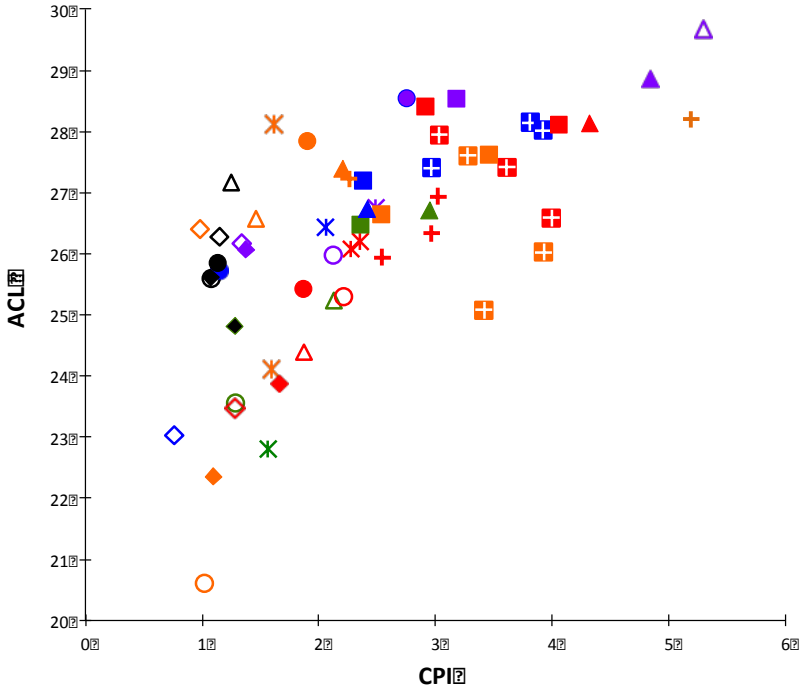
- Bottom water geochemical signatures, especially in the ETM, are imprinted by marsh OC, which is delivered to the estuary via lateral circulation.

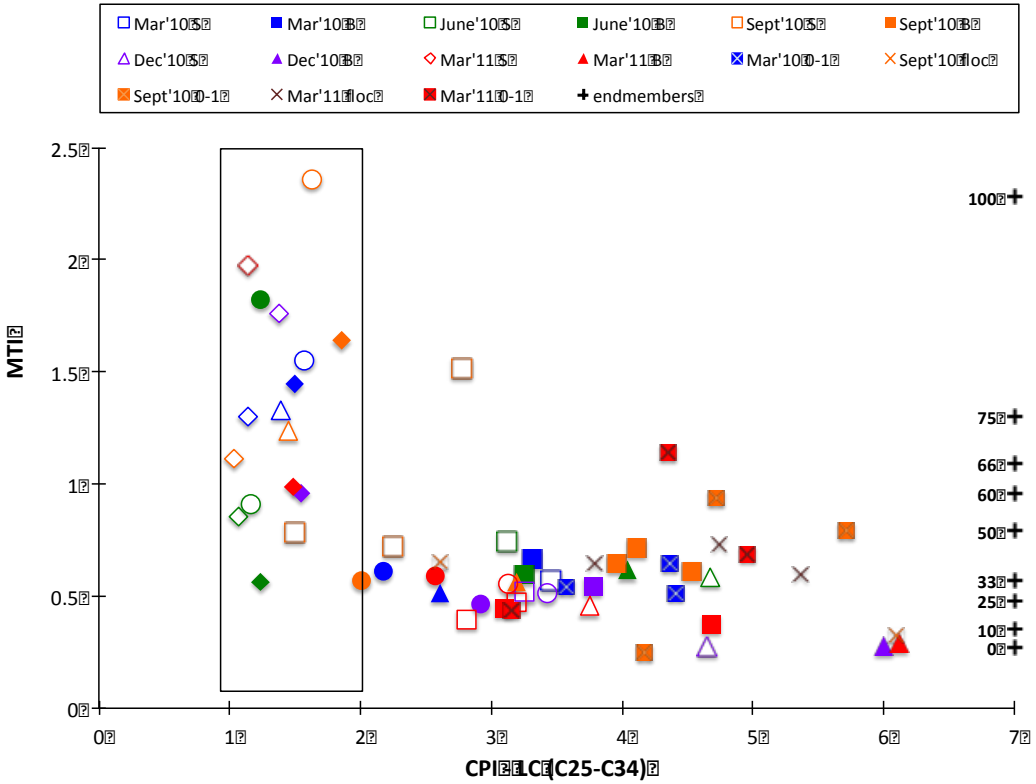
- **The land-derived OC reaching the marine OC cycle may have a different reactivity than previously thought due to its different pathway of delivery.**

