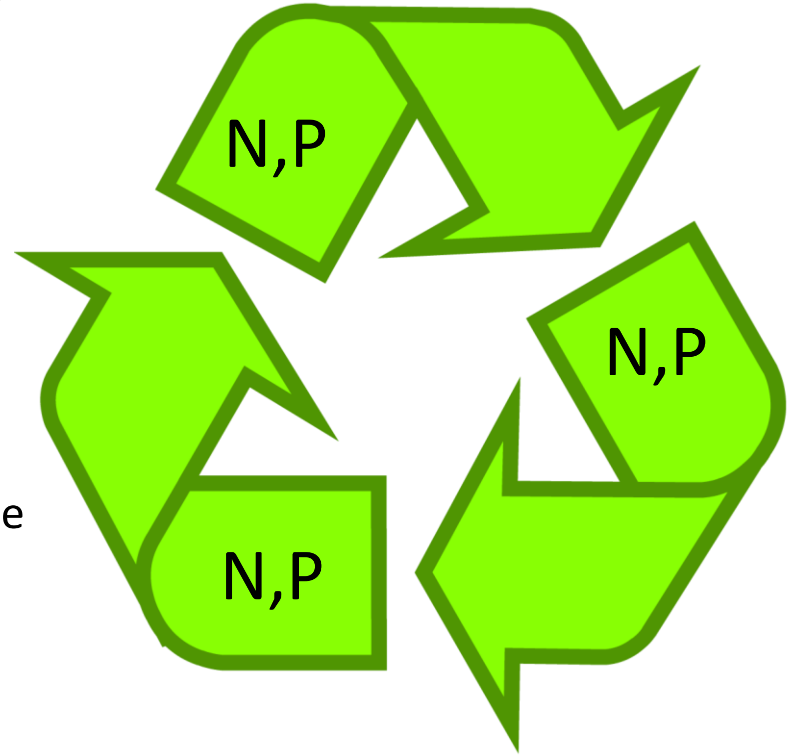
How do input loads and internal cycling affect hypoxia in Chesapeake Bay?

......and how does hypoxia affect internal cycling and fate of input loads in the estuary?



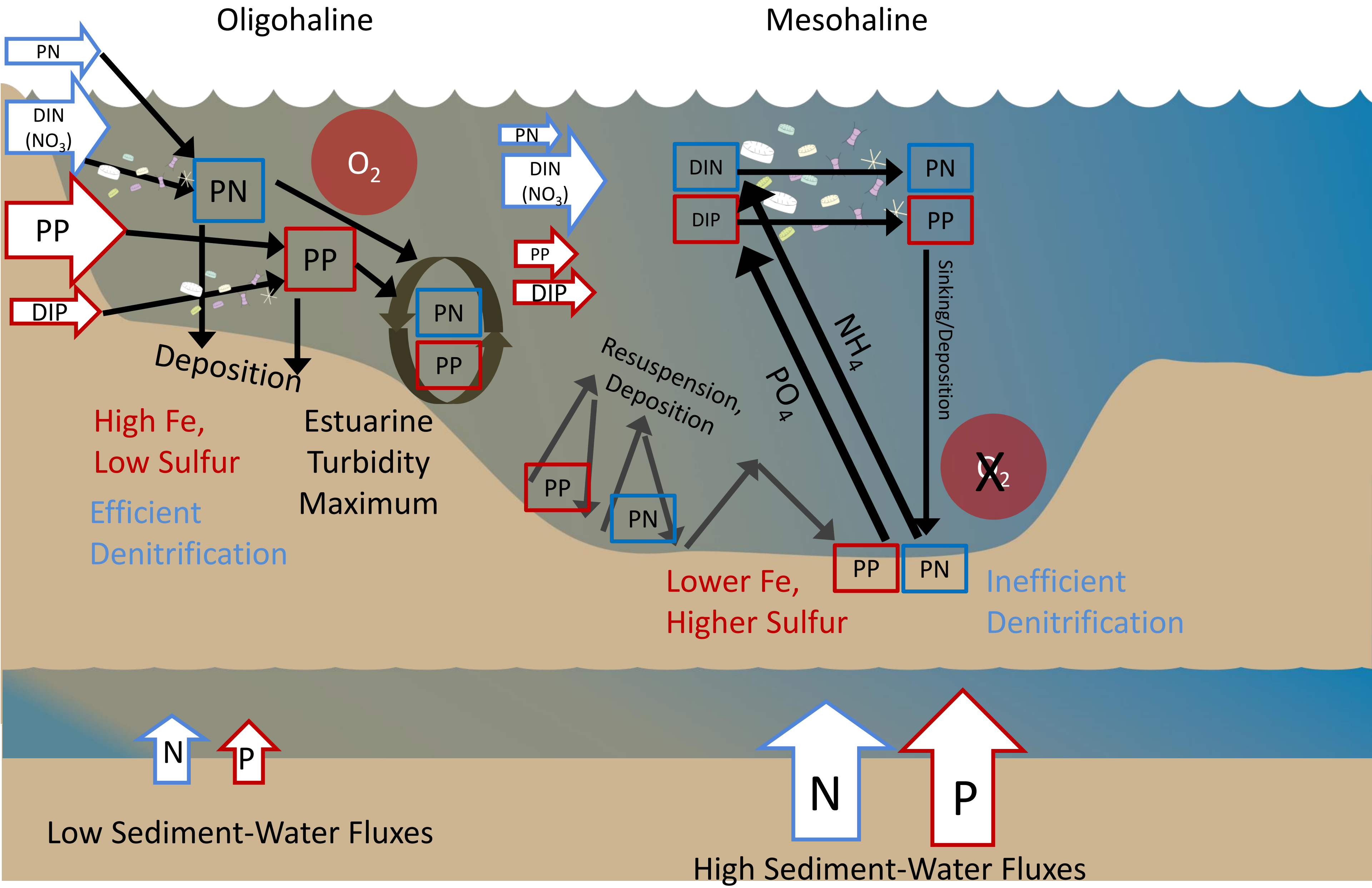
Jeremy Testa
University of Maryland Center for Environmental Science
Chesapeake Biological Laboratory
Solomons, Maryland, USA

University of Maryland
CENTER FOR ENVIRONMENTAL SCIENCE

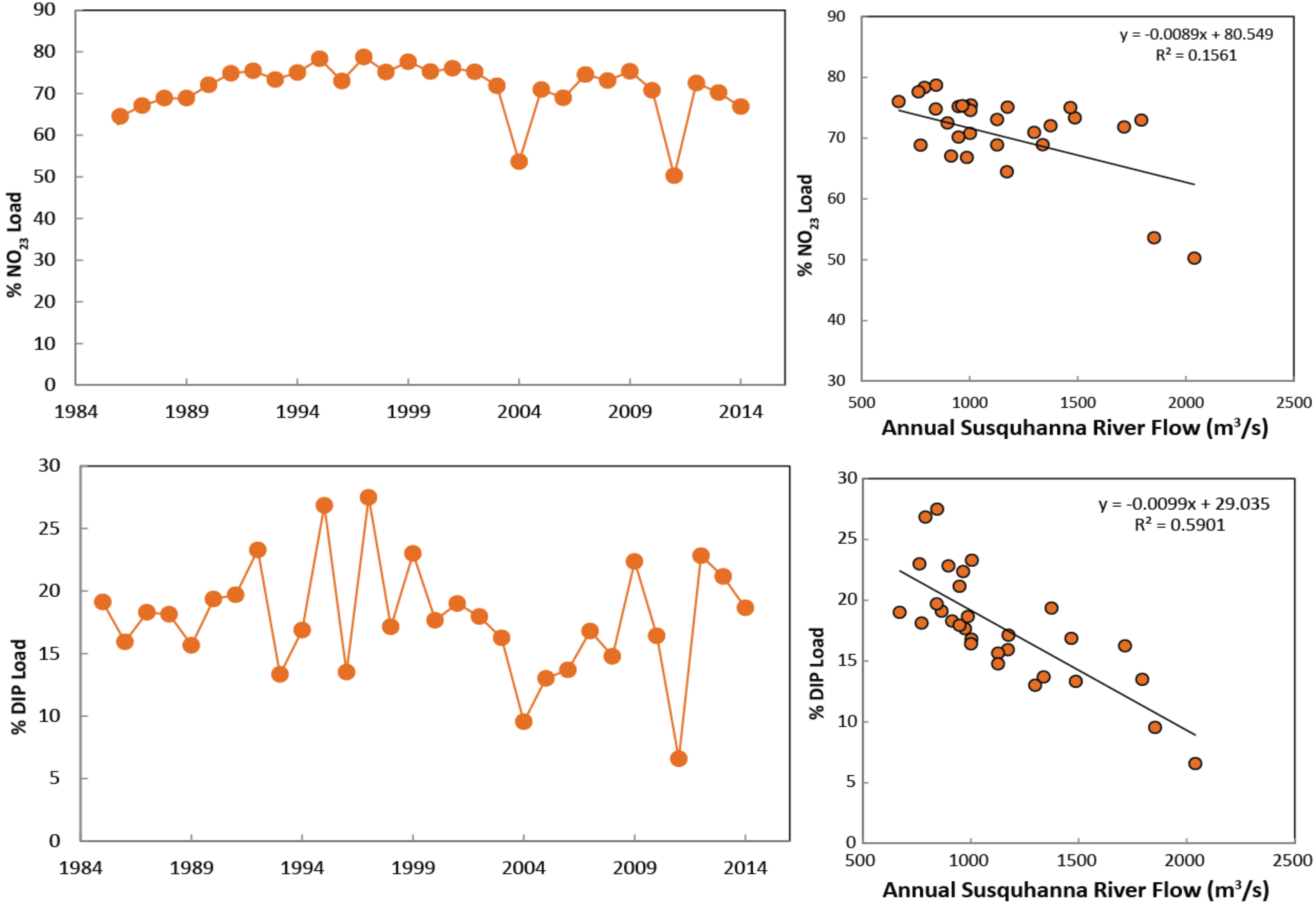
Outline

- A conceptual picture of how watershed-derived nutrients are distributed and processed within the estuary
- The modes in which these nutrients drive hypoxia
- The potential for non-dissolved materials to become bioavailable and measurably impact hypoxia
- The role and control of internal processing (i.e., ‘internal loading’) of nutrients and implications for eutrophication

Regional Variability in Inputs, Transport and Biogeochemistry



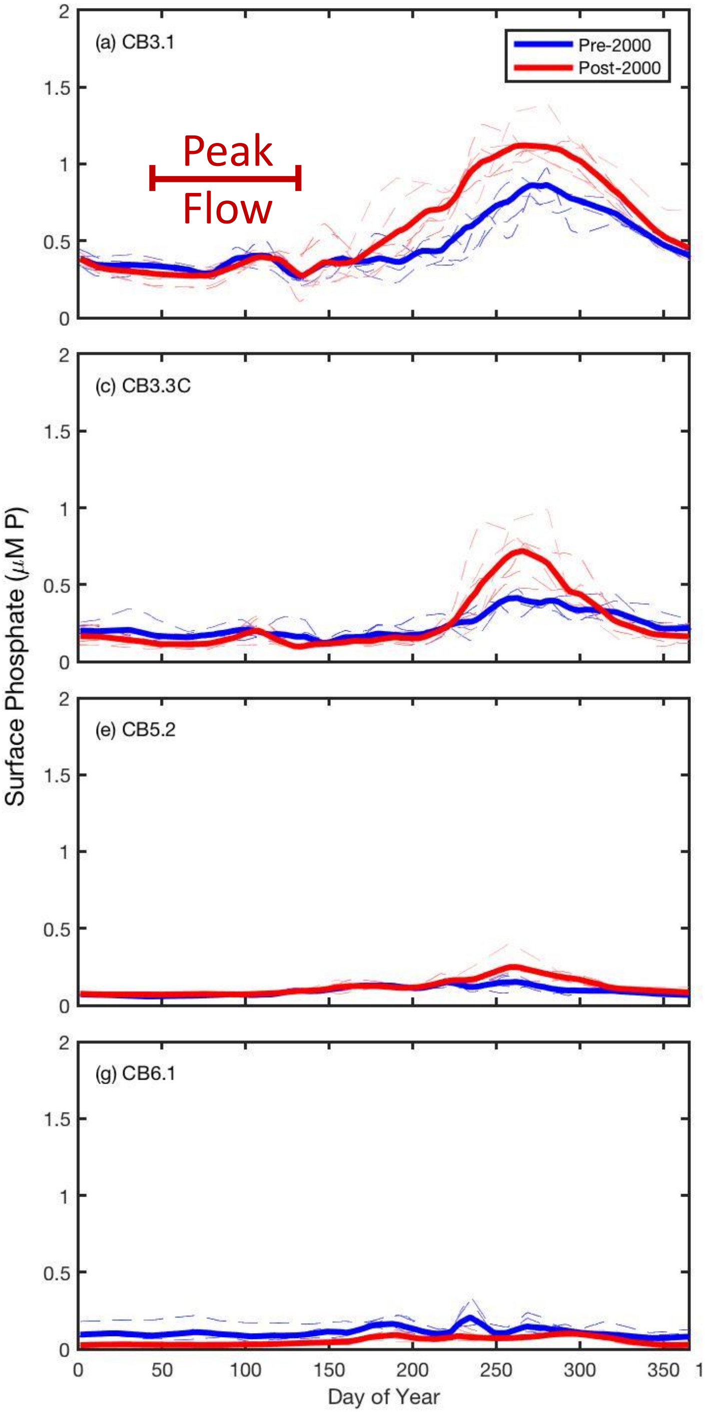
Dissolved N Dominates TN Input, Particulate P Larger Fraction of TP

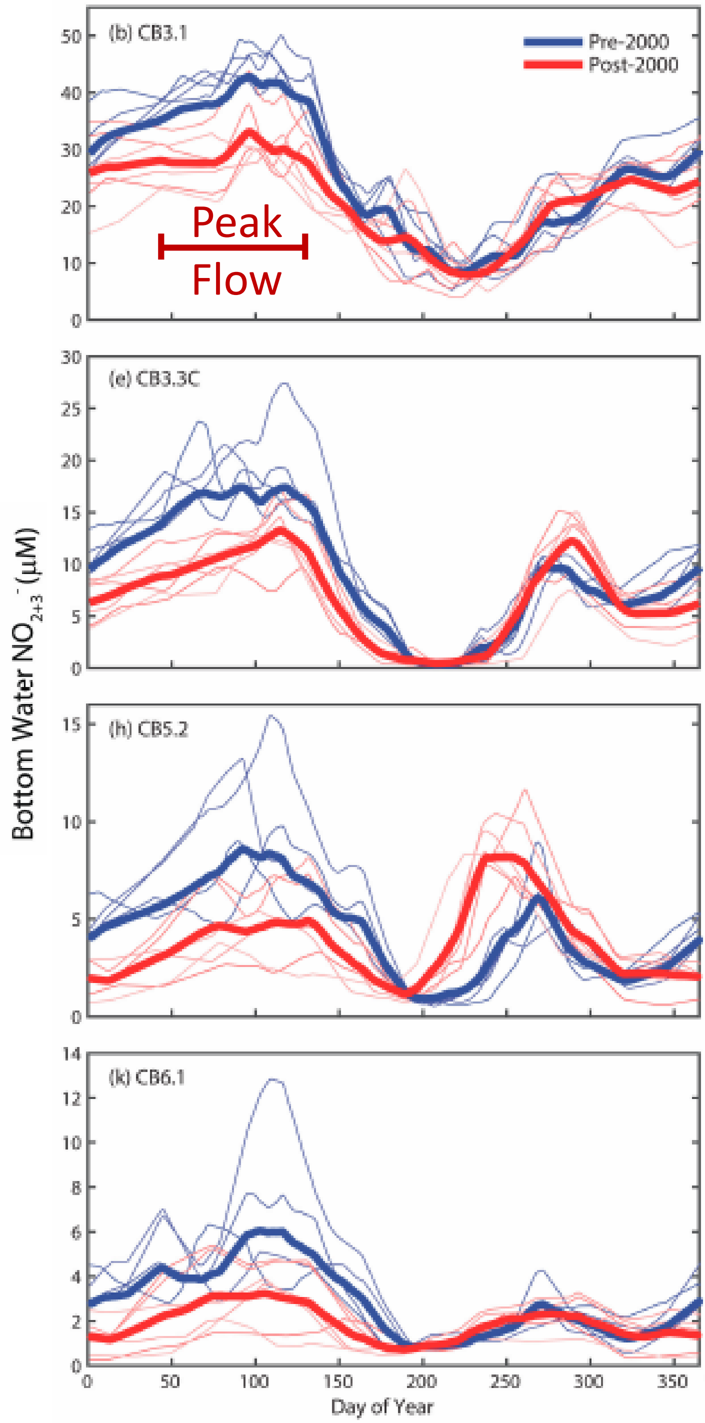


Data reanalyzed from Zhang et al. (2016)

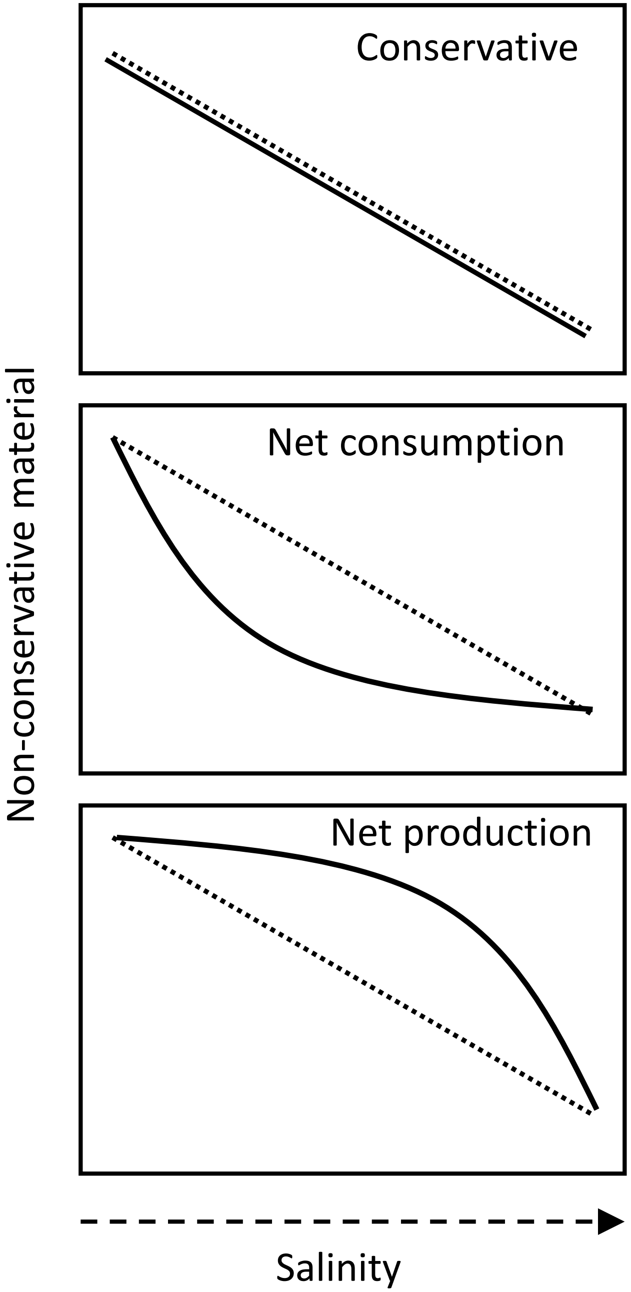
Dissolved N, P in Estuary Reveal Role of DIN, TP Input

