A satellite map of the Texas-Louisiana shelf. The land is shown in green and brown, with a large river delta (the Mississippi River) extending into the Gulf of Mexico. The water is dark blue, with a large area of lighter blue and green indicating hypoxia formation. The text is overlaid on the map.

# Monomethylmercury Concentrations on the Texas-Louisiana Shelf During Hypoxia Formation

Sara Keach

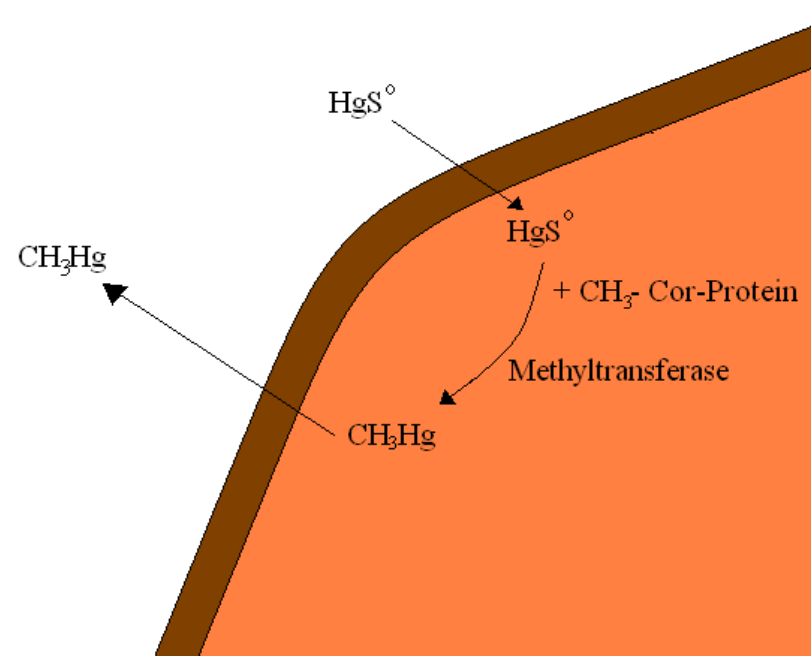
12-8-05

# Hg Cycle



# Sulfate Reducing Bacteria

- Principle Methylators
  - Passive Diffusion
  - $\text{CH}_4$  Transfer to Absorbed Hg
- Hg Methylation
  - Suitable SRB Environment
  - Neutral Hg Species

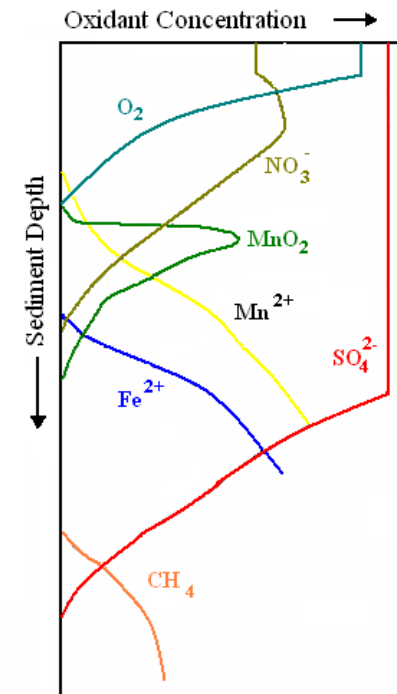


# Environmental Parameters Controlling Methylation

- Dissolved Oxygen\*
- Sulfate/Sulfide
- Salinity\*
- Temperature\*
- Organic Matter
- Benthic Flux\*

# Environmental Parameters Controlling Methylation

- Dissolved Oxygen
- Sulfate/Sulfide
- Salinity
- Temperature
- Organic Matter
- Benthic Flux
- SRB → Anaerobic
- Anoxic, Hypoxic (<1.4 mL/L)



# Environmental Parameters Controlling Methylation

- Dissolved Oxygen
- **Sulfate/Sulfide**
- Salinity
- Temperature
- Organic Matter
- Benthic Flux
- SRB:  $\text{SO}_4^{2-} \rightarrow \text{HS}^-$
- Sulfate
  - Increases Methylation
- Sulfide
  - Byproduct
  - Inhibits Methylation
    - $\text{HgS}_2^{2-}$ ,  $\text{HgSOH}^-$