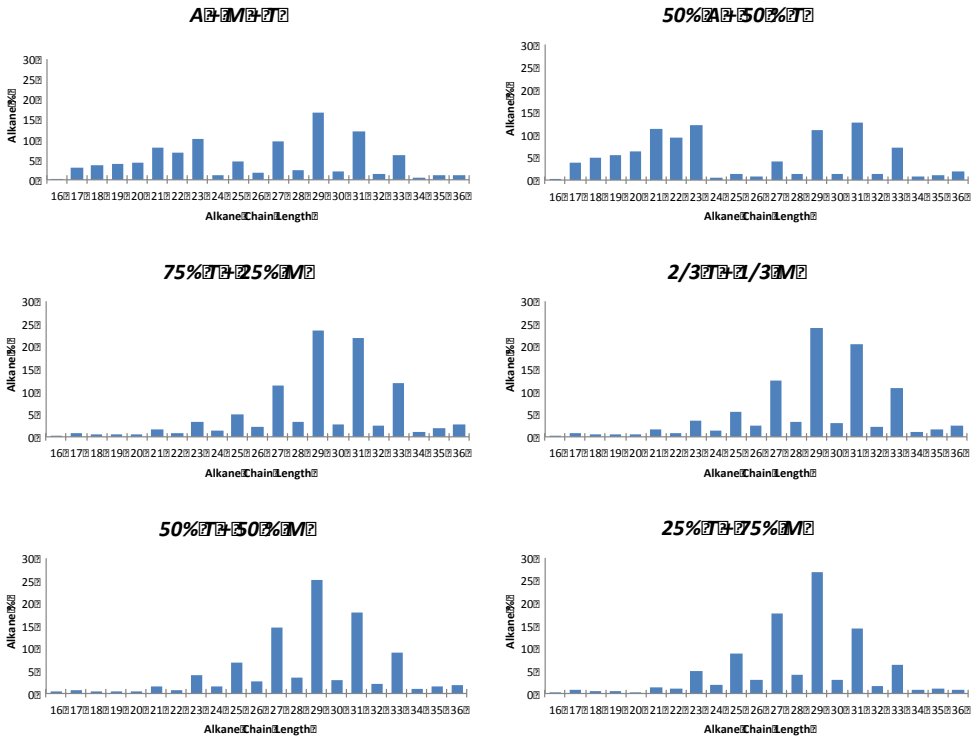
Wet chemistry flow chart

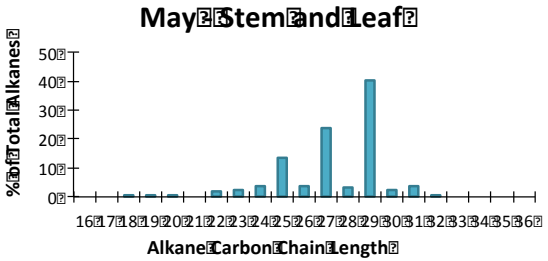


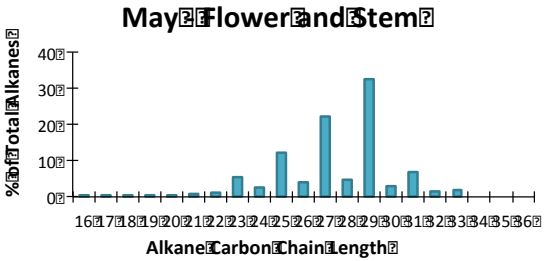
Sediments in the upper estuary are strongly terrestrial.

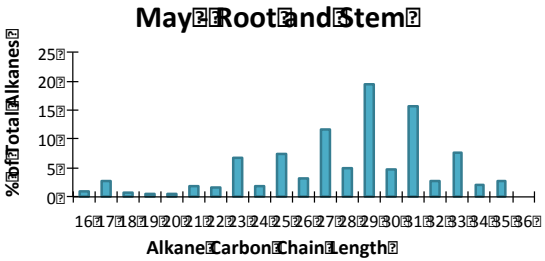


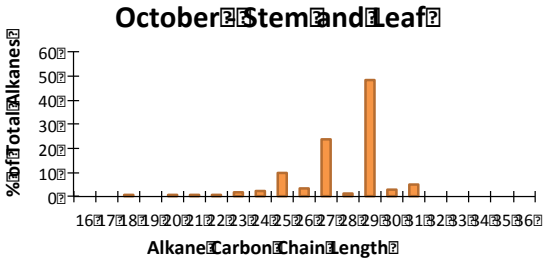

Mar'10
Mar'10
June'10
June'10
Sept'10
Sept'10
Dec'10
Dec'10
Mar'11
Mar'11
Mar'10
Sept'10
Sept'10
Mar'11
Mar'11
endmembers
MTI
2.5
2
1.5
1
0.5
0
0
1
2
3
4
5
6
7
CPI
LCE
(C25-C34)
100
75
66
60
50
33
25
10
0

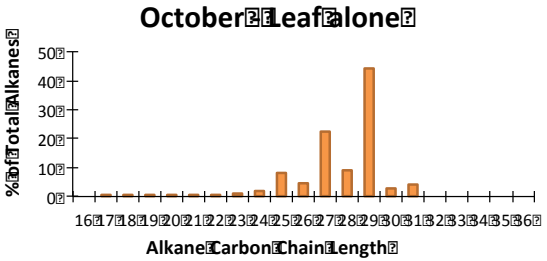

A + M + T
50% A + 50% T
75% T + 25% M
2/3 T + 1/3 M
50% T + 50% M
25% T + 75% M
Alkane %
Alkane Chain Length
16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36
0 5 10 15 20 25 30