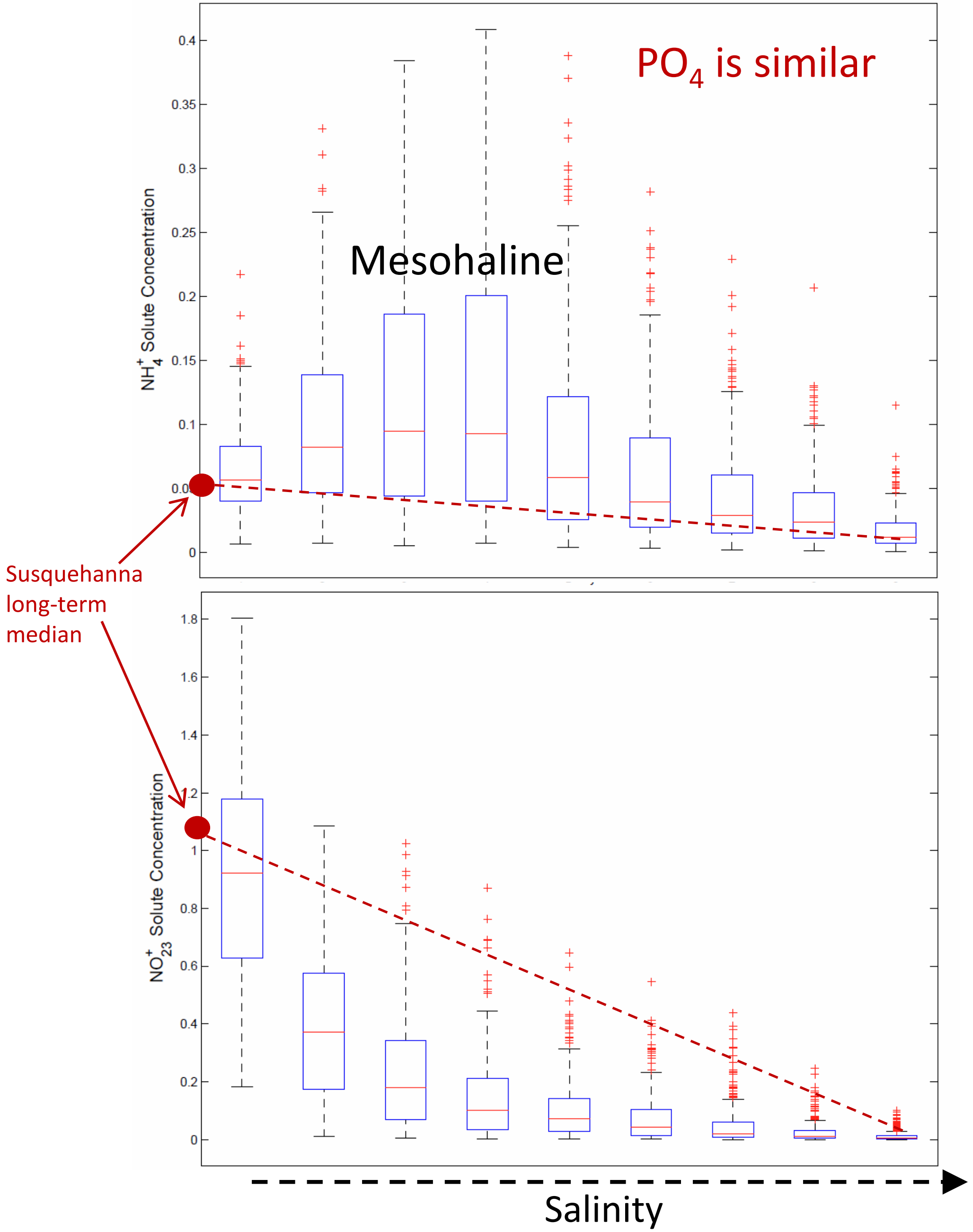
- No PO_4 peaks during peak flow
- PO_4 peaks in late summer everywhere
- NO_{23} peaks in winter-spring with peak flow





Mixing Diagrams to Interpret Estuarine Transformations




PO_4 is similar

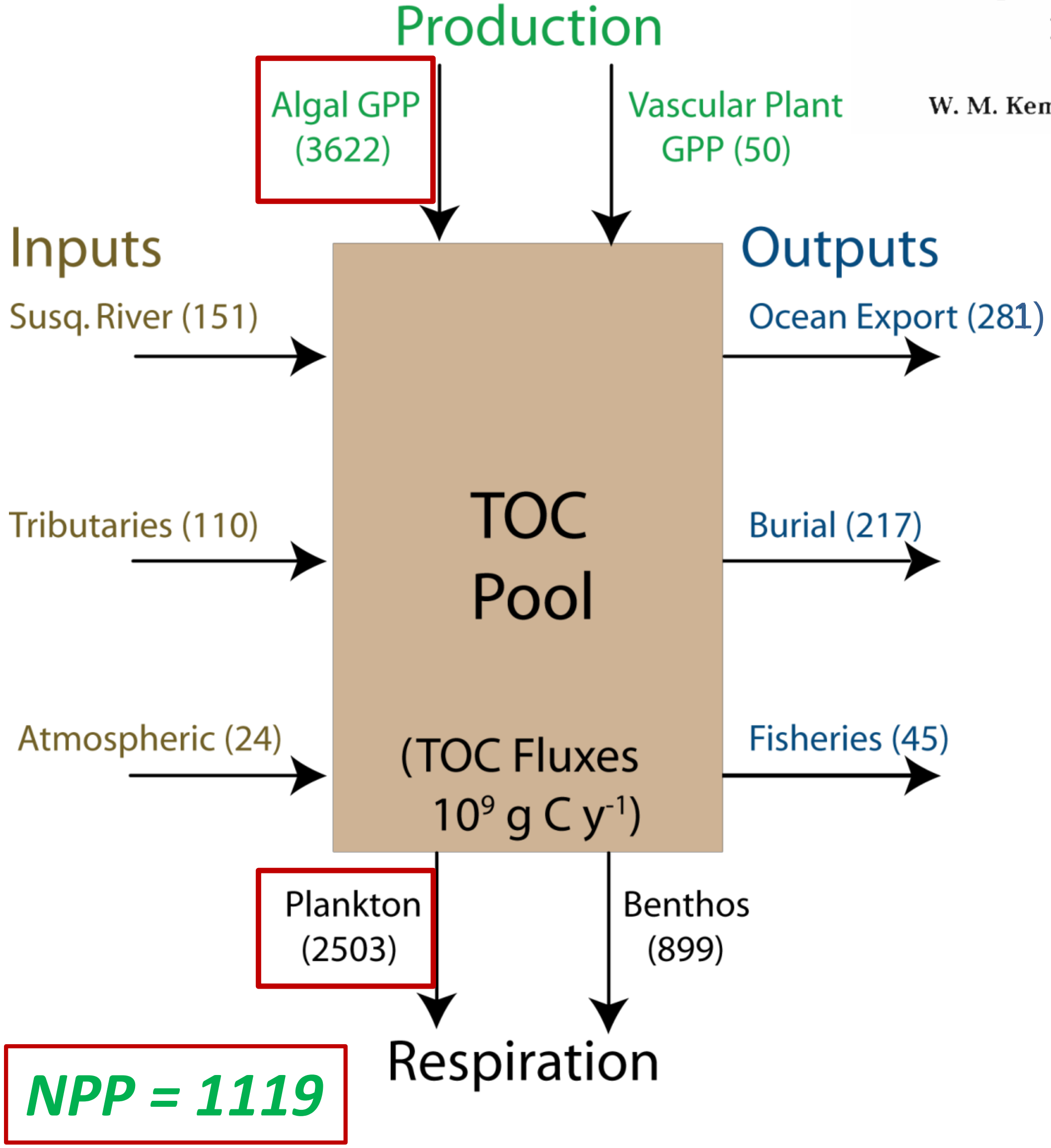
Mesohaline

Susquehanna long-term median

Vol. 150: 229–248, 1997 | MARINE ECOLOGY PROGRESS SERIES
Mar Ecol Prog Ser | Published April 30

Organic carbon balance and net ecosystem metabolism in Chesapeake Bay

W. M. Kemp[1,*], E. M. Smith[1], M. Marvin-DiPasquale[2,**], W. R. Boynton[2]



Production

Algal GPP (3622)

Vascular Plant GPP (50)

Inputs

Susq. River (151)

Tributaries (110)

Atmospheric (24)

TOC Pool

(TOC Fluxes 10^9 g C y^{-1})

Outputs

Ocean Export (281)

Burial (217)

Fisheries (45)

Plankton (2503)

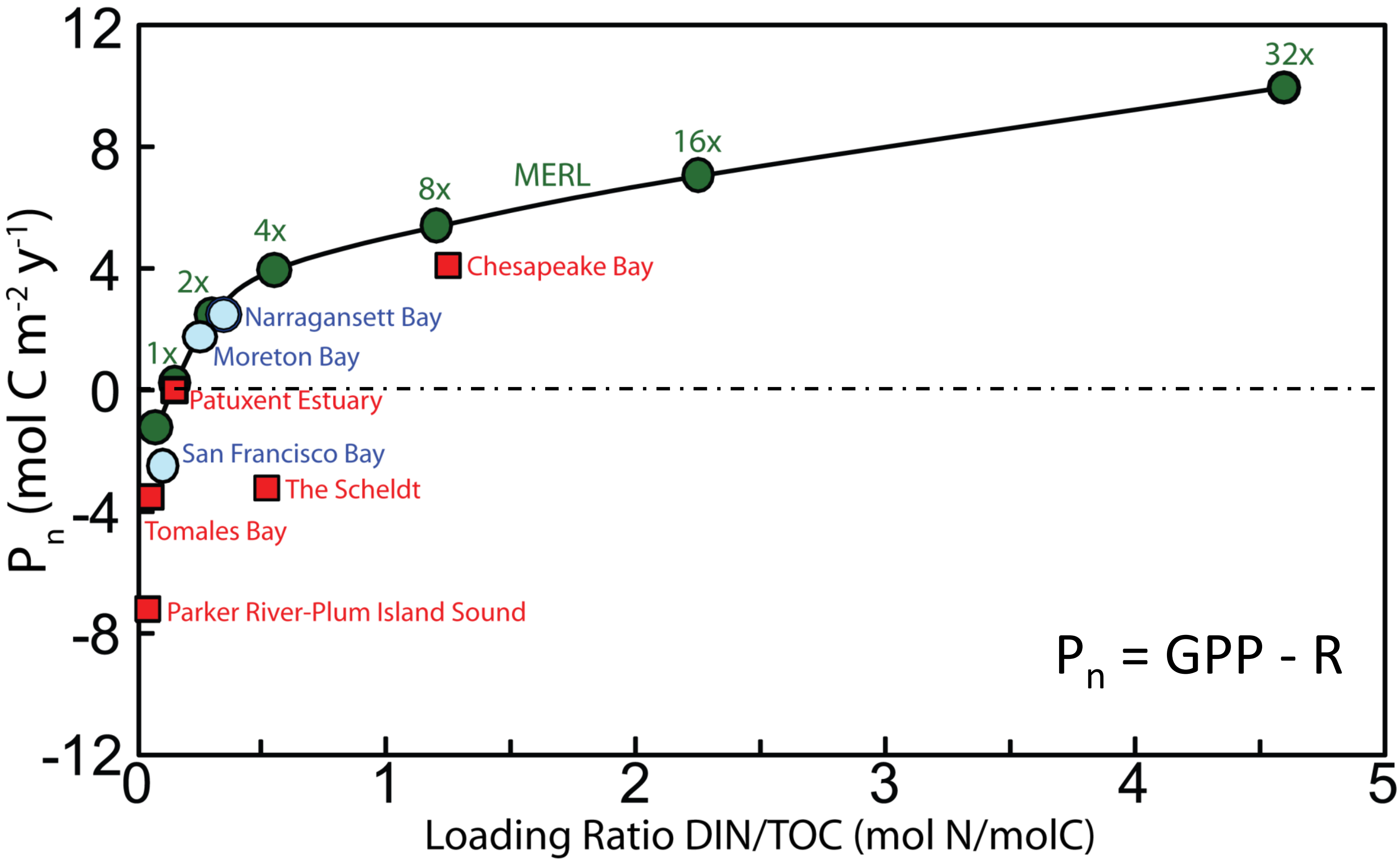
Benthos (899)

Respiration

NPP = 1119

- Phytoplankton dominate organic matter pools
- Our ability to control hypoxia rests with controlling these pools
- Nutrients that support these pools primarily enter in dissolved form
- The recycling of these nutrients in driven by a combination of processes varying over space, time

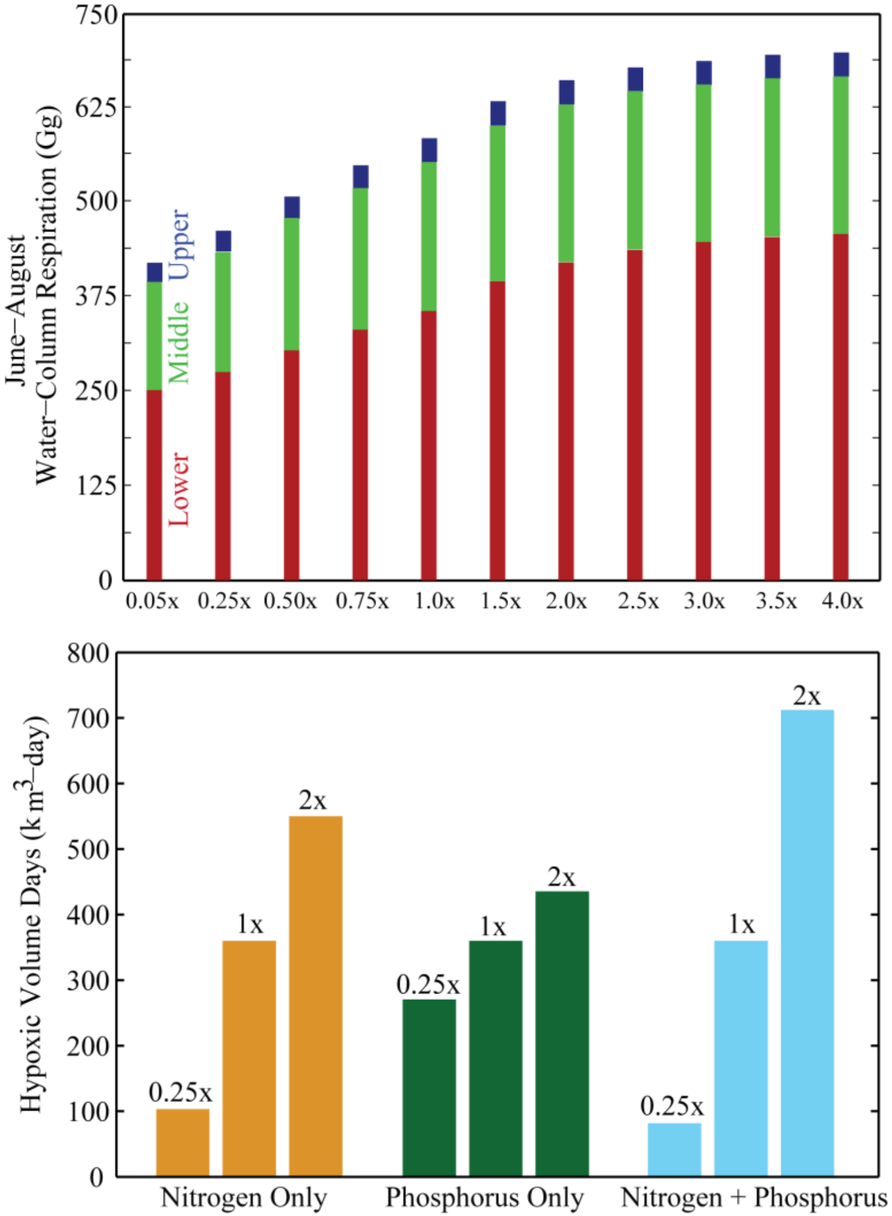
Net Algal Carbon Production To Support Hypoxia Supported by Relative DIN Excess in Load



$P_n = GPP - R$

Kemp et al. 1997, Herrmann et al. 2015

Most Models Suggest that Hypoxia Responds to Both Nitrogen and Phosphorus Load Changes



Testa et al. 2016

- Experimental N and P enrichment, holding physics constant
- More sensitive to N than P – mostly a function of far greater N-limited waters in modeled mainstem
- Increase in oxygen consumption driven by seaward waters

What Do We Know About the Cycling of N and P within the Estuary?

Particulate Phosphorus “Bioavailability”

Water Column

- Desorption in the water column (± salinity) driven by physical chemistry or biological uptake
- Decomposition of organic P
- pH-related Fe-bound P release

Sediment

- Release of P adsorbed/co-precipitated with Fe oxides via iron reduction (w/o sulfides)
- Release of Fe oxide-bound P via conversion of Fe oxides to Fe sulfides
- Release of Fe-bound P via high pH
- *Not all Fe-bound P is released in sulfidic CB sediments – (0.16 mg P g^{-1} buried)*[1]

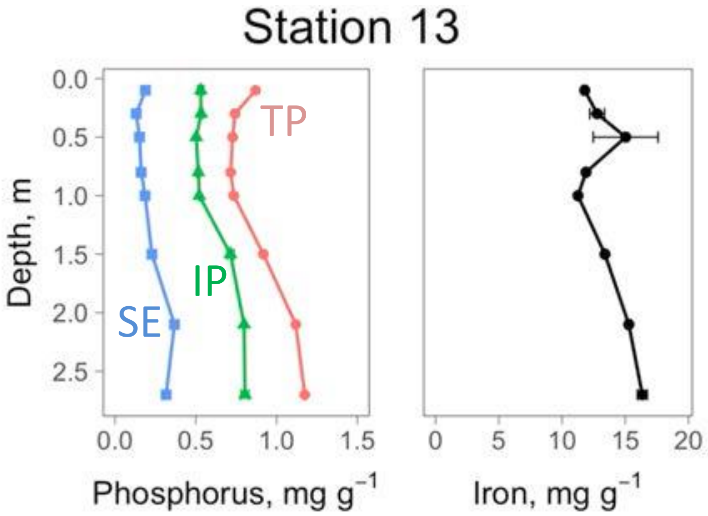
[1] Joshi, S. R., R. K. Kukkadapu, D. J. Burdige, M. E. Bowden, D. L. Sparks, and D. P. Jaisi. 2015. Organic Matter Remineralization Predominates Phosphorus Cycling in the Mid-Bay Sediments in the Chesapeake Bay. Environmental Science & Technology 49: 5887-5896.

