Methylmercury Production in the Coastal Zone: An Important Source of Methylmercury to Marine Fish?

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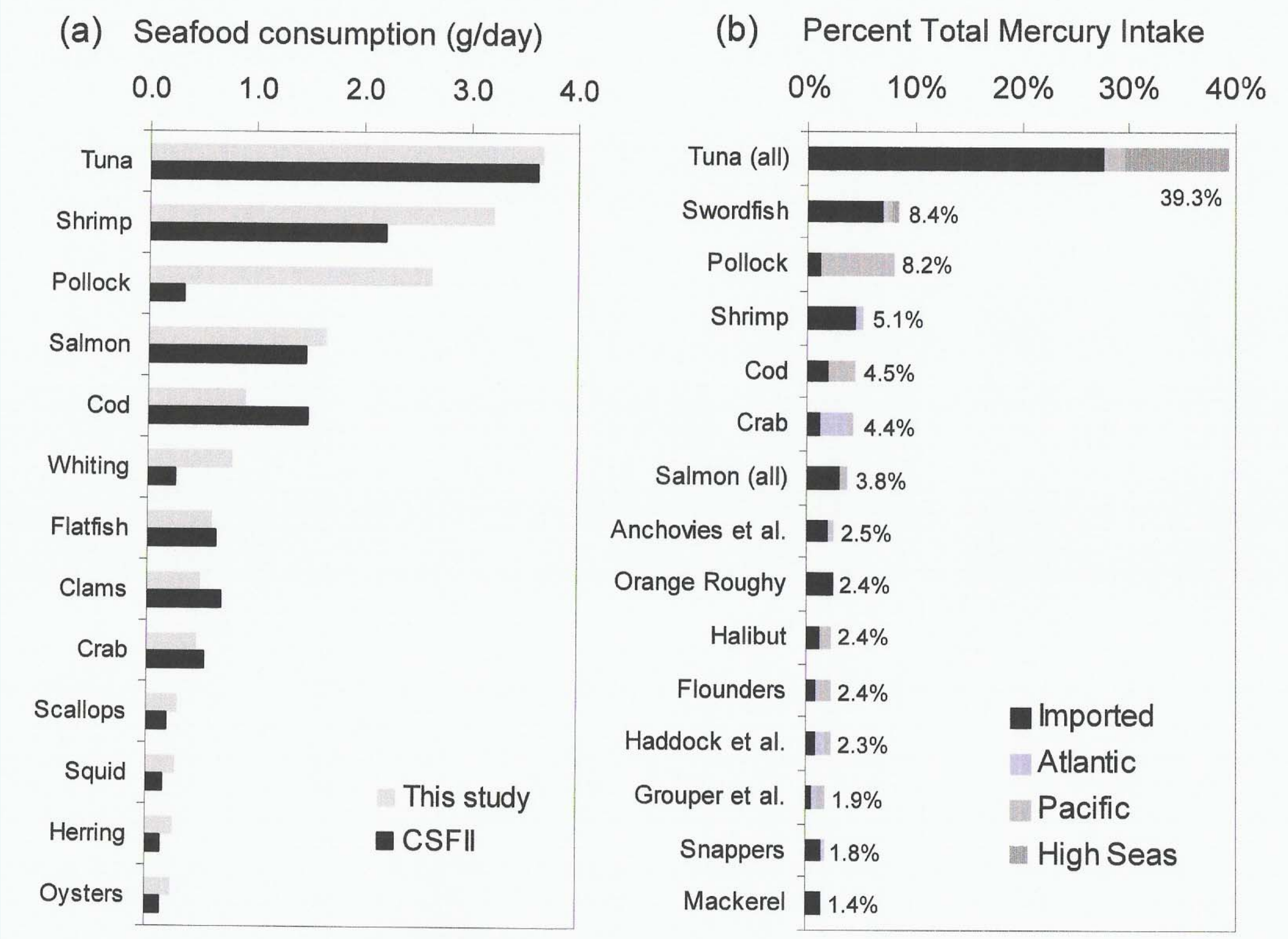
Outline

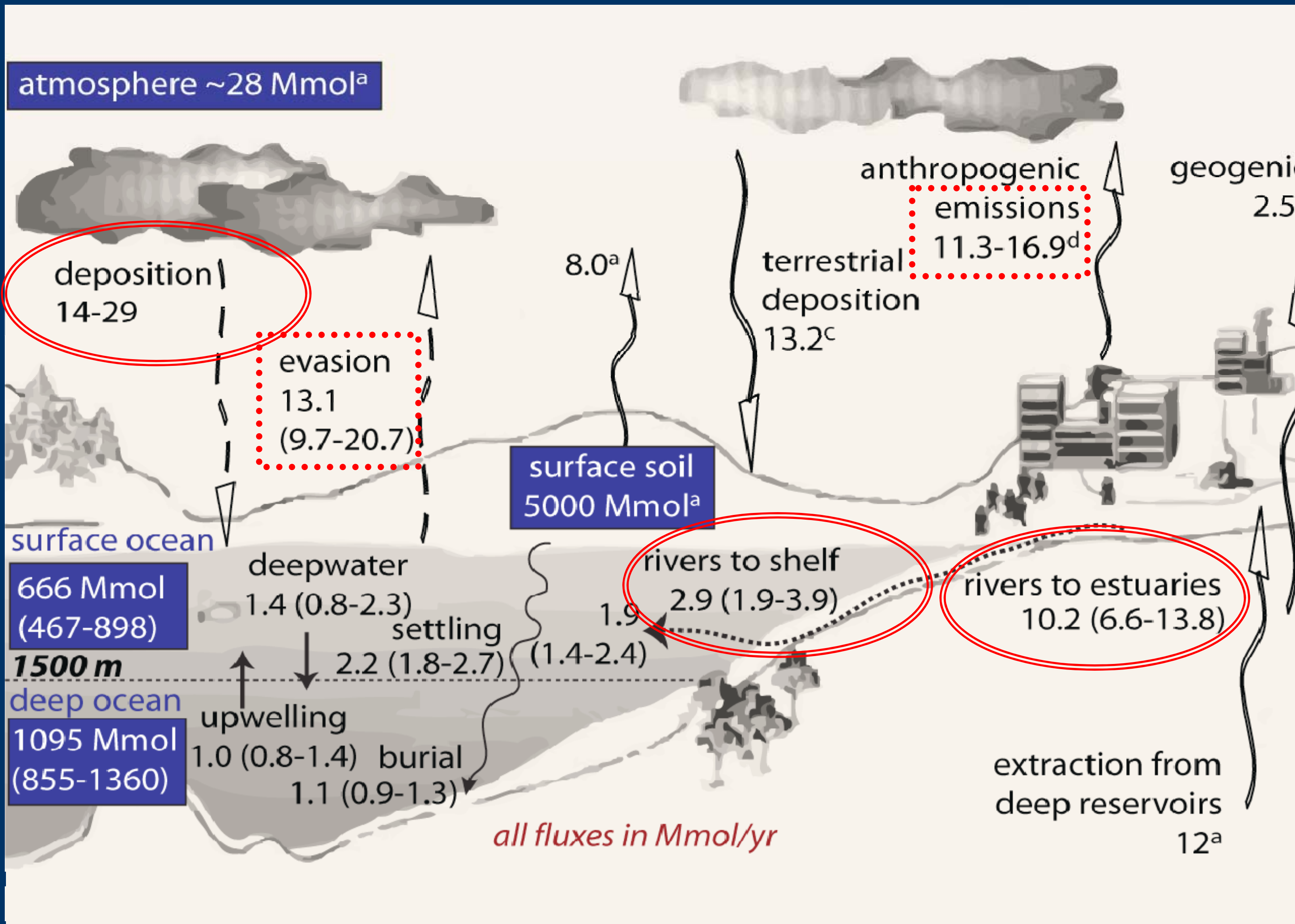
- Brief background on Mercury in the Environment
- Methylmercury in Ocean Fish, and its Sources
- Mercury Methylation in Coastal Waters
- Importance of Extreme Events in Mercury Cycling and Fate
- Is the Coastal Zone Important?

Consumption Patterns and Percent of Population-Wide Mercury Intake by Fish Species & Geographic Source Region for the "Average" Consumer

Sunderland (2007)

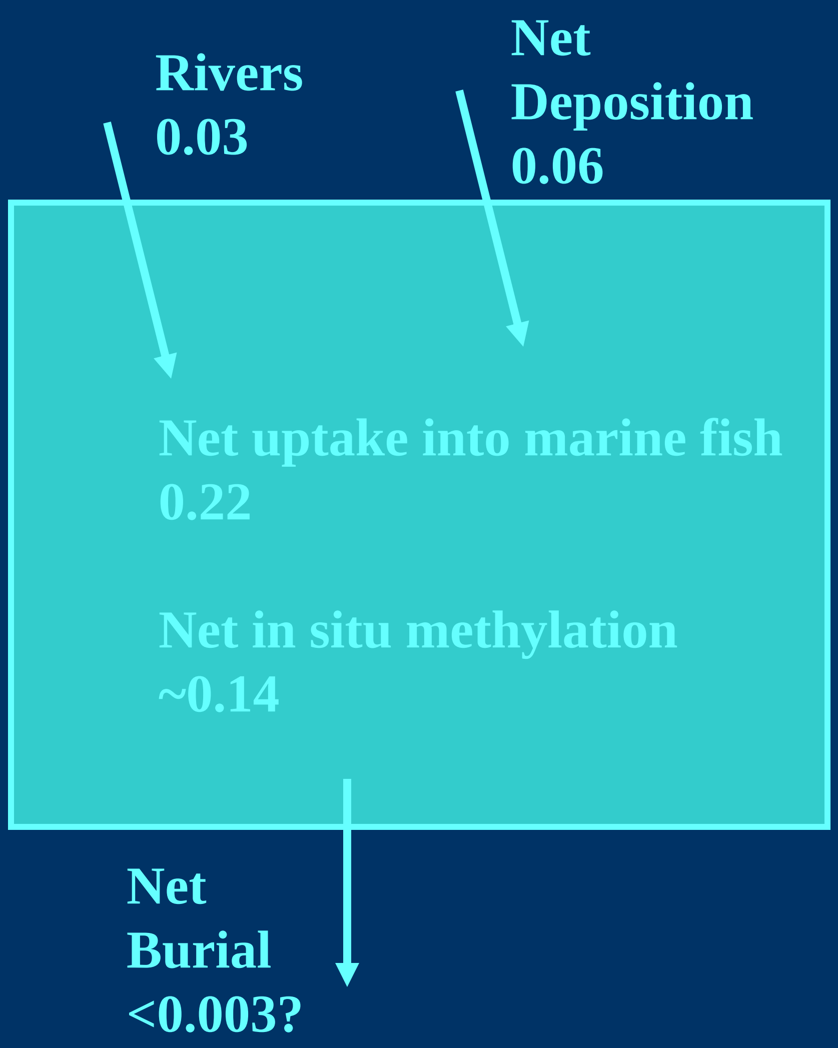


EPA's RFD exceeded by 1% of the "average consumers"



Source: Sunderland & Mason, 2007

We know about the inputs to the ocean of inorganic Hg (mostly atmospheric). But, where does the methylmercury come from?



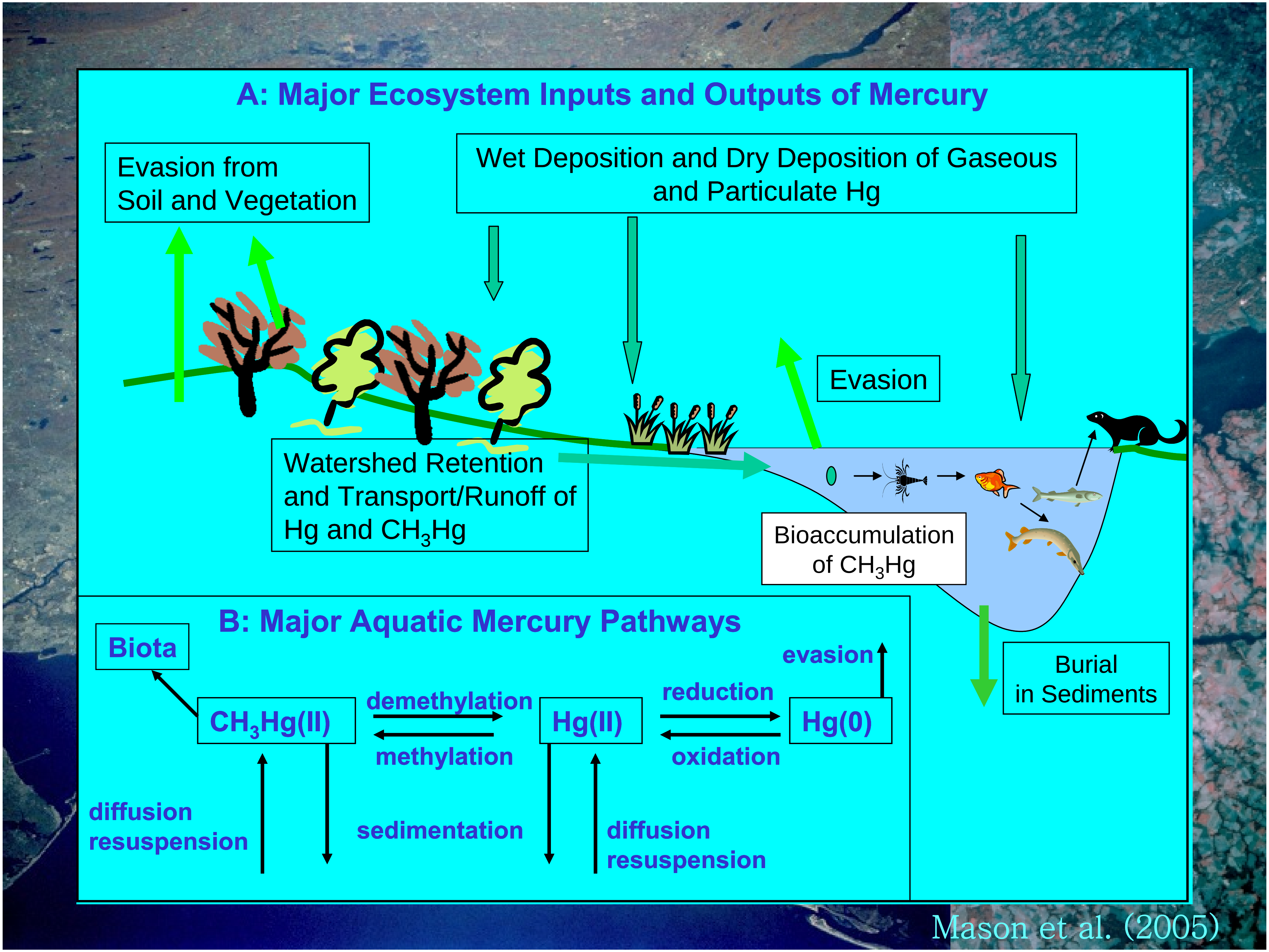
<u>Ratio: Pluvial/Fluvial</u>

Hg	~15
MeHg	~2

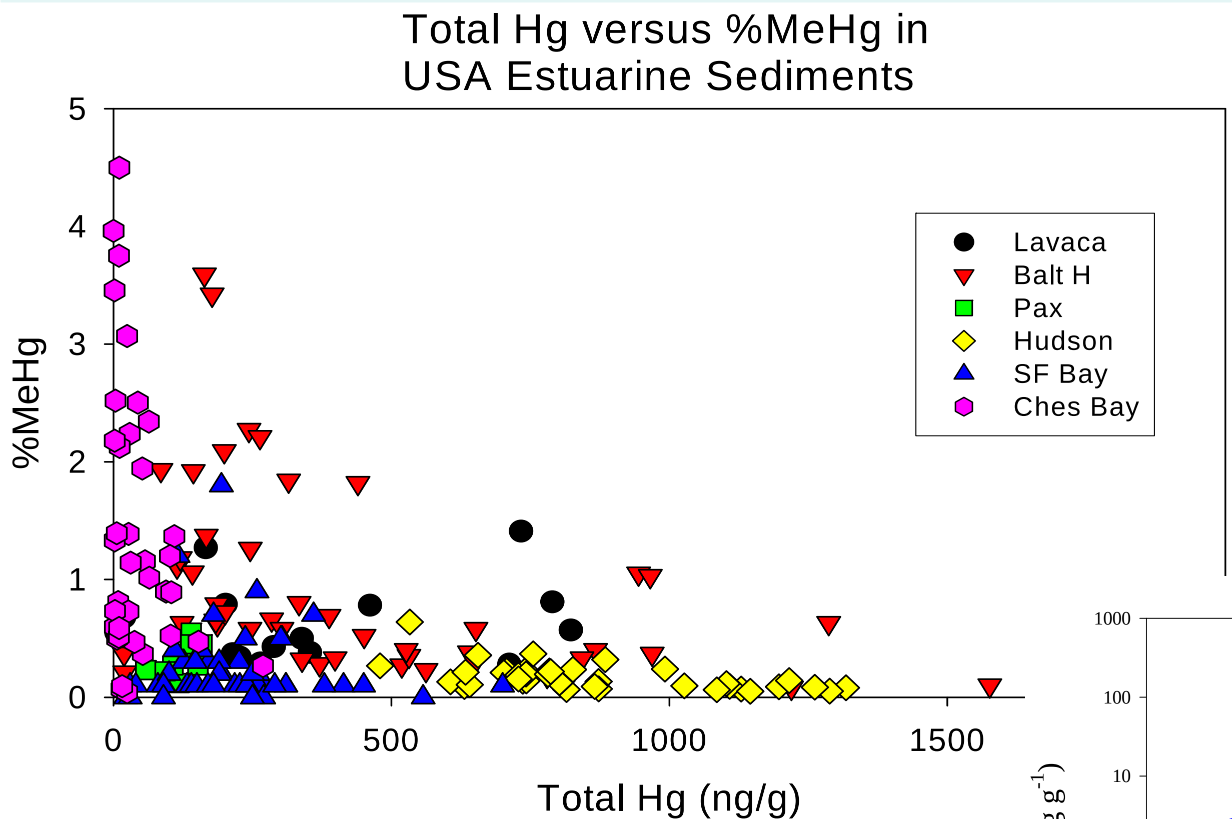
Major source of MeHg is *in situ* production

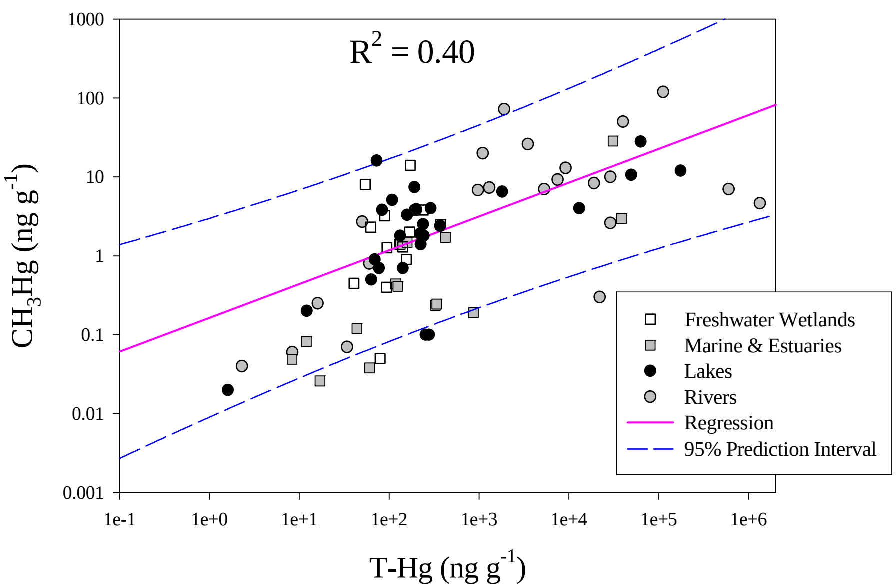
But where?