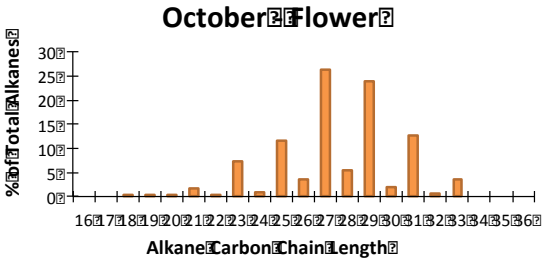

May Stem and Leaf
% of Total Alkanes
Alkane Carbon Chain Length

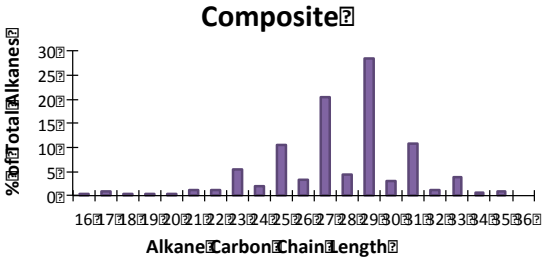

May Flower and Stem
% of Total Alkanes
Alkane Carbon Chain Length


May Root and Stem
% of Total Alkanes
Alkane Carbon Chain Length

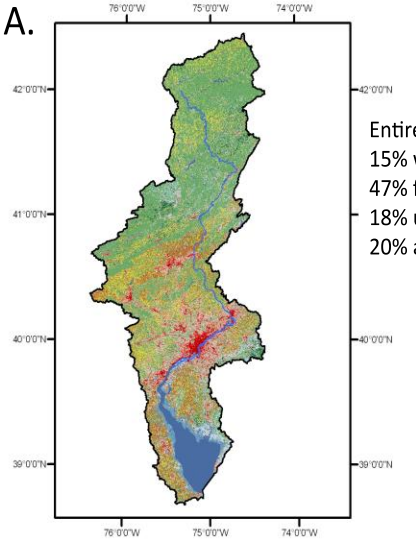

October Stem and Leaf
% of Total Alkanes
Alkane Carbon Chain Length


October Leaf alone
% of Total Alkanes
Alkane Carbon Chain Length


October Flower
% of Total Alkanes
Alkane Carbon Chain Length

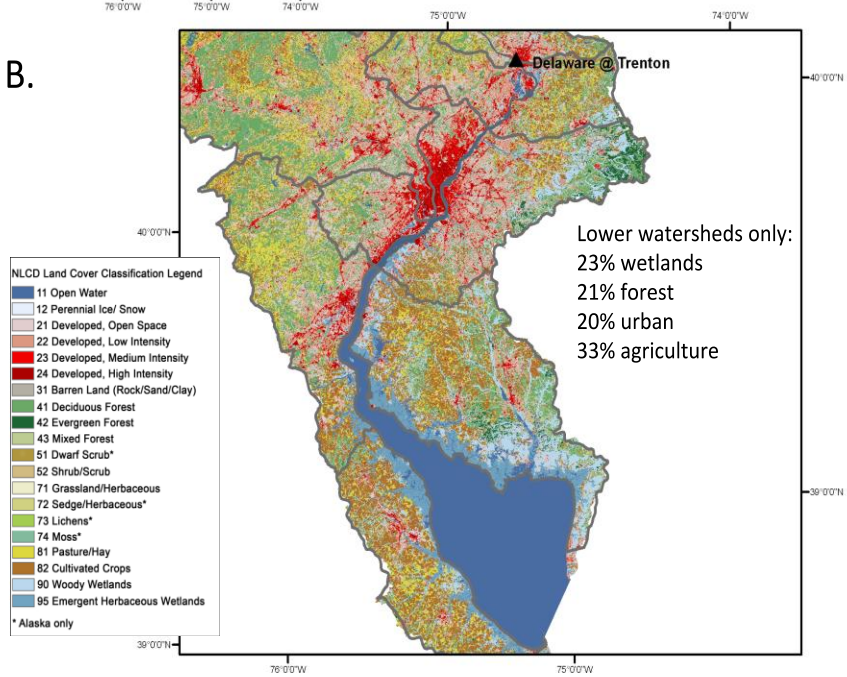

Composite
% of Total Alkanes
Alkane Carbon Chain Length

A.



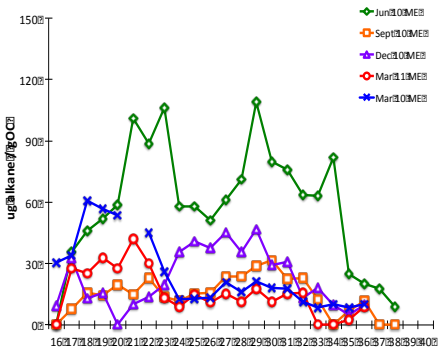
Entire watershed:
15% wetlands and open water
47% forest
18% urban
20% agriculture

B.