Particulate N “bioavailability” is relatively simple

– a matter of reactivity of OM and denitrification

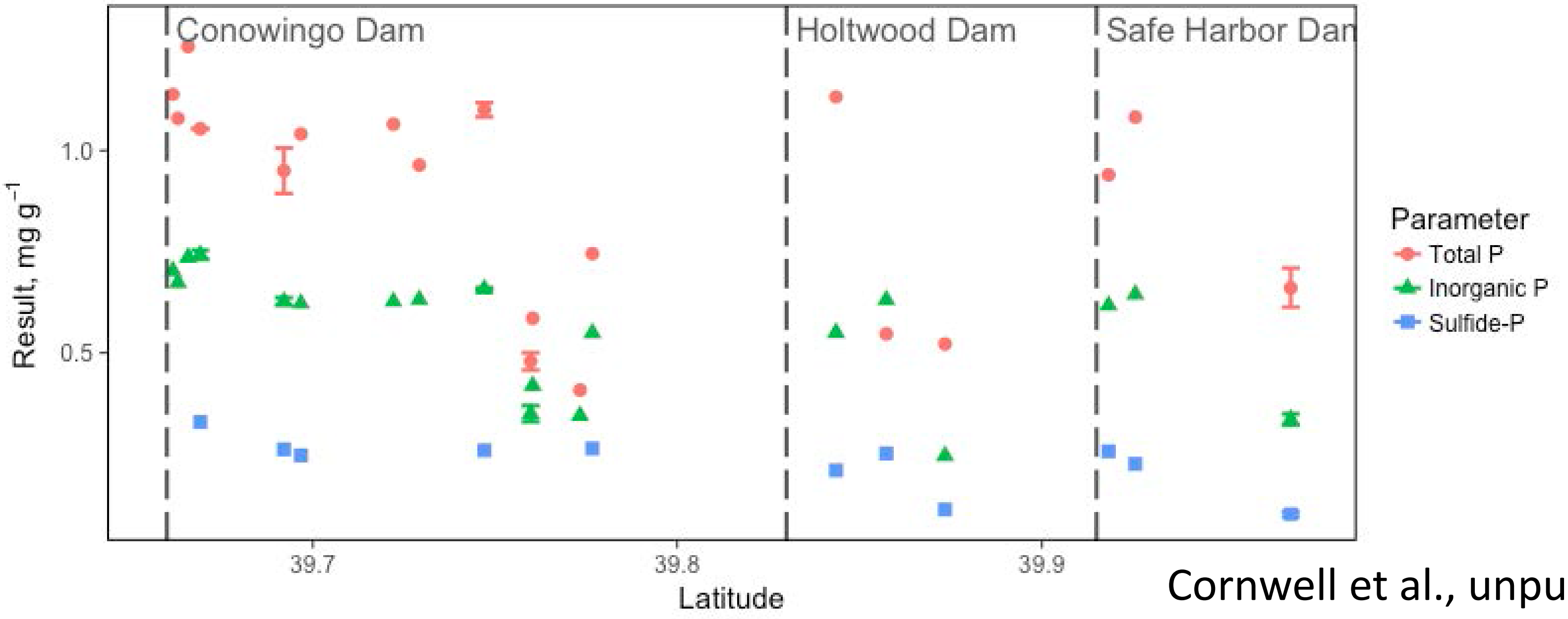
‘Small’ Fraction of Scoured P Could be Remineralized in Bay

Sulfide-Extractable P, Inorganic P, Total P From Susquehanna Reservoirs



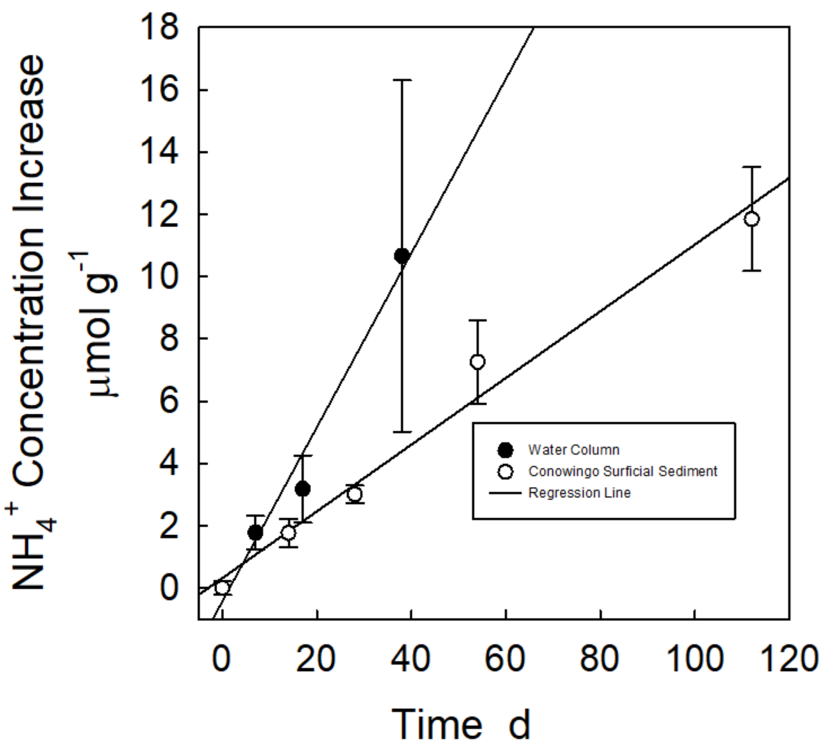
About ¼ to ⅓ of TP is sulfide-releasable

Consistent across lower Susquehanna River reservoirs



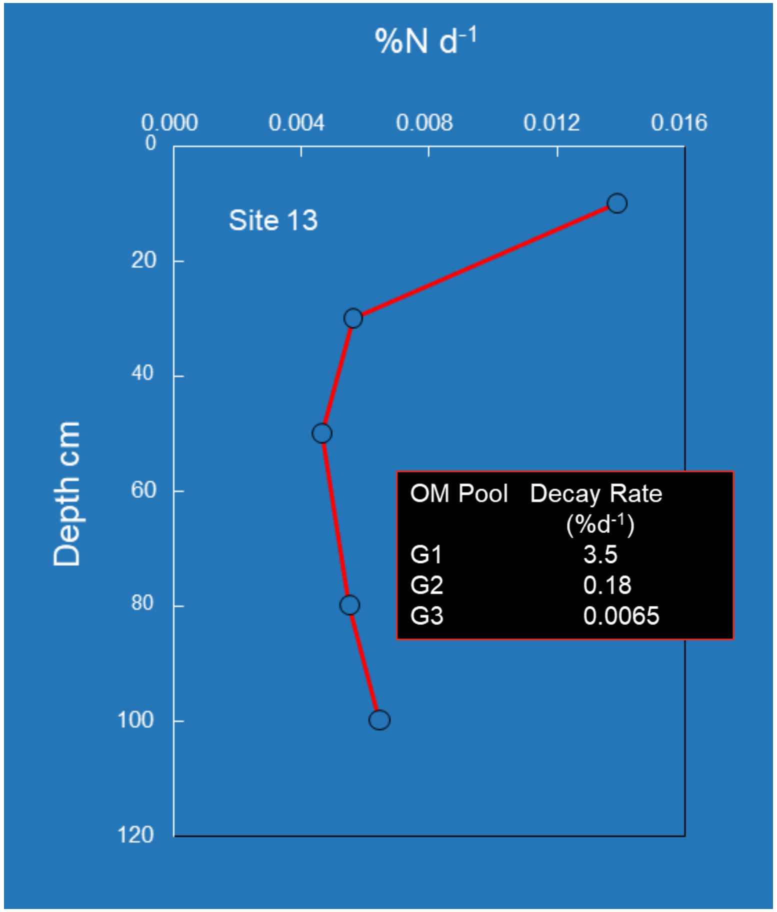
Cornwell et al., unpublished

Reservoir Sediments, River Particulates Are Not Highly Reactive

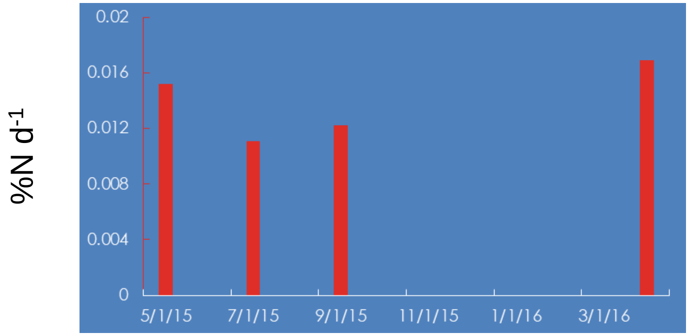


The average individual time course regressions were 0.05±0.03 and 0.34±0.37 µmol g^{-1} d^{-1} for sediment and water column (at dam).

The N remineralization are << than rates expected from algal-derived organic matter



OM Pool	Decay Rate (%d^{-1})
G1	3.5
G2	0.18
G3	0.0065



So,

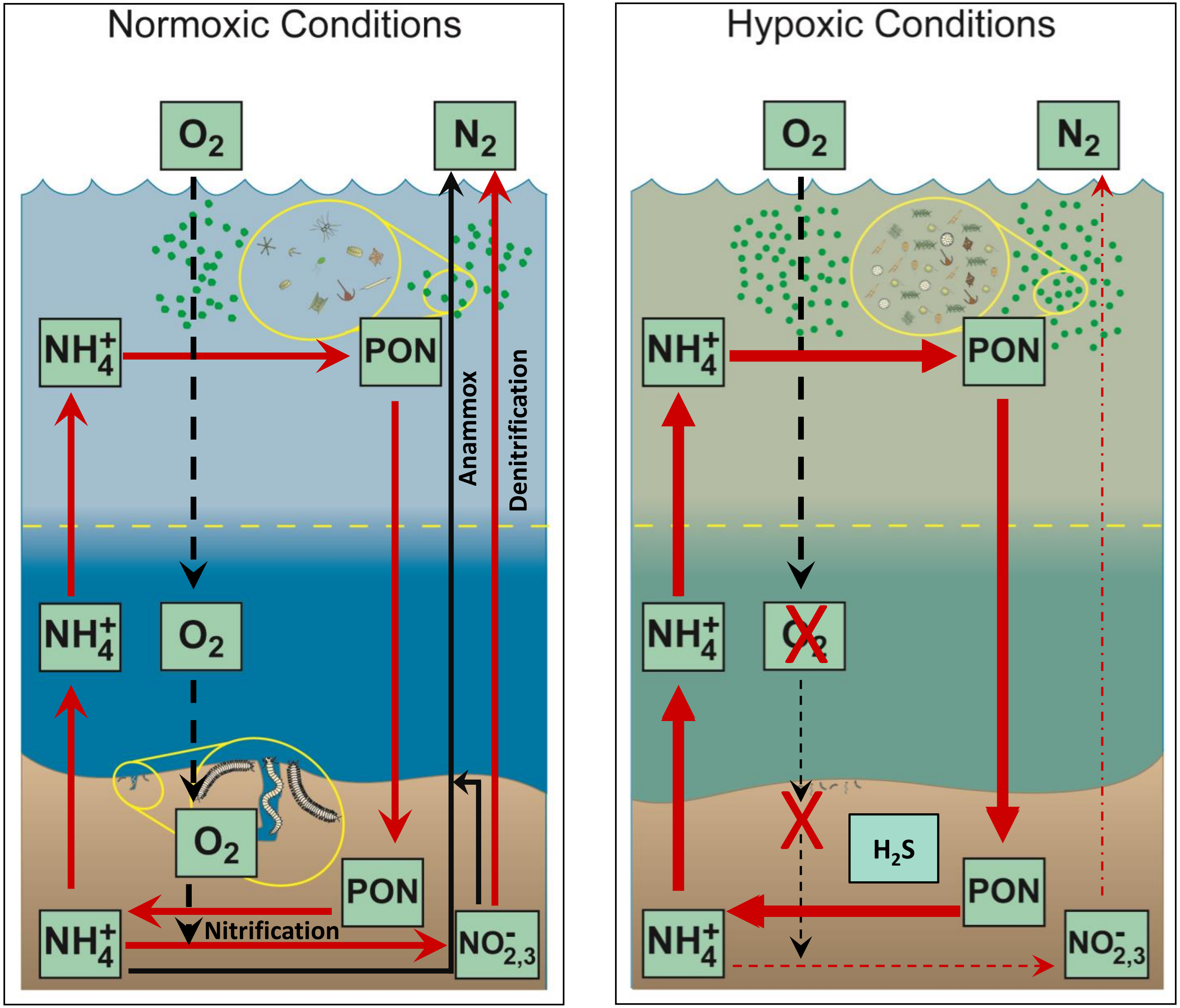
Dissolved nutrients are key drivers of phytoplankton P_n and hypoxia

Particulate N inputs are small, poorly reactive

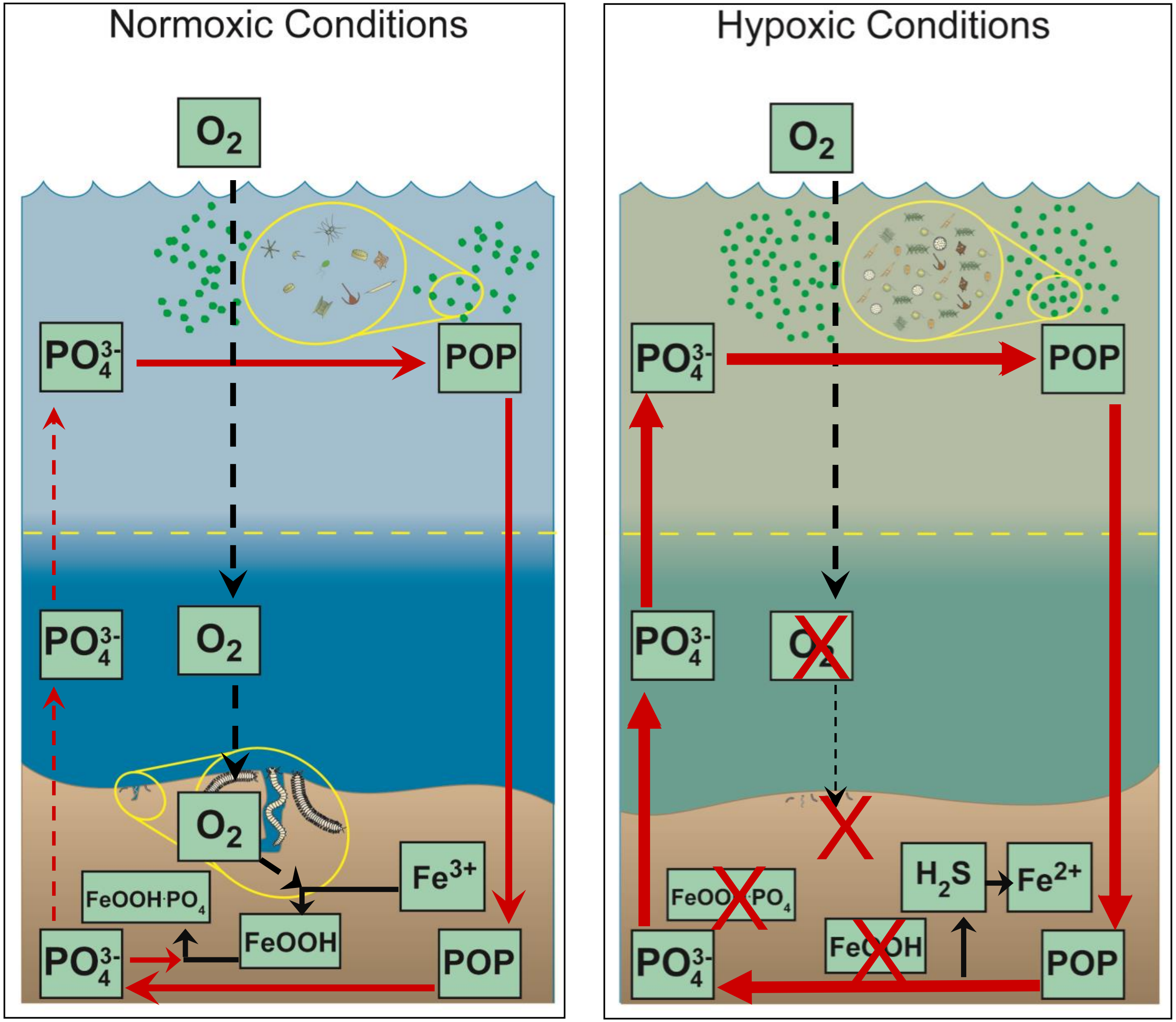
Particulate P inputs are large, somewhat unreactive

But how is the ultimate reactivity related to the estuarine conditions in which these particulates ultimately land?

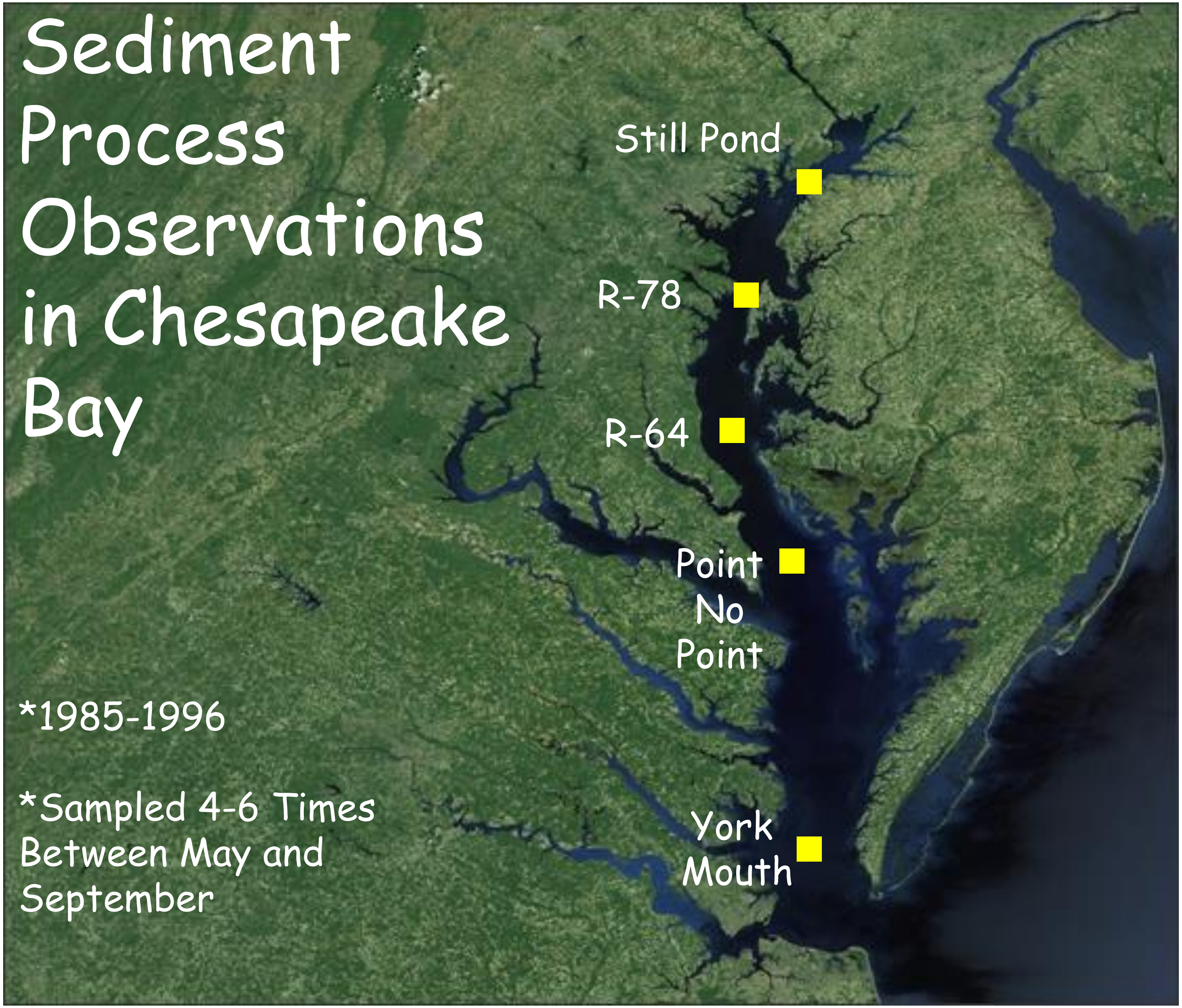
Conceptual Model of O_2 Interactions with N-Cycle