1. Deep ocean sediments
(ala Kraepiel et al., 2003)
2. Water column in low oxygen environments
(ala Mason et al)
3. Shelf and slope sediments
(ala Mason and Fitzgerald et al)

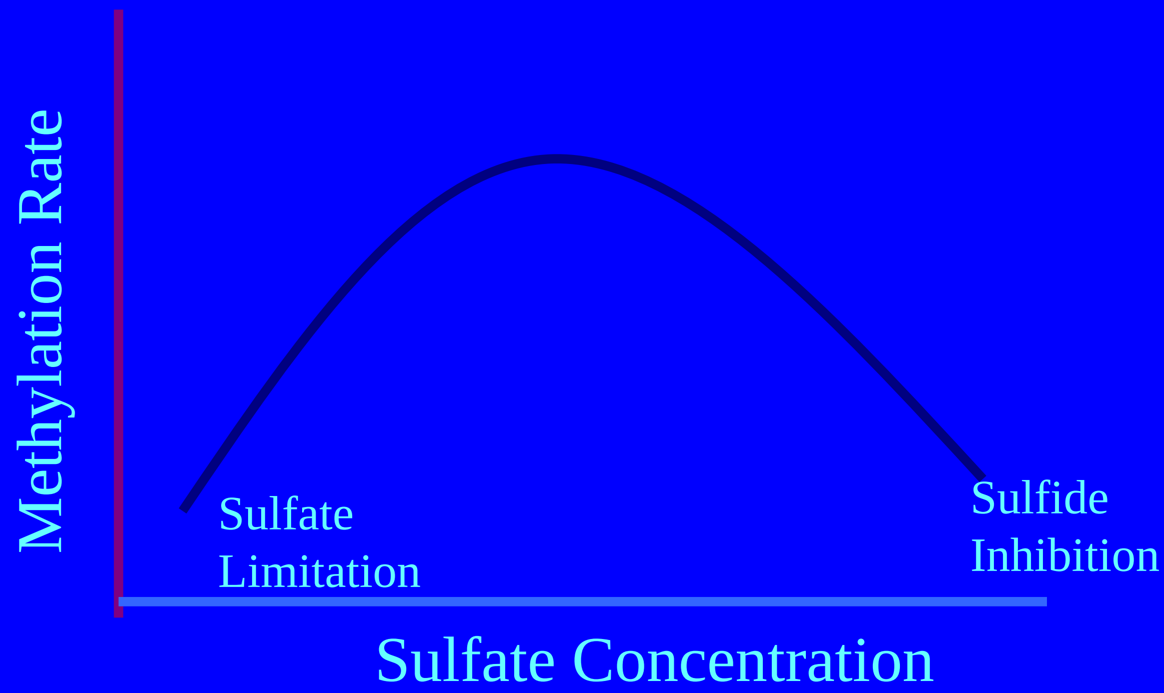

A: Major Ecosystem Inputs and Outputs of Mercury
Evasion from Soil and Vegetation
Wet Deposition and Dry Deposition of Gaseous and Particulate Hg
Evasion
Watershed Retention and Transport/Runoff of Hg and CH_3Hg
Bioaccumulation of CH_3Hg
Burial in Sediments
B: Major Aquatic Mercury Pathways
Biota
$CH_3Hg(II)$
demethylation
methylation
Hg(II)
reduction
oxidation
Hg(0)
evasion
diffusion resuspension
sedimentation
diffusion resuspension
Mason et al. (2005)

The fraction of total mercury that is methylmercury appears to decrease with increasing mercury concentration in estuaries. Also, it is different for different types of ecosystems





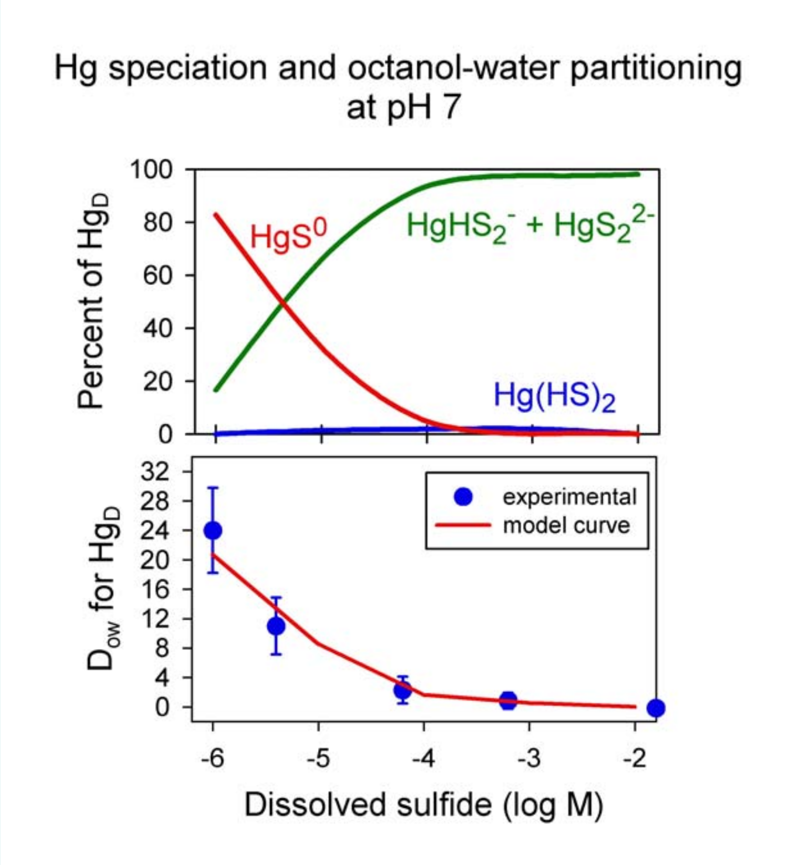
An Often-Observed Empirical Relationship Between Mercury Methylation and Sulfate/Sulfide levels

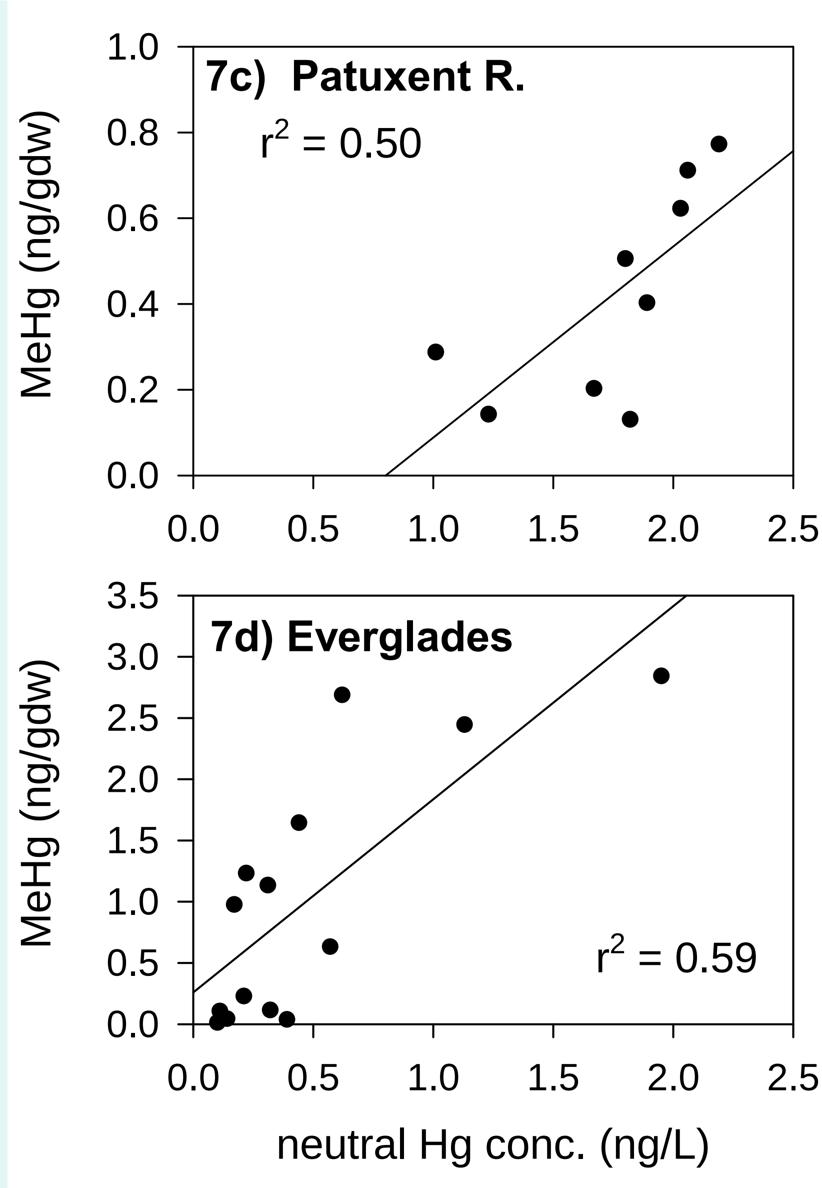


- At low sulfate, microbes are limited by sulfate concentration and methylation is lower.

- At high sulfate, inhibition of methylation appears to coincide with high sulfide. However precipitation of insoluble HgS does not appear to be controlling factor

The Role of Mercury Speciation

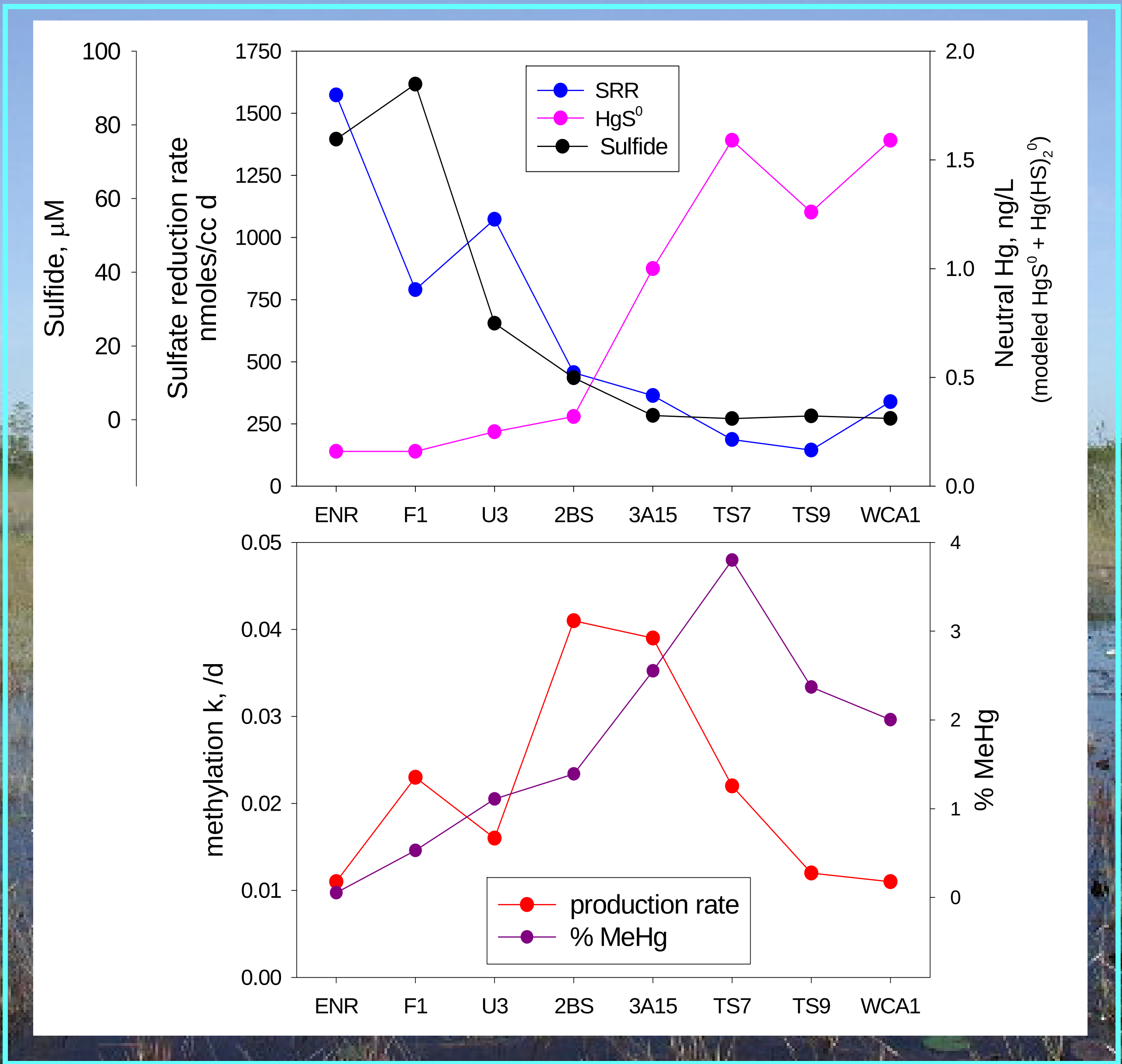




Hypothesis: Neutral Hg-sulfide species concentration controls methylation rate as this is the form of the Hg taken up by bacteria. The fraction as the neutral complexes is a function of sulfide conc. Thus, methylation rate, or in-situ MeHg conc. is a function of dissolved speciation

Benoit et al., 1999a; 1999b

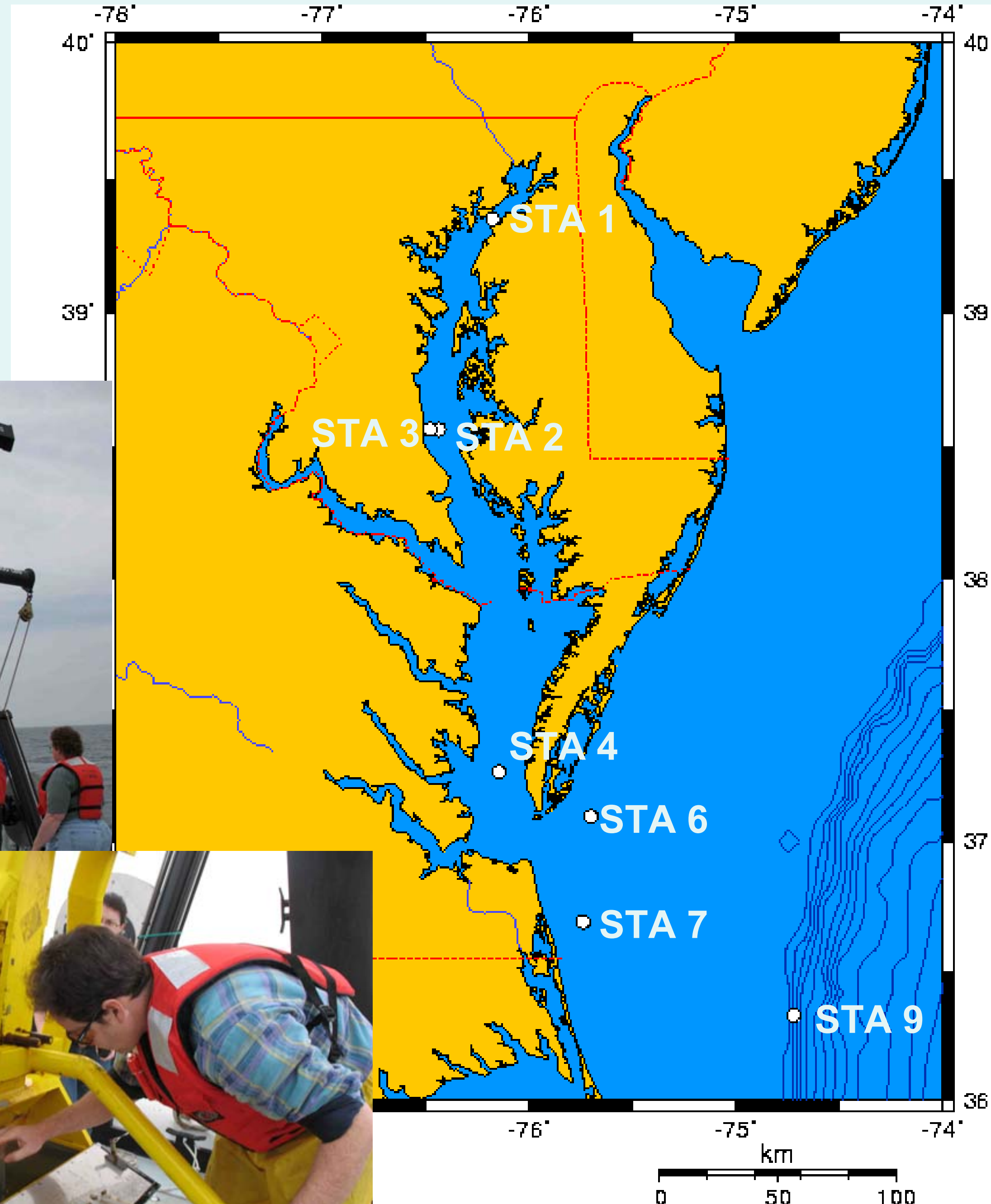
Everglades – Changes across stations in ~ N-S direction
Illustrates the importance of chemistry and Hg speciation



Benoit et al., 2003

Experimental Method

Undisturbed sediment was collected from stations in the Chesapeake Bay and mid-Atlantic shelf and slope



Experimental Method

- Solid phase
  - Hg_T
  - MeHg
  - Ancillary - C, N, S, Fe(II), Fe(III)
- Pore water
  - Hg_T
  - MeHg
  - Ancillary - SO_4^{2-}, HS^-, Cl^-, Mn, Fe
- Bacterial activity
  - CO_2 and CH_4 production
  - SO_4^{2-} reduction
- Hg methylation and MeHg demethylation rates
  - Stable mercury isotope incubations

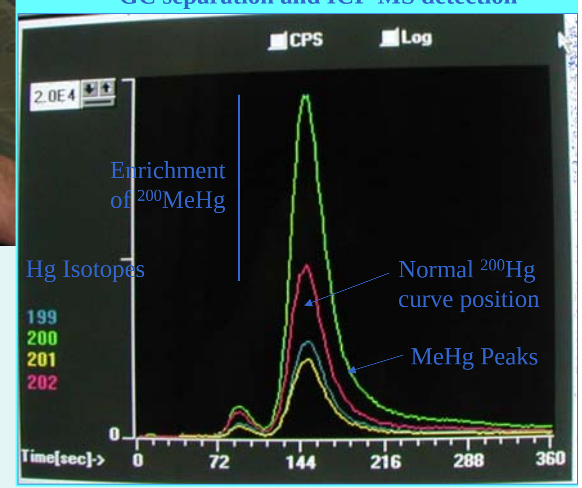
$$^{201}Hg(II) \xrightarrow{k_m} Me^{201}Hg$$

$$Me^{199}Hg \xrightarrow{k_{dm}} {}^{199}Hg(II)$$

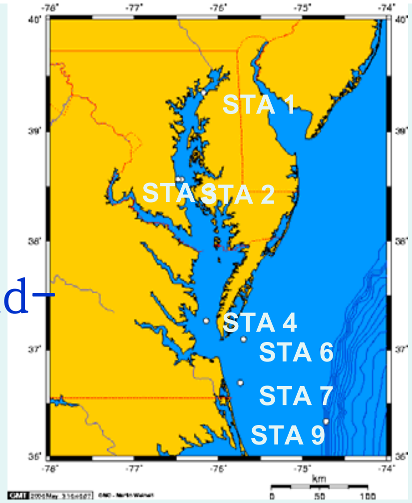
$$k_m = \frac{[Me^{201}Hg]}{[^{201}Hg]t}$$

$$k_{dm} = \frac{1}{t} \times \ln\left[\frac{[Me^{199}Hg]}{[Me^{199}Hg]_0}\right]$$

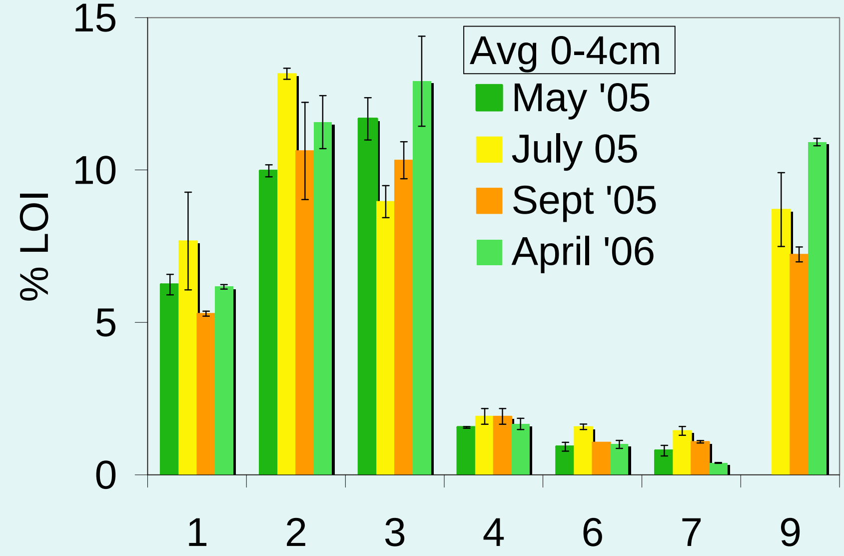
MeHg analysis by aqueous ethylation GC separation and ICP-MS detection

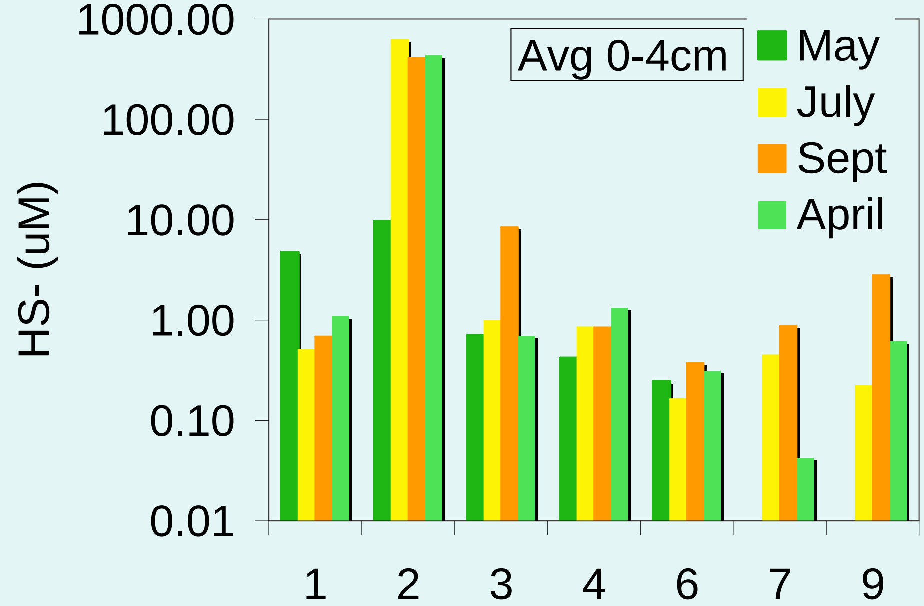


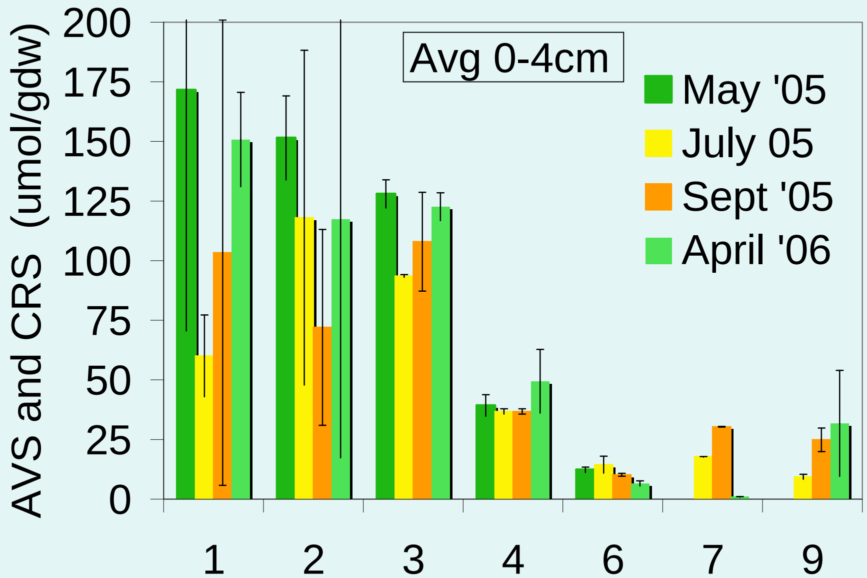
Results – Ancillary Data



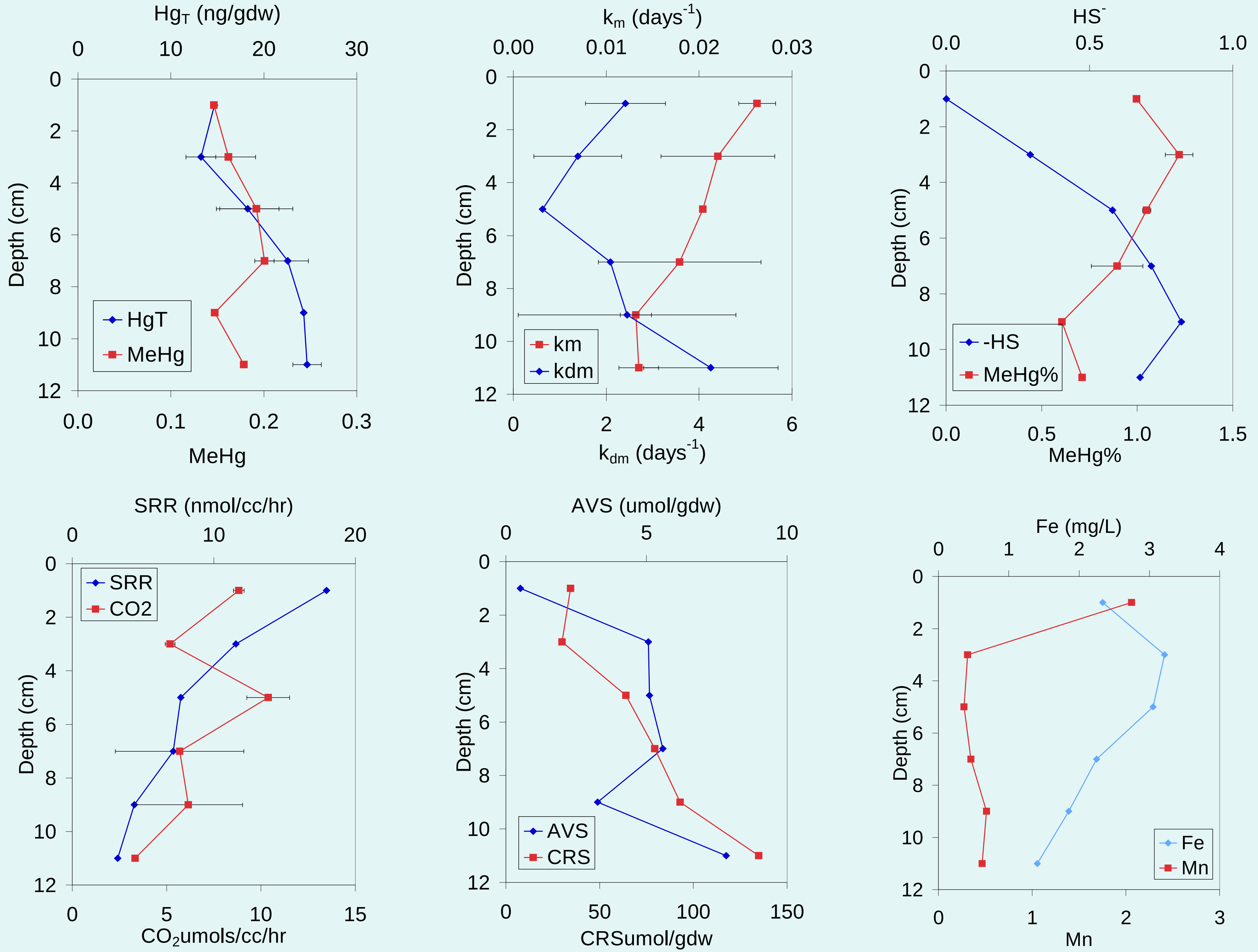
Sediment organic content (as %LOI) is high in the mid-Bay and low on the shelf. The slope (~600 m) site has higher OC than Sts. 4-7. Sulfide varies from very low offshore values to high values at the mid-Bay site. Shows a strong seasonal cycle in the Bay related to sulfate reduction