# Environmental Parameters Controlling Methylation

- Dissolved Oxygen
- Sulfate/Sulfide
- **Salinity**
- Temperature
- Organic Matter
- Benthic Flux
- Freshwater > Marine
- Hg Diffusion
- Freshwater
  - $\text{Hg}(\text{OH})_2$ ,  $\text{HgCl}_2$
- Marine
  - $\text{HgCl}_3^-$ ,  $\text{HgCl}_4^{2-}$

# Environmental Parameters Controlling Methylation

- Dissolved Oxygen
- Sulfate/Sulfide
- Salinity
- **Temperature**
- Organic Matter
- Benthic Flux
- Stimulates Bacterial Activity

# Environmental Parameters Controlling Methylation

- Dissolved Oxygen
- Sulfate/Sulfide
- Salinity
- Temperature
- **Organic Matter**
- Benthic Flux
- Quality
  - Food
  - Bacterial Activity
- Quantity
  - HgS → Hg-DOM
  - Bioavailable → Not

# Environmental Parameters Controlling Methylation

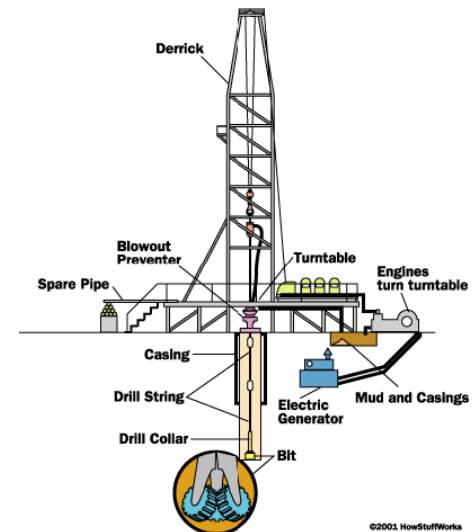
- Dissolved Oxygen
- Sulfate/Sulfide
- Salinity
- Temperature
- Organic Matter
- **Benthic Flux**
- Sediment ↔ Water
- Bioaccumulation
- Positive Flux
  - Low Oxygen
  - Low Light
  - Temperature
  - Low pH

# Hg in the Gulf of Mexico

- Elevated Hg in Species → Elevated Hg in Environment (Gilmour et al., 1998)
  - King Mackerel: 1.05 ppm (Ache et al., 2000)
  - Crabs: 0.21 – 0.3 ppm (Ache et al., 2000)
  - Oysters: 0.05 – 0.2 ppm (Ache et al., 2000)

# Hg Sources to the Gulf of Mexico

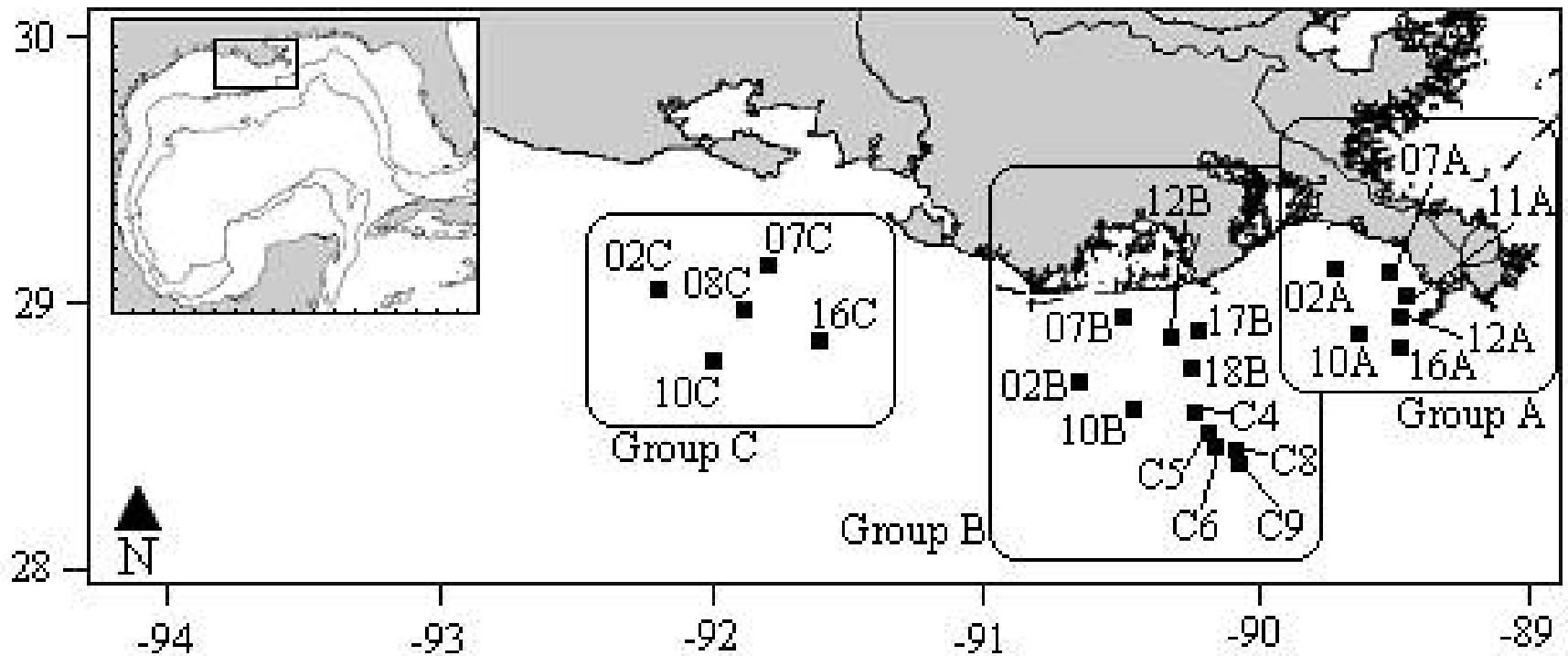
- Oil Rigs
  - Barite Muds to Drill (0.5 ppm THg)
- Mississippi & Atchafayla Rivers
  - 0.3 - .46 ng/L MMHg Acadian-Pontchartrain Basin (Krabbenhoft et al., 1999)
  - 4 ng/L THg (Garbarino et al., 1995)
- Hypoxic Zone
  - ??



