Application of a Polymeric Equilibrium-Based Passive Sampler for Methylmercury to Measure a Sediment Porewater Depth Profile

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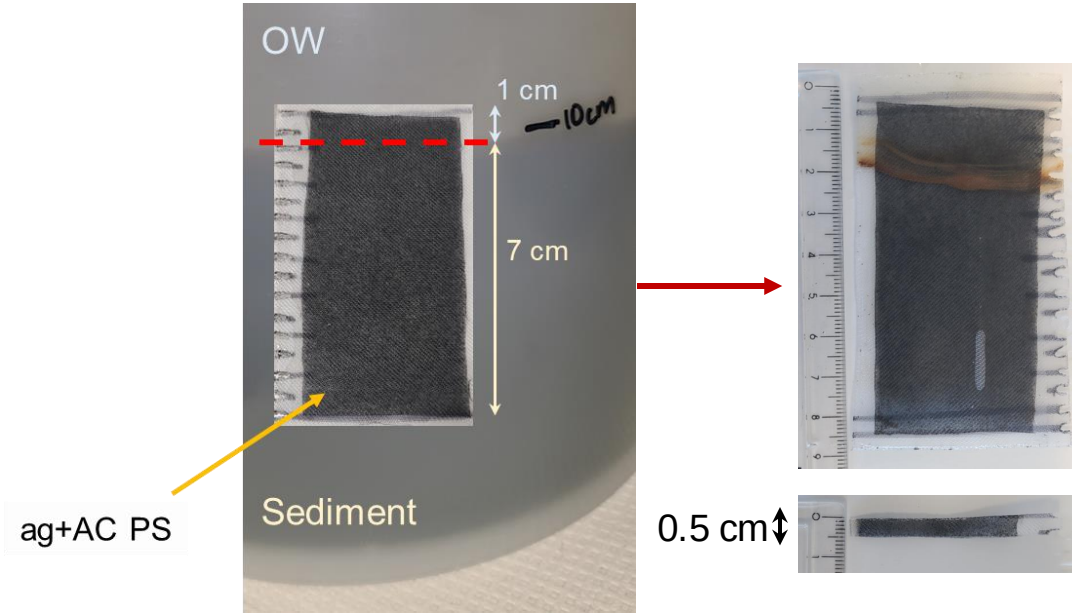
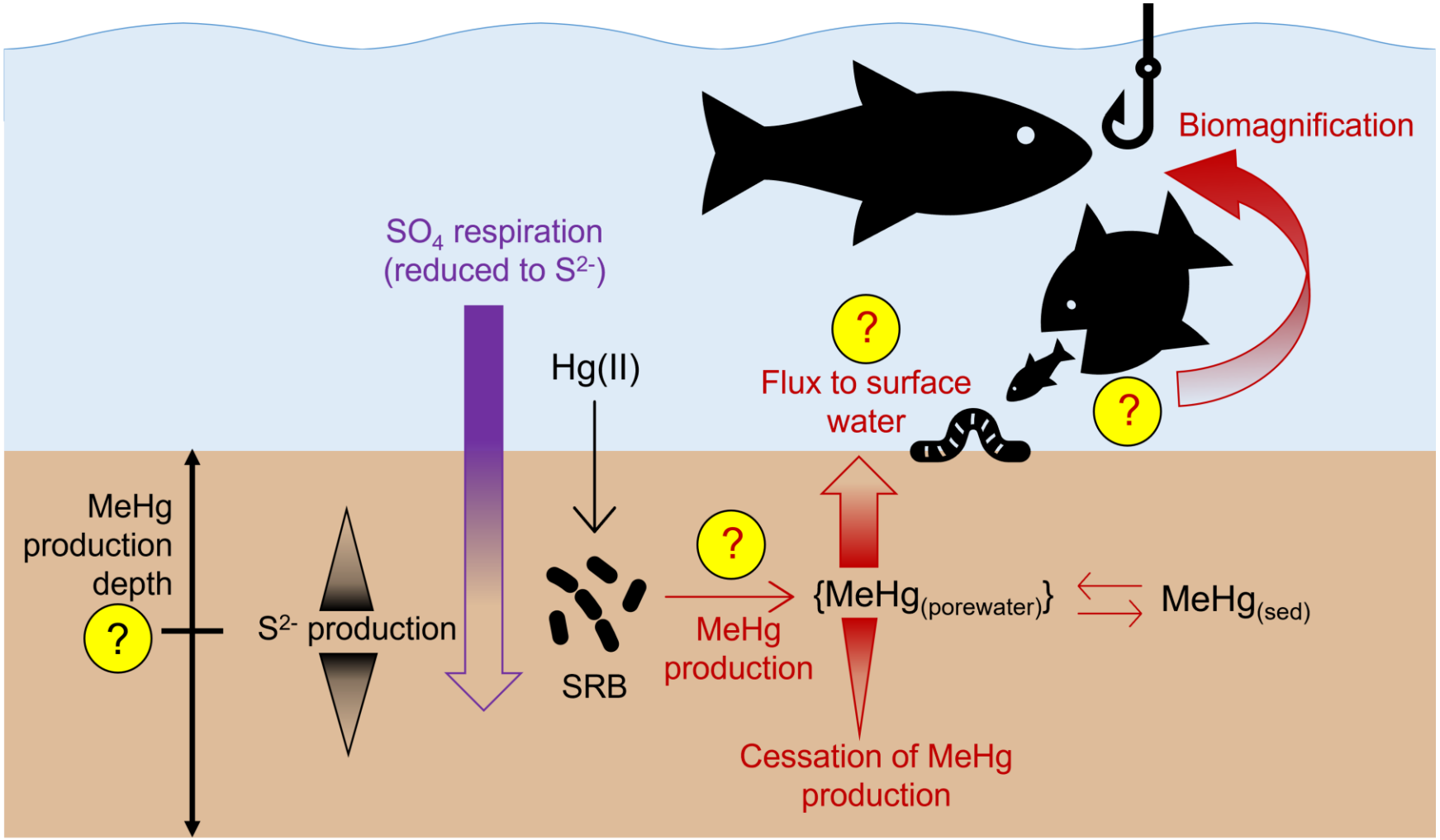