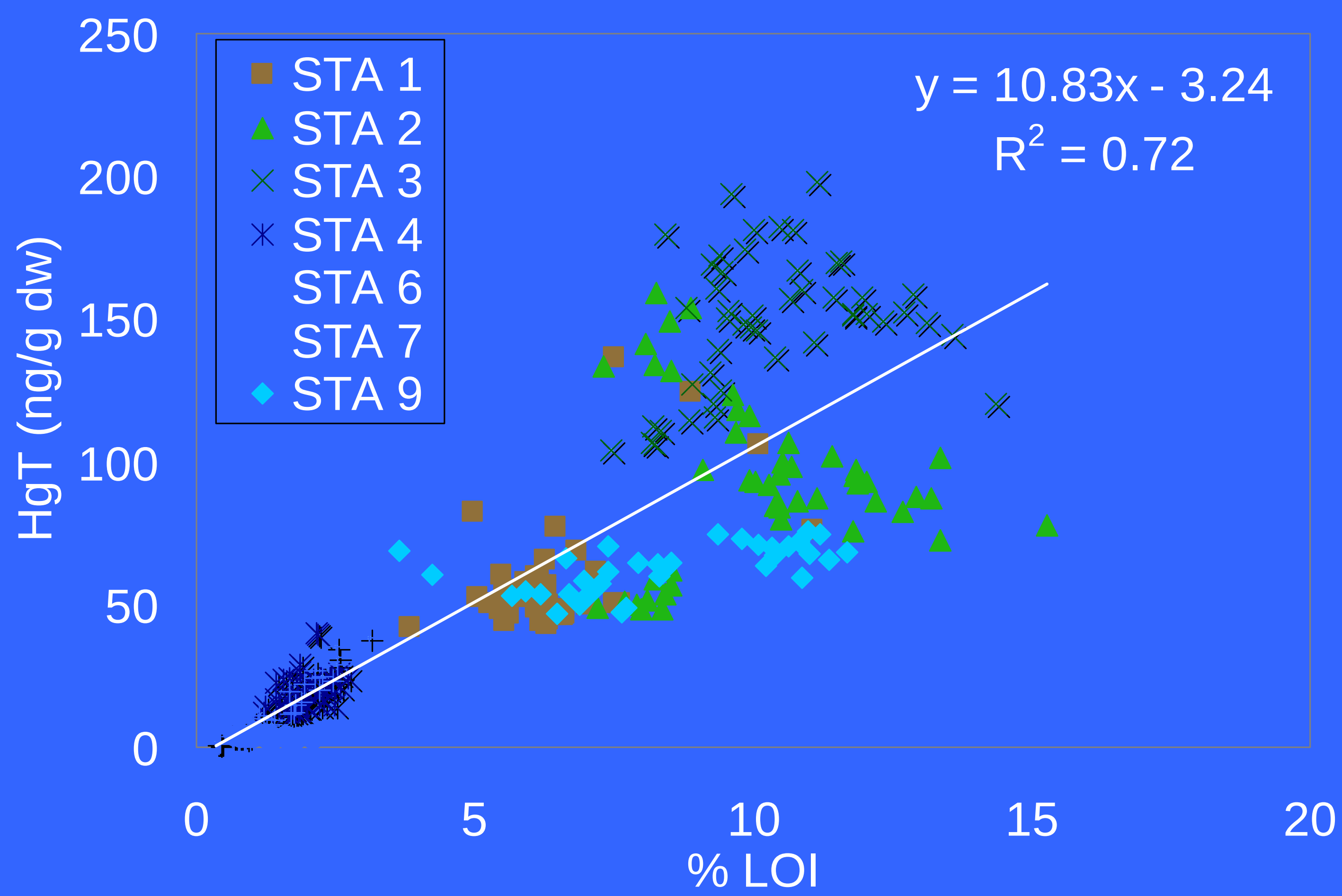




Vertical profiles for the sediments at St. 4

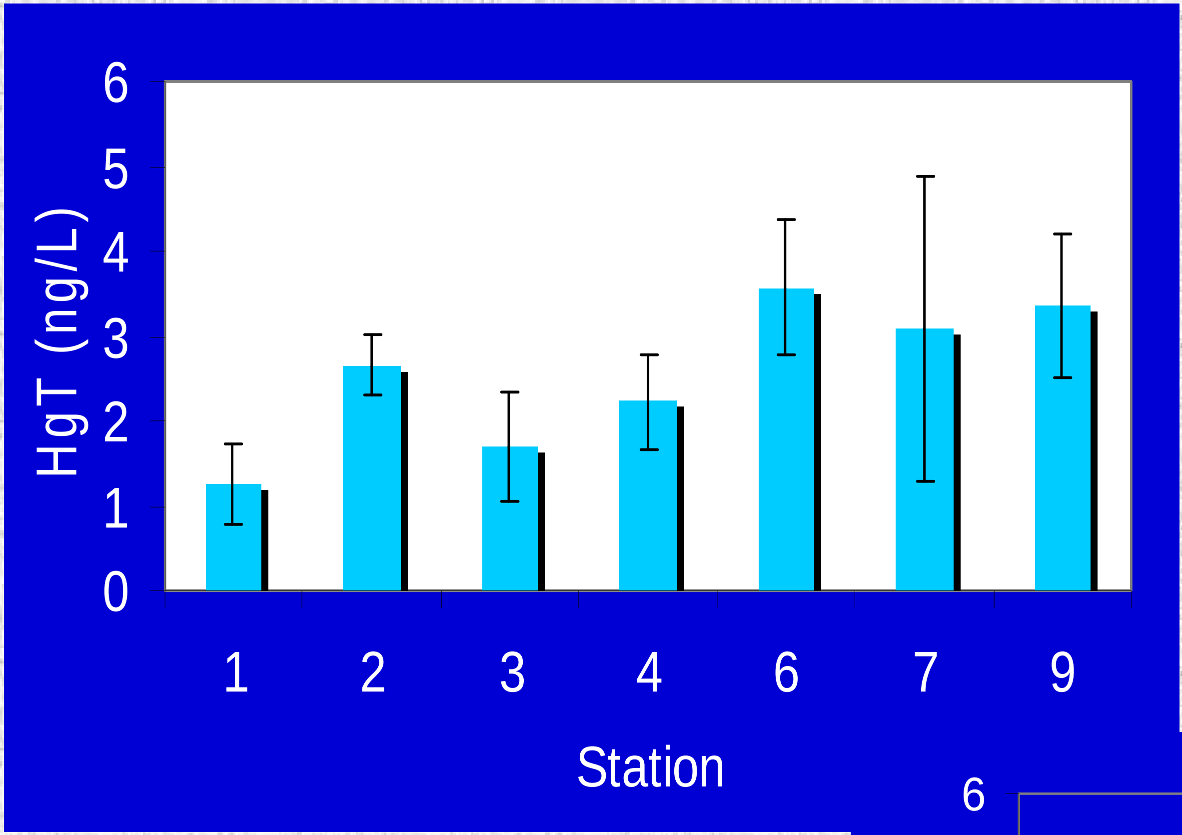


Results - Controls of Hg_T speciation



	Adj r^2	y-intercept	% LOI	AVS/CRS	HS-
1	0.724	-5.16	11.0		
2	0.769	-10.97	8.91	0.180	
3	0.810	-15.00	9.85	0.210	-0.0444

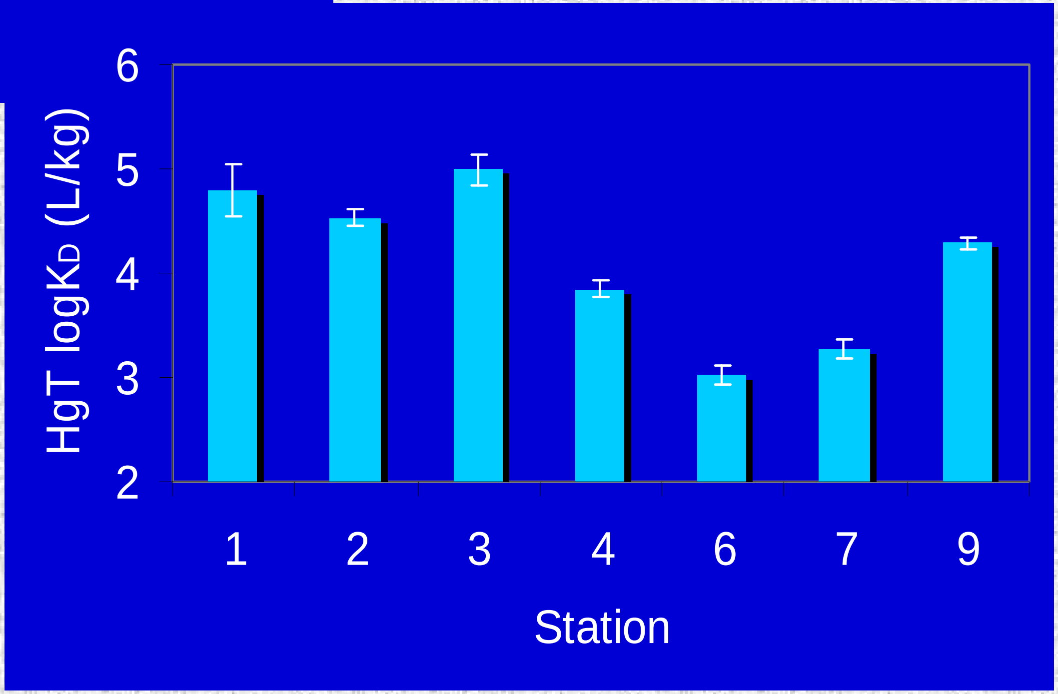
Fe(II) and Fe(III) not significant.



Porewater concentrations are of the same order for the offshore sandy sites compared to the organic rich Bay sites, suggesting differences in the dissolved-solid partitioning between these locations

$$K_D = \frac{[Hg_{solid}]}{[Hg_{dissolved}]}$$

In the upper sediments, therefore, the K_D differences are largely driven by differences in the solid phase concentration

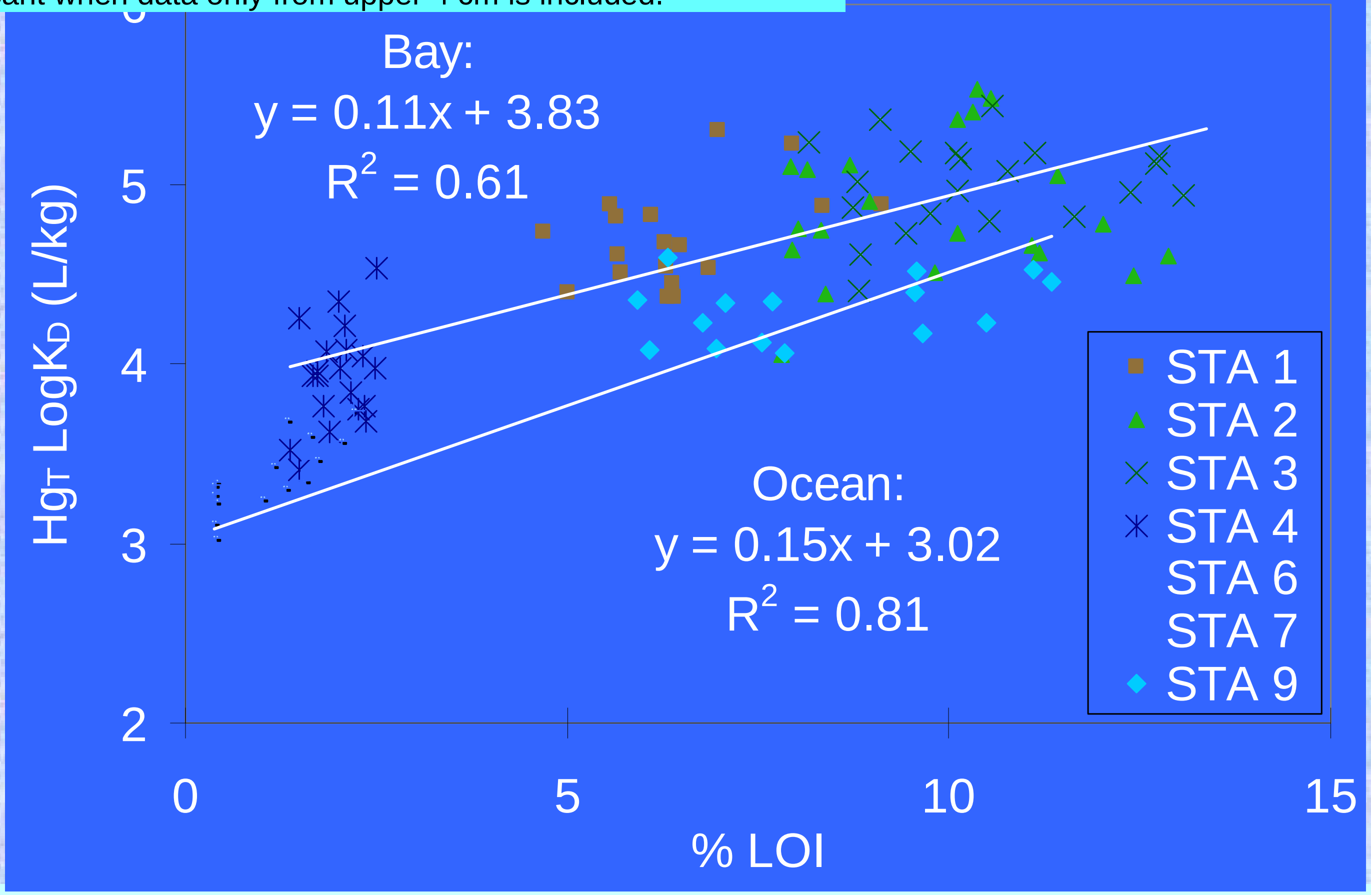


Stepwise Multiple Linear Regression for Hg_T $LogK_D$

	Adj. r^2	y-intercept	% LOI	AVS/CRS
1	0.726	3.27	0.161	
2	0.810	3.18	0.113	0.00375

Not significant: HS^-, Fe(II), Fe(III)

HS- becomes significant when data only from upper 4 cm is included.

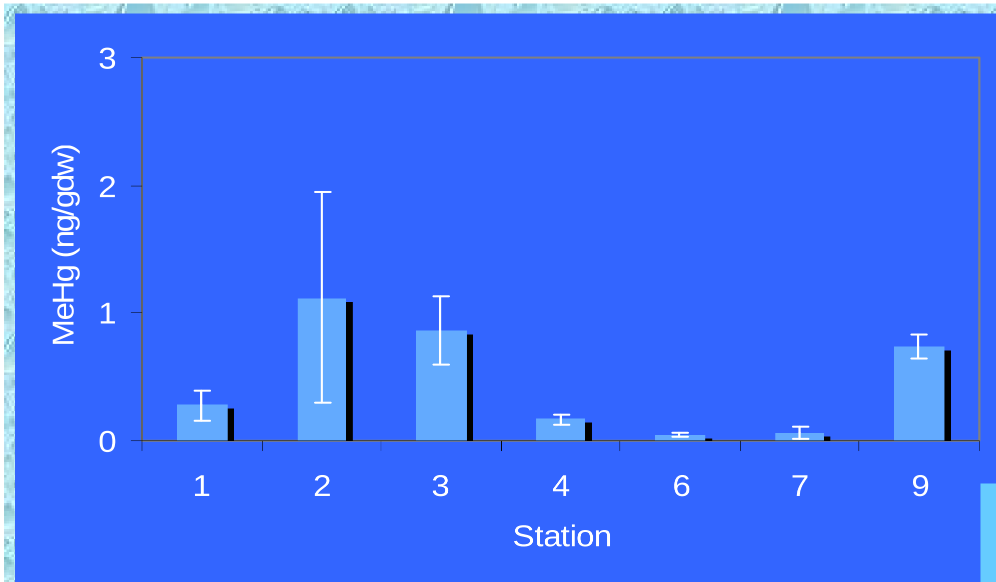


Hammerschmidt and Fitzgerald (2006): LIS and Shelf

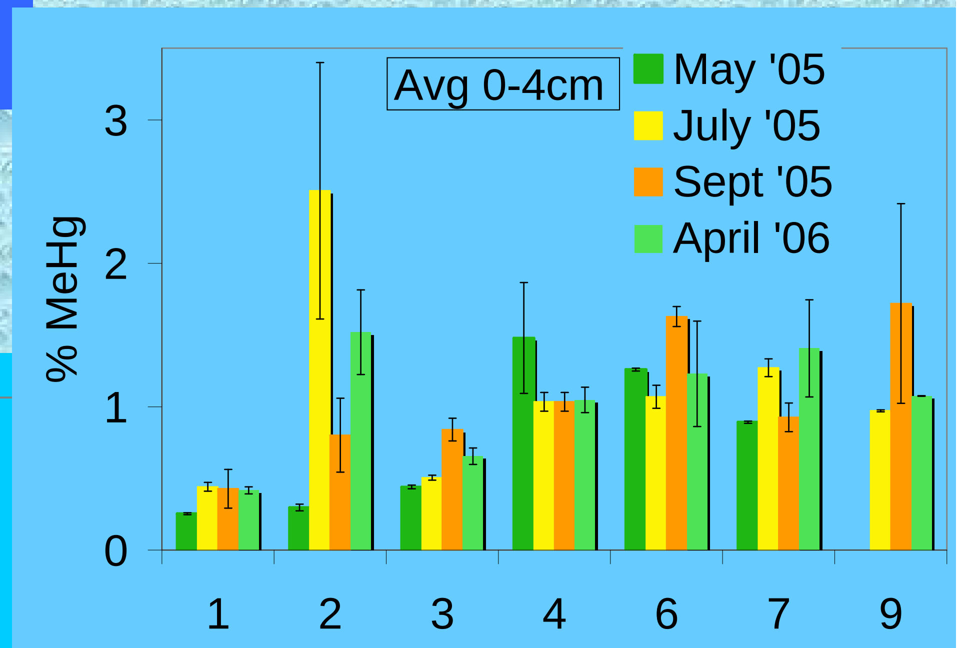
$Log(K_D)=0.15[\%OM] + 3.13$; $r^2=0.75$, $p<0.01$

Senn et al (in review) Gulf of Mexico; Much lower %OM - <3%

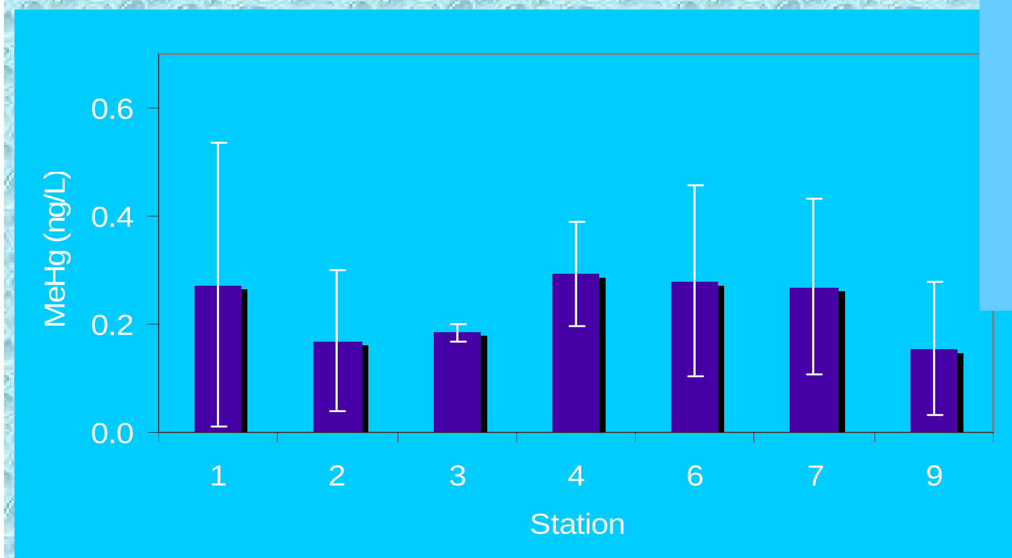
$Log(K_D) = 0.59[\%OM] + 3.2$; $r^2 = 0.65$, $p<0.01$