Conceptual Model of O_2 Interactions with P-Cycle



Sediment Process Observations in Chesapeake Bay

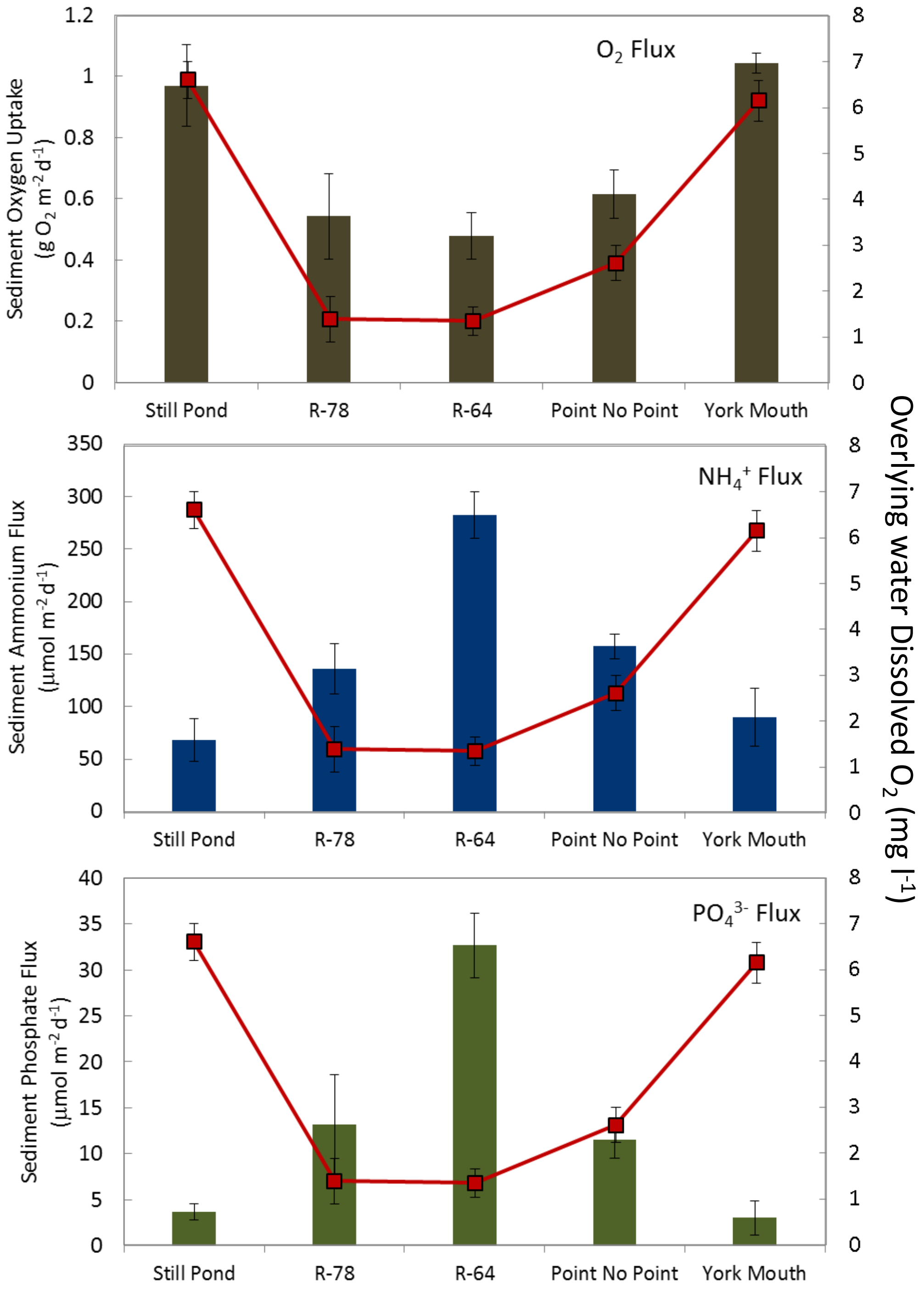


*1985-1996

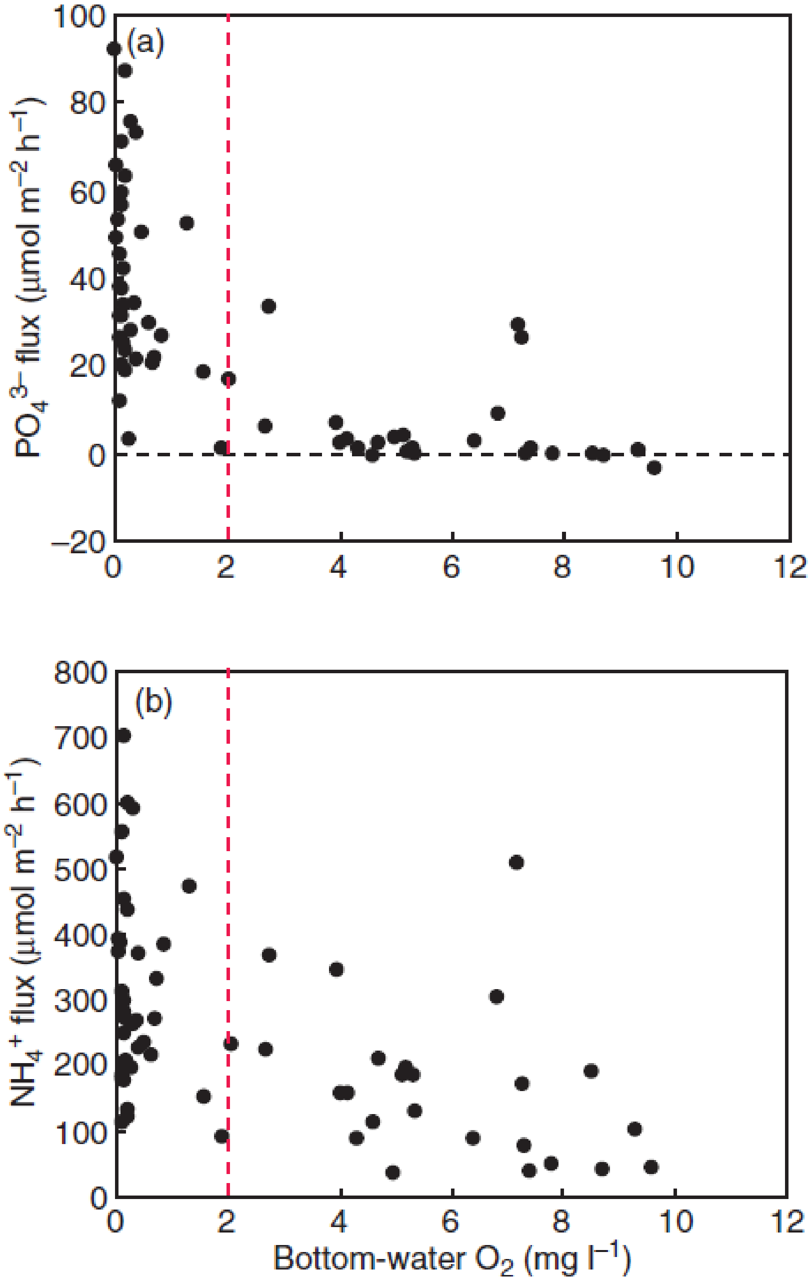
*Sampled 4-6 Times Between May and September

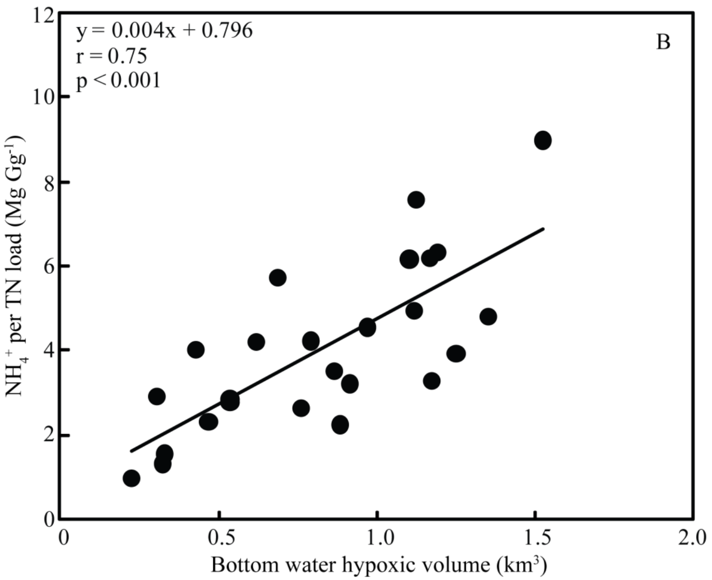
Spatial Variation in Sediment-Water Fluxes

- Sediment O_2 Uptake lowest in region between Bay Bridge and Patuxent
- NH_4^+ and PO_4^{3-} fluxes peak in mid-Bay
- Bottom-water O_2 low where N and P fluxes peak

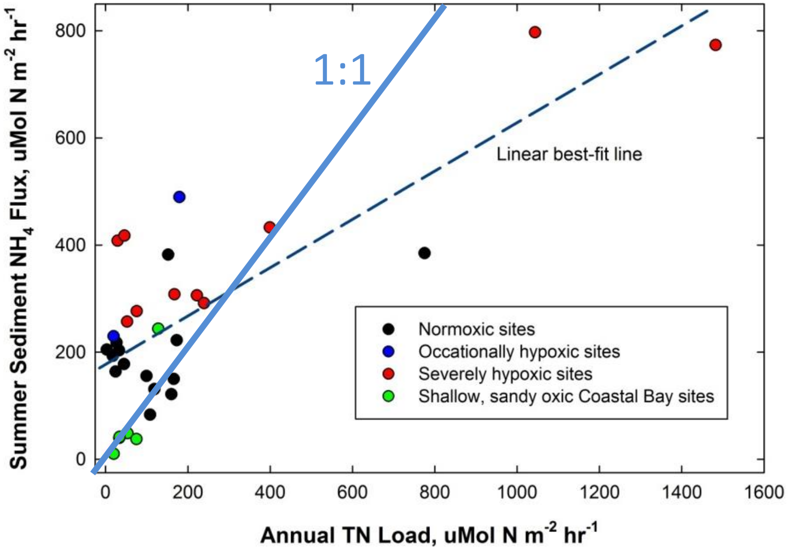


Hypoxia, Sulfide Stimulates Dissolved N, P Recycling



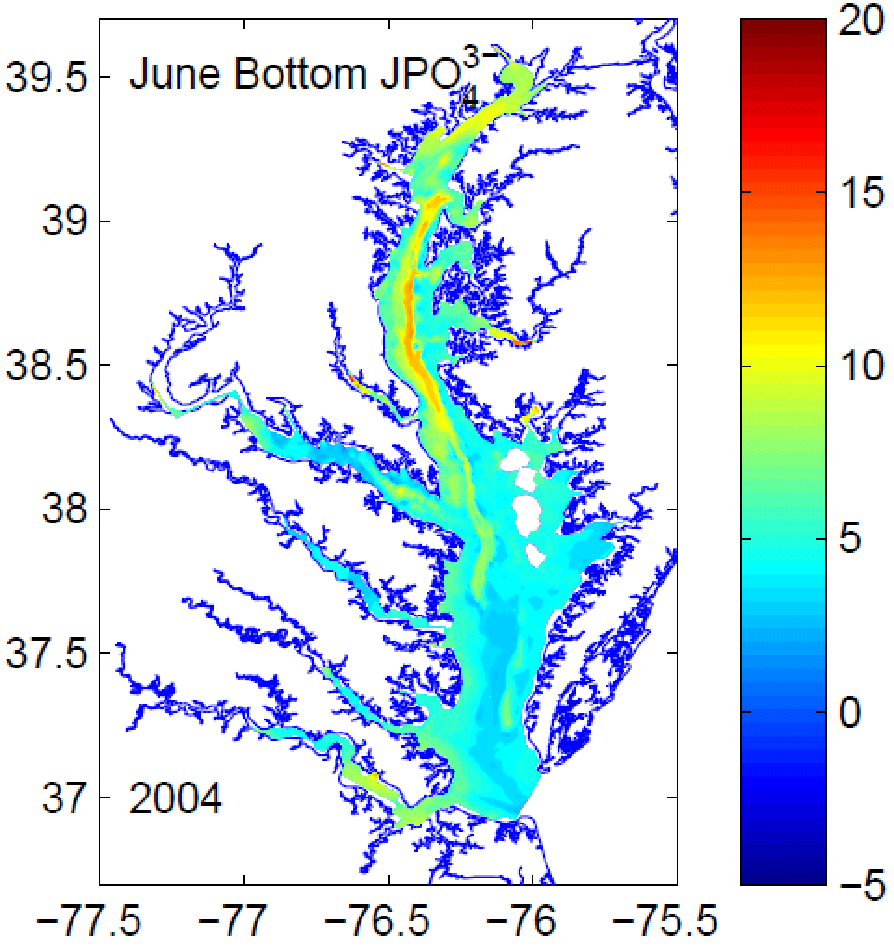


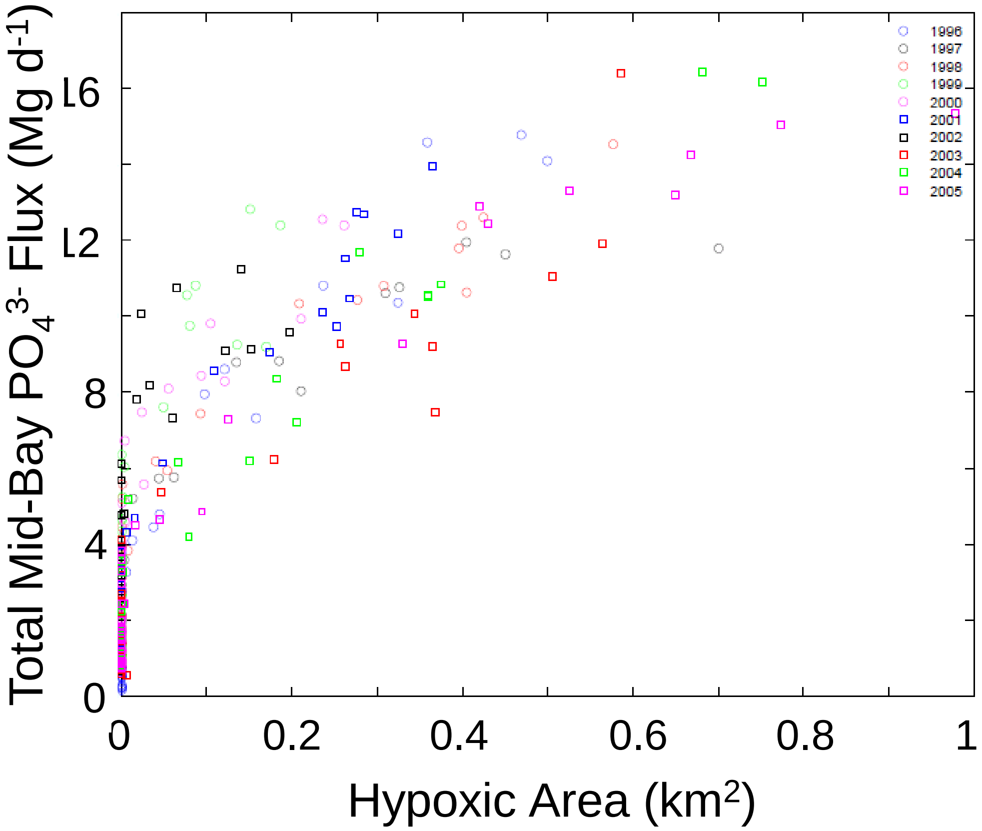
- *Larger N and P pool generated for a given load* with *higher hypoxic volumes*



Data from Walter Boynton, published in Testa and Kemp 2011, 2012

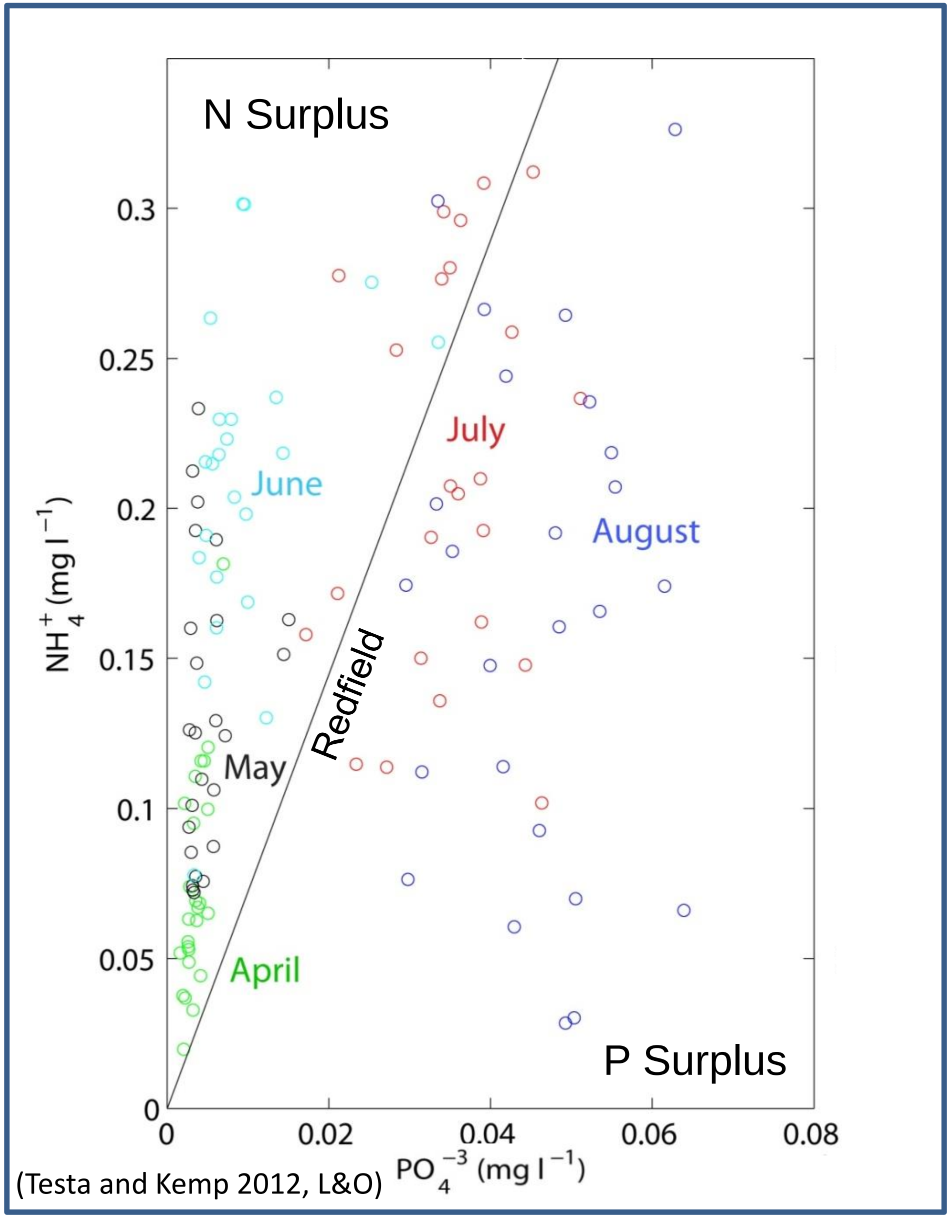
Numerical Model Distributions of P Flux



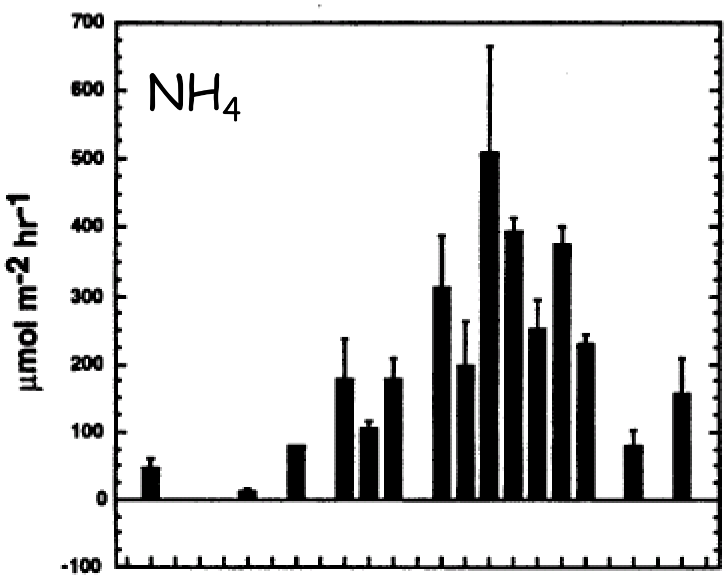


Model Simulations reported in Testa et al. 2014

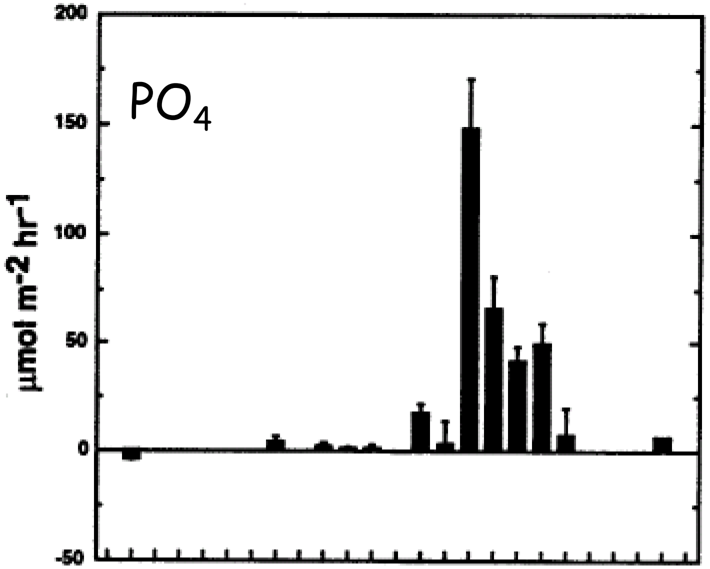
Temporal Mismatch in Fluxes Drives N:P Ratios



(Testa and Kemp 2012, L&O)