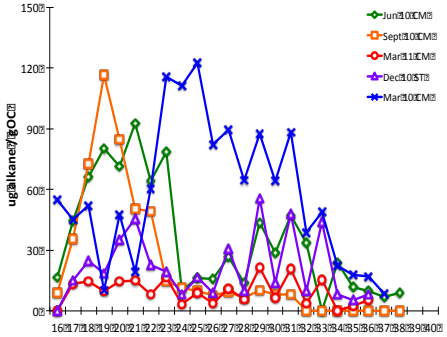


Lower watersheds only:
23% wetlands
21% forest
20% urban
33% agriculture

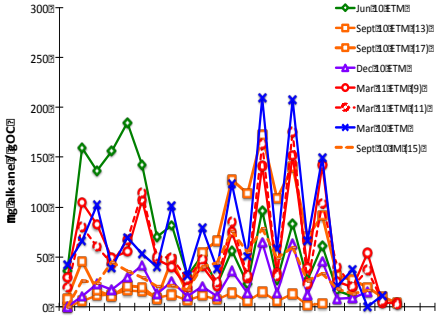
Marine Endmember Surface Water



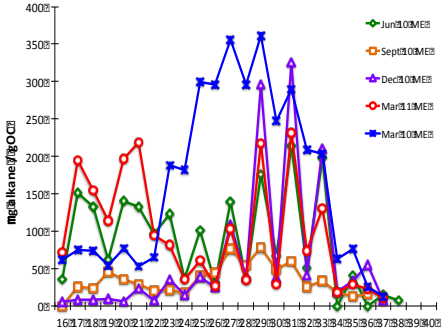
Delaware Bay Surface Water



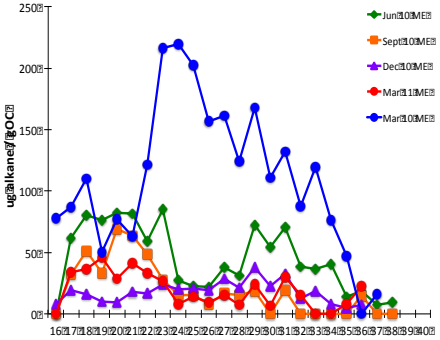
ETM Surface Water



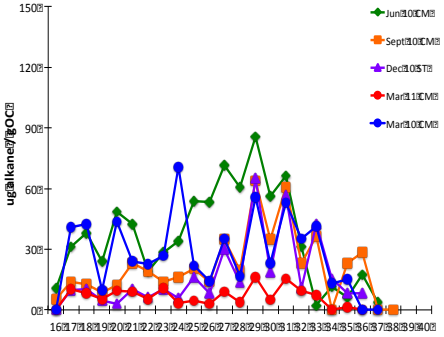
RE Surface Water



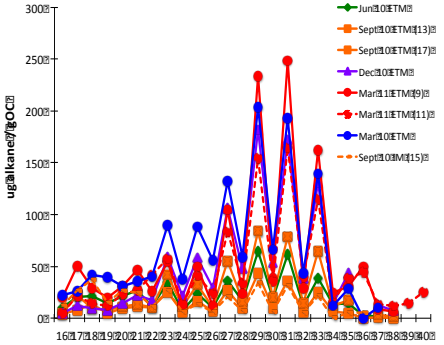