# Research Objectives

- Is the Hypoxic Zone a Source of MMHg to the Gulf?
  - Seasonal Trends
  - Role of Environmental Parameters
  - Benthic Flux

# Sampling



# Sampling

- Field Blanks
- Sample Collection
- Acidification
- Storage



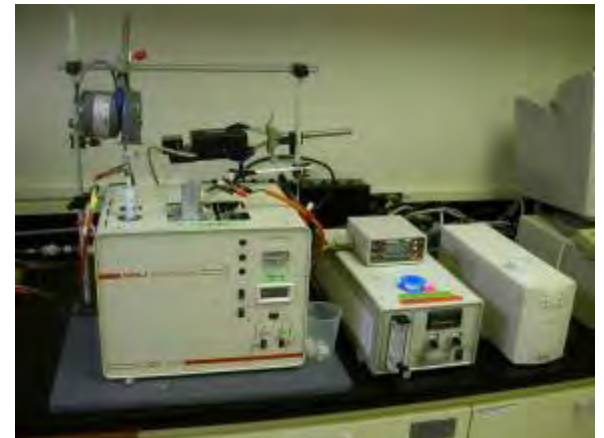
# Analysis - Water

Distillation

Ethylation



GC/CVAFS



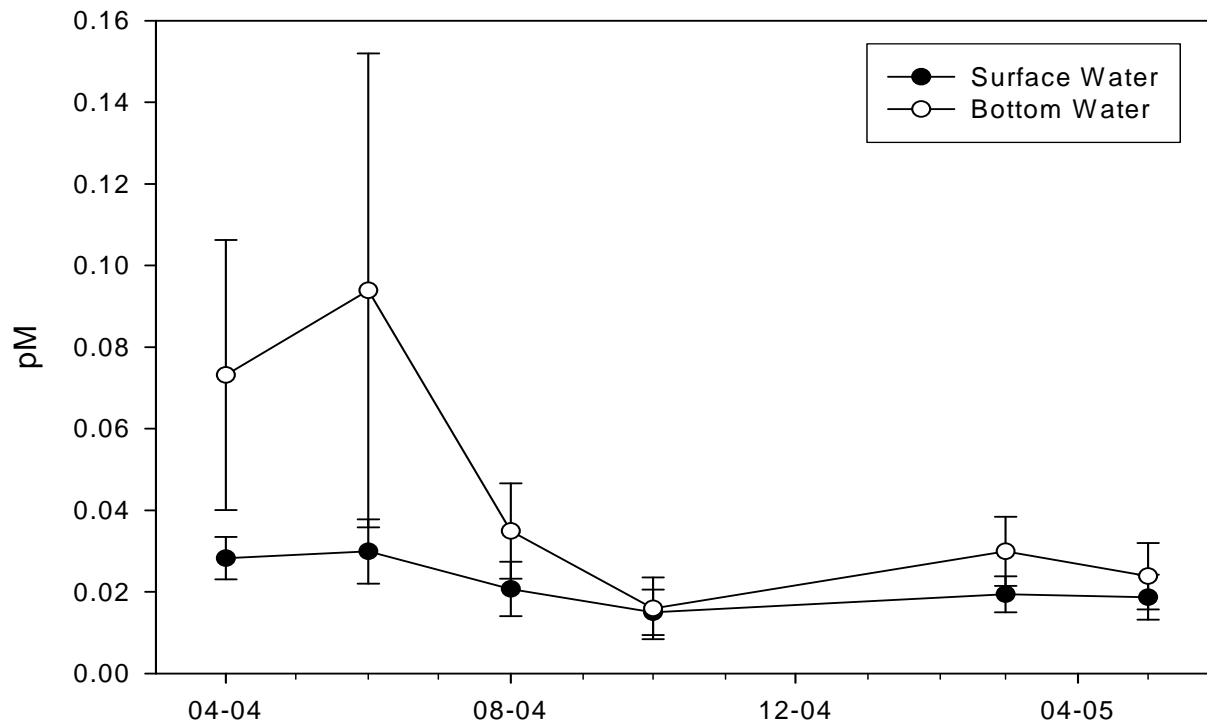
# Analysis - Sediment

MMHg: Extraction & CVAFS

THg: Direct Hg Analyzer

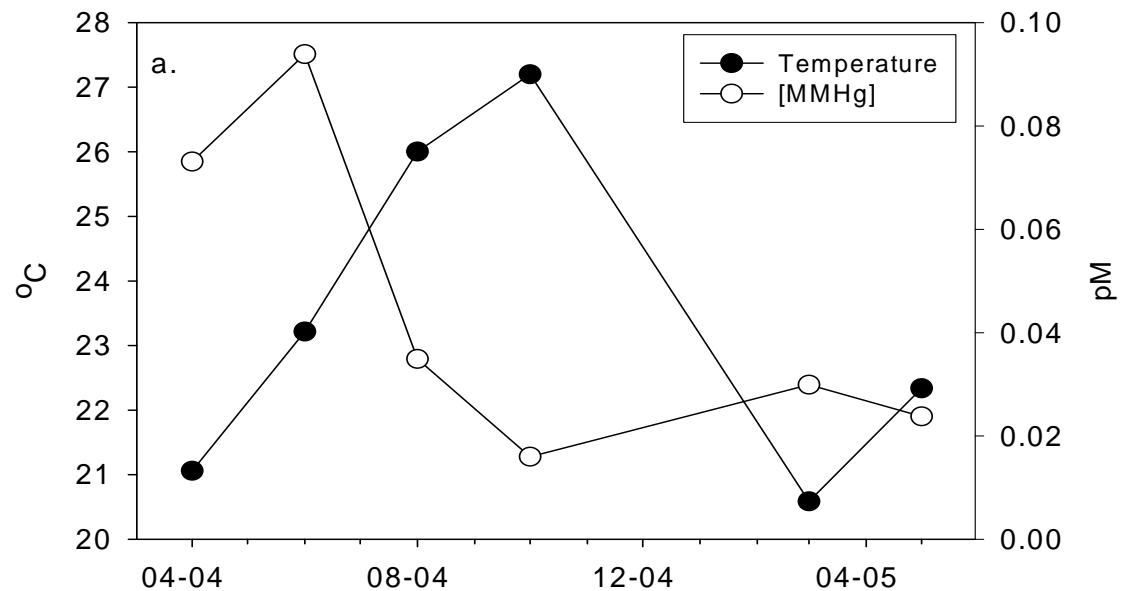


# Results

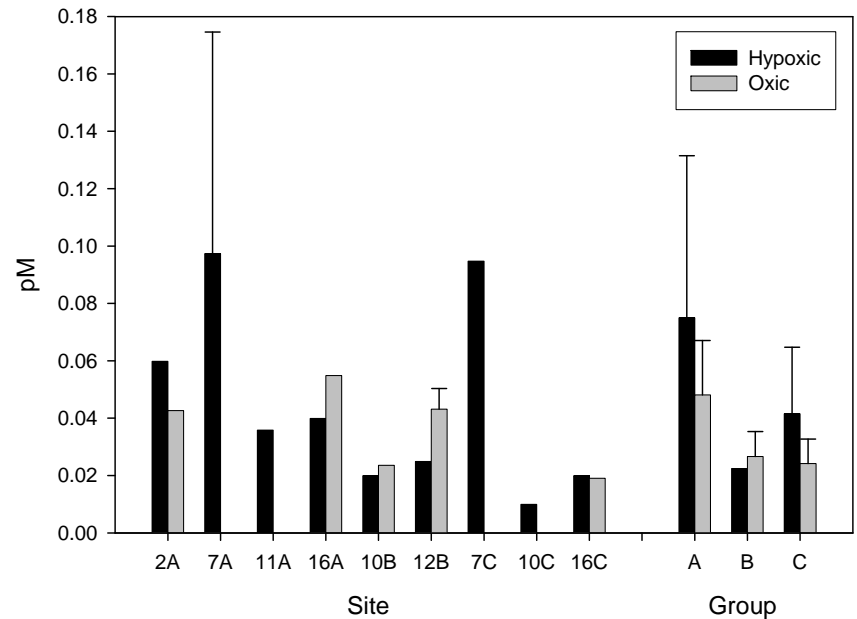
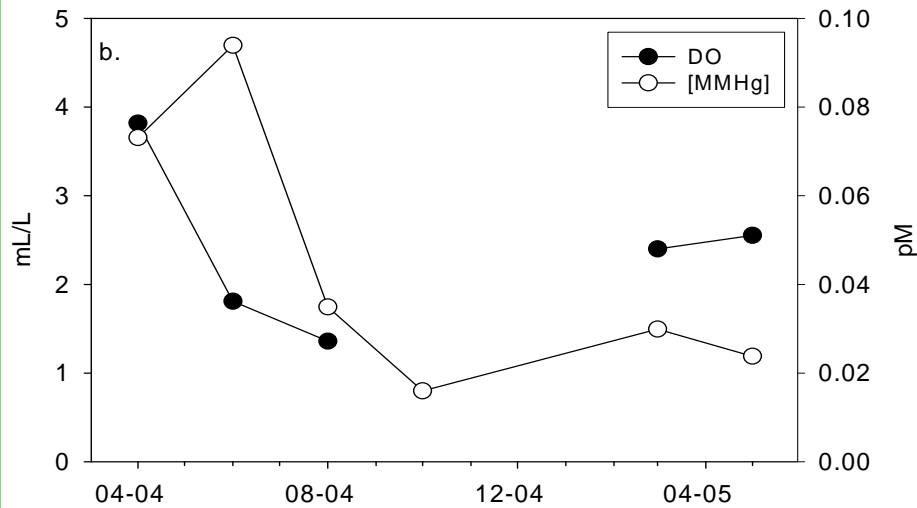


# Results - [MMHg] and Temp

- Not a Direct Relationship
- Too Warm?
- Sulfide-Hg Interactions?  
(Covelli et al. 1999)