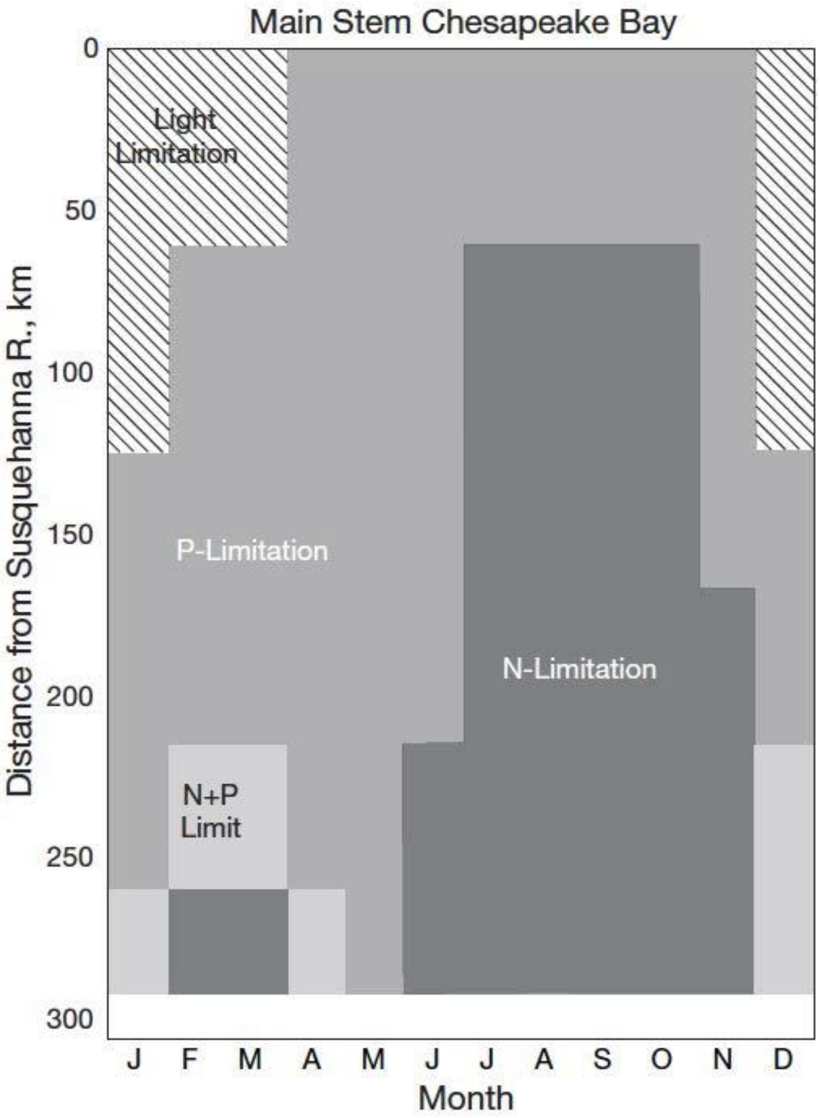
(Cowan and Boynton 1996)



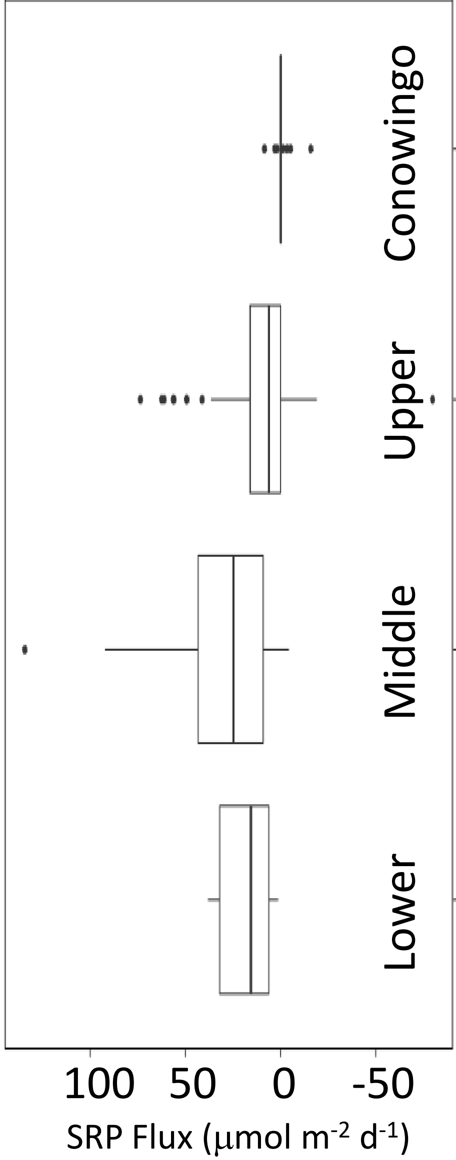
P:N in late summer >>>phytoplankton

- **It is all about location**

- Low upper bay SRP releases are in a zone of P limitation
- High mid-bay releases are in a more N-limited area

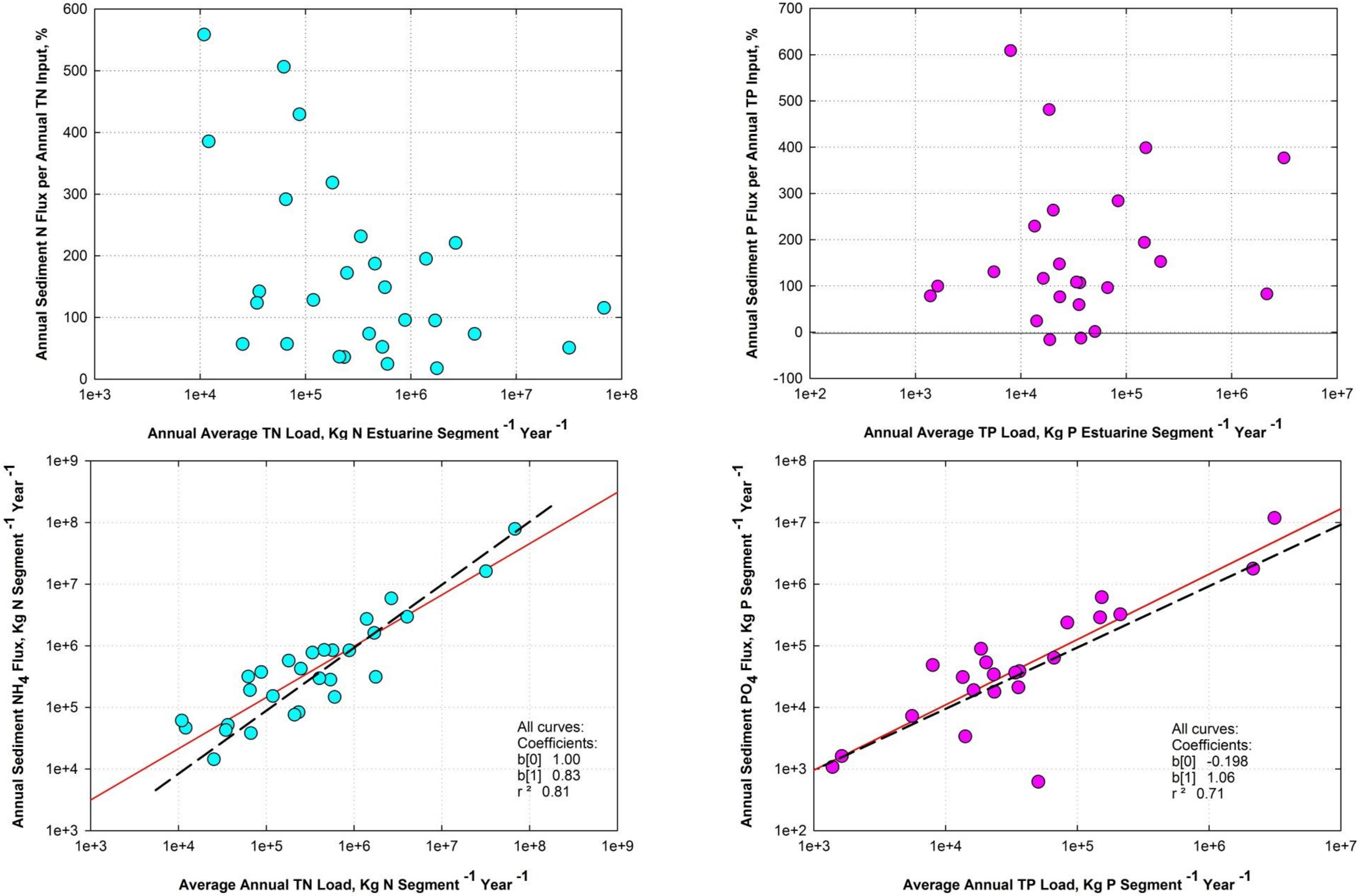


Kemp, W. M. and others 2005. Eutrophication of Chesapeake Bay: historical trends and ecological interactions. Marine Ecology-Progress Series 303: 1-29.



Estuarine “Internal Loading”

Watershed Input and Sediment Flux Are Related



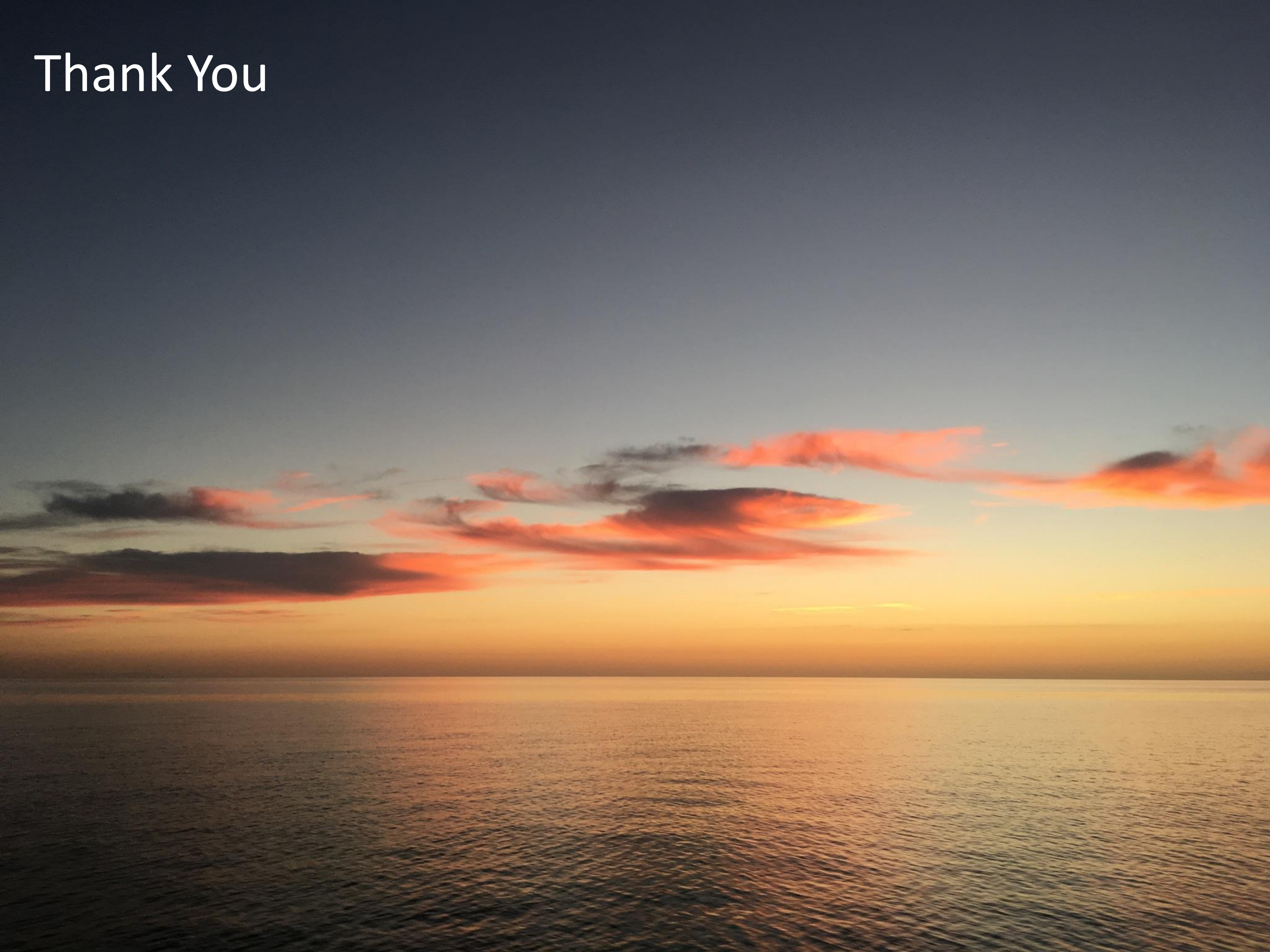
*At peak rates, sediments support 85% of N and 215% of P needed for primary production

Boynton and Testa, in prep

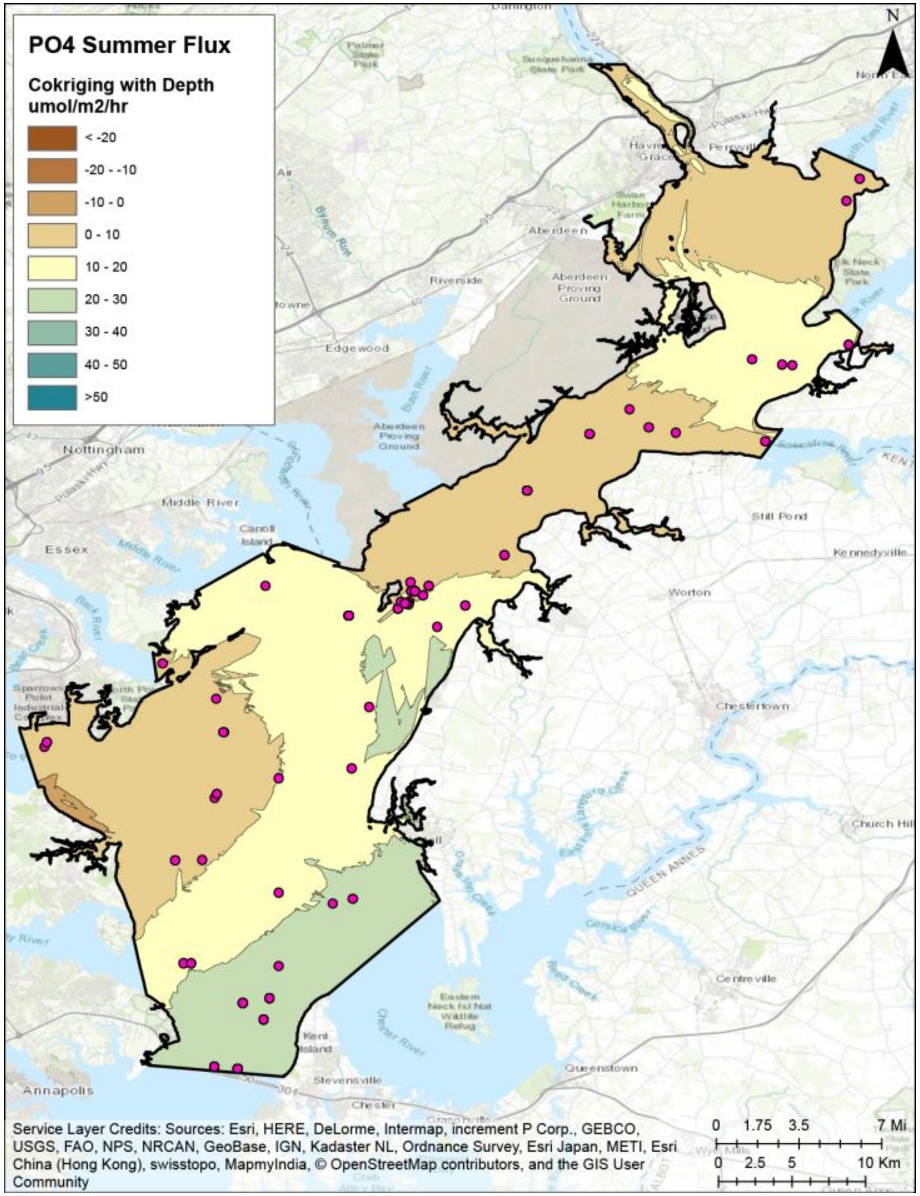
In Conclusion.

- Phytoplankton drive biological contribution to hypoxia
- Dissolved forms of N and P are the most direct form of input to fuel phytoplankton
- Input PP is large, can be remobilized as DIP to be made bioavailable, direct PN loads a small piece of TN puzzle
- Fate of particulate N and P depends on where the are remineralized in estuary
- Hypoxia enhances the potential for N and P recycling, drives shift in N to P ratio

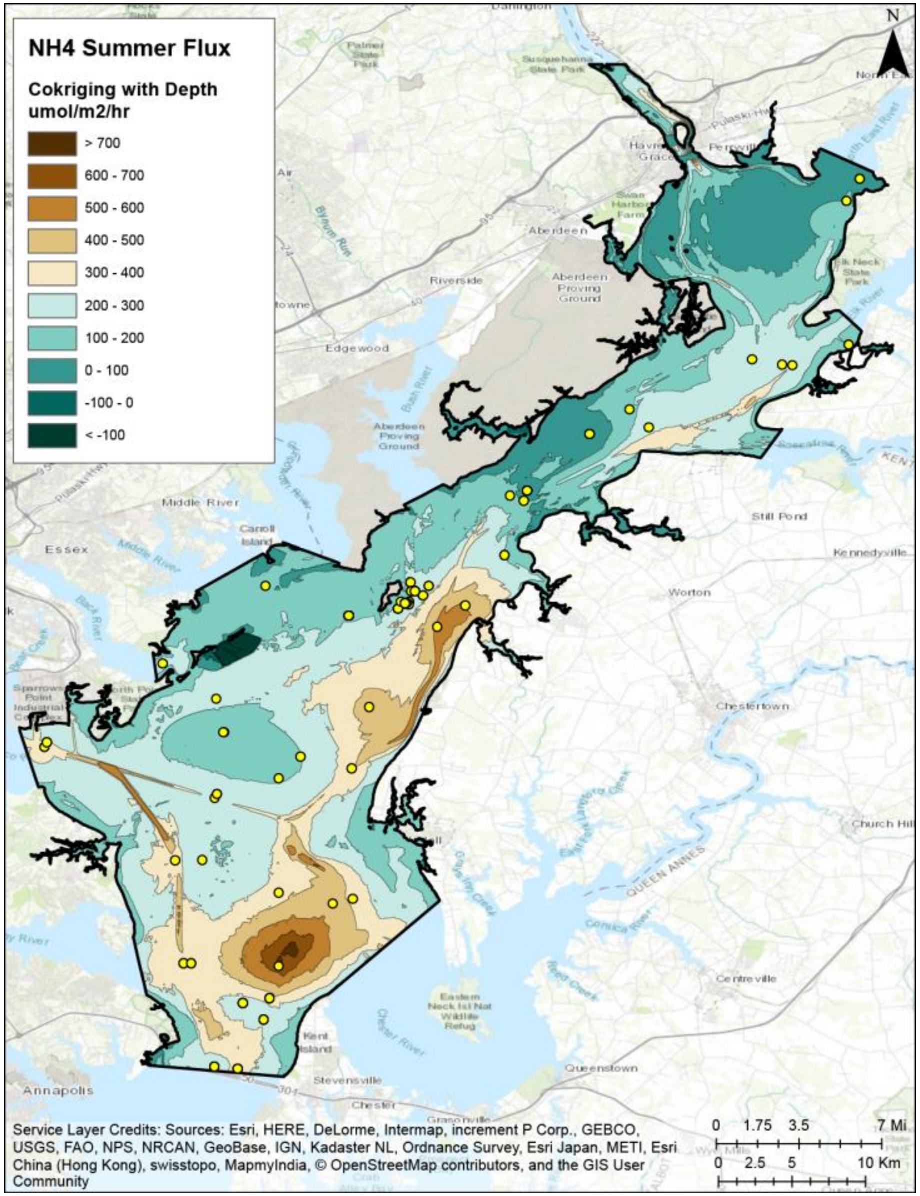
Thank You



Upper Bay Nutrient Fluxes are Low or Directed into Sediment



Service Layer Credits: Sources: Esri, HERE, DeLorme, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), swisstopo, MapmyIndia, © OpenStreetMap contributors, and the GIS User Community