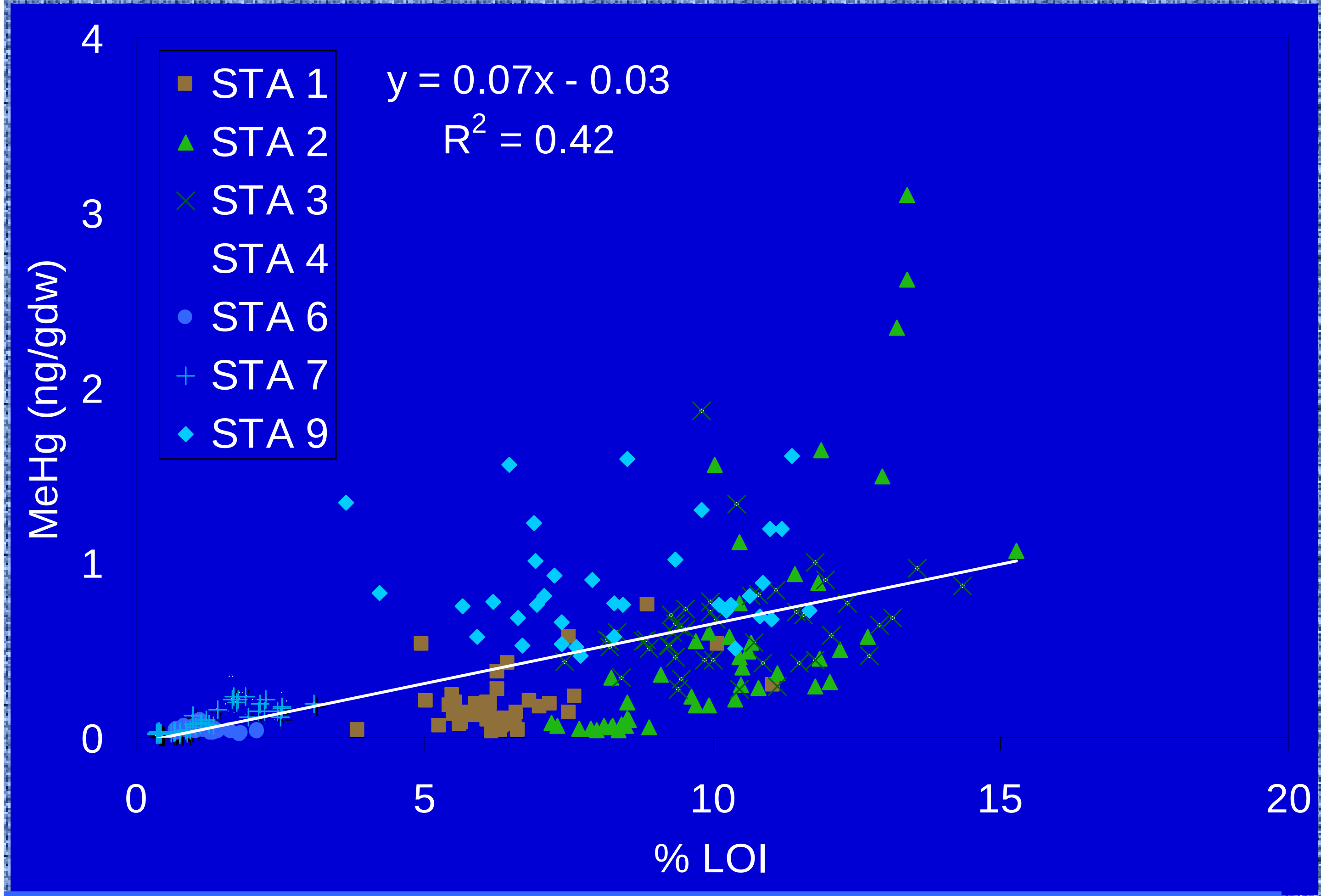
While MeHg concentrations are higher in the bulk phase for the high OC Bay sites, there is much less difference in terms of porewater concentration. Overall, the fraction of Hg as MeHg is higher for the offshore sites



Station 2 has high variability in all parameters; may reflect the fact that this site has seasonal water column anoxia; water column methylation occurs at St. 2



The relationship between total Hg and MeHg is not strong, as found elsewhere. %MeHg is relatively high cf. other coastal systems.



Hammerschmidt and Fitzgerald (2006): LIS/Shelf
y=0.13x + 1.55
r2=0.77

Stepwise Multiple Linear Regression for bulk-phase MeHg concentration

	Adj. r^2	y-intercept	% LOI	AVS/CRS	k_m
1	0.419	-0.0353	0.0682		
2	0.605	0.0650	0.101	-0.00288	
3	0.630	-0.0440	0.0966	-0.00236	3.84

Not significant: $Hg_{T(pw)}$, Fe_{dis}, SO_4, k_m*$Hg_{T(pw)}$, HS^-

Sites sampled in July 06., in estuary, on the shelf and slope, including a transect at Station 9

Sta #	Dpth (m)	Type
STA 2	16	mud
STA 3	6	mud
STA 4	16	sandy mud
STA 6	16	dry clayey sand
STA 7	15	sand
STA 9	646	mud
STA 9A	85	coarse, worms
STA 9B	107	sandy mud
STA 10	48	coarse sand/shell
STA 11	227	clayey sand
STA 12	600	organic, mud
STA 13	30	sand
STA 14	38	sand
STA 15	50	coarse grain

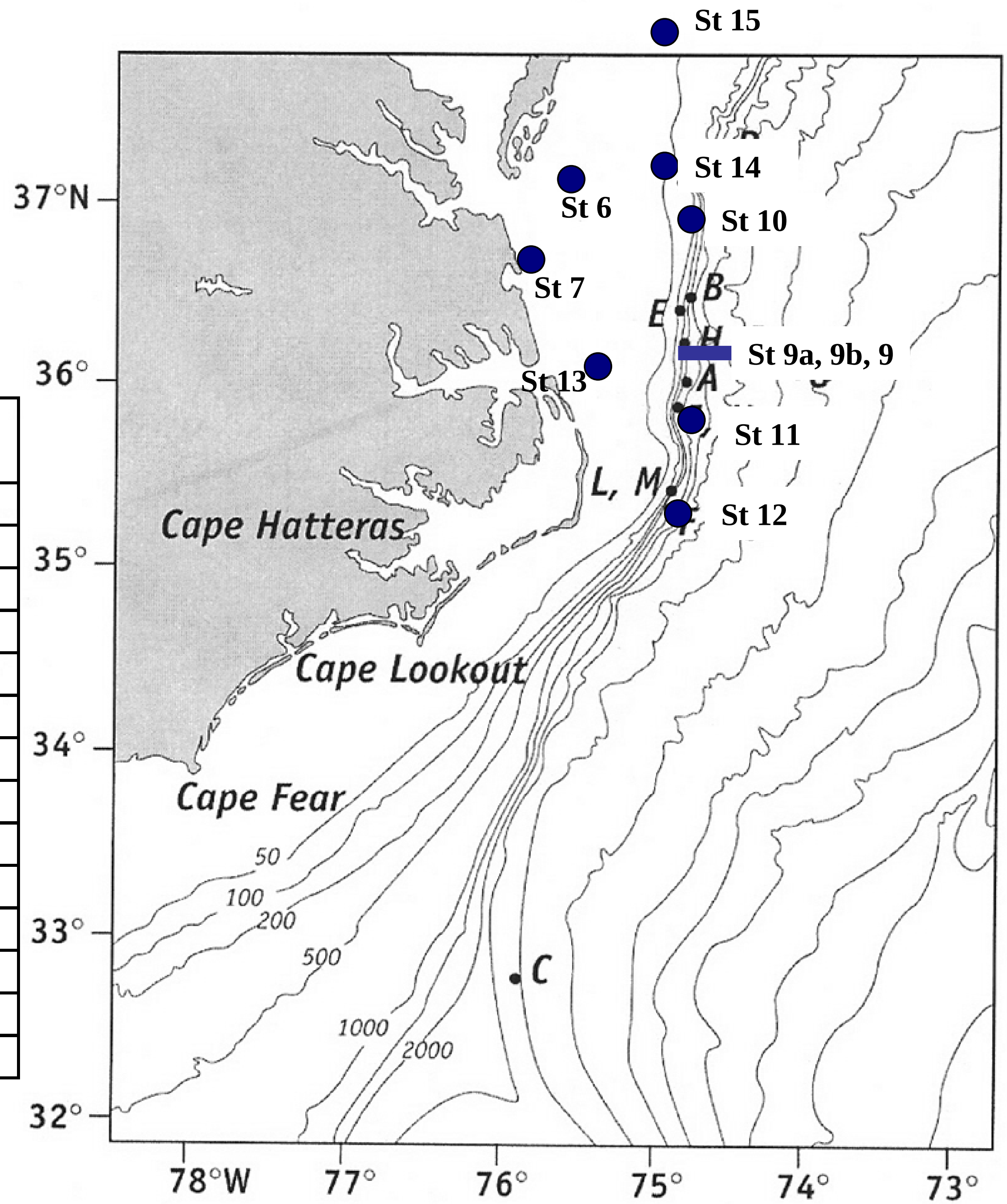
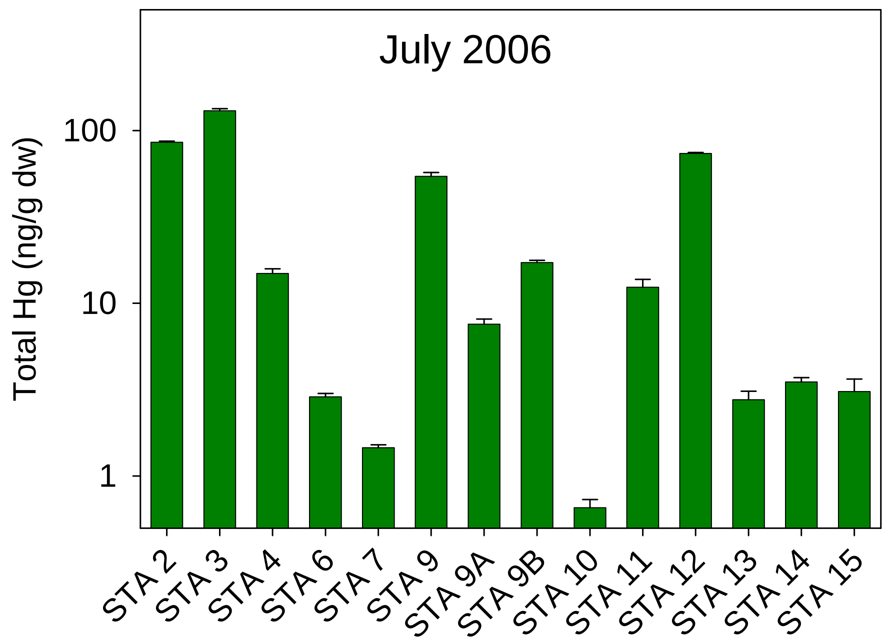
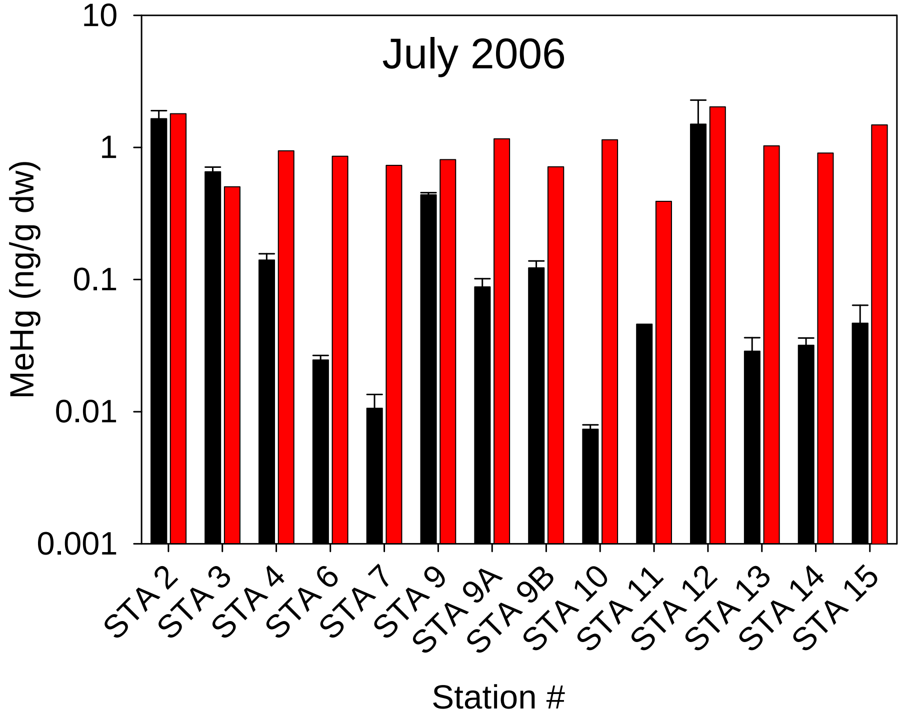
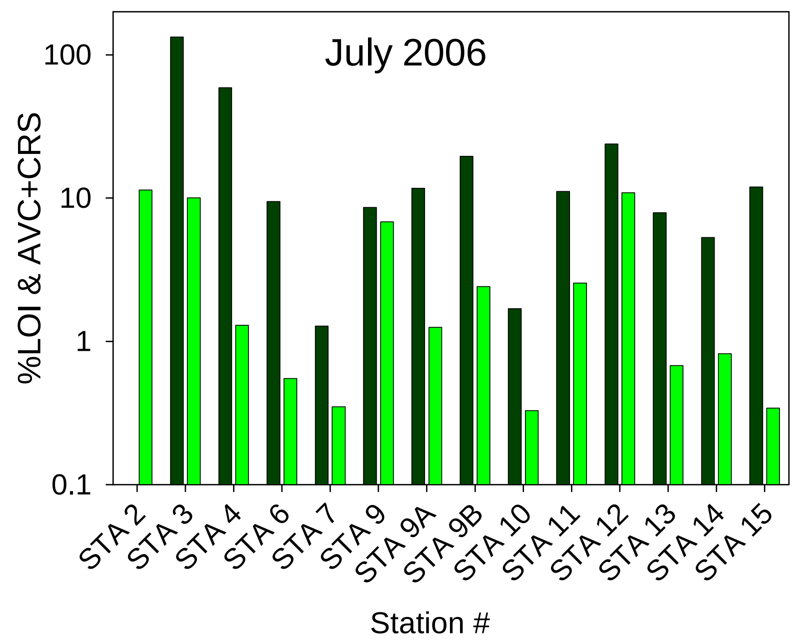


Fig. 1. Locations of in situ benthic flux chamber deployment sites.

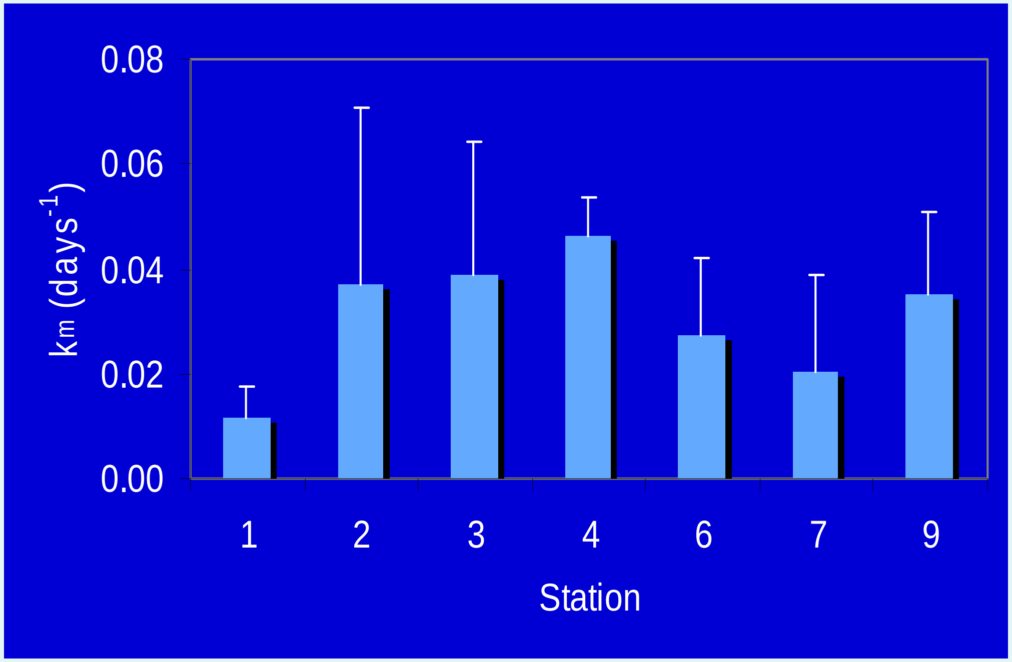

July 2006
Total Hg (ng/g dw)
100
10
1
STA 2
STA 3
STA 4
STA 6
STA 7
STA 9
STA 9A
STA 9B
STA 10
STA 11
STA 12
STA 13
STA 14
STA 15

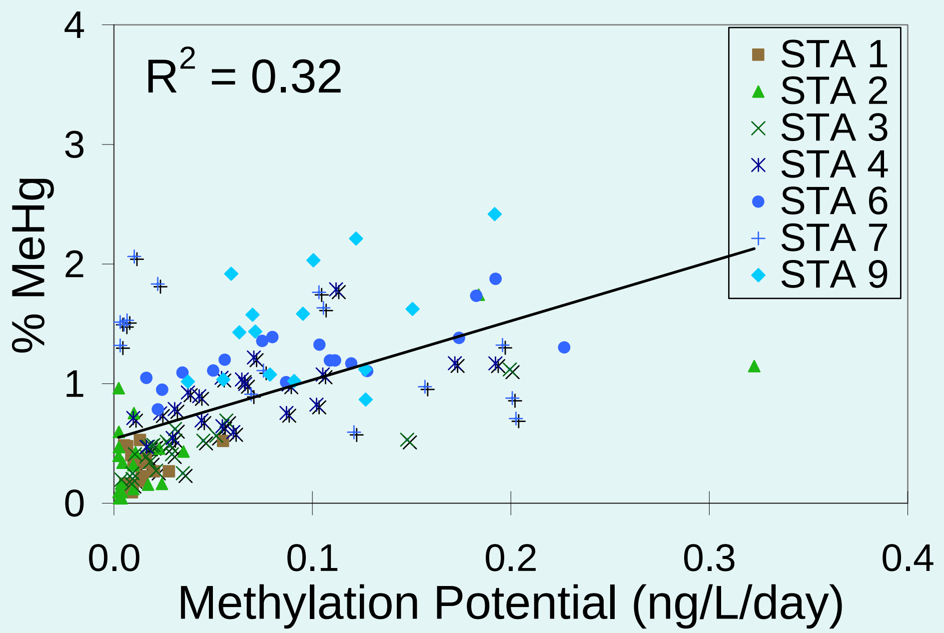

July 2006
MeHg (ng/g dw)
10
1
0.1
0.01
0.001
STA 2
STA 3
STA 4
STA 6
STA 7
STA 9
STA 9A
STA 9B
STA 10
STA 11
STA 12
STA 13
STA 14
STA 15
Station #

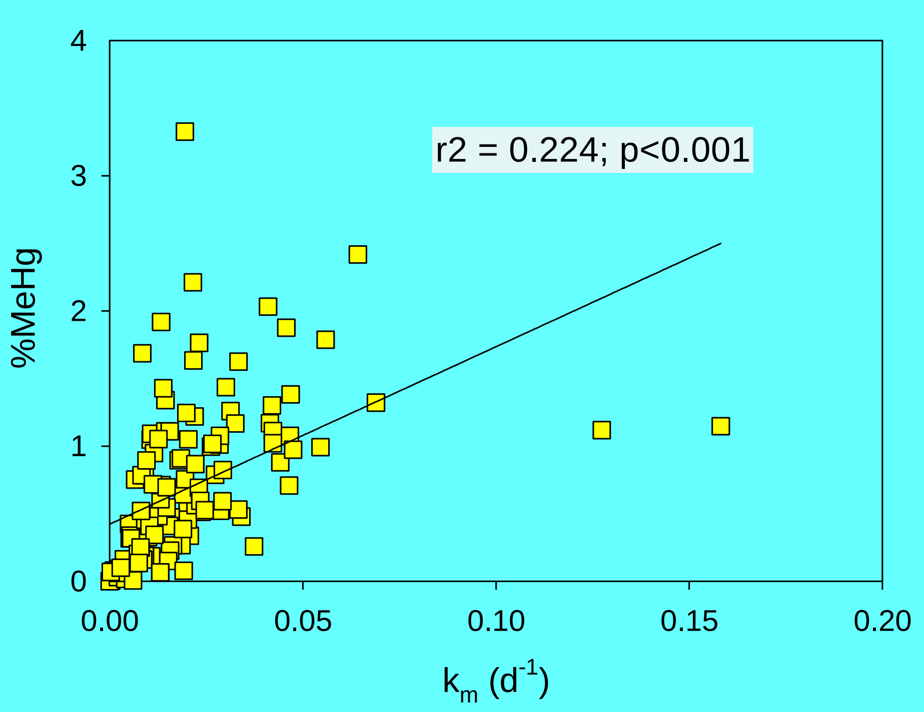

July 2006
%LOI & AVC+CRS
100
10
1
0.1
STA 2
STA 3
STA 4
STA 6
STA 7
STA 9
STA 9A
STA 9B
STA 10
STA 11
STA 12
STA 13
STA 14
STA 15
Station #