# Results – [MMHg] and DO

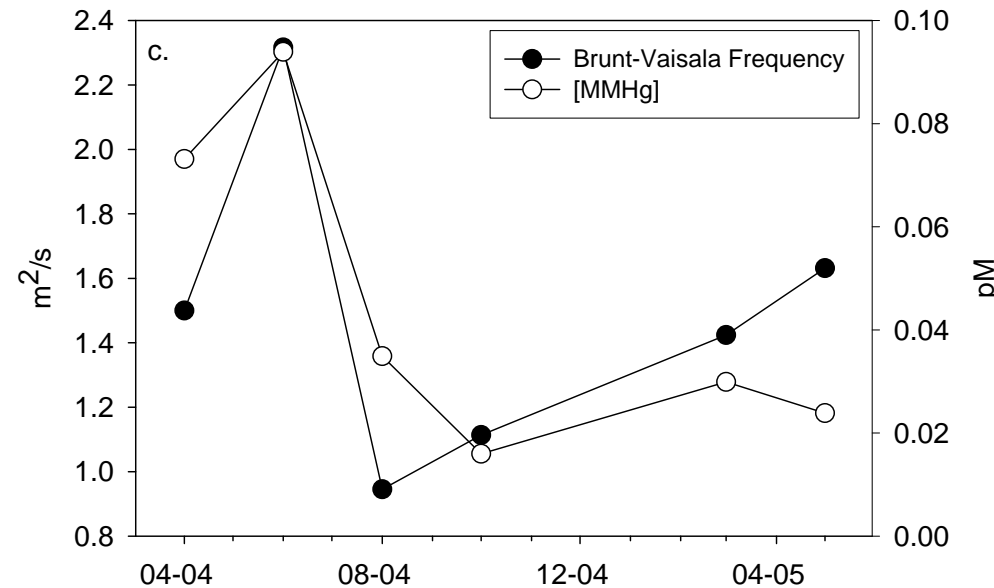


# Results

- Salinity, PAR, Particulate Conc. are Constant
  - Temperature: June/July < August
  - DO: June/July > August
  - But MMHg: June/July > August
- 
- So What's Controlling Bottom Water [MMHg]?

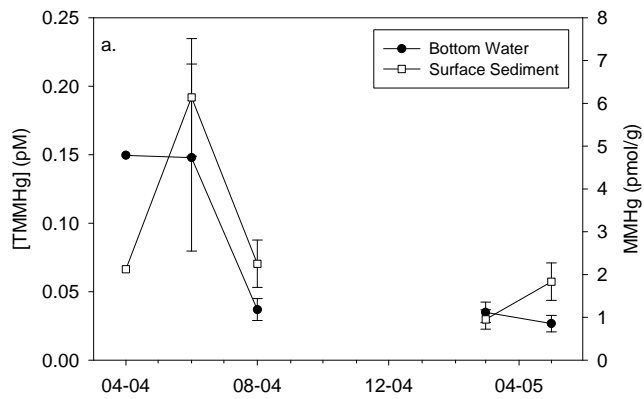
# Results – [MMHg] and Stratification

- $N^2_{(m^2/s)} = \left( \frac{g}{\rho_o} \right) \left( \frac{\partial \rho}{\partial z} \right)$
- Increased Methylation at Pycnocline or Oxycline
- Barrier