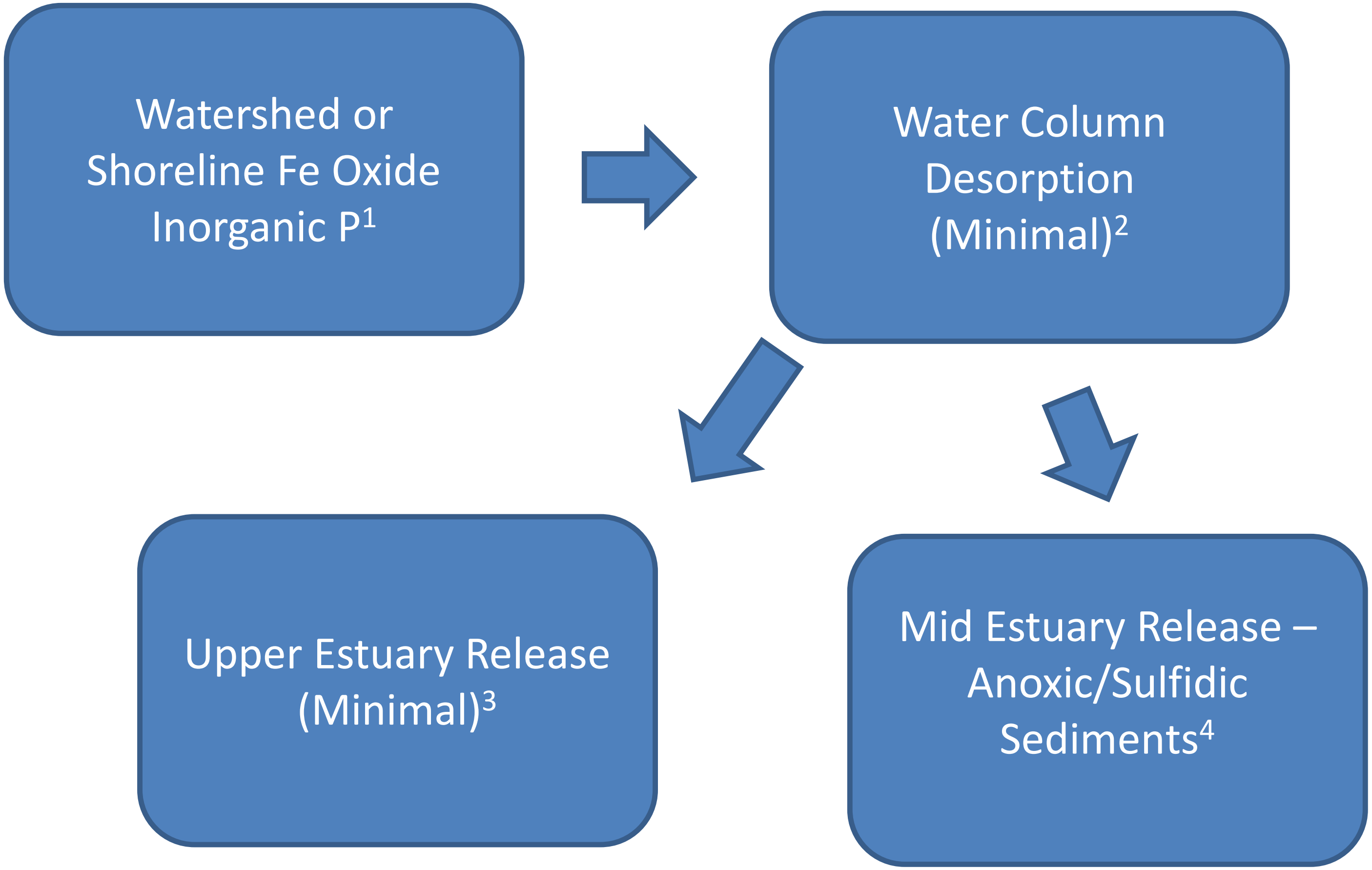


Service Layer Credits: Sources: Esri, HERE, DeLorme, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), swisstopo, MapmyIndia, © OpenStreetMap contributors, and the GIS User Community

…….except in the most seaward, deeper sections

Testa et al. (2018)

Major SRP Releases From Watershed-Derived Particulates Are Likely Diagenetic



Watershed or Shoreline Fe Oxide Inorganic P[1]

Water Column Desorption (Minimal)[2]

Upper Estuary Release (Minimal)[3]

Mid Estuary Release – Anoxic/Sulfidic Sediments[4]

[1] Jordan, T. E., J. C. Cornwell, W. R. Boynton, and J. T. Anderson. 2008. Changes in phosphorus biogeochemistry along an estuarine salinity gradient: The iron conveyer belt. Limnology and Oceanography **53: 172-184.**

[2] Spiteri, C., P. Van Cappellen, and P. Regnier. 2008. Surface complexation effects on phosphate adsorption to ferric iron oxyhydroxides along pH and salinity gradients in estuaries and coastal aquifers. Geochimica Et Cosmochimica Acta 72: 3431-3445.

[3] Boynton, W. R., and E. M. Bailey. 2008. Sediment Oxygen and Nutrient Exchange Measurements from Chesapeake Bay, Tributary Rivers and Maryland Coastal Bays: Development of a Comprehensive Database & Analysis of Factors Controlling Patterns and Magnitude of Sediment-Water Exchanges. UMCES Technical Report Series No. TS-542-08. University of Maryland Center for Environmental Science.

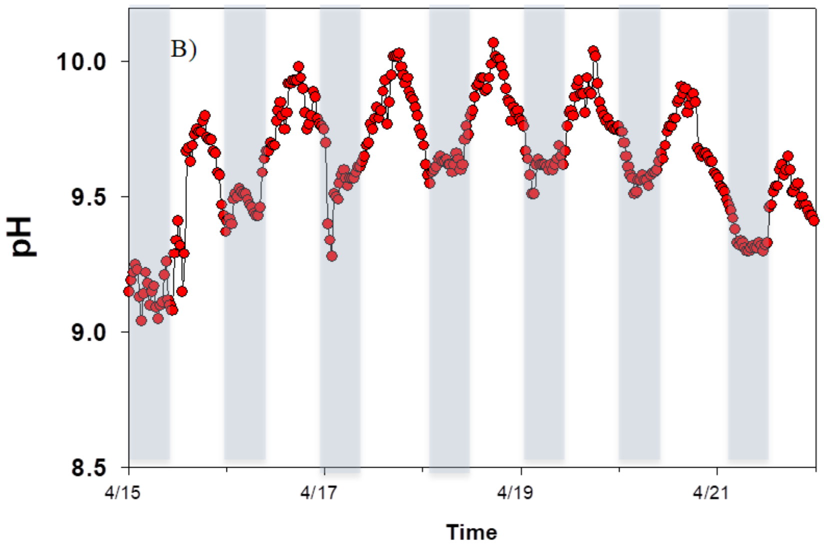
[4] Testa, J. M., and W. M. Kemp. 2012. Hypoxia-induced shifts in nitrogen and phosphorus cycling in Chesapeake Bay. Limnology and Oceanography 57: 835-850.

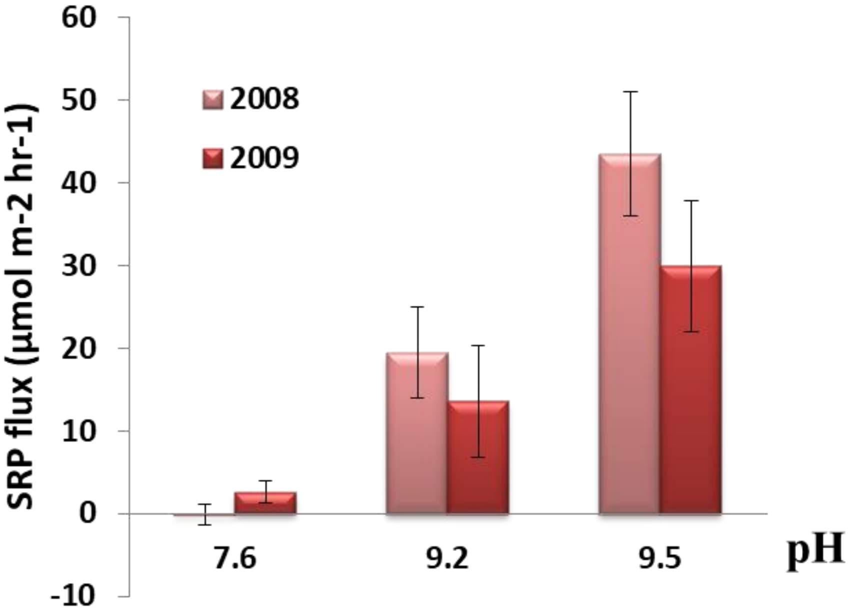
Observations From Sassafras River Sediments

Cyanobacteria blooms results in elevated pH

At pH's ≥ 9.2, desorption of SRP from Fe oxides occurs

[Also, coupled nitrification-denitrification is inhibited]

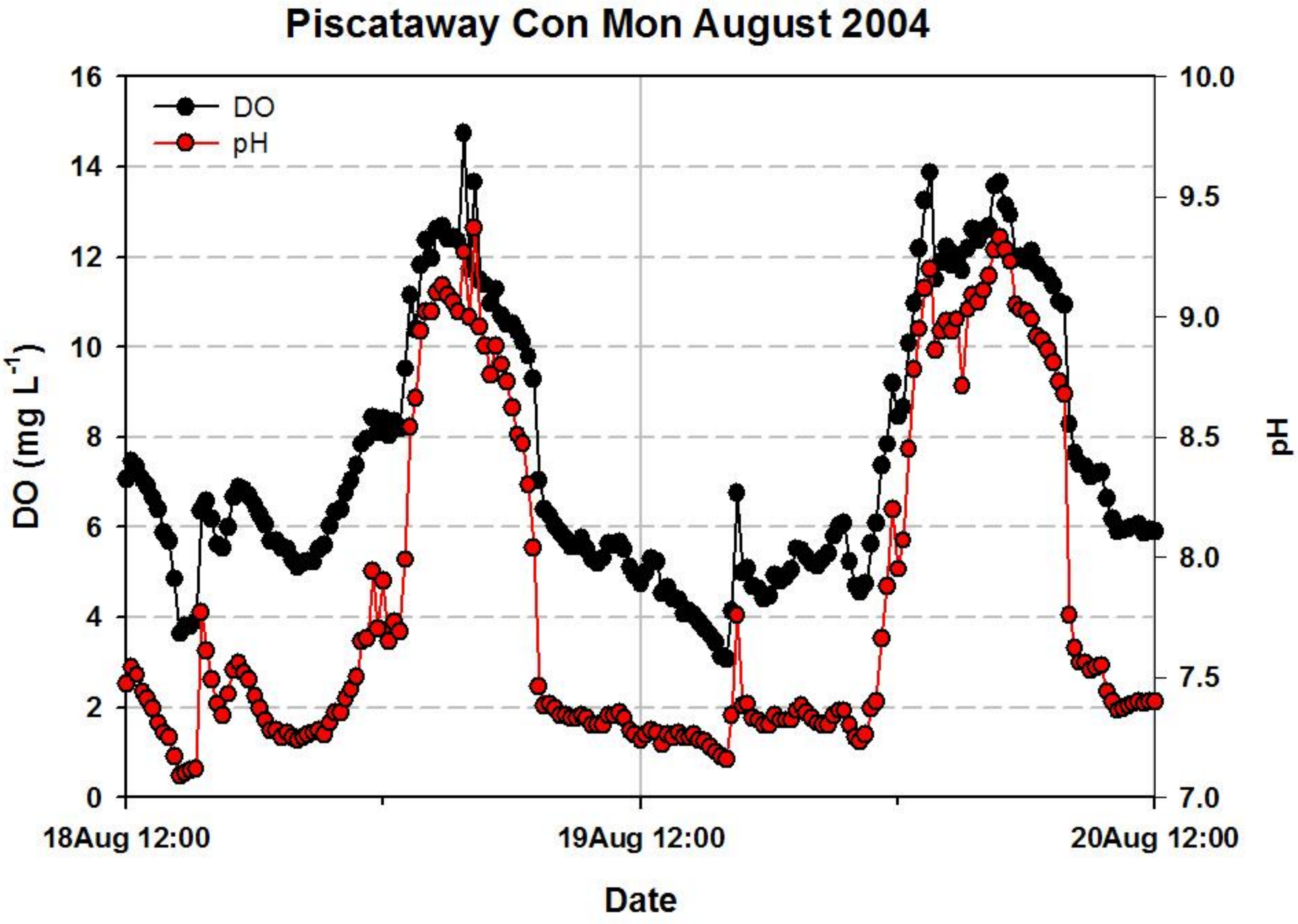




Gao, Y., J. C. Cornwell, D. K. Stoecker, and M. S. Owens. 2012. Effects of cyanobacterial-driven pH increases on sediment nutrient fluxes and coupled nitrification-denitrification in a shallow fresh water estuary. Biogeosciences **9: 2697-2710.**

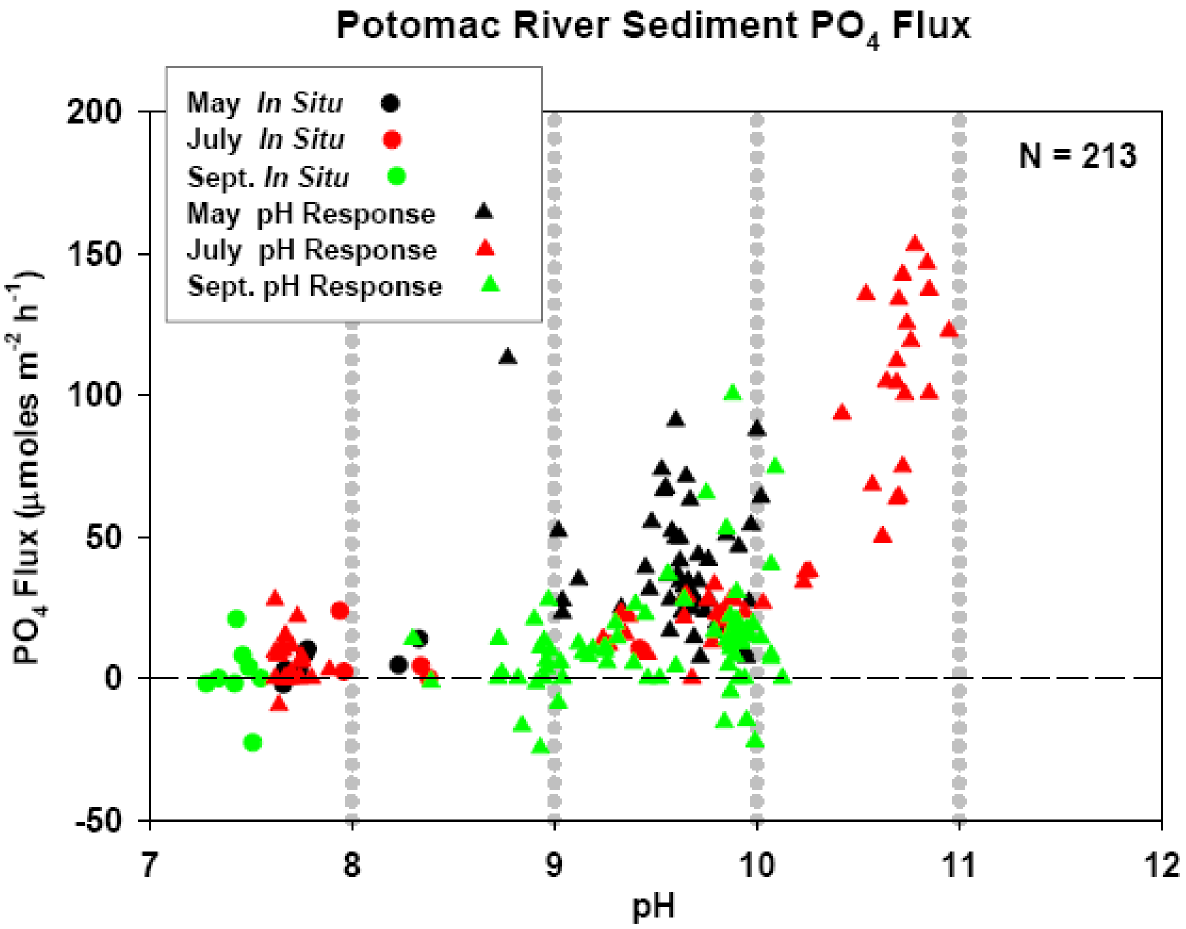
pH also influences sediment P flux:

An enriched creek of the Potomac

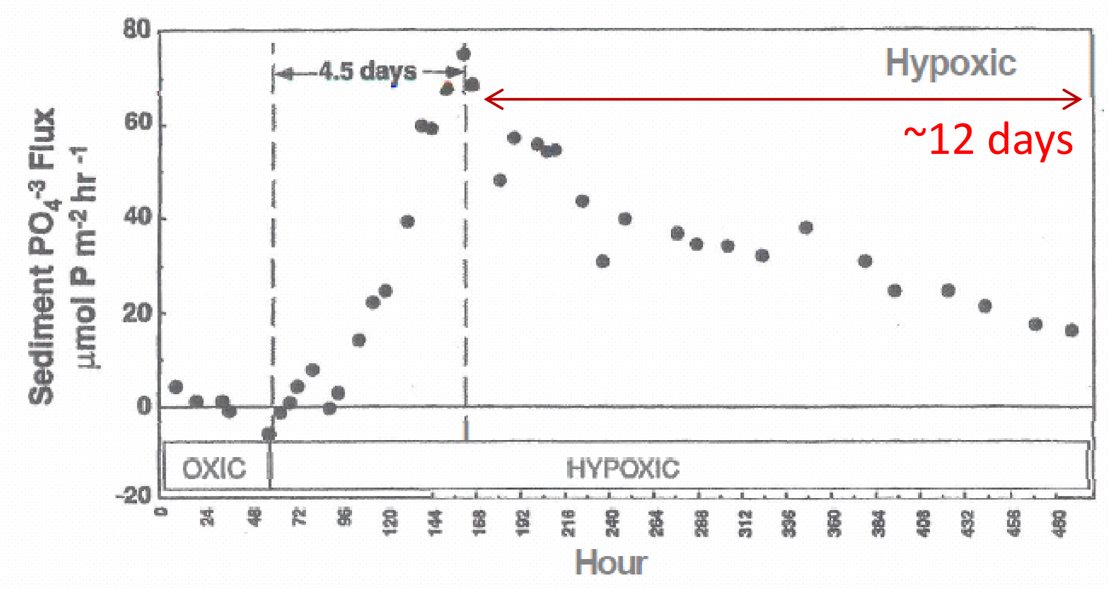


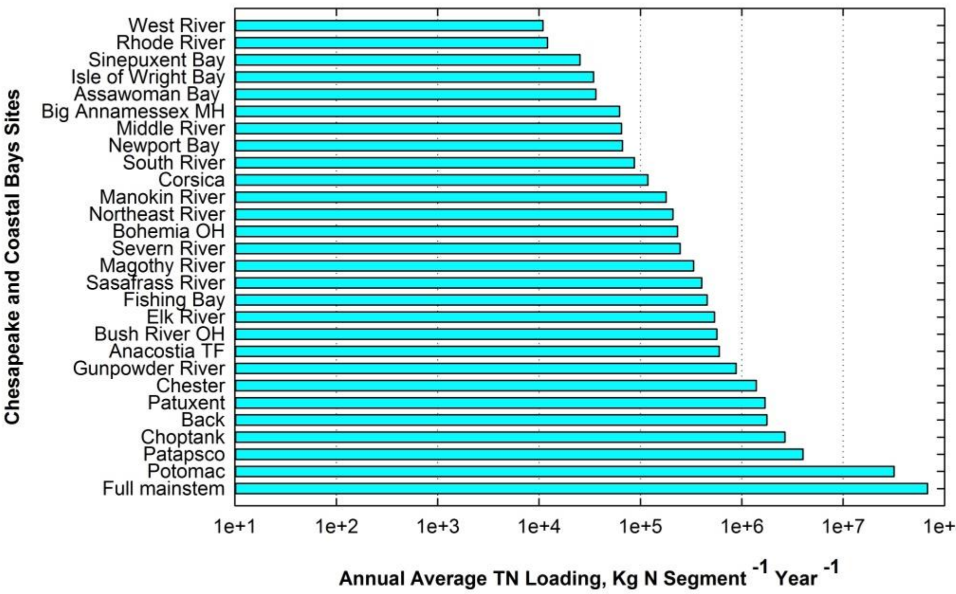
A Synthesis of Sediment P flux vs pH

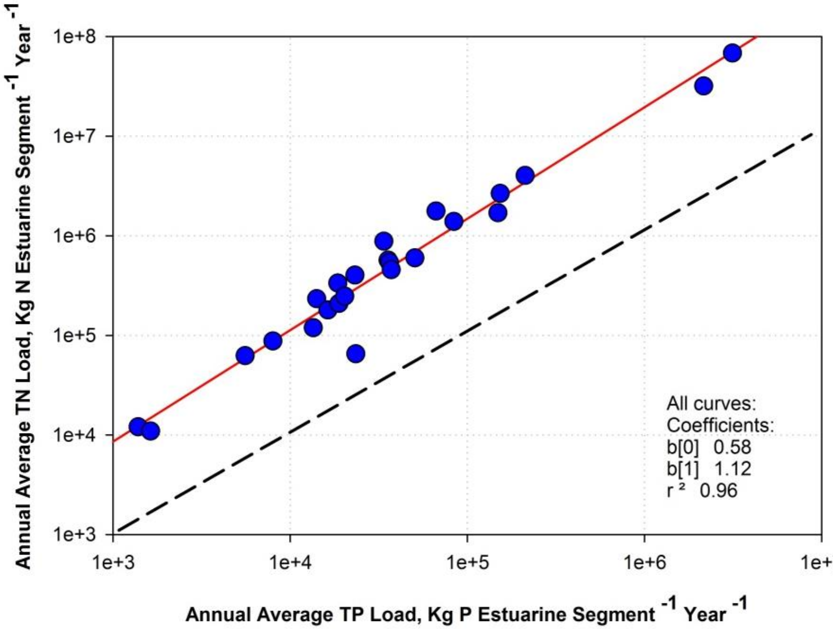
- Potomac River data
- In the tidal freshwater, pH can be important, especially during algal blooms
- Sediment P release rates increase rapidly at pH > 9.3