Marine Endmember Bottom Water



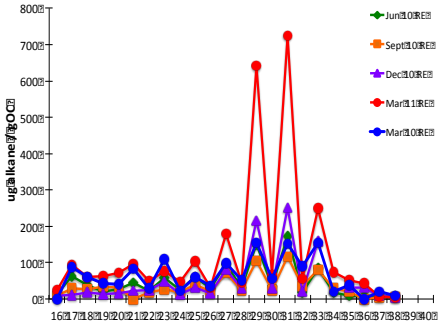
Delaware Bay Bottom Water

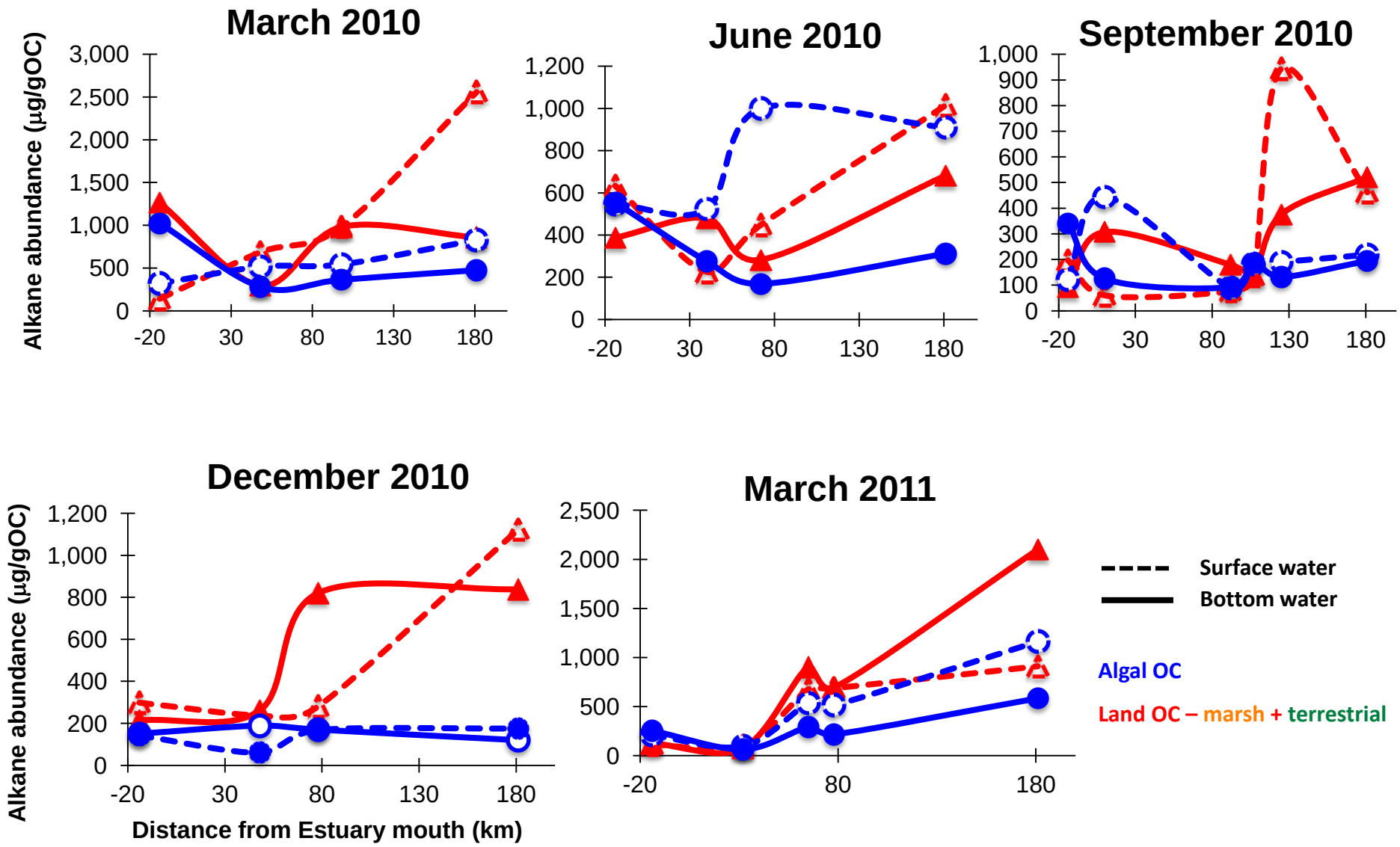


ETM Bottom Water

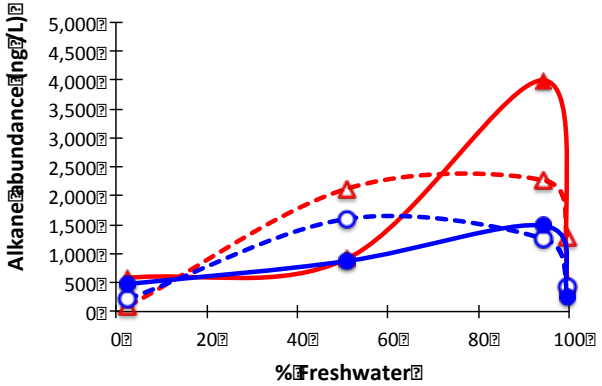


RE Bottom Water

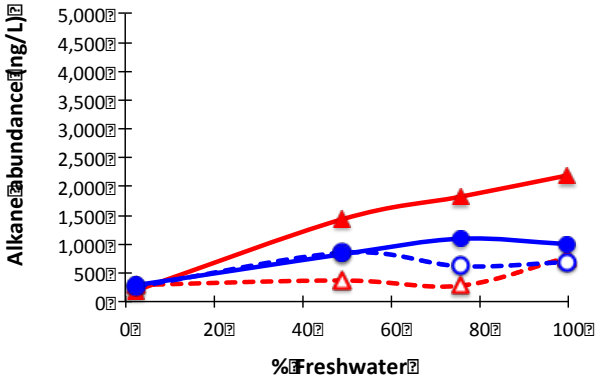



March 2010
June 2010
September 2010
December 2010
March 2011
Alkane abundance (µg/gOC)
Distance from Estuary mouth (km)
Surface water
Bottom water
Algal OC
Land OC – marsh + terrestrial