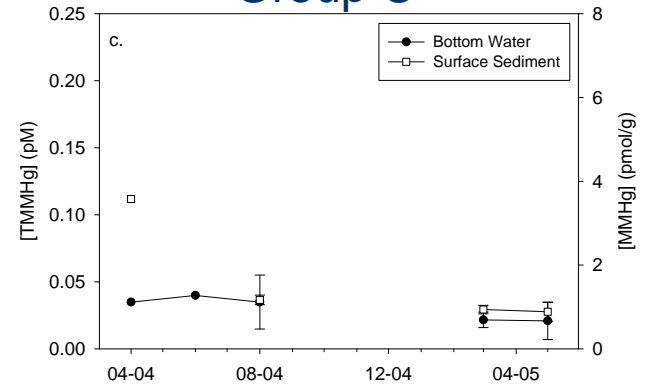


# Results

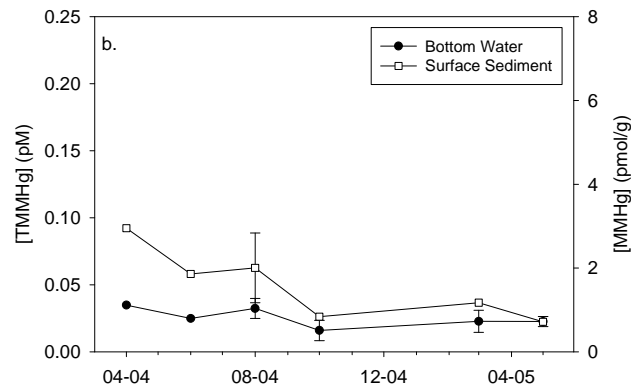
## Group A



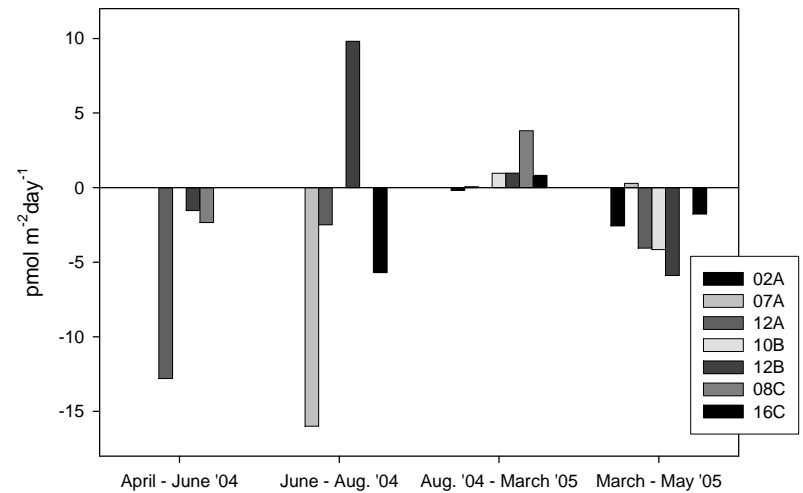
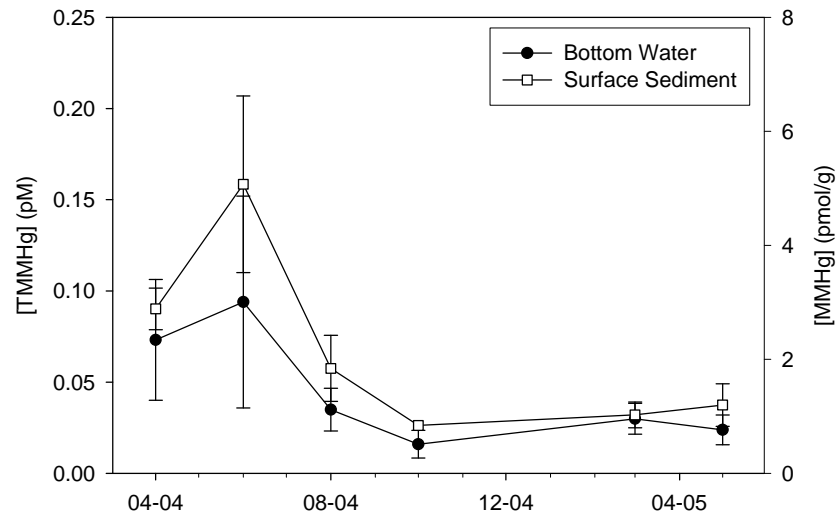
## Group C