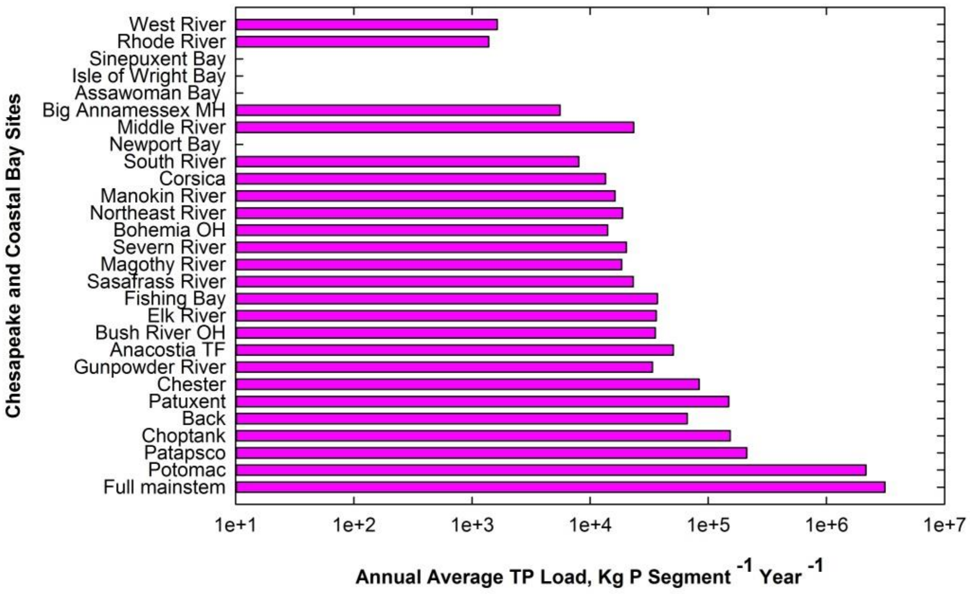


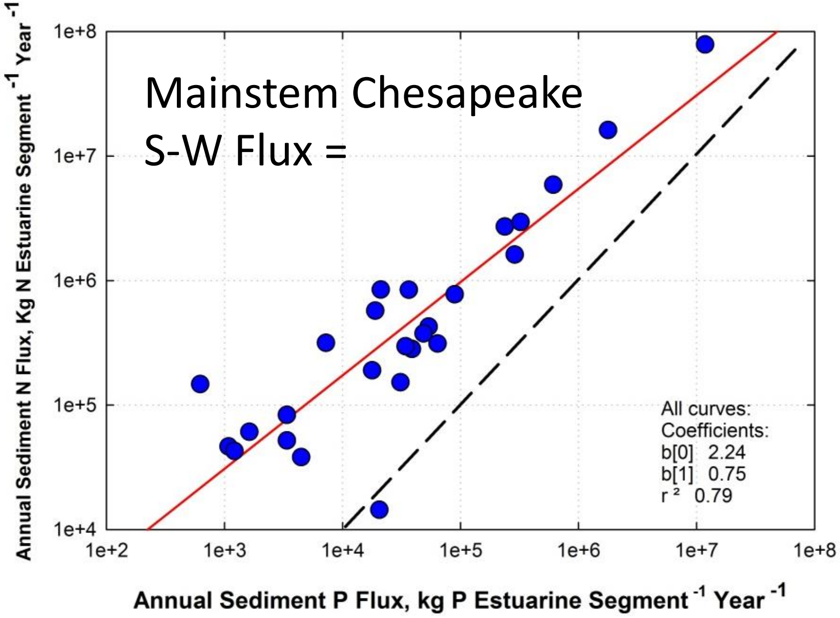
Bailey et al. 2006


Sediment PO$_4^{-3}$ Flux
µmol P m^{-2} hr^{-1}
80
60
40
20
0
-20
4.5 days
Hypoxic
~12 days
OXIC
HYPOXIC
0
24
48
72
96
120
144
168
192
216
240
264
288
312
336
360
384
408
432
456
480
Hour

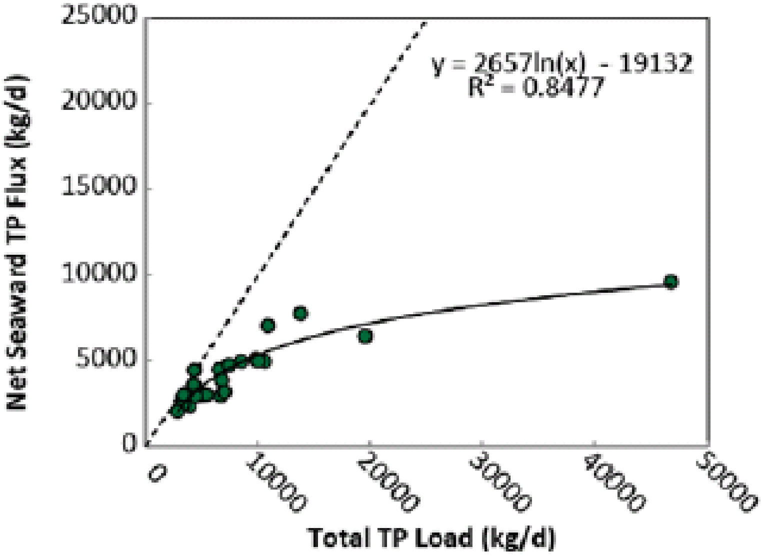




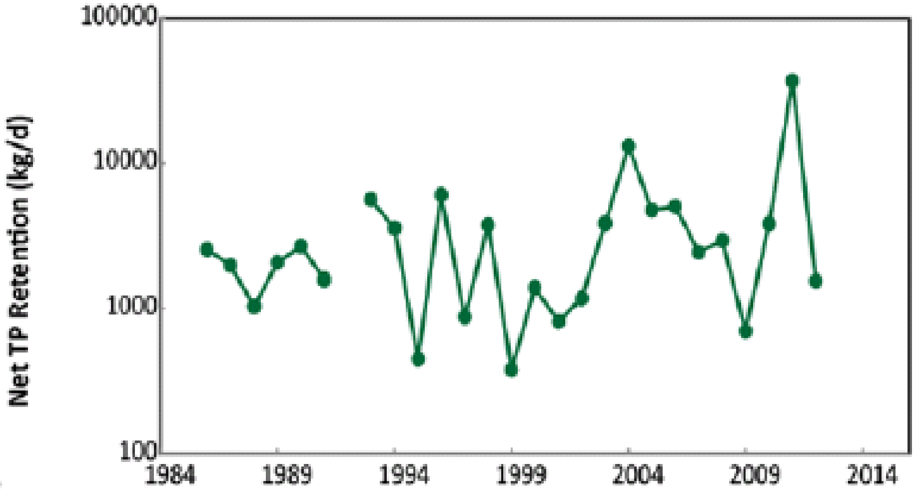




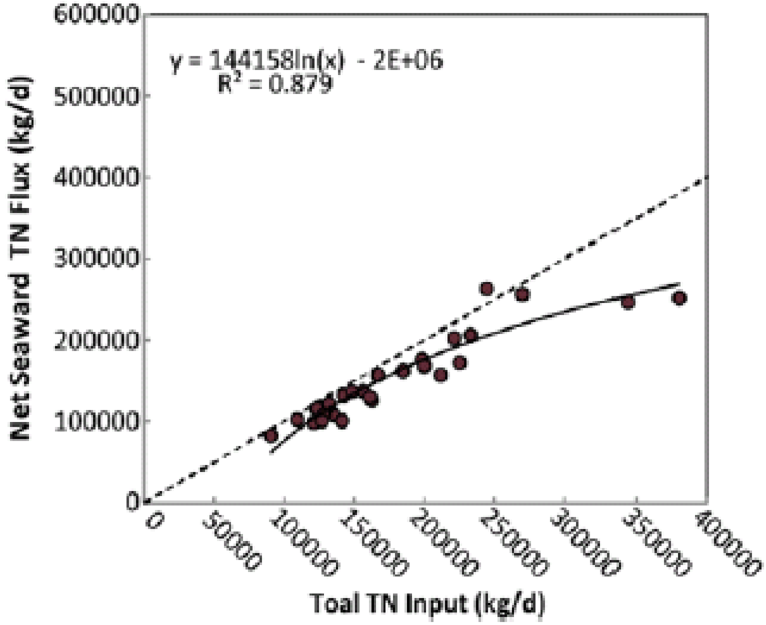
Mainstem Chesapeake
S-W Flux =



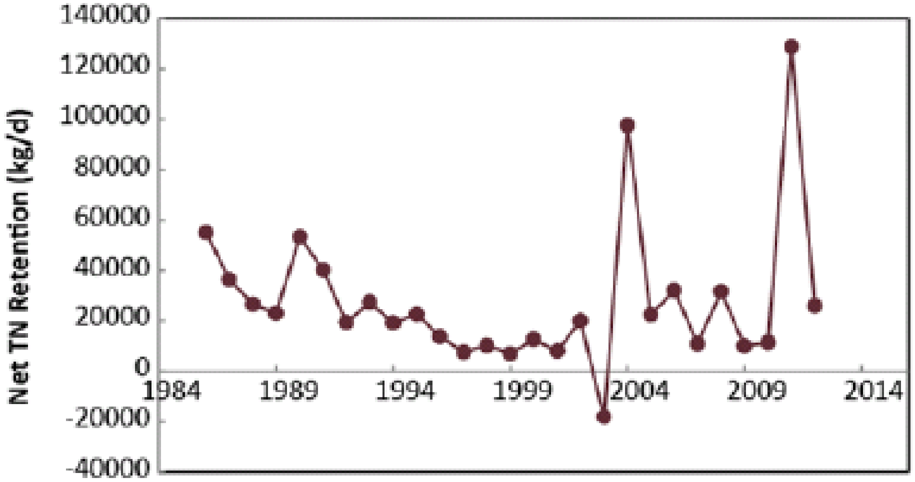
25000
20000
15000
10000
5000
0
0
10000
20000
30000
40000
50000
y = 2657ln(x) - 19132
R^2 = 0.8477
Net Seaward TP Flux (kg/d)
Total TP Load (kg/d)



100000
10000
1000
100
1984
1989
1994
1999
2004
2009
2014
Net TP Retention (kg/d)

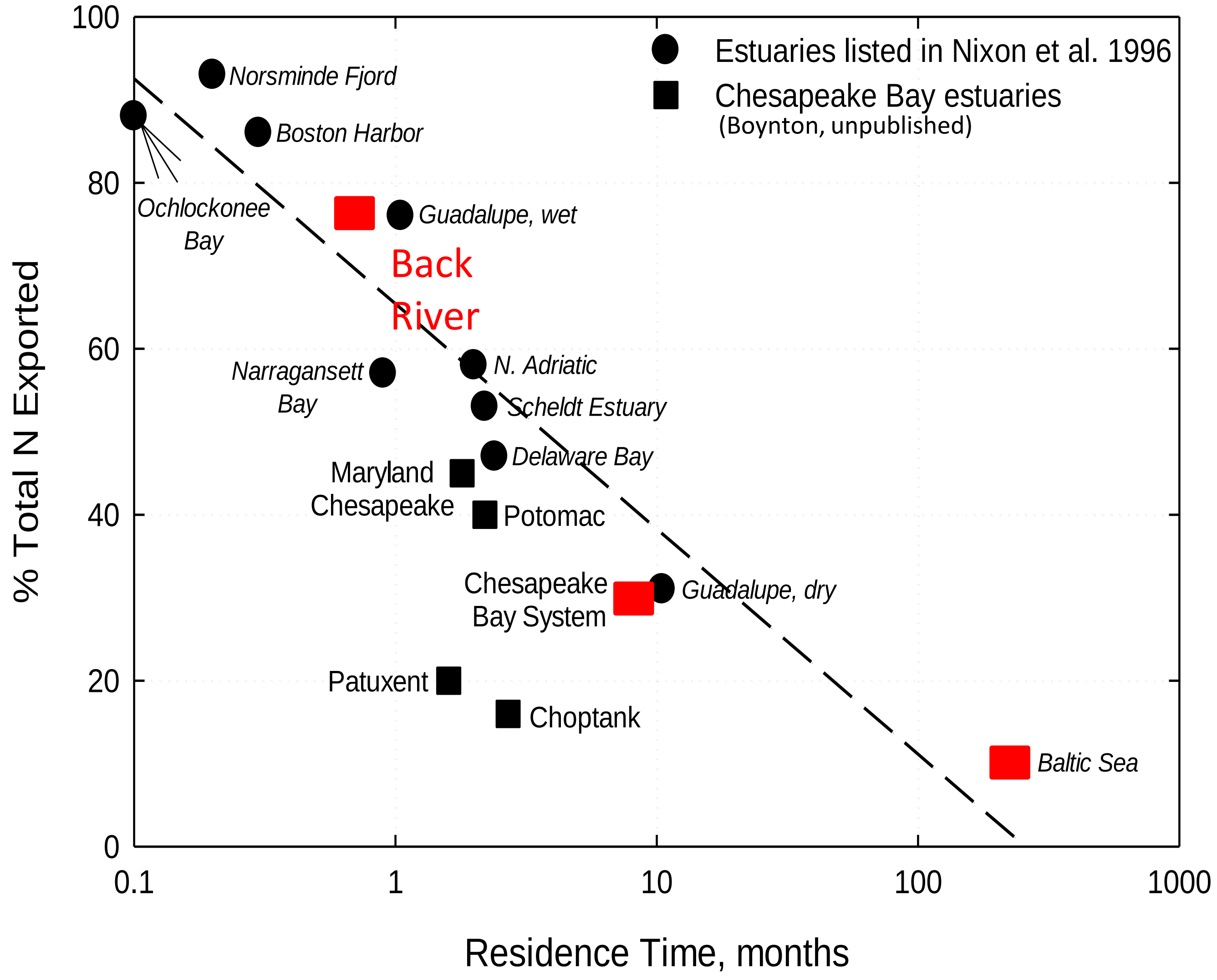


600000
500000
400000
300000
200000
100000
0
0
50000
100000
150000
200000
250000
300000
350000
40000
y = 144158ln(x) - 2E+06
R^2 = 0.879
Net Seaward TN Flux (kg/d)
Toal TN Input (kg/d)

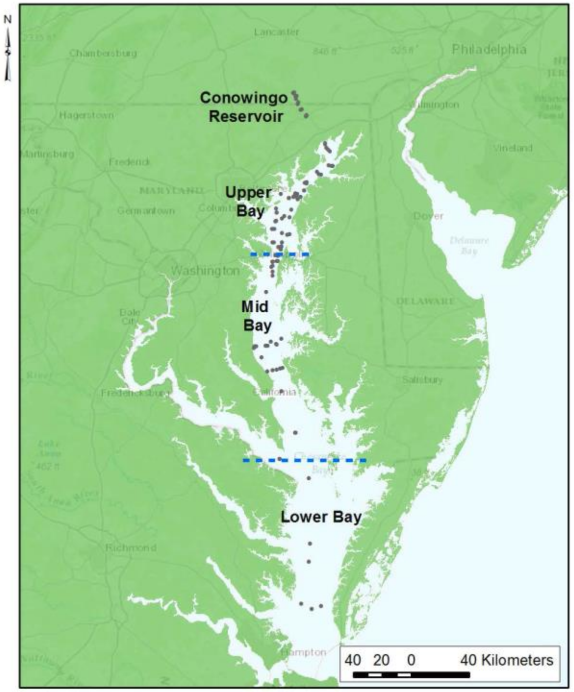


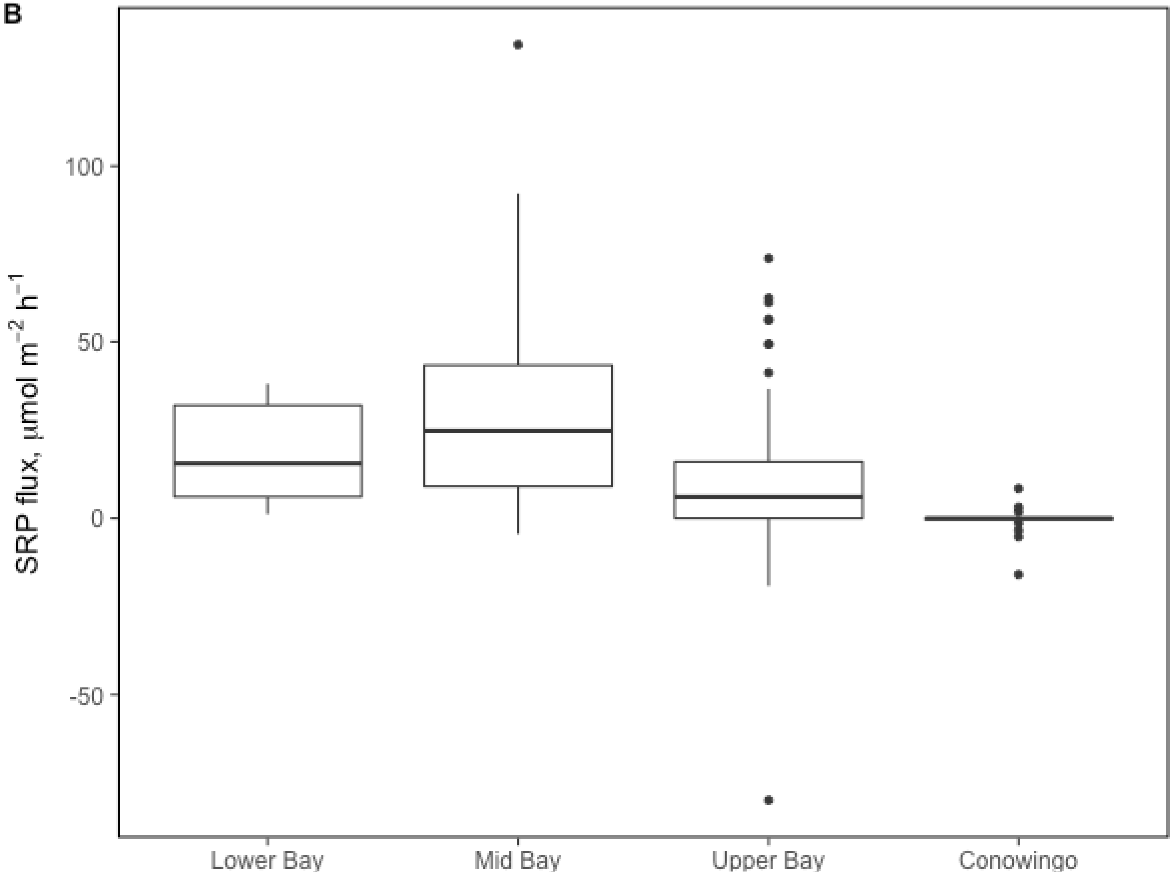
140000
120000
100000
80000
60000
40000
20000
0
-20000
-40000
1984
1989
1994
1999
2004
2009
2014
Net TN Retention (kg/d)