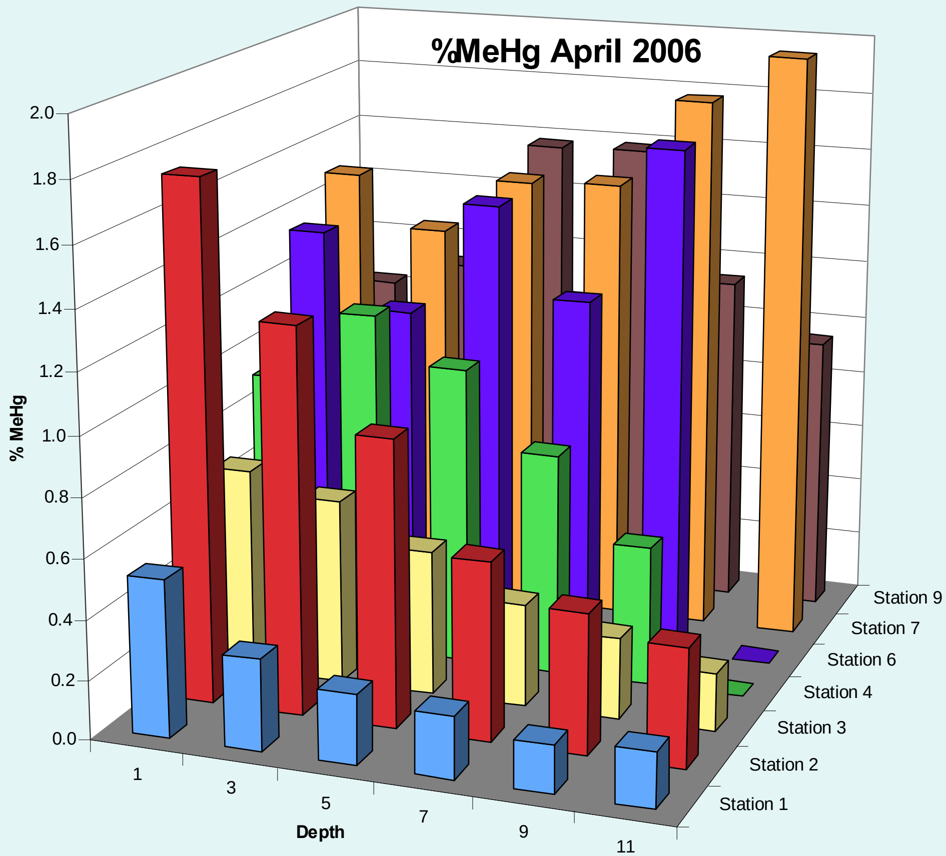
Mercury Methylation

The estimated methylation rate, and the potential rate ($k[Hg_T]$), correlate with the in situ %MeHg. Such a relationship is valid if methylation/demethylation are psuedo reversible first order reactions and demeth rates are relatively constant across sites

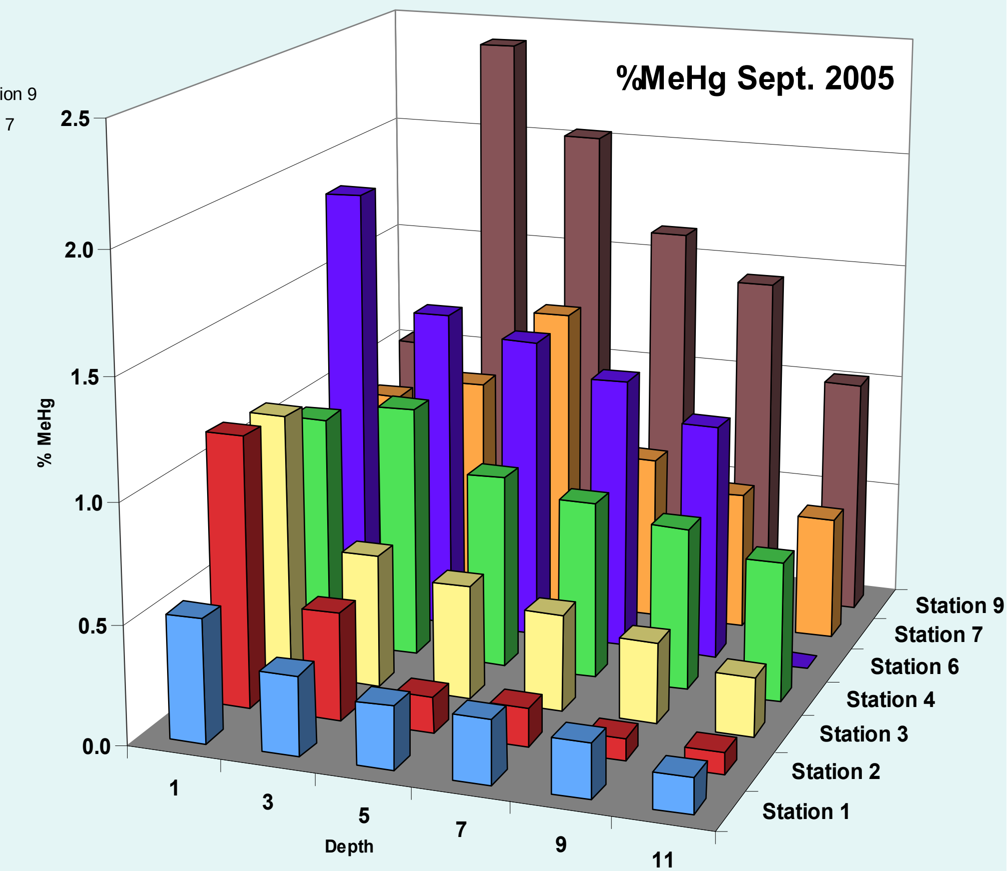






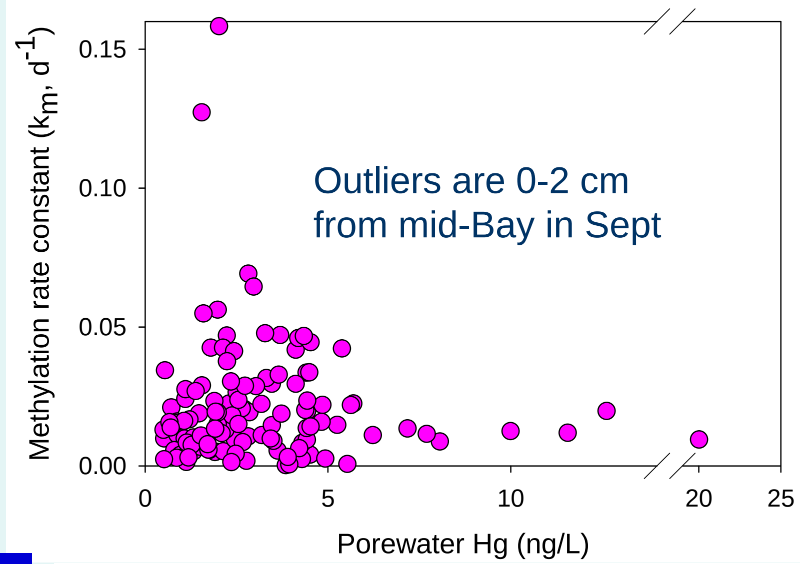


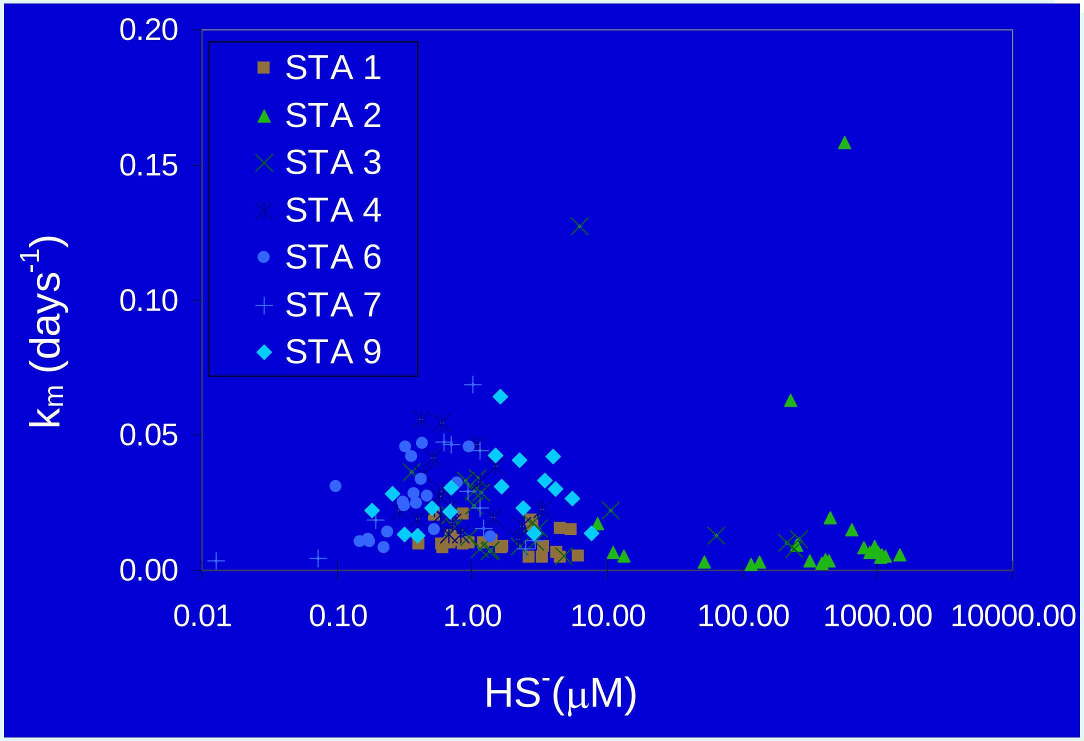
3D Plot of Station #, sediment depth and %MeHg for two of the sampling periods (early spring and early fall) for the Chesapeake Bay/shelf

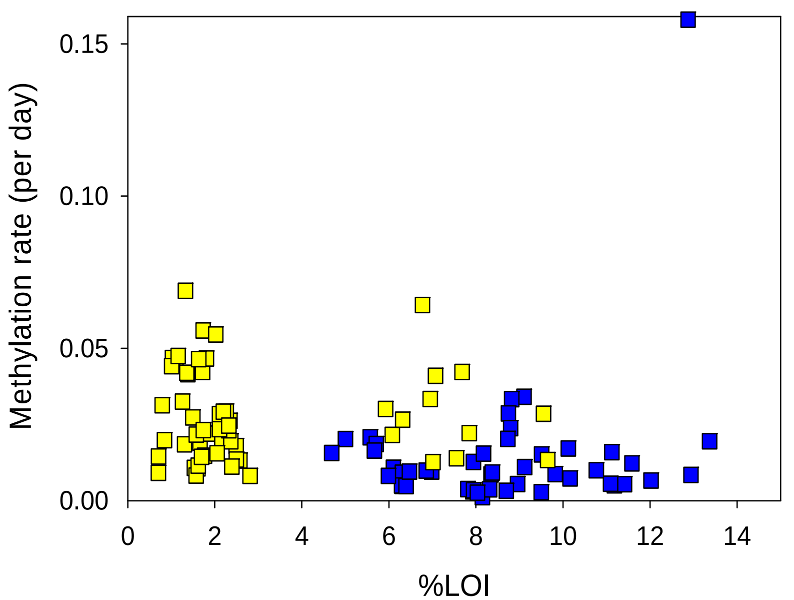


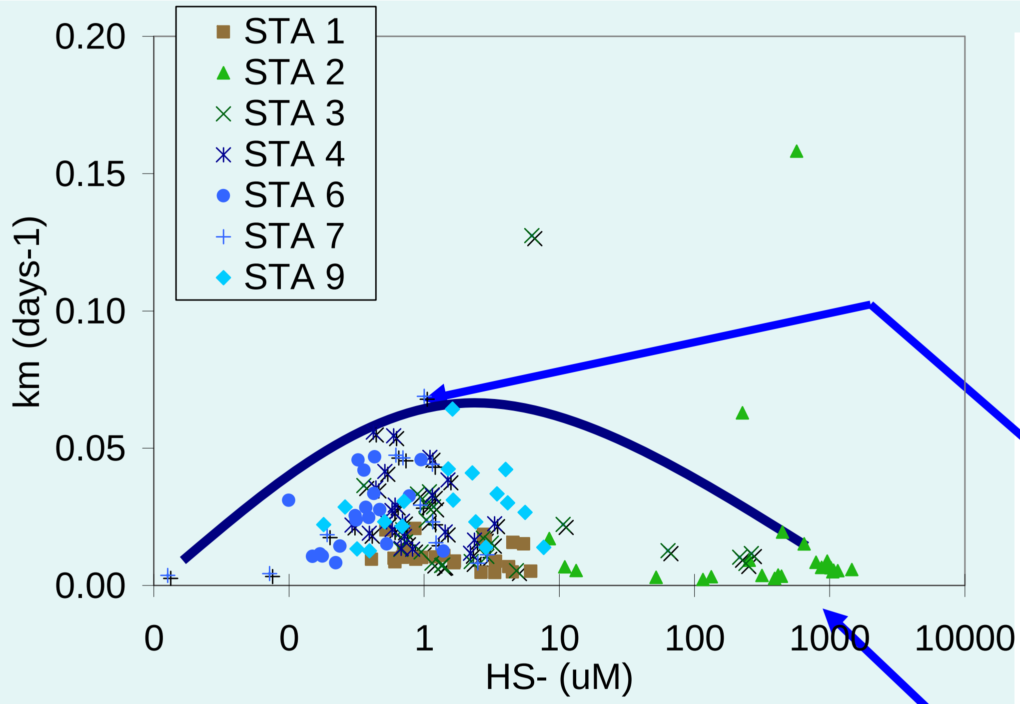
The %MeHg is highest in the surface sediments for the estuarine sites and decreases markedly with depth. For the shelf sites, there is a larger depth interval over which the %MeHg is relatively high. Overall the integrated signal is higher for the shelf sediments

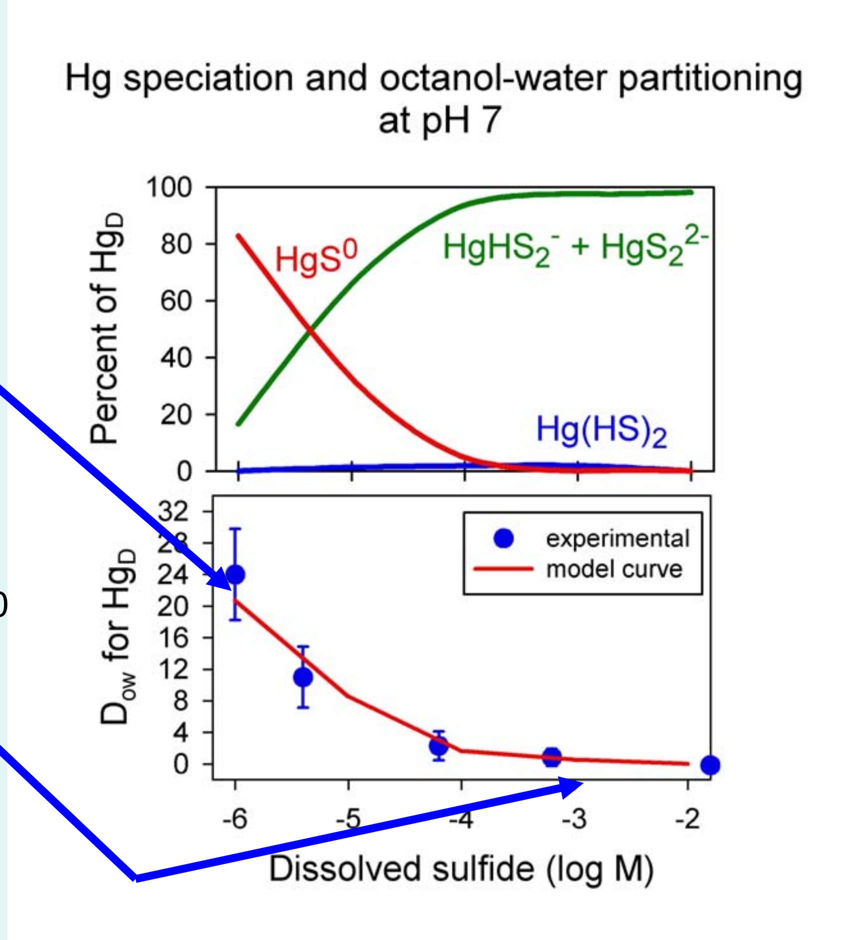
- For the Chesapeake Bay/shelf, the methylation rate constant does not correlate well with porewater Hg
- Does not appear to be strongly related to sediment organic carbon
- Looks to be lower at high sulfide and can be high at low sulfide
- **What's going on?**











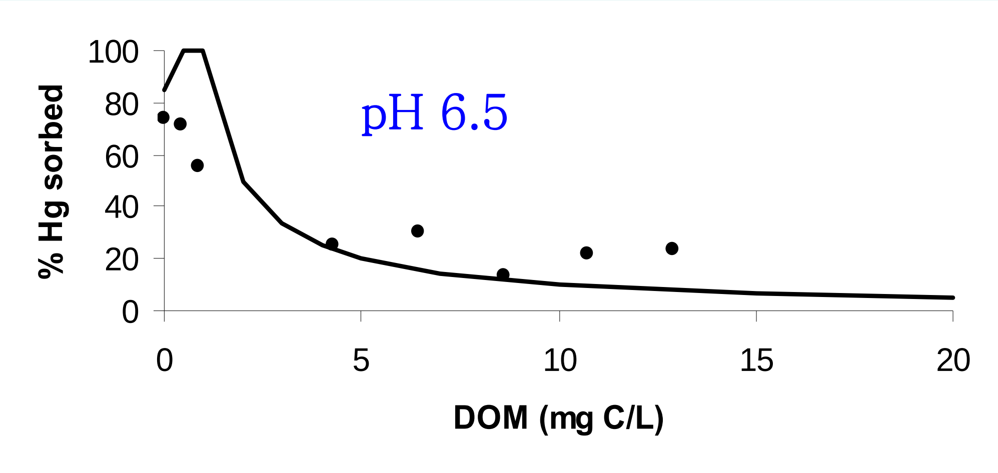
At least, qualitatively, the results fit with the predicted impact of sulfide on Hg bioavailability to the methylating organisms.

But what about the variability at intermediate sulfide? There appears to be other factors that are as important

Besides sulfide, other factors that could also impact methylation are other complexing agents such as DOC, also pH, and clearly the bacterial community structure

This is all dandy, but what other factors should be considered (DOM, sulfide, solid sulfide etc)?

- For **hydrous Fe-Oxide**, Hg bound strongly in the absence of DOM. Binding was reduced as DOM increased.



$$\equiv FeSH + Hg^{2+} \leftrightarrow \equiv FeSHg^{+} + H^{+}$$
$$\log K = 29.6$$

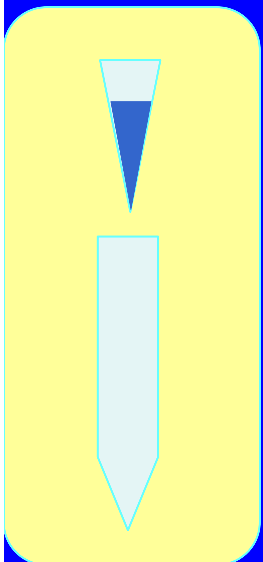
$$\equiv FeSH + MeHg^{+} \leftrightarrow \equiv FeSMeHg + H^{+}$$
$$\log K = 6.0$$

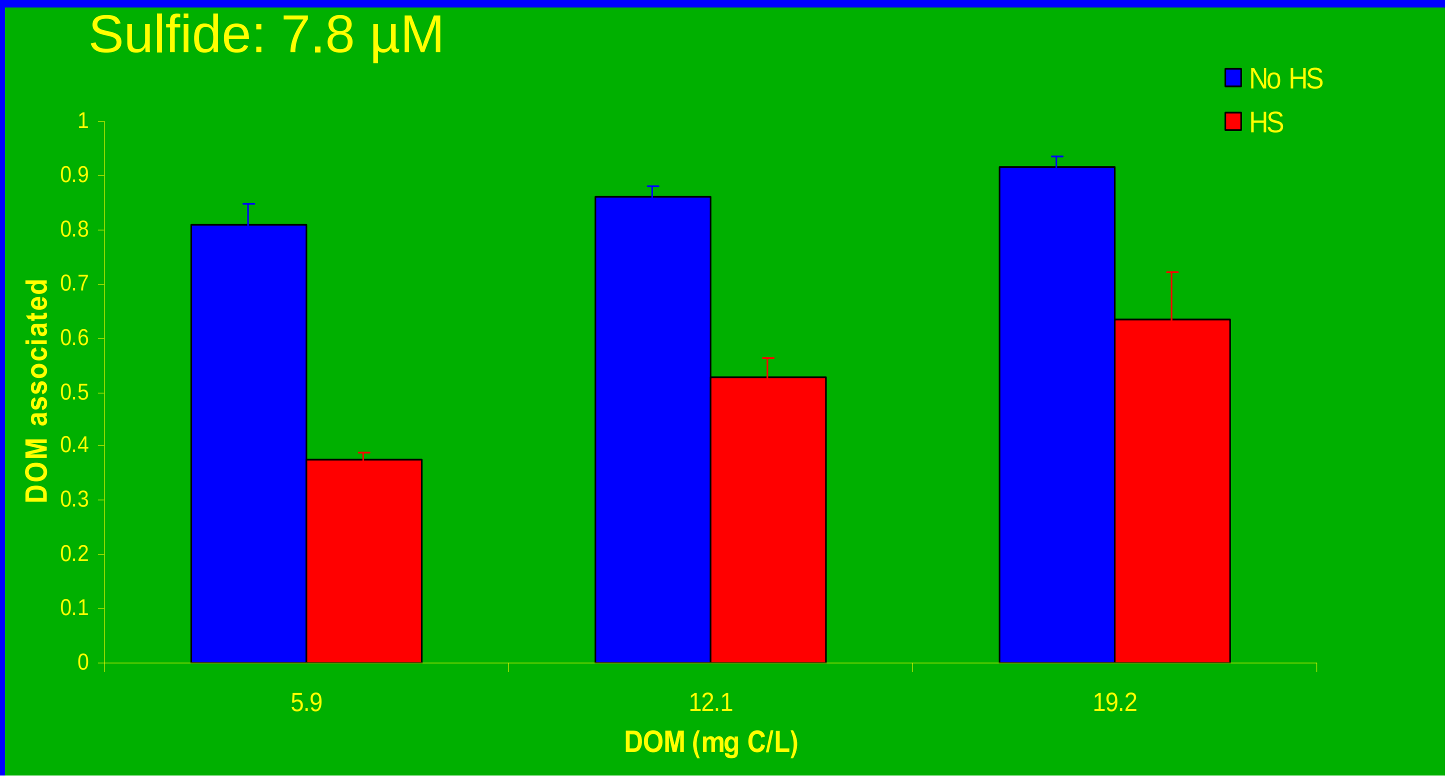
Hg, MeHg Sorption to FeS?