## Group B



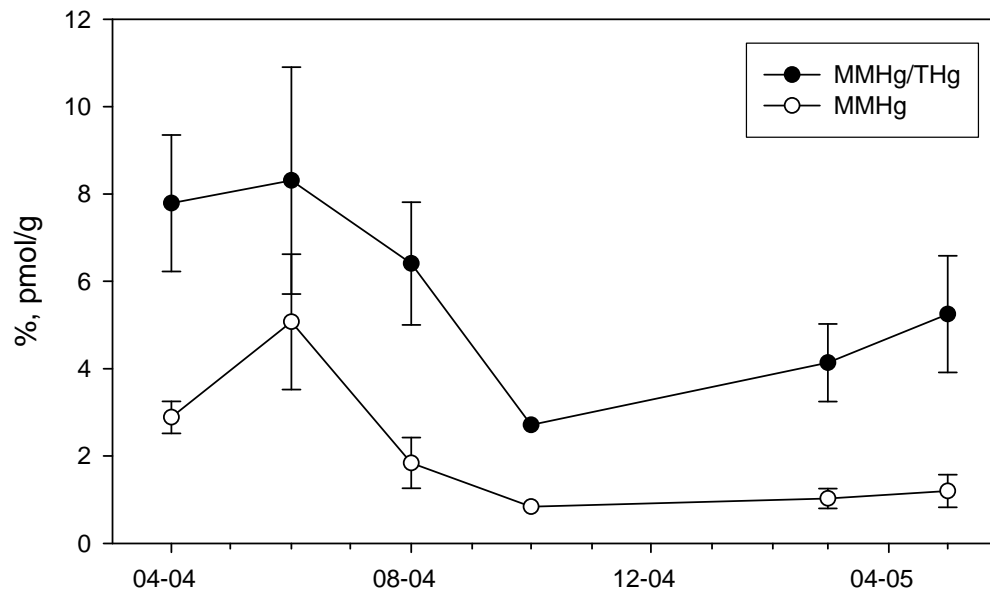
# Results - Benthic Flux



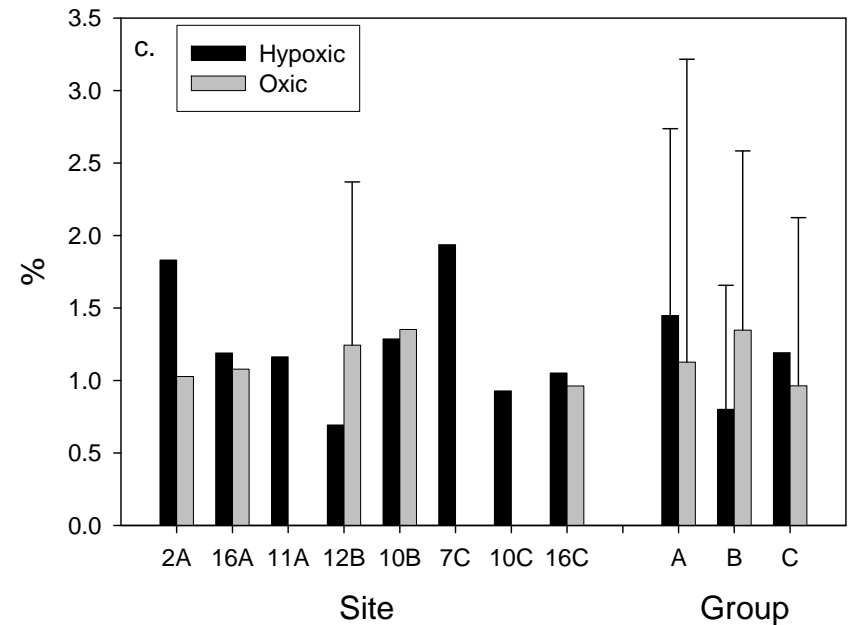
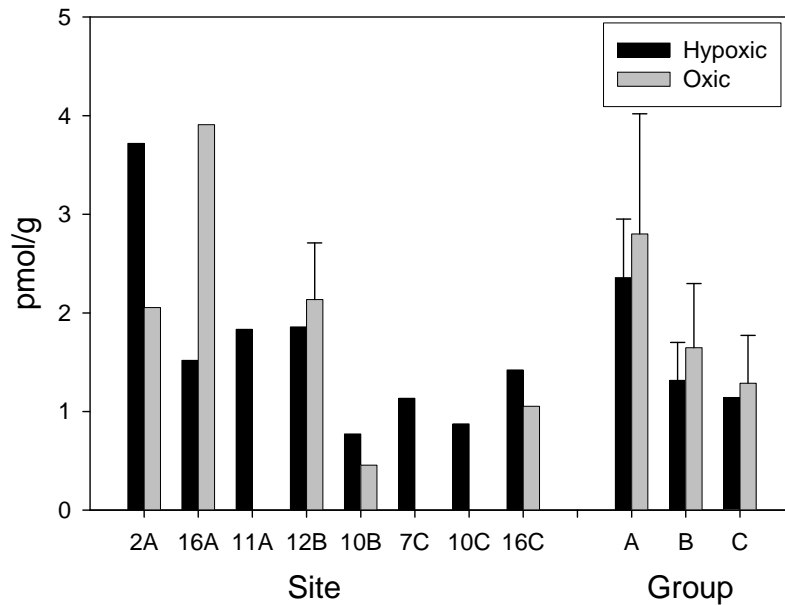
# GOM Fluxes

- Benthic Flux: -16 – 9.8 pmol/m<sup>2</sup>/day
- Wet Deposition: 2.4 pmol/m<sup>2</sup>/day (NADP/MDN)
- Mississippi River: 1.72 – 99.8 pmol/m<sup>2</sup>/day

# Results - Sediment



# Results – [MMHg] and DO



# Comparison (Sediment)

- Trefry et al. (2002)
  - MMHg:  $2.19 \pm 1.35$  pmol/g
  - THg: 54.8 - 458.7 pmol/g
- This Work
  - MMHg:  $1.86 \pm 1.86$  pmol/g
  - THg:  $159.2 \pm 102.9$  pmol/g

# Conclusions

- DO
  - Peak Methylation in the Middle of Range
  - Hypoxia → Increased Methylation
- Temperature
  - Inverse Relationship ... Inhibition?
- Stratification
  - Major role in Controlling/Containing [MMHg]

# Conclusions

- Mississippi River
  - Timing of peak Methylation
  - Increases MMHg ...Stratification? Direct Source?
- Benthic Fluxes
  - Relocation of MMHg
  - Important in GOM

# Thanks to ...

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- My Committee
  - Gary Gill, Steve Dimarco, Peter Santchi, Jay Rooker
- Hg Lab
  - Ron Lehman, Key-Young Choe
- Everyone Aboard the Gyre Who Helped Me Collect Samples