Positive Feedbacks and Residence Time



Sediment SRP Releases More Important in Saline Part of Bay



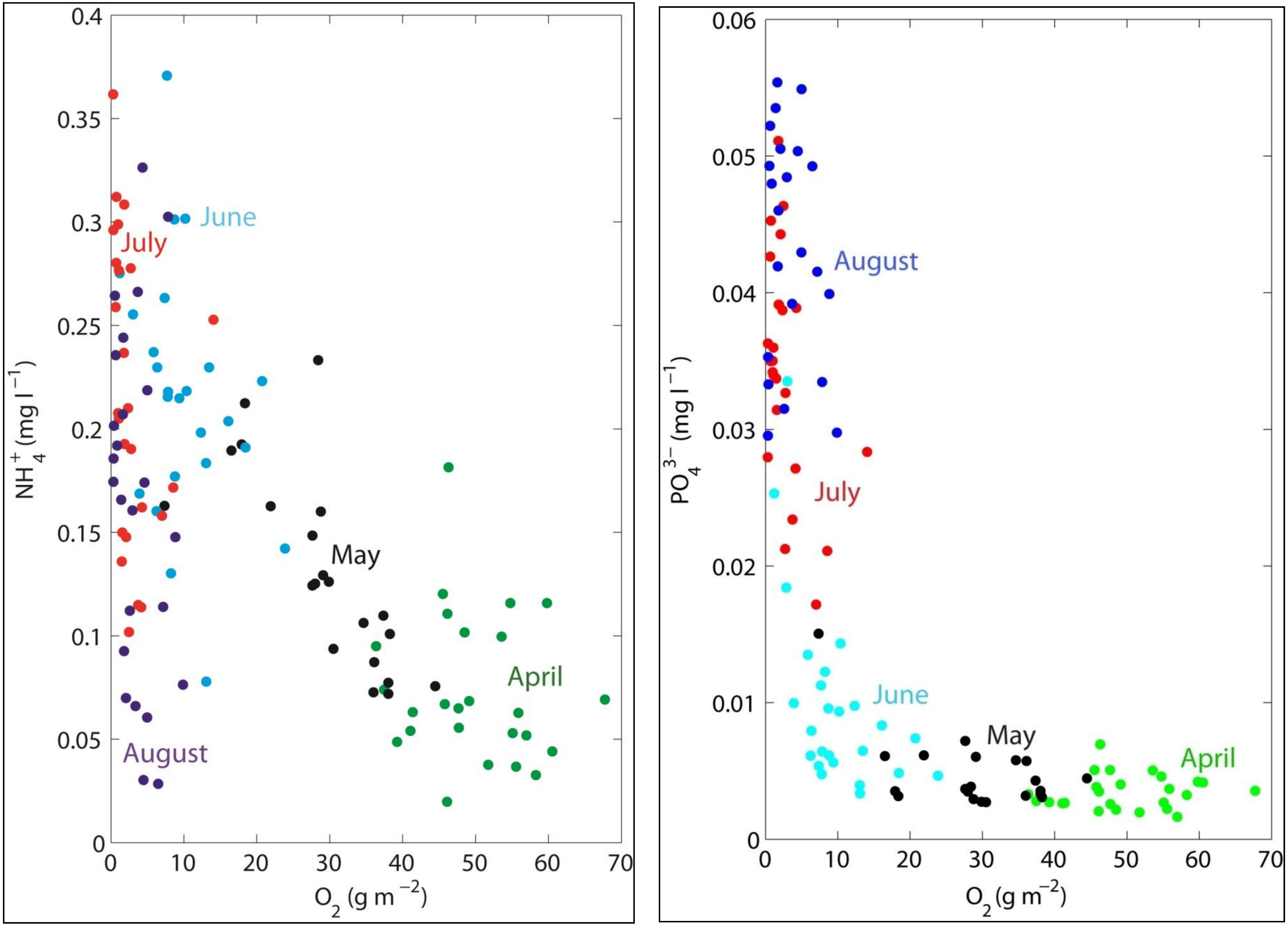


Boynton, W. R., and E. M. Bailey. 2008. Sediment Oxygen and Nutrient Exchange Measurements from Chesapeake Bay, Tributary Rivers and Maryland Coastal Bays: Development of a Comprehensive Database & Analysis of Factors Controlling Patterns and Magnitude of Sediment-Water Exchanges. UMCES Technical Report Series No. TS-542-08. University of Maryland Center for Environmental Science.

Cornwell, J. C., M. S. Owens, H. Perez, and Z. Vulgaropulos. 2017. The Impact of Conowingo Particulates on the Chesapeake Bay: Assessing the Biogeochemistry of Nitrogen and Phosphorus in Reservoirs and the Chesapeake Bay. Final Report to Exelon Generation and Gomez and Sullivan. UMCES Contribution UMCES.

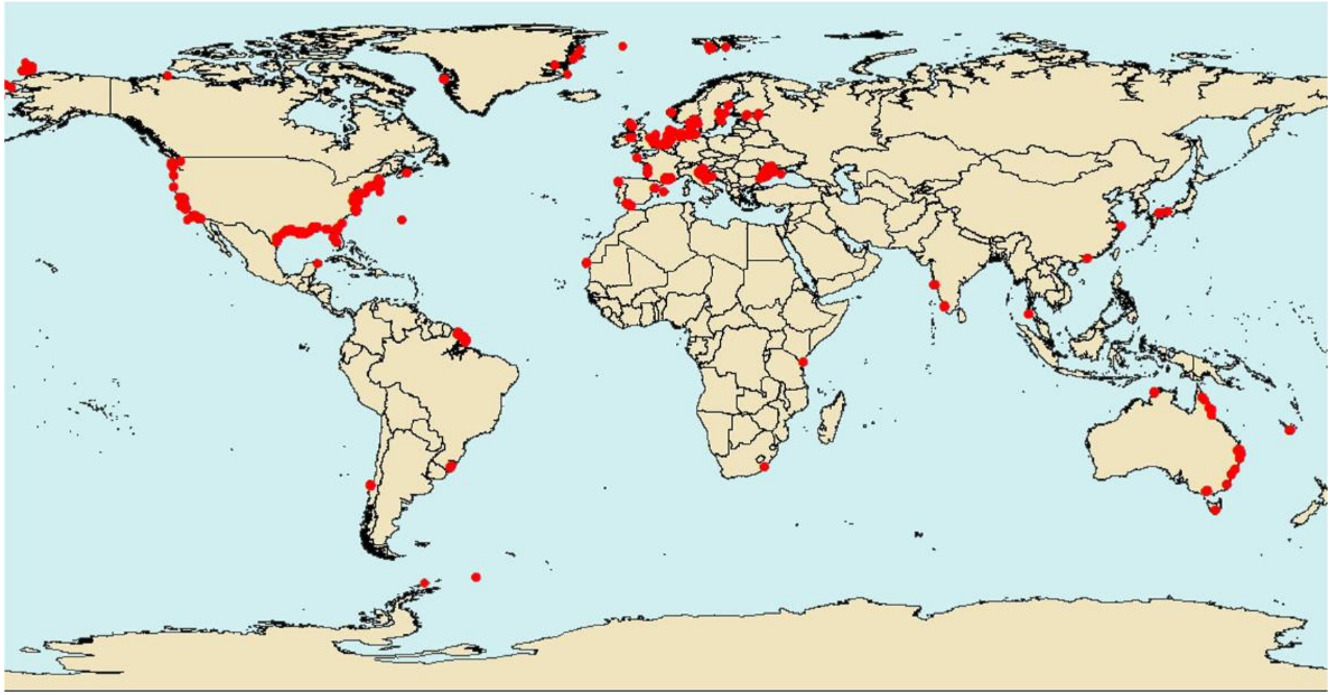
Vulgaropulos, Z. L. 2017. Reservoir Scour as a Major Source of Bioavailable Phosphorus to a Coastal Plain Estuary? MEES Program, M.S. Thesis, University of Maryland, College Park.

Seasonal Trends in Bottom NH_4^+ & PO_4^{3-} vs. O_2



(Testa and Kemp 2012, L&O)

Estuarine “Internal Loading”



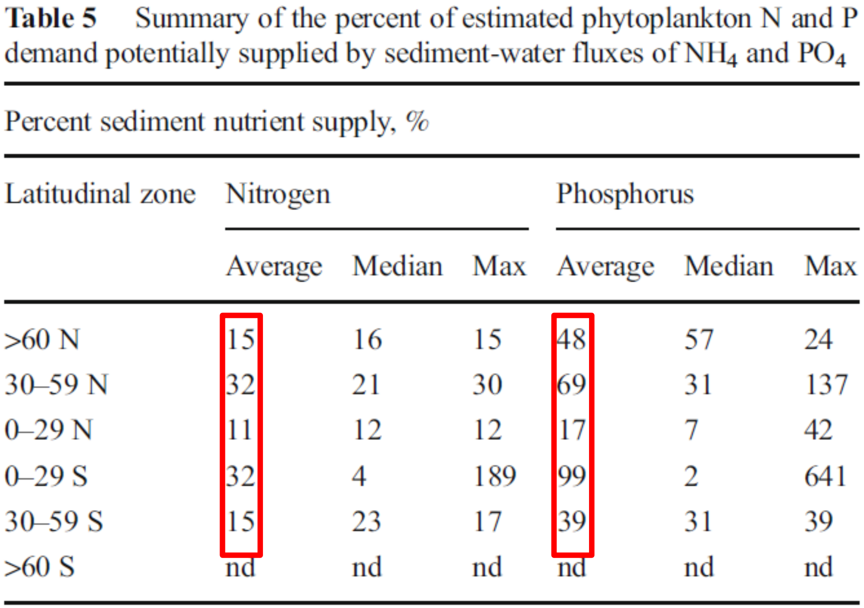


Table 5 Summary of the percent of estimated phytoplankton N and P demand potentially supplied by sediment-water fluxes of NH_4 and PO_4

Percent sediment nutrient supply, %

Latitudinal zone	Nitrogen			Phosphorus		
	Average	Median	Max	Average	Median	Max
>60 N	15	16	15	48	57	24
30–59 N	32	21	30	69	31	137
0–29 N	11	12	12	17	7	42
0–29 S	32	4	189	99	2	641
30–59 S	15	23	17	39	31	39
>60 S	nd	nd	nd	nd	nd	nd

Boynton et al. (2017)

PRELIMINARY: Chesapeake Bay Phosphorus Budget

10^6 kg/yr	TP	PO_4-P
Susquehanna River[λ]	2.7 (±7.2)	0.4 (±0.4)
Net exchange with Tributaries[ξ]	4.0 (±2.4)	1.1 (±0.9)
Net Input From Atlantic Ocean[Φ]	1.8	0.6
Net sediment-water exchange[β]	8.9 (±0.47)	8.9 (±0.47)
Sediment burial	-14.5	N/A

[Φ] Computed from box model for 1987-2015; [λ] Computed at USGS RIM stations 1985-2017 (Zhang); [ξ] Computed from net exchange in QUAL-ICM model 1985-2005; [φ] Computed from Phase 6 Chesapeake Bay watershed model 1985-2014; [β] from 30-year ROMS-RCA simulation (Shen et al., unpublished); [Δ] from Boynton et al. 1995 for entire Chesapeake System

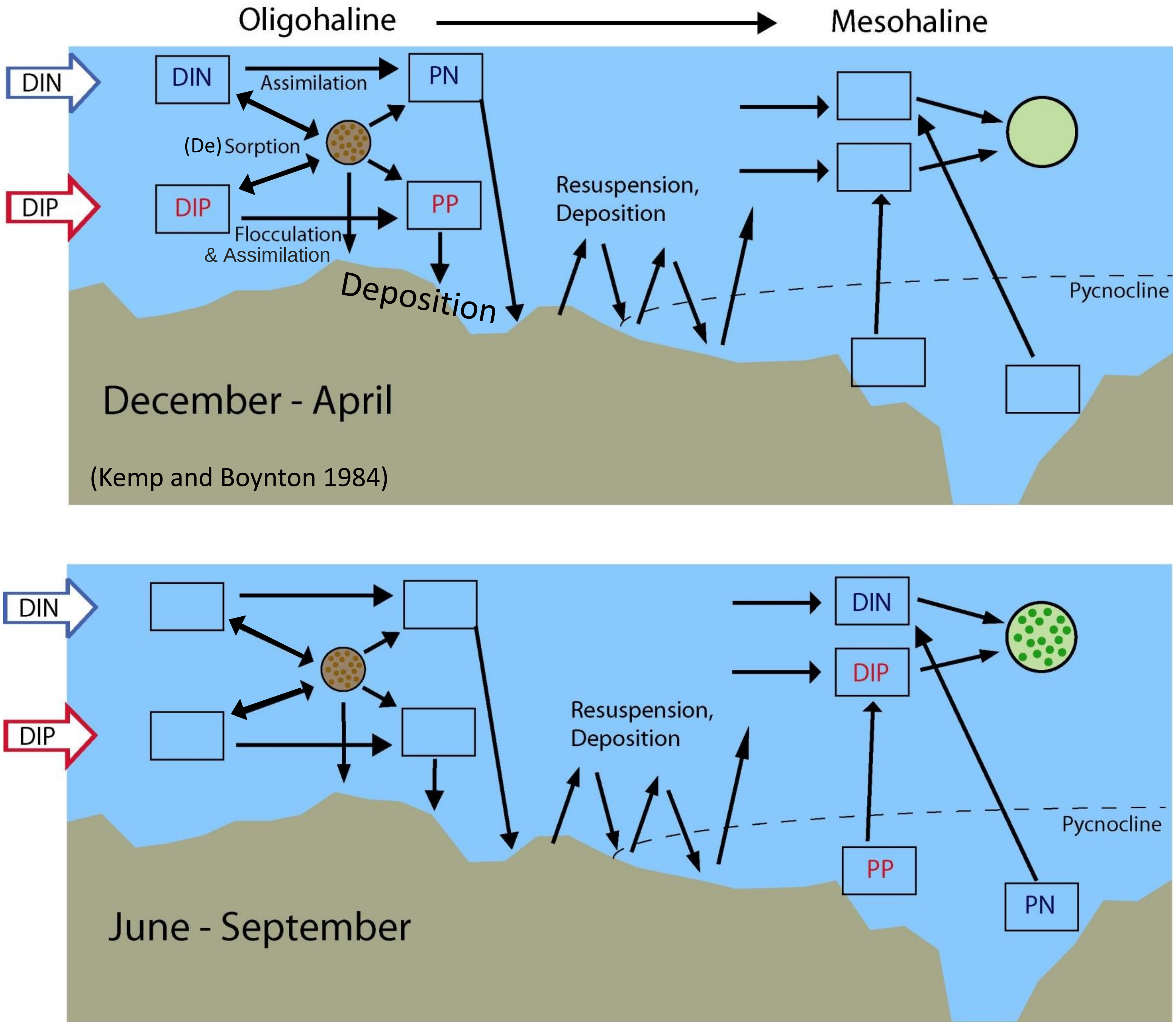
PRELIMINARY: Chesapeake Bay Nitrogen Budget

10^6 kg/yr	TN	NOx-N
Fall Line Total[λ]	61.5 (±58)	42.7 (±34.5)
Net exchange with Tributaries[ξ]	64.2 (±33.3)	10.9 (±13.5)
Net Input From Atlantic Ocean[Φ]	-39.4	4.5
Net sediment-water exchange[β]	25.4 (±7.1)	25.4 (±7.1)
Atmospheric Deposition	2.5	2.5
Denitrification[β]	-40.9 (±4.84)	-40.9 (±4.84)
Sediment burial[Δ]	-52.8	N/A

[Φ]Computed from box model for 1987-2015; [λ]Computed at USGS RIM stations 1985-2017 (Zhang); [ξ]Computed for DIN from net exchange in QUAL-ICM model 1985-2005; [φ]Computed from Phase 6 Chesapeake Bay watershed model 1985-2014; [β]from 30-year ROMS-RCA simulation (Shen et al., unpublished); [Δ]from Boynton et al. 1995 for entire Chesapeake System

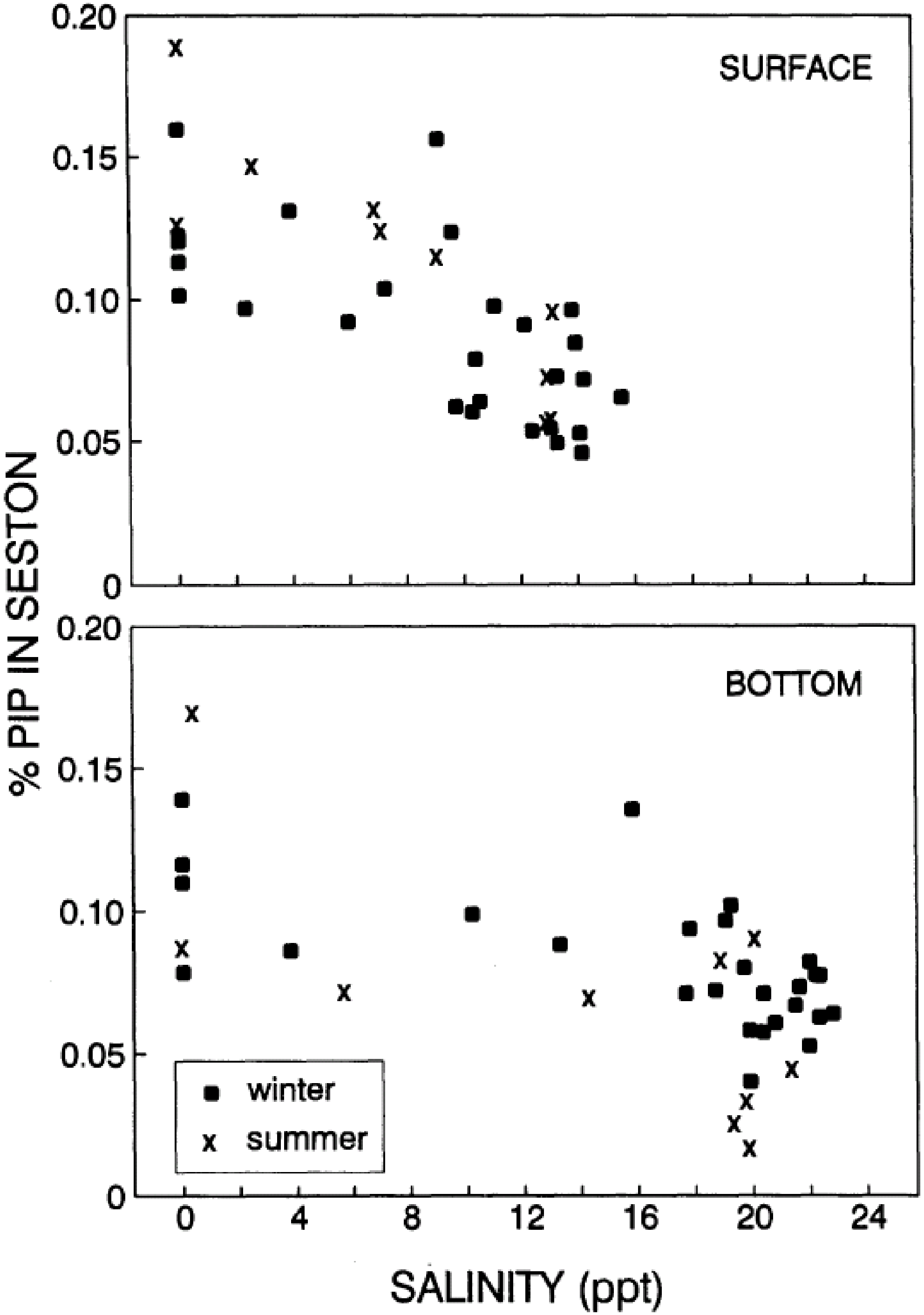
Denitrification = 30% of TN Load

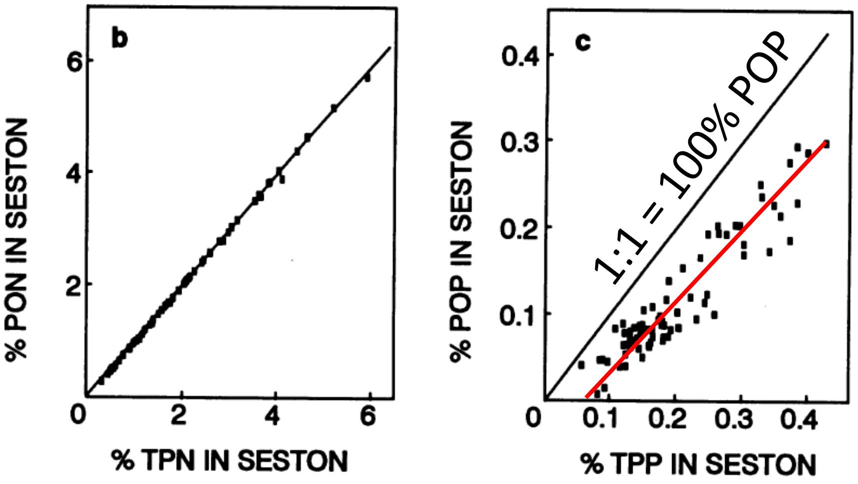
Regional and seasonal variability in physical transport and biogeochemistry



(Kemp and Boynton 1984)

Particulate Inorganic Contribution to PP highest in Low Salinity Waters, ***Low Overall***





Keefe (1994)