Sampling difficulties limit understanding of Hg fate & transport

which is heavily influenced by the site's biogeochemistry

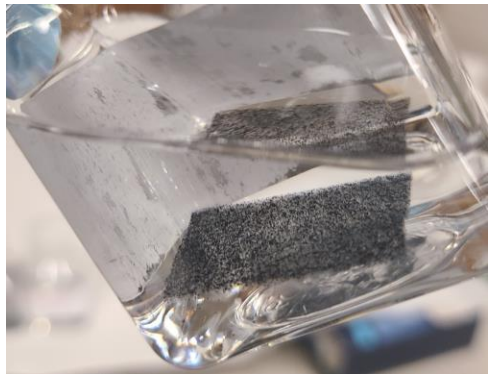


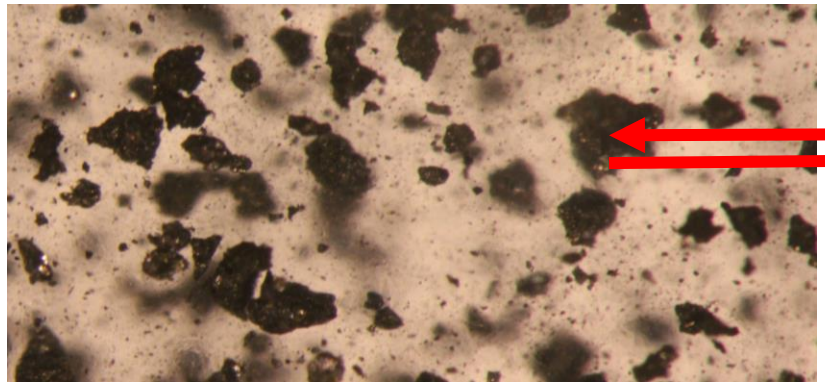
Traditional Sampling Difficulties

- **Low $[MeHg]_{aq}$**: large sample needed for detection
- **Redox Sensitivity**: after collection, sediment core oxygenation influences Hg sediment:porewater dynamics and redox chemistry
- **Temporal Variability**: natural events can cause day-to day variations, which may necessitate continuous sampling
- **Spatial Variability**: porewater MeHg reaches a peak somewhere down the porewater column