- Hg, MeHg strongly adsorbed (>99.9% in lab exps). DOM no effect. Complexation constants were determined.
- In oxic sediments, Hg bound to POC
- Organic matter and FeS likely responsible for sorption under anoxic conditions

The interaction between Hg, Sulfide & DOM was investigated using ultrafiltration experiments

- Amicon Ultra 15 mL centrifuge filters (5000 Da)
- DOM > 5000 Da in all experiments
  - Hg associated with DOM remained in extract
- Inorganic Hg-sulfide complexes < 5000 Da
  - Pass through or sorbed onto filter
- Stable isotope used for all experiments





At these sulfide levels, thermo-dynamic models predict all the Hg should be associated with sulfide

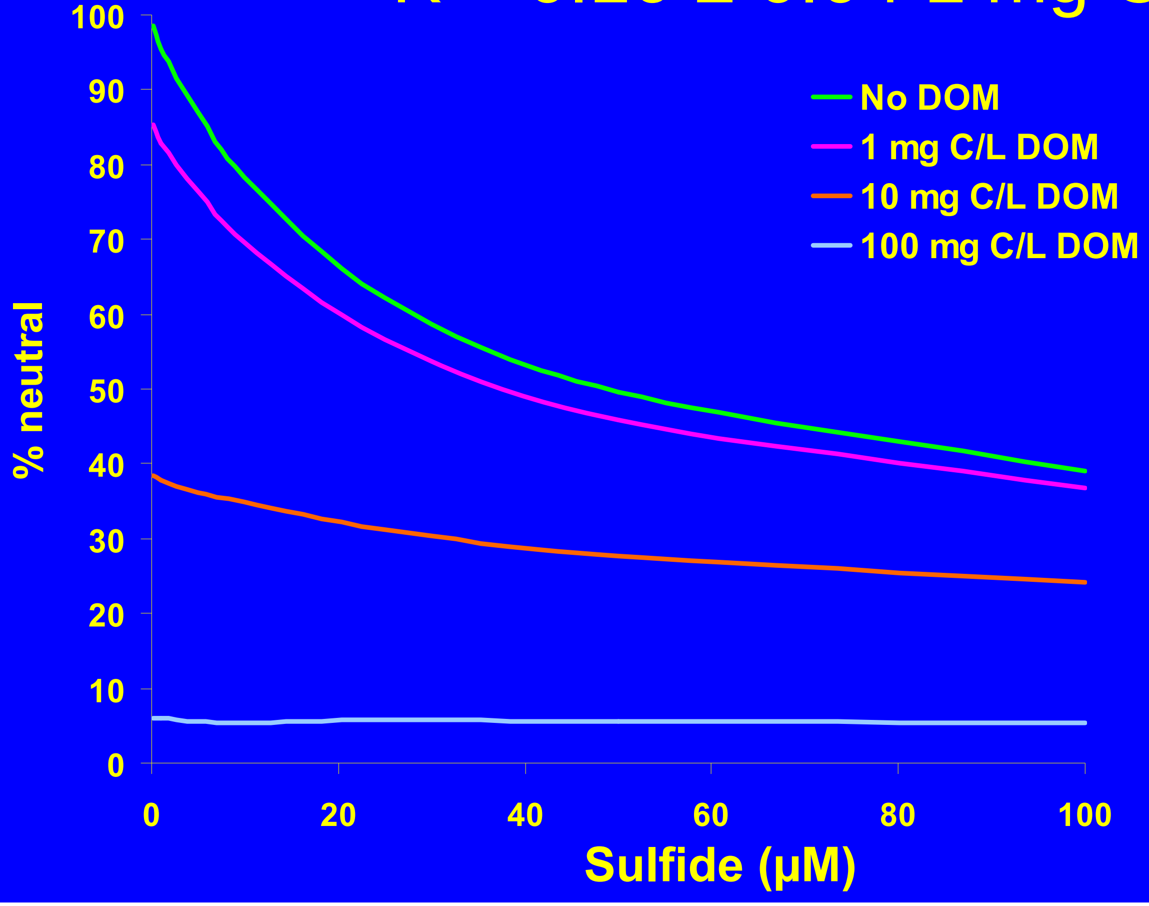
Miller et al., 2007

Conclusion: Neutral Hg-S complexes interact with DOM thereby reducing their concentration in solution and the bioavailability of Hg to bacteria

Stability constant for the interaction

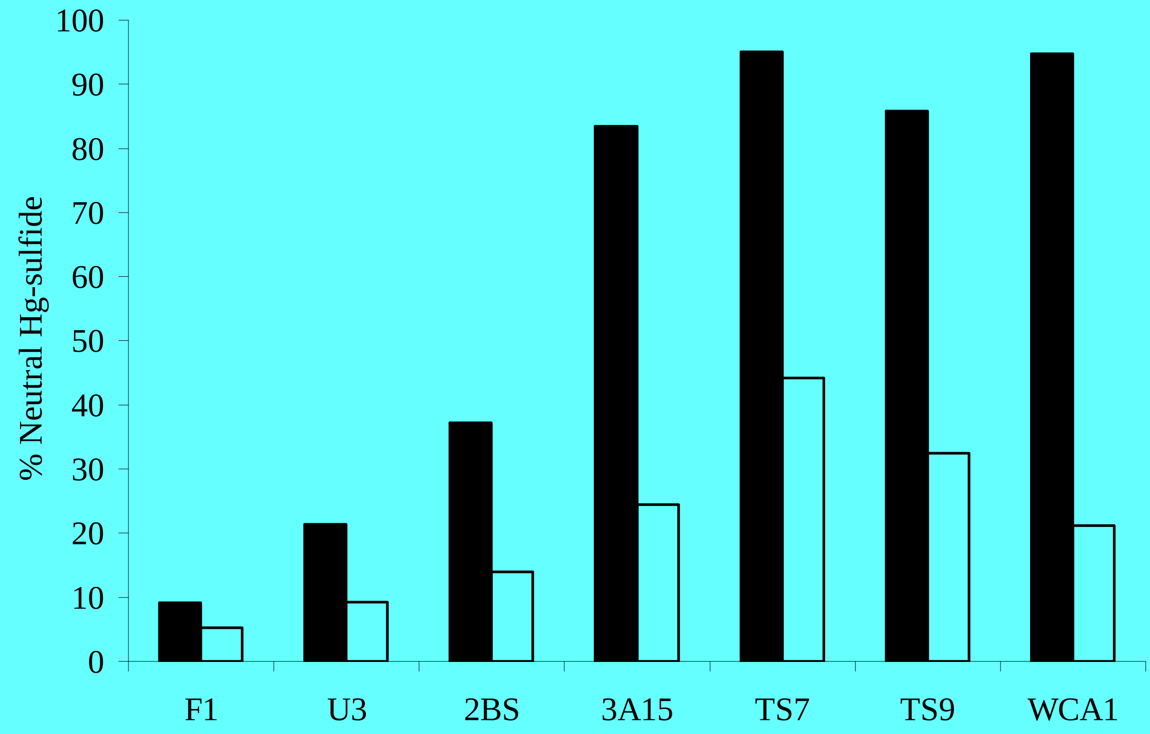
$$HgSulfide_N + DOM \leftrightarrow (HgSulfide_N)DOM$$

$$K = 0.16 \pm 0.04 \text{ L mg C}^{-1}$$

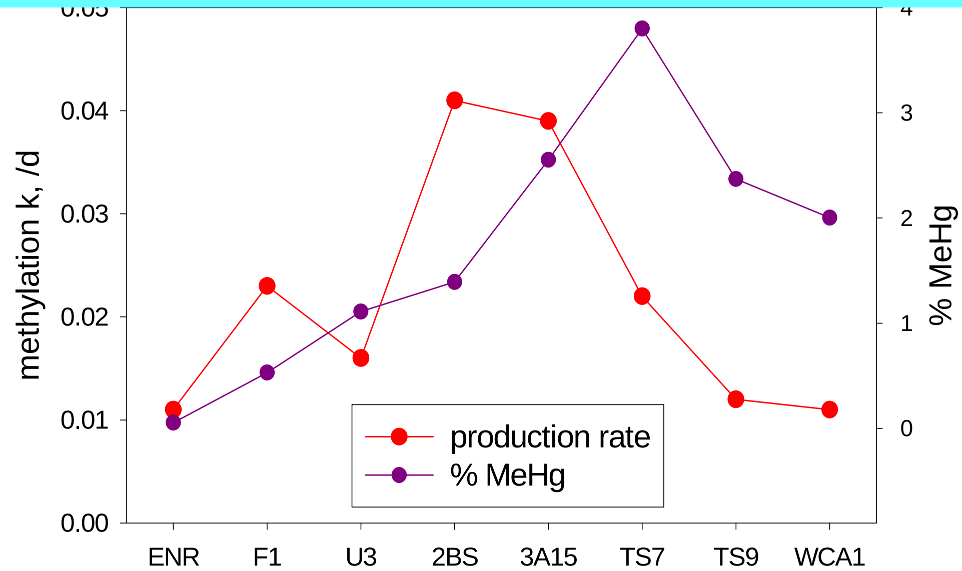


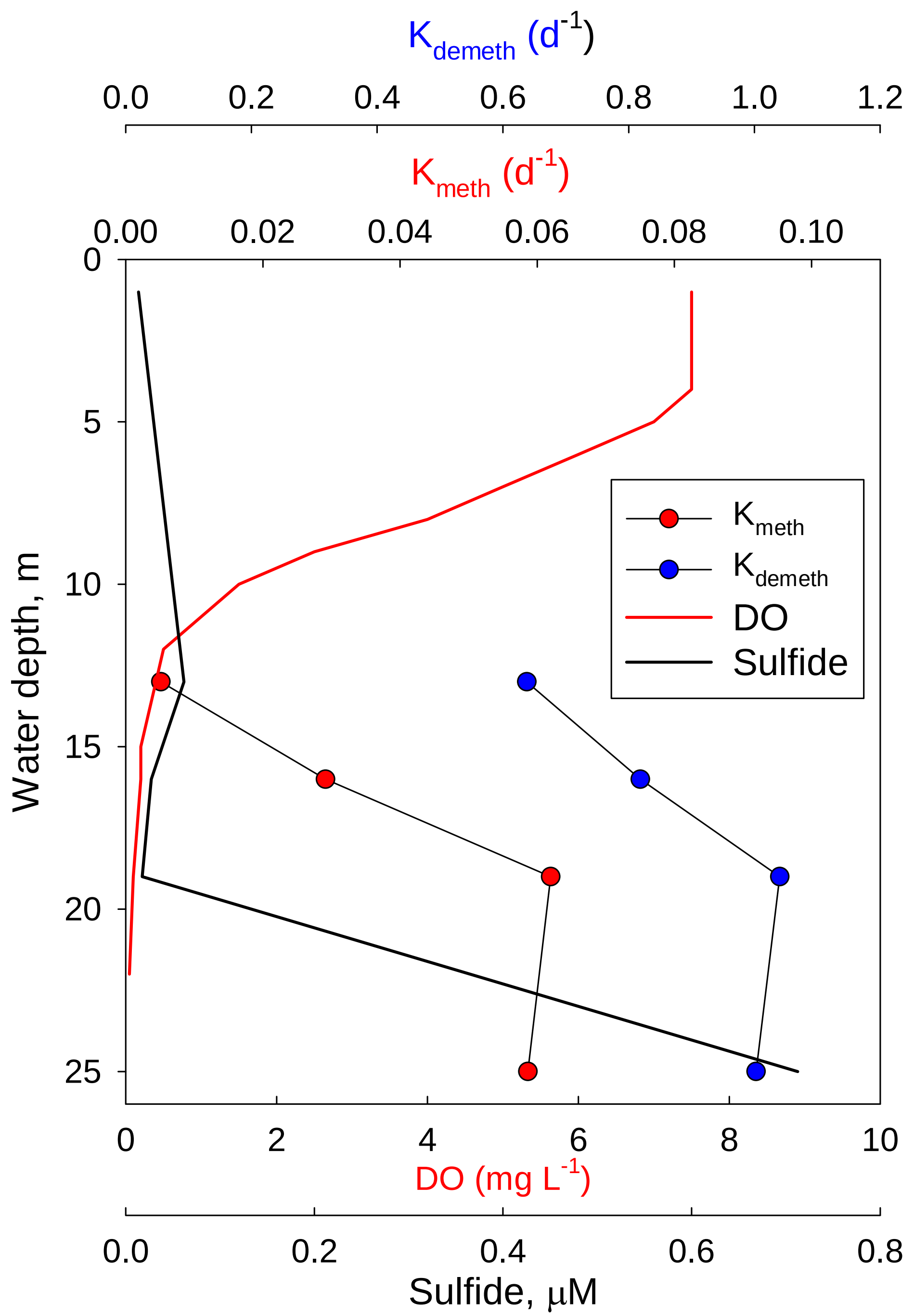
Miller et al., submitted

Calculated abundance of neutral Hg−sulfide complexes in surficial soil pore waters for seven sites across the Florida Everglades without (filled bars) and with (open bars) the interaction involving HgS−DOM included in the model. Overall while the magnitude changes, the overall trends are similar. The calculated concentrations with the interaction match the %MeHg more closely overall



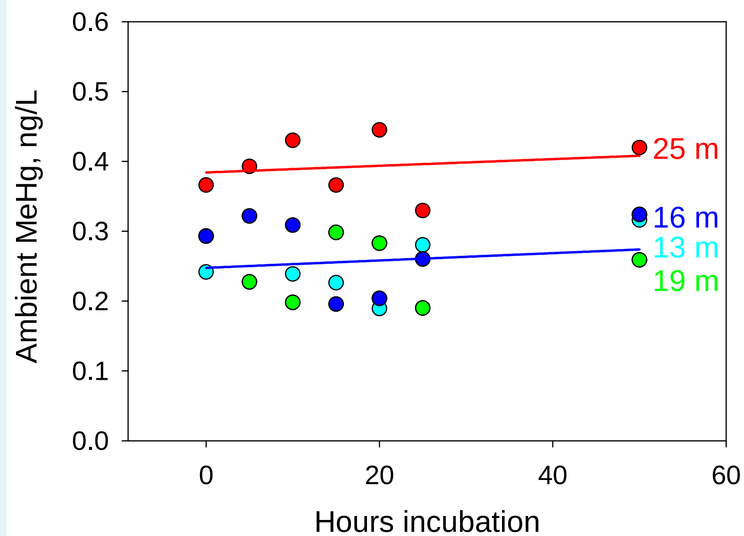
Miller et al., submitted





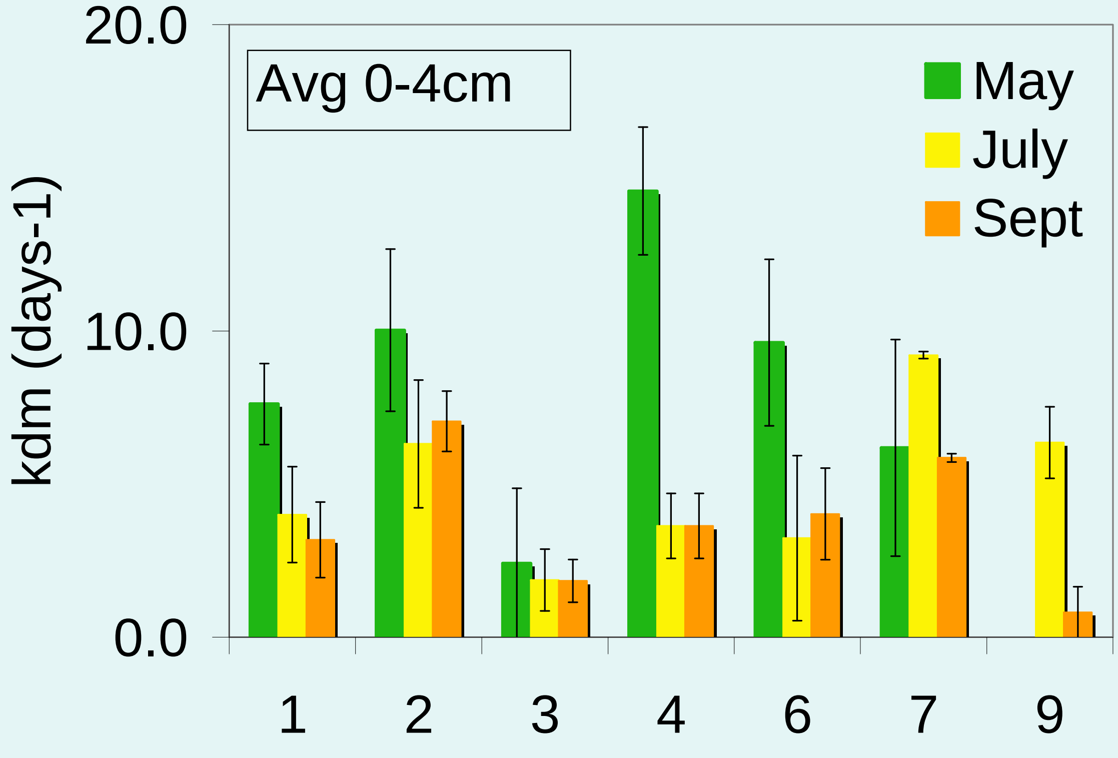
Station 2 – the importance of water column methylation

1. **Sulfide levels in the bottles were low throughout the incubations (<0.2 µM) although there was a suggestion of higher levels overall at the final timepoint.**
2. **pH increased over time of the incubations from initial values of 7.3-7.4 to 7.8-8.0 at the end of the incubations**



And finally, we should not ignore the reverse reaction – demethylation

Results - k_{dm}

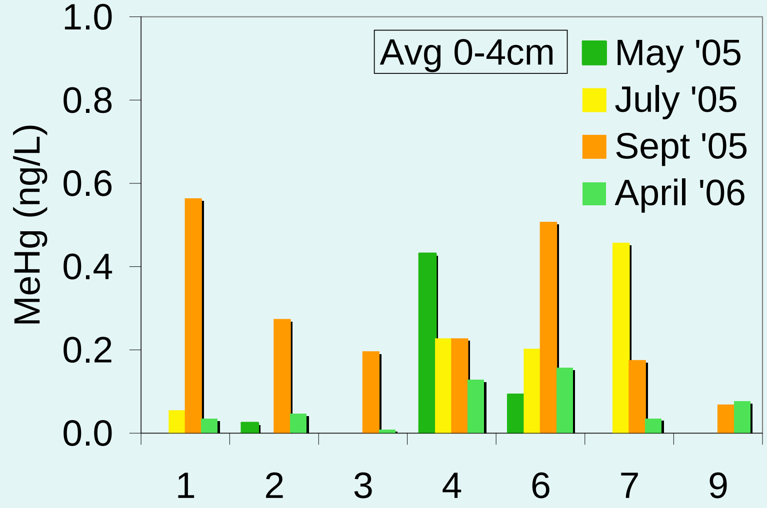


Rates are relatively variable across sites

Demethylation rate constants DO NOT correlate with:

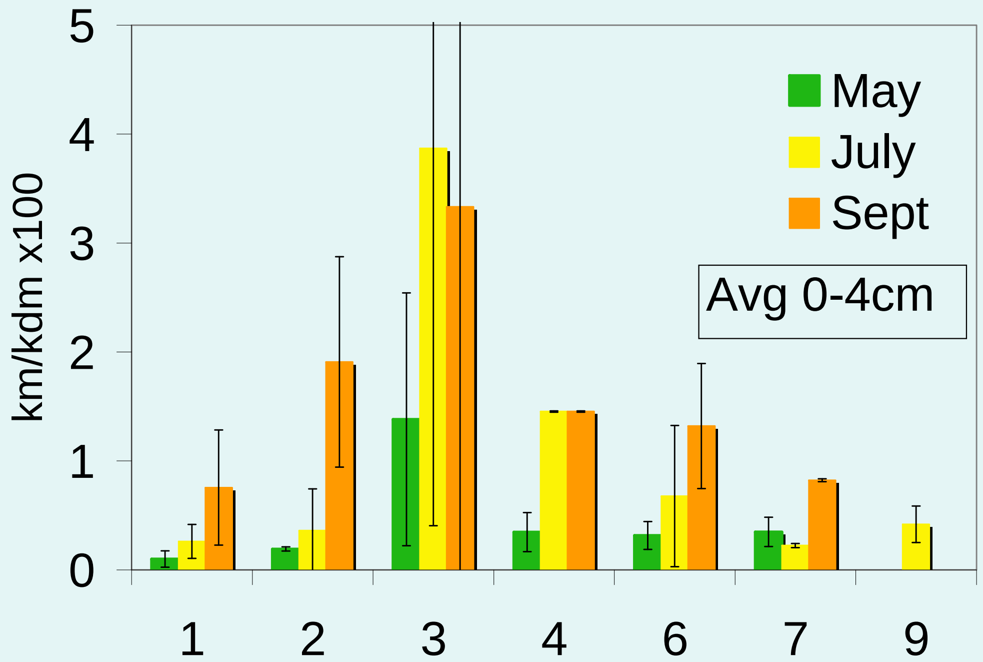
%LOI, Porewater sulfide, Sediment MeHg, AVS

Sulfate reduction rate



Questions:

1. What form of MeHg is taken up?
2. What microbes are responsible?
3. What is the relationship with depth?



The ratio of the rate constants for the Chesapeake Bay/shelf data is comparable to that of other estuarine and coastal systems, which are not highly contaminated. Also, as found elsewhere, the ratio of the rate constants is comparable to the range in %MeHg found in the sediments

Location Type and Method[a]	k_1 ($\times 10^{-2}$) (d^{-1})	k_2 (d^{-1})	k_1/k_2 ($\times 10^{-3}$)	$[MeHg]_{tot}/[Hg]_{tot}$ ($\times 10^{-3}$)	Refs
Hudson River (S)	0.2	15	0.1	2.0	Heyes et al., 2005
Bay of Fundy (S)	4.4	3.6	12	3.3	Sunderland et al., 2004
Mesocosm Studies (S)	3.1	16	2.3	2.8	Kim et al., 2005[b]
San Pablo Bay (R)	1.4	0.3	56	18	Marvin- DiP et al., 03
Berry's Creek, NY (R)	1-18	0.06-0.12	10-150	4-8	Cardona-Marek, PhD
Delaware River, DE (S)	0.7-3	3-15	~2	~2	Cardona-Marek, PhD

a: Method – S = Stable isotopes used; R = Radioisotopes used.