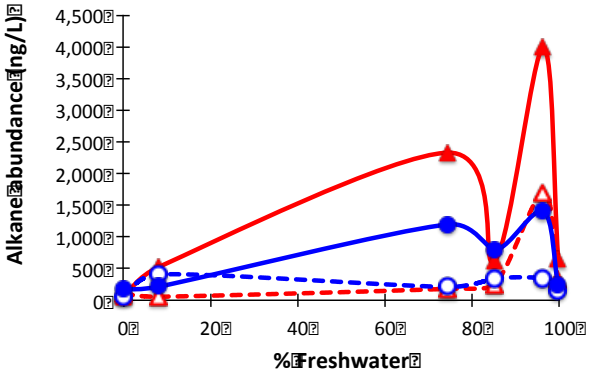
March 2010



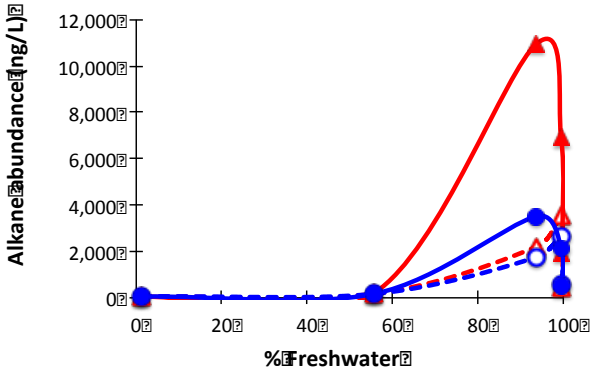
June 2010



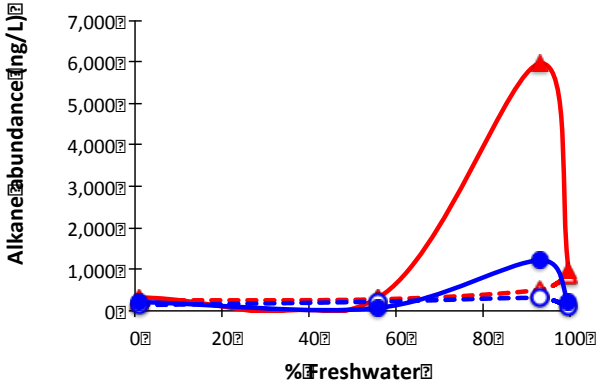
September 2010



March 2011



December 2010

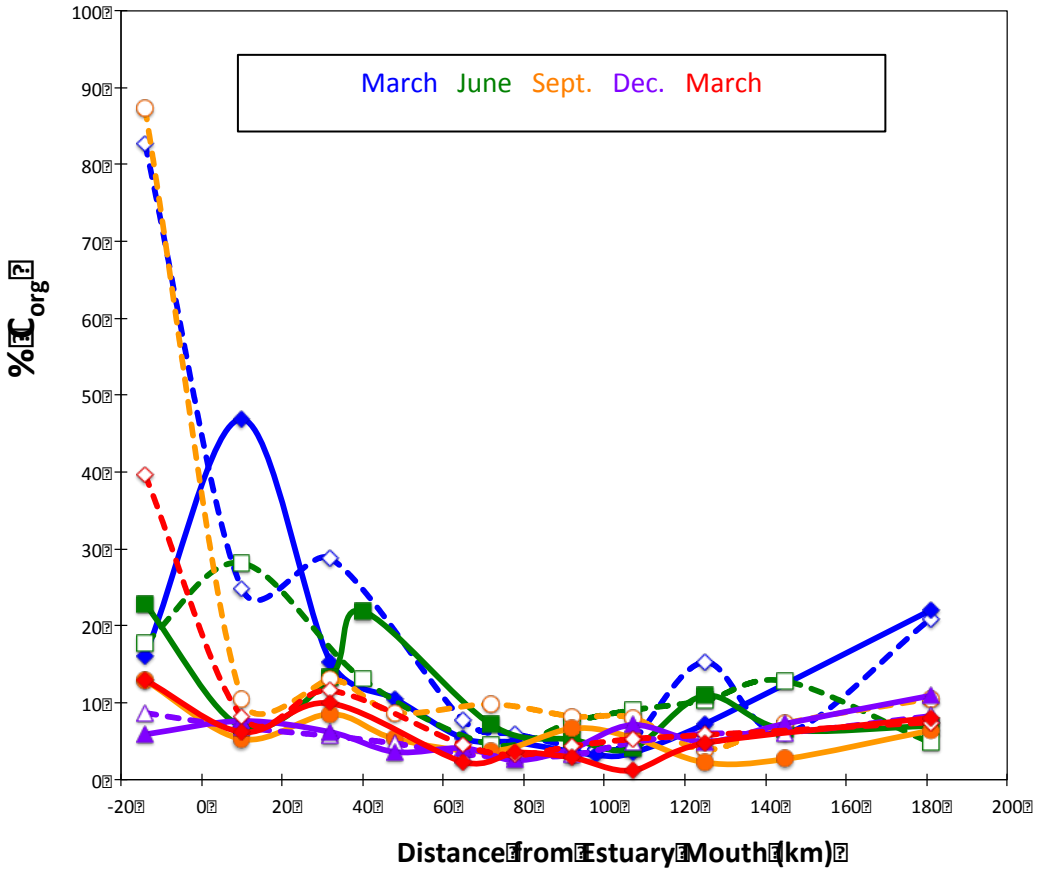


Surface water

Bottom water

Algal OC

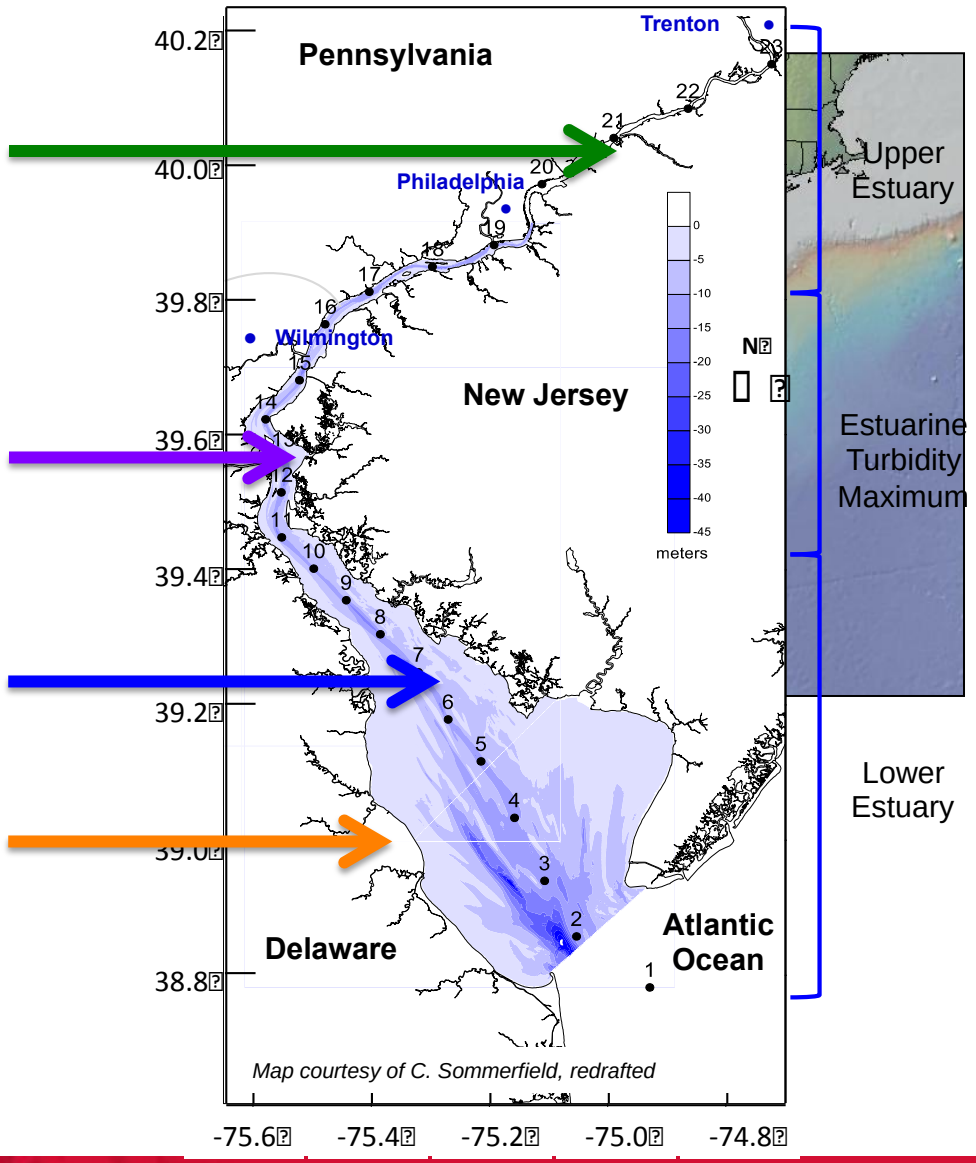