Activated Carbon *Equilibrium* Passive Sampler (PS) developed to overcome challenges with traditional sampling methods

ag+AC
Activated carbon suspended in agarose gel sheet (1 mm thick)





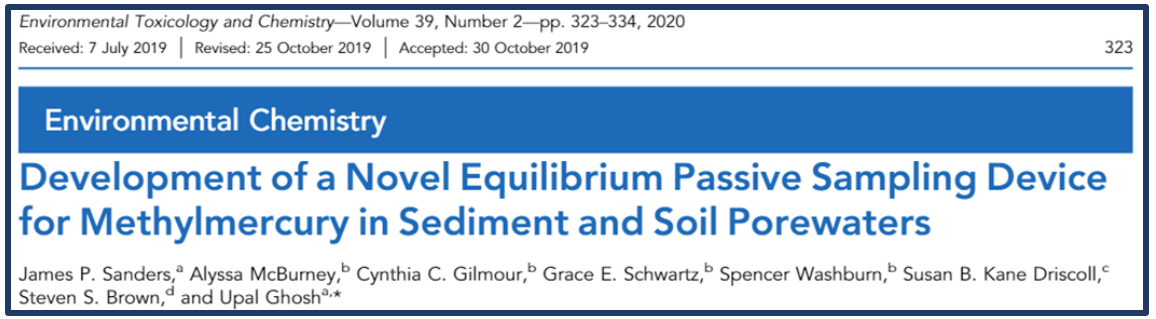
$[MeHg]_{aq}$

$$[MeHg]_{aq} = \frac{[MeHg]_{PS}}{K_{PS}}$$

Demonstrations from Current Publications

- **Improved Detection** ($K_{PS} \cong 10^3$)
- **Applicable in a variety of chemical environments**
  - *Tight K_{PS} range for MeHg complexes with several aquatic dissolved organic matter of varying character*
  - *minimal effects on sediment-PW dynamics*
- **Time-averaged measurements**
  - *PS-water reversible equilibrium reached in 14-28 days*
- **Measured a 2-point spatial $[MeHg]_{aq}$ profile**
  - *using a single polymer* **placed across the sediment-water interface.** *Comparable* **w/in a factor of 4 to grab sample** *measurements*

Next Step: fine-scale porewater profiling



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Environmental Chemistry

Development of a Novel Equilibrium Passive Sampling Device for Methylmercury in Sediment and Soil Porewaters

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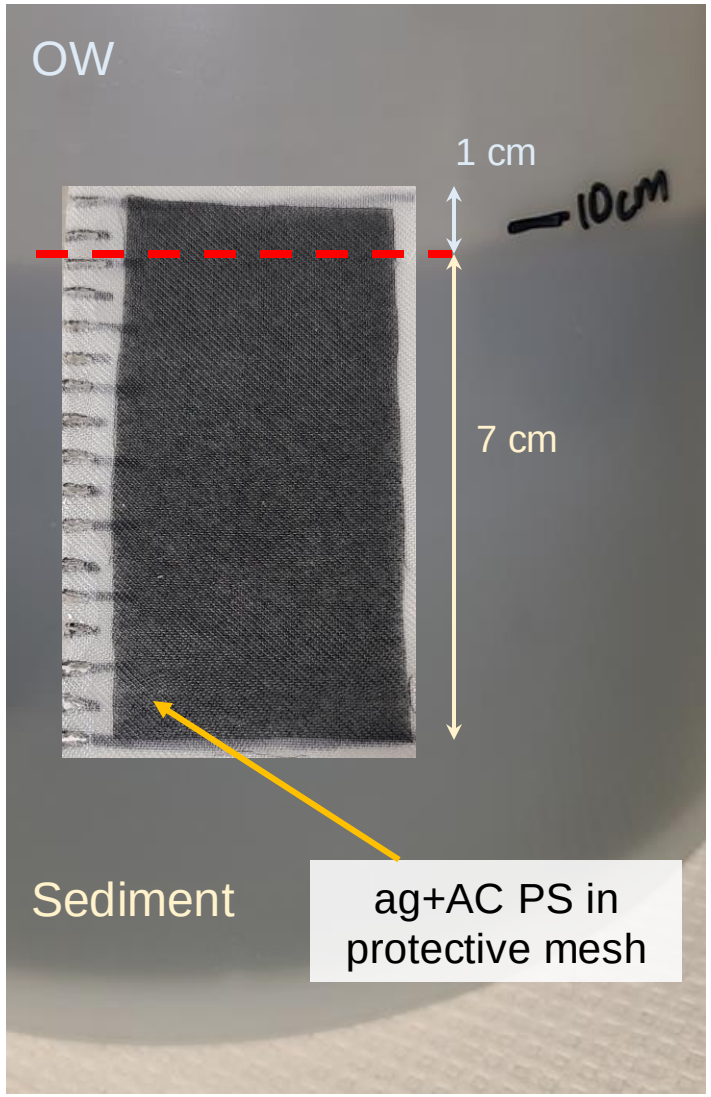
Environmental Chemistry