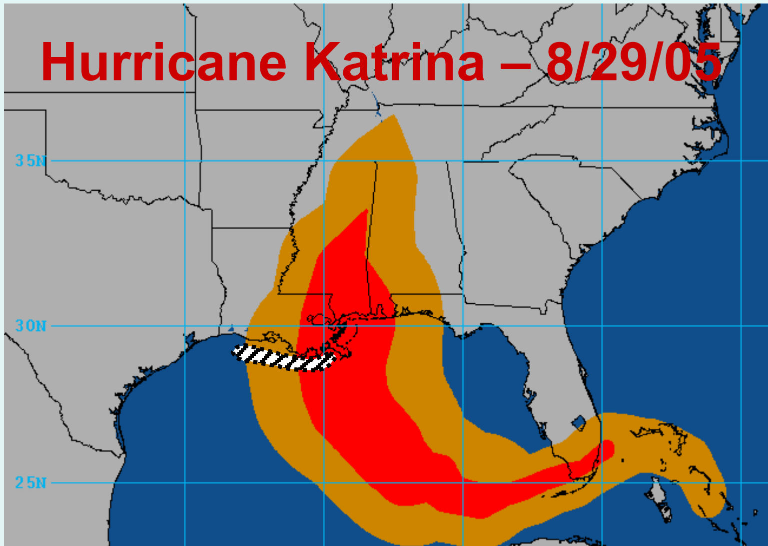
b: average values for both R and NR systems in the top sediment layer (0-0.5 cm).

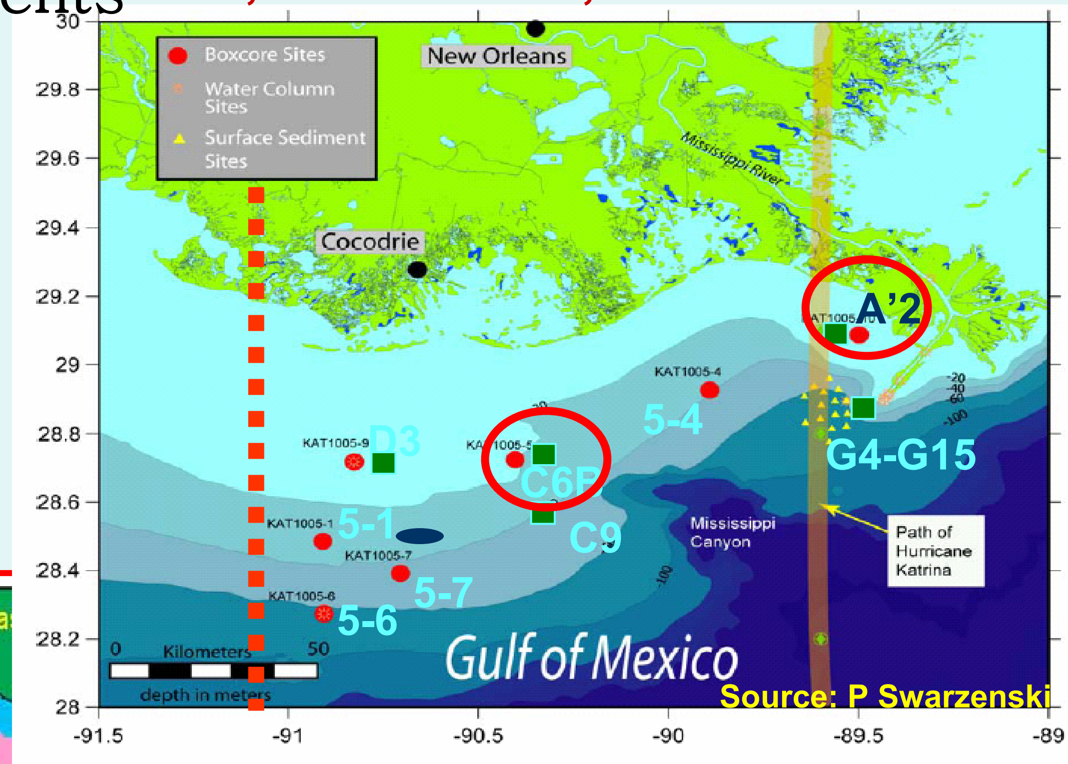
The focus has been on chemical factors, but what about?

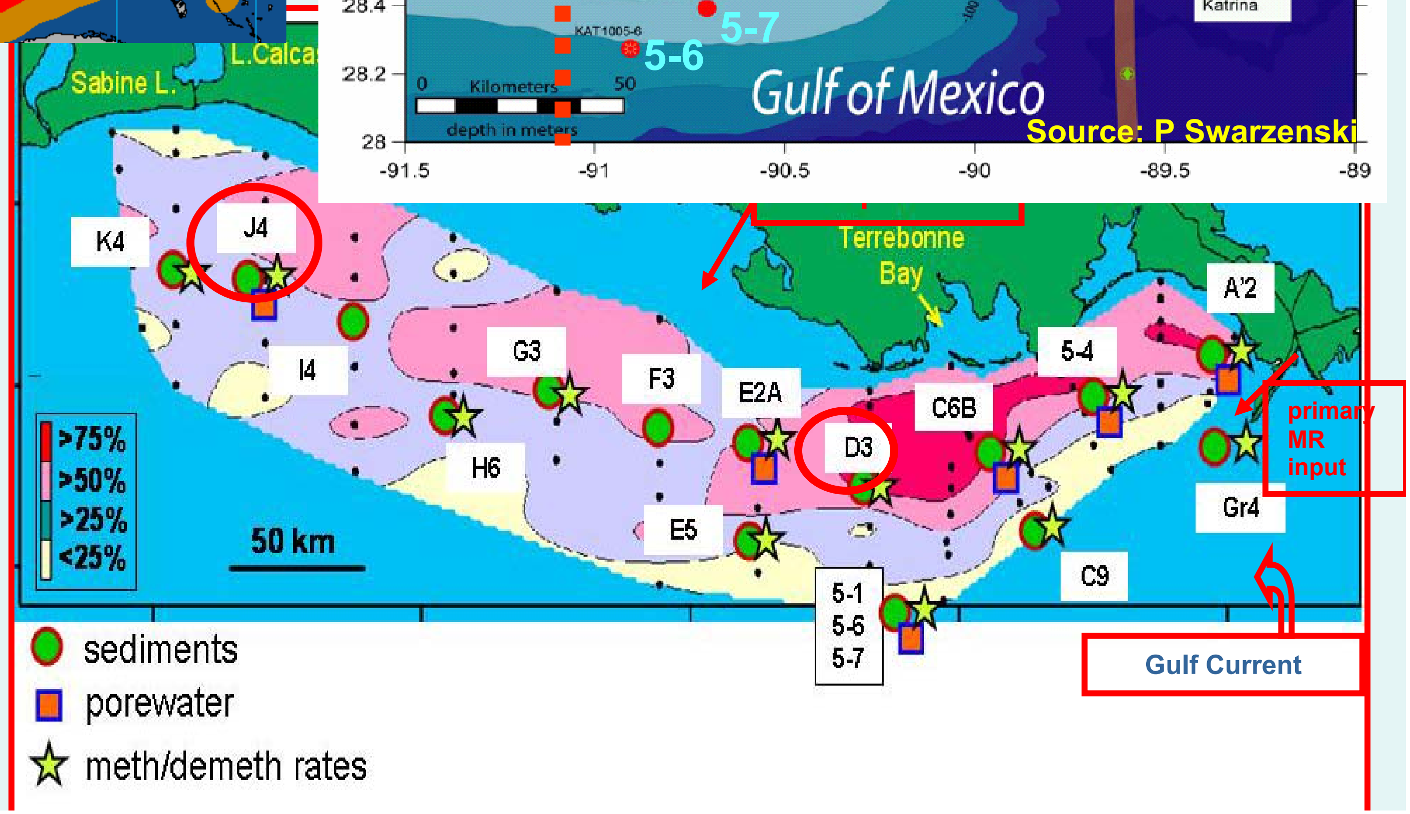
- **Biological**: Differences in community structure and the ability to methylate Hg. Not all SRB's methylate. Some Fe reducers do. What about the impact of C supply? Other limitations (sulfate etc)
- **Physical:** Disturbance is important in "resetting" the system. Tidal resuspension can enhance methylation. Wetting/drying leads to sediment oxidation/enhance methylation
- What about **extreme events**?

The Impact of Extreme Events

, Jul & Oct 05, Mar & Jul 06



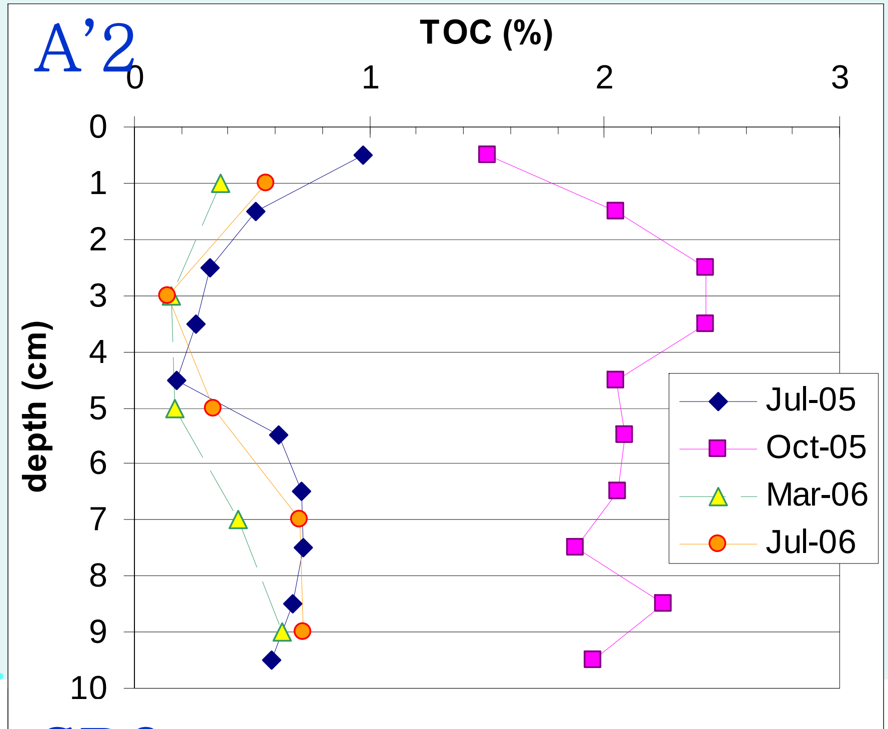


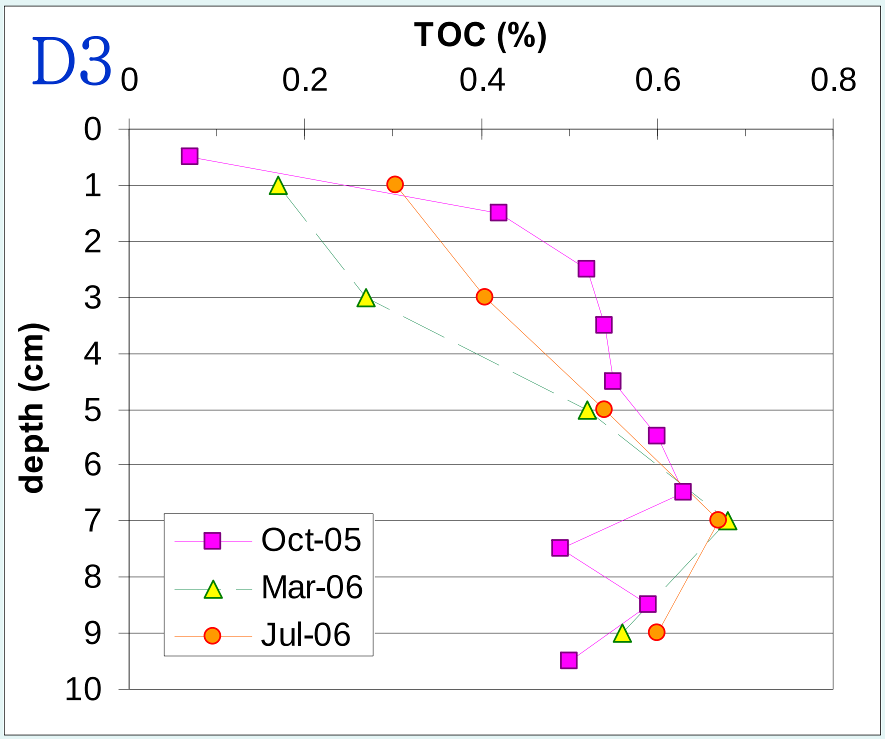


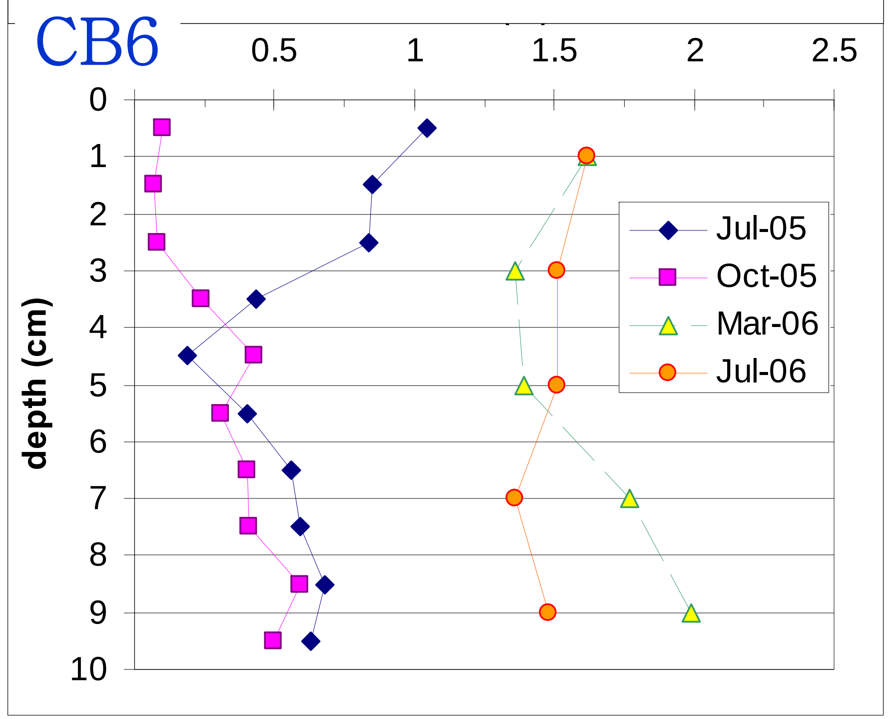
Stations A'2 was directly impacted by Katrina while J4 was less directly impacted by Katrina but was impacted by Rita; D3 was on the outskirts of both storms

At station D3, there is little change in %TOC over the various sampling periods.
At A’2, there is a very different sediment %TOC in Oct 05 compared to the other times
At CB6, there appears to be a complex signal which shows a decrease in %TOC from Jul 05 to Oct 05 for the upper 4 cm but a very different %TOC after that at all depths

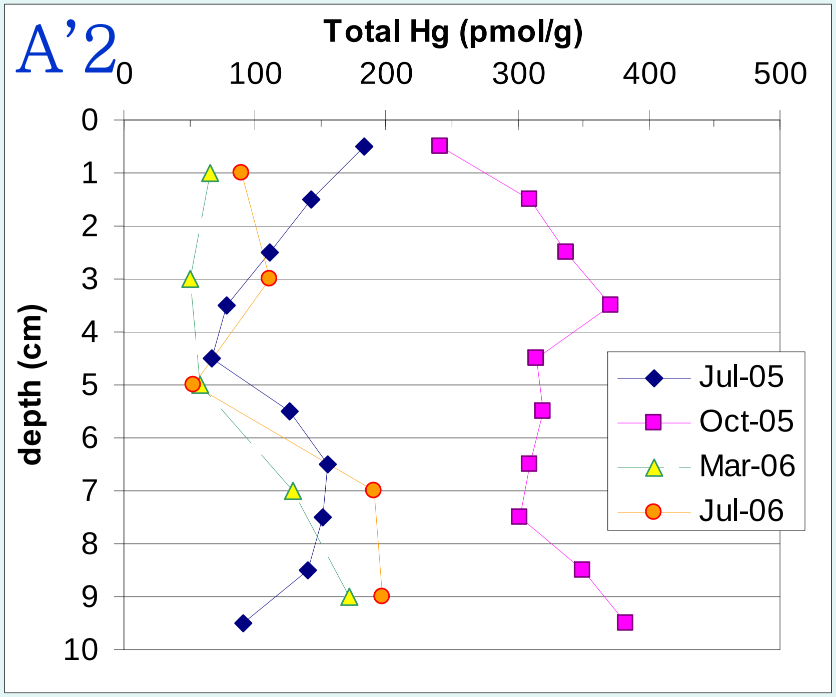
Liu et al., in rev.



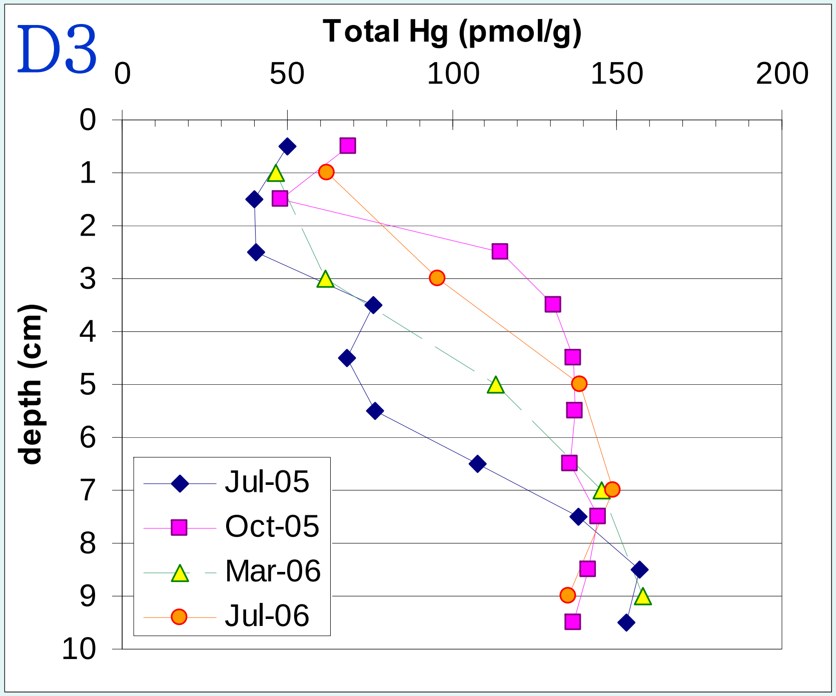


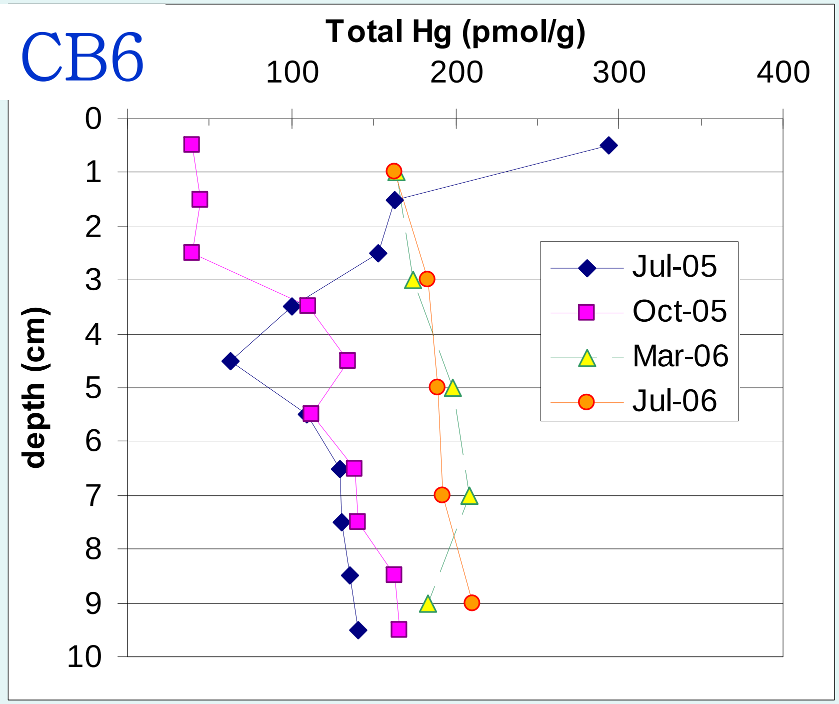


The total Hg concentrations mimic those of %TOC. It appears that both are reflecting similar changes in the sediment profile
For station D3, little change over time
For A'2, much higher in Oct 05, rest similar
For CB6, decrease in upper sediment in Oct 05, then increase throughout

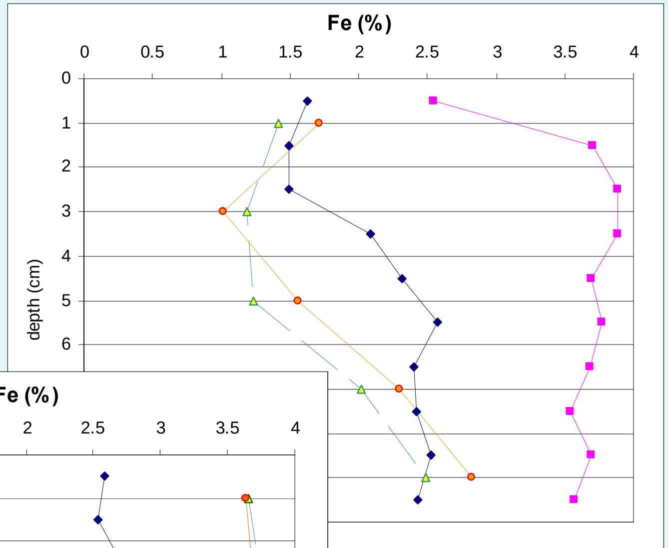


Liu et al., in rev.