Land OC – marsh + terrestrial

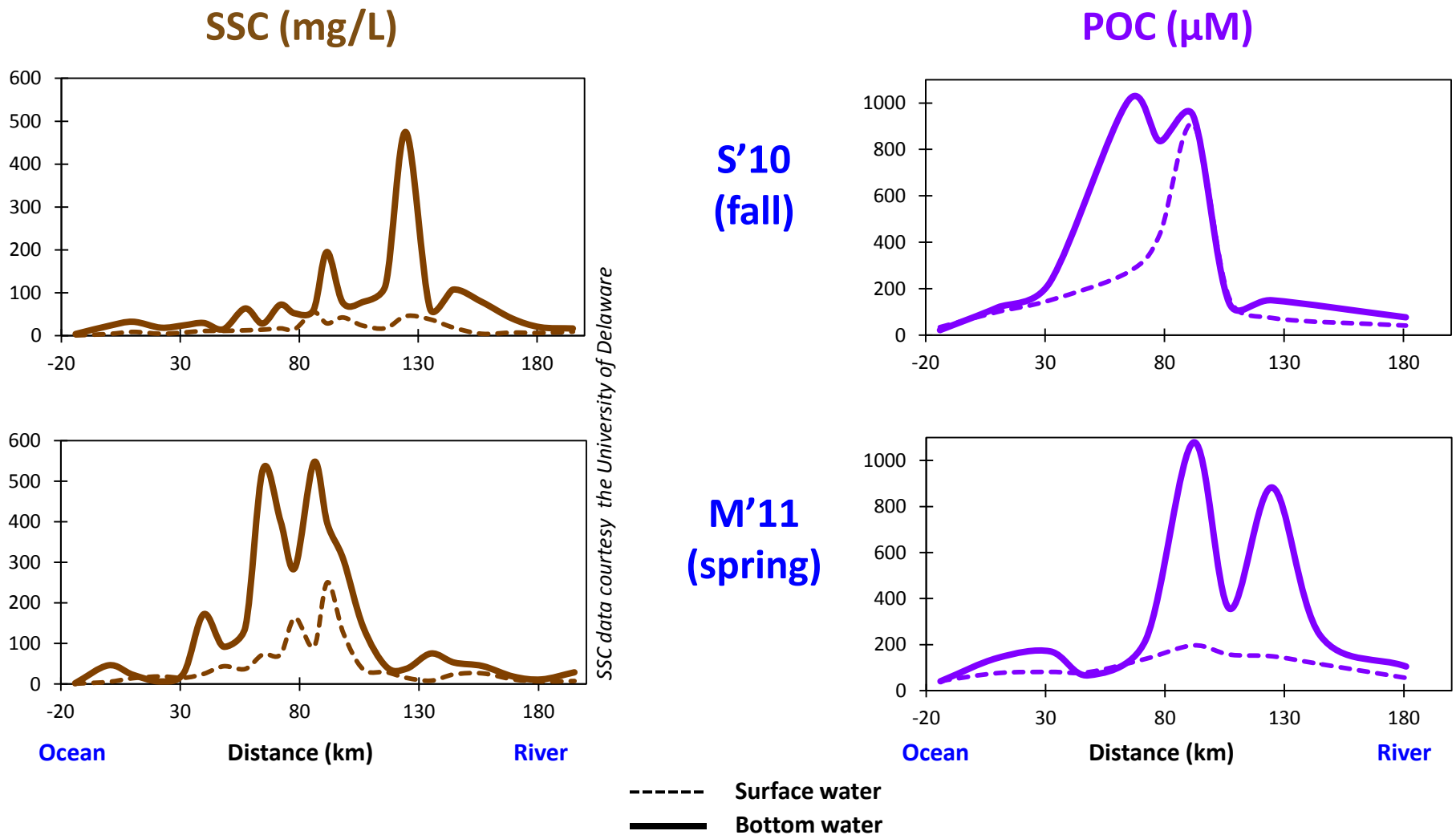

March June Sept. Dec. March
100
90
80
70
60
50
40
30
20
10
0
-20
0
20
40
60
80
100
120
140
160
180
200
%C_org
Distance from Estuary Mouth (km)

The Delaware Estuary is a model system to assess OC cycling.

Reasons why:

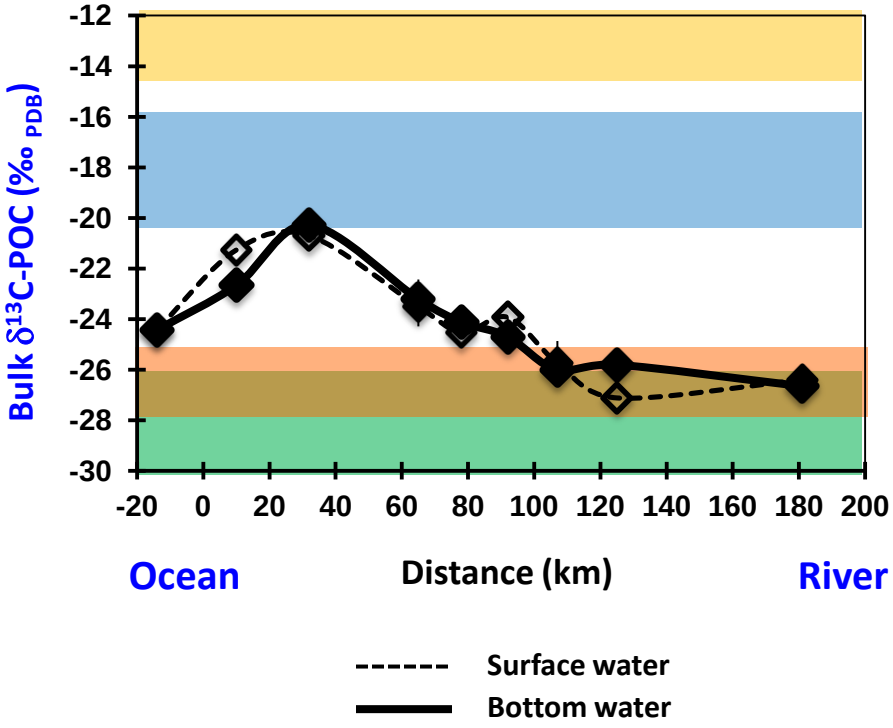
- Well-studied
- Archetypal coastal plain estuary
- Multiple sources of OC
  - **Terrestrial OC** from Delaware River
  - **Algal OC** from seasonal blooms
  - Extensive wetlands – **marsh OC**
- **ETM –** particle trap and MIXING ZONE! (Sommerfield and Wong, 2011, *J. of Geophys. Res.*)

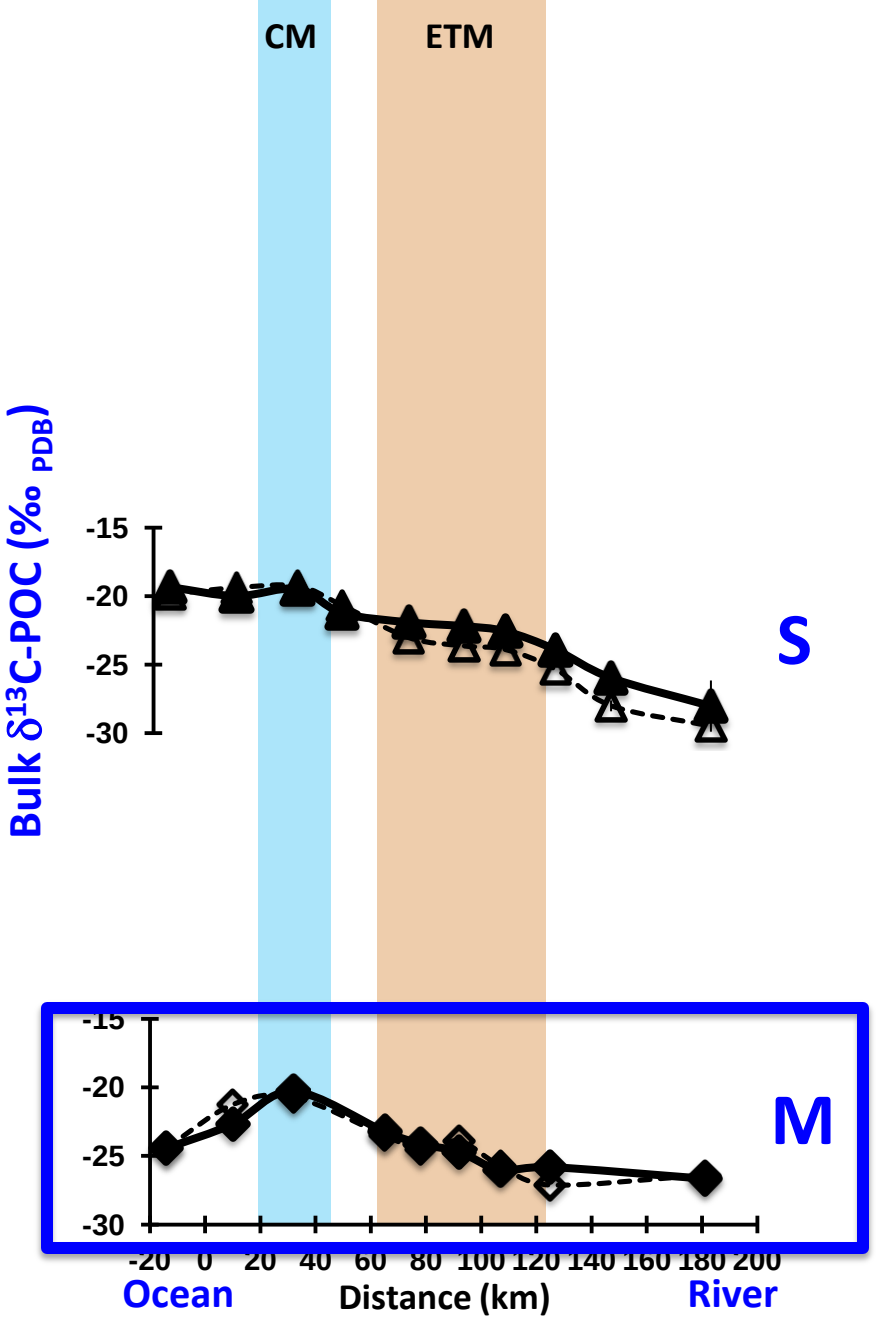




Sus More OC in bottom water than surface water! catter.

M - 2011





The bulk stable carbon isotopic composition of POC differentiates seasonal **algal** blooms in the lower estuary and **C3 vascular plant** OM in the upper estuary.

- Preen and Kirchman 2004