Uptake Mechanisms of a Novel, Activated Carbon-Based Equilibrium Passive Sampler for Estimating Porewater Methylmercury

Spencer J. Washburn,[a,*] Jada Damond,[b] James P. Sanders,[c] Cynthia C. Gilmour,[a] and Upal Ghosh[b,*]

Demonstration 1: measure a $[MeHg]_{aq}$ profile (0.5 cm resolution) with ag+AC PS and observe corresponding biogeochemistry



Deployed 8 x 4 cm ag+AC PS in freshwater sediment microcosms

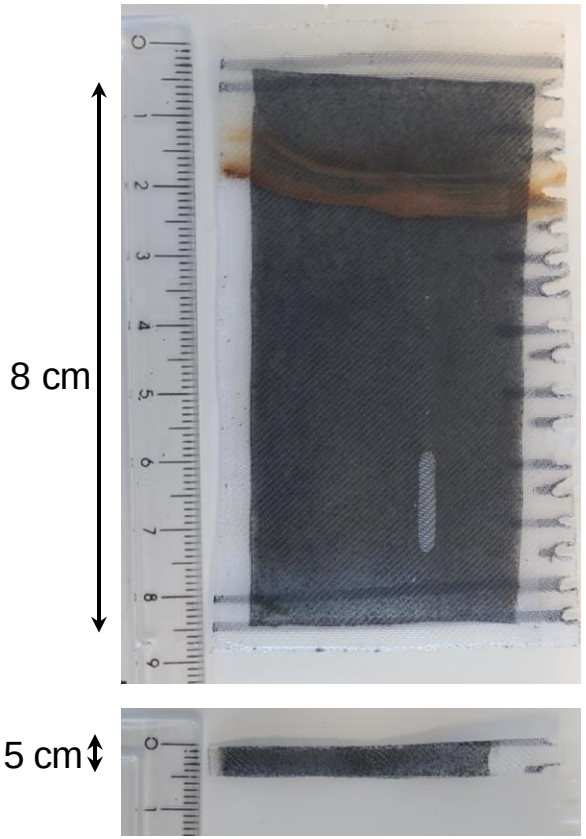
- Hg-laden sediment (BCSA) diluted with pristine freshwater sediment (SERC) & homogenized
- Overlying water (OW) collected from freshwater stream (SERC). Aerated throughout experiment
- 14-day incubation followed by 29-day PS deployment

Initial Levels

$[THg]_{Sed}$ (mg/kg)	$[MeHg]_{Sed}$ (µg/kg)	$[MeHg]_{PW}$ (ng/L)	$[SO_4^{2-}]_{OW}$ (µM)	$[SO_4^{2-}]_{PW}$ (µM)
4.4	2.3	0.56	154	2,854

The ag+AC PS method was compared to collecting and sectioning sediment cores to provide a porewater profile