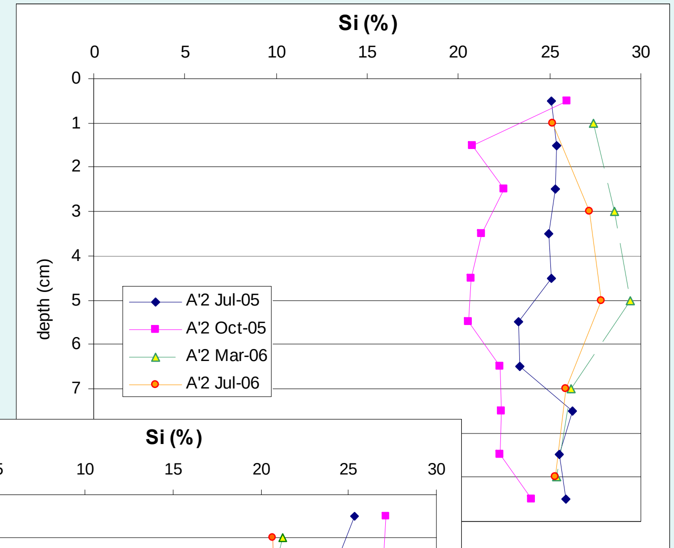




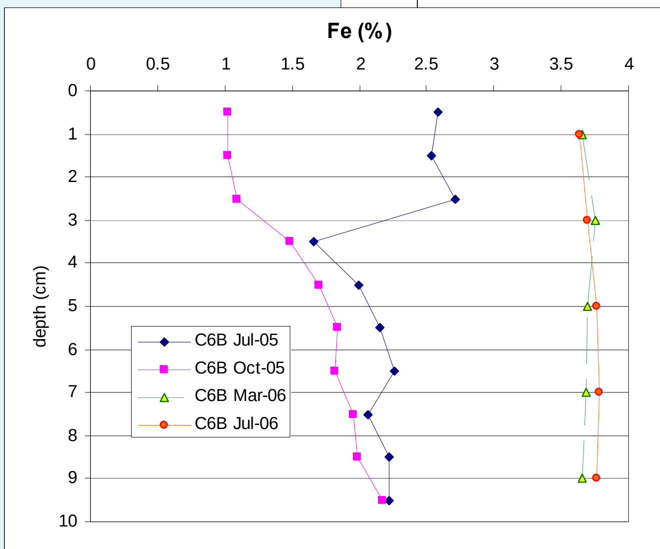
A'2 Fe



A'2 Si

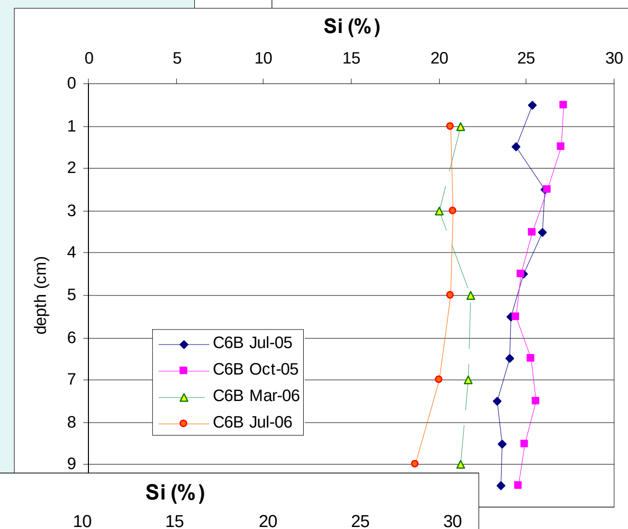


CB6 Fe

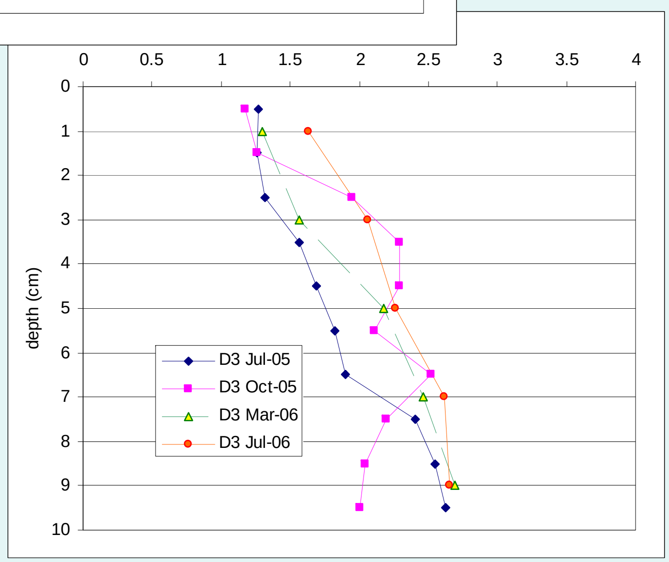


Overall, Fe trends similar to Hg/TOC. Si opposite

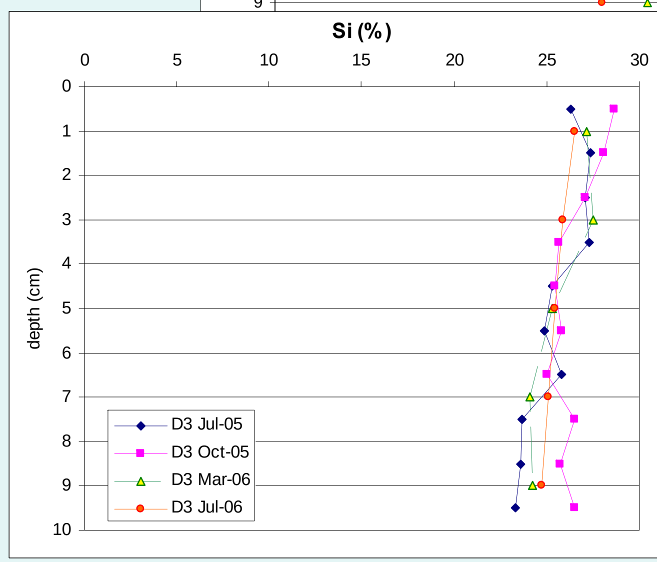
CB6 Si



D3 Fe

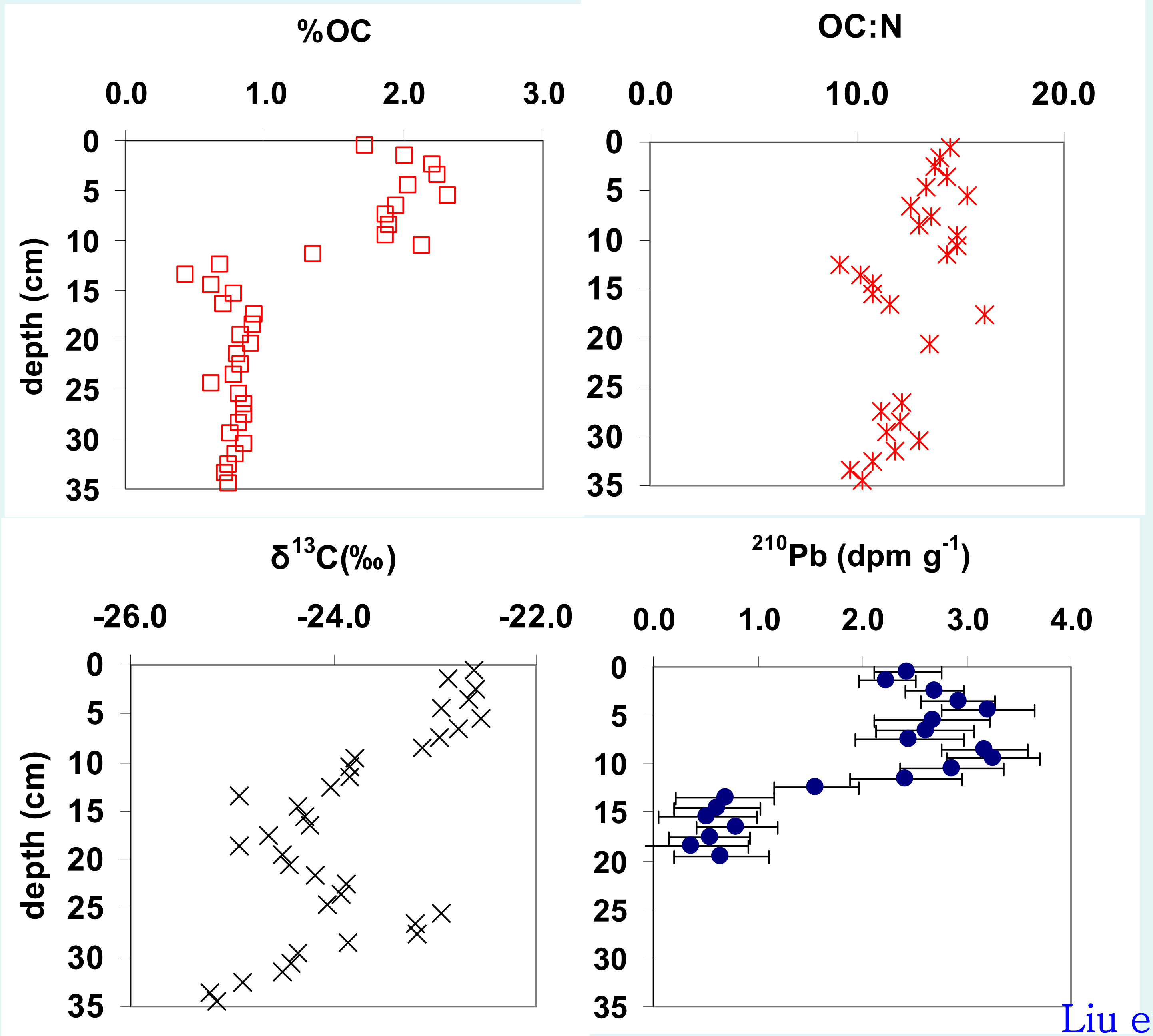


D3 Si



Liu et al., in rev.

Other parameters also indicate a substantial disturbance at Station A'2

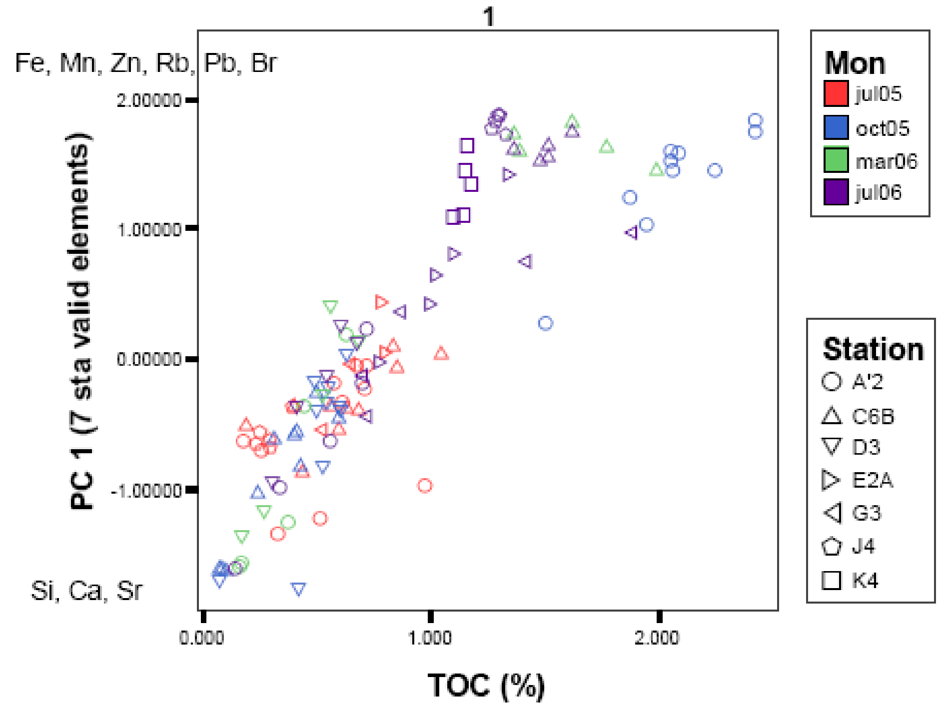


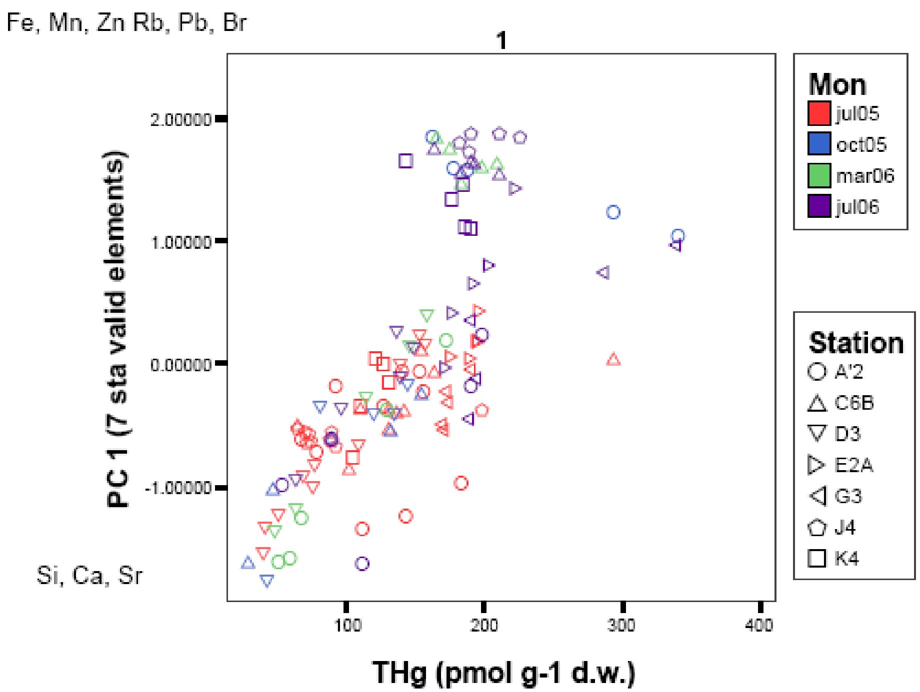
Liu et al., in rev.

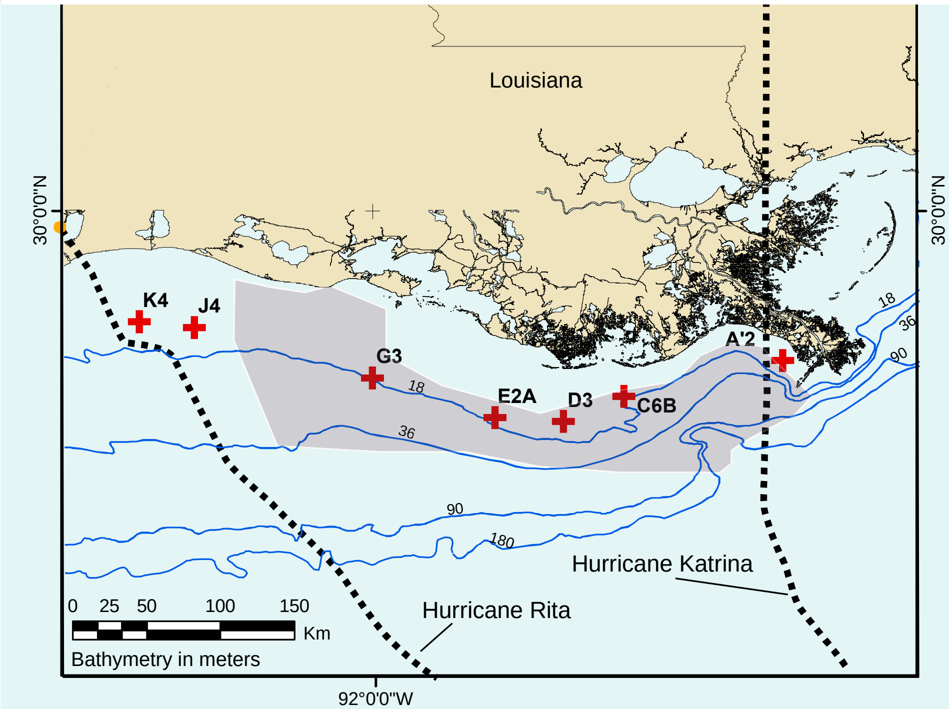
Results from PCA suggest that the sediments from A'2 & K4 in Oct 05, from C6B in Mar 06 and Jul 06 may differ from the rest.

This suggests there was sediment movement both during and in the months after the hurricanes

Liu et al., in rev.







Goni et al. (07) calculate that 1.2×10^{15} g of sediment and 1.4×10^{13} g org-C were redistributed during the hurricanes, as indicated on the map.

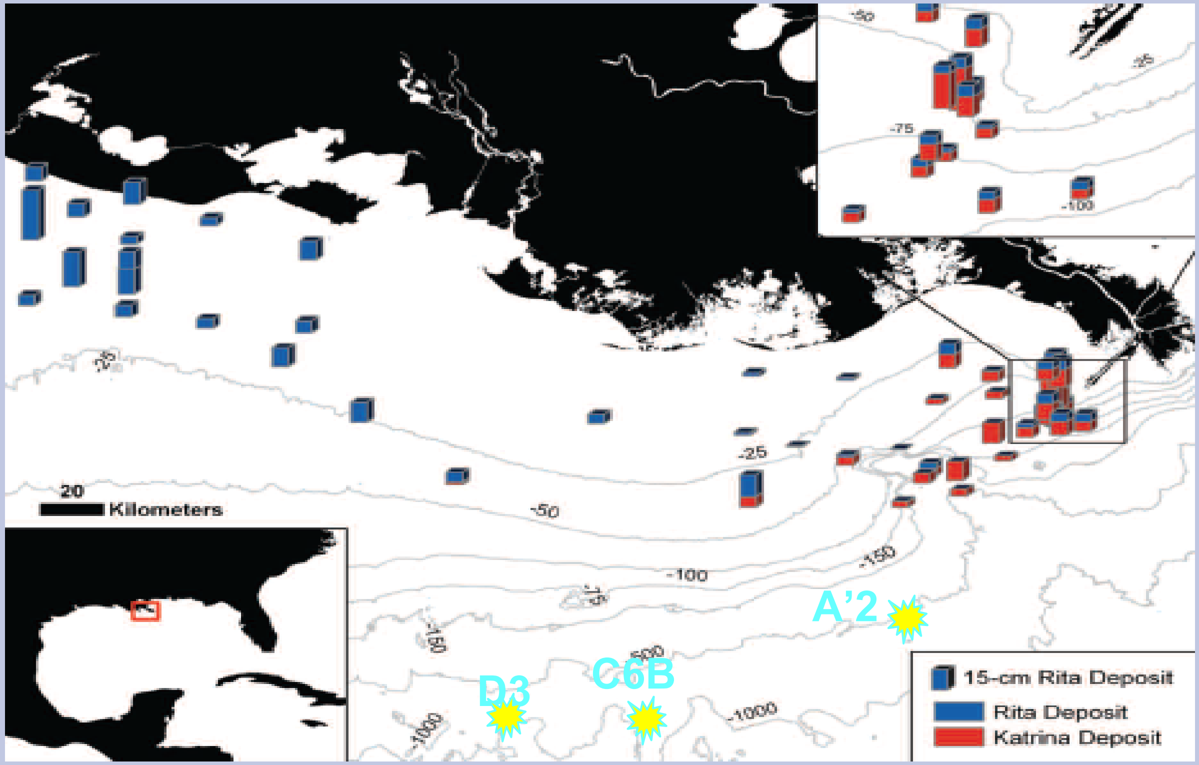


Figure 2. Map illustrating the thickness of sediment deposits associated with Hurricanes Katrina and Rita.

Goni report March 2007. *The Sedimentary Record* 5(1).

Based on these org-C estimates and the THg-TOC correlation, we estimate that ~50 tons of Hg were redistributed by the hurricanes. This is 3-5 times the annual river Hg input (10 ton/year) and atmosphere (2.5 ton/year) combined.

Liu et al., in rev.

Finally, to answer the initial question, and returning to the Chesapeake/shelf……….

We find….

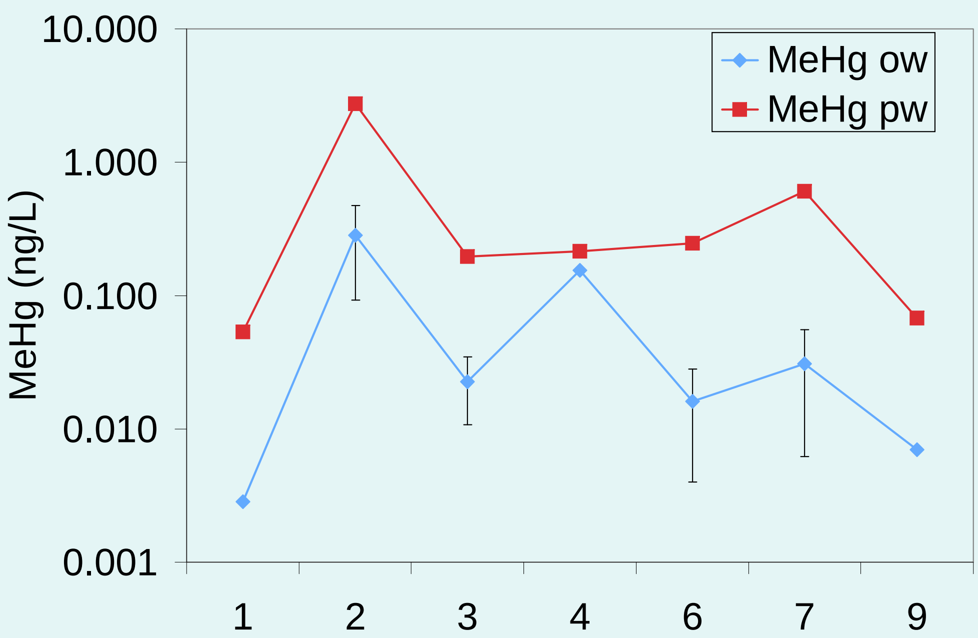
- High Hg_T and MeHg in solid phase of organic-rich bay and slope sediment, low in sandy shelf
- Comparable Hg_T and MeHg in porewater of all sediment
- %MeHg relatively high compared to other systems
- Seasonal trends consistent with biotic production
- Environmental factors that control Hg bioavailability elucidated - Particulate organic matter impacts K_D; Sulfide effects K_D and Hg_{pw} and both impact bioavailability

1. Is methylation in coastal zone important?
   - Net MeHg production substantial at all sites
   - But is the flux out of the sediments important?

Results - Sediment-water MeHg Diffusive Flux

Estimated Diffusive Flux, F (Gill et al., 1999)

- D_w MeHg-MOM = 2×10^{-6} cm^2 $s^{-1;}$ D_w MeHgSH = 1.3×10^{-5} cm^2 s^{-1}



Studies in other systems suggest that the actual flux is higher than that estimated assuming simple diffusion and also MeHg flux appears to be enhanced under low oxygen conditions

Assuming MeHgSH is species diffusing:

Site	Depth (m)	F (pg m^{-2} hr^{-1})	Time (yr)
Bay	10	52.3 ± 40.4	0.217 ± 0.11
Shelf	16	163.6 ± 91.9	0.339 ± 0.16
Slope	620	28.3	17.5

Results suggest that sediments could be an important source of MeHg to coastal waters. Also, shelf and slope sediments have abundant macrofauna and therefore there is substantial potential for bioaccumulation through the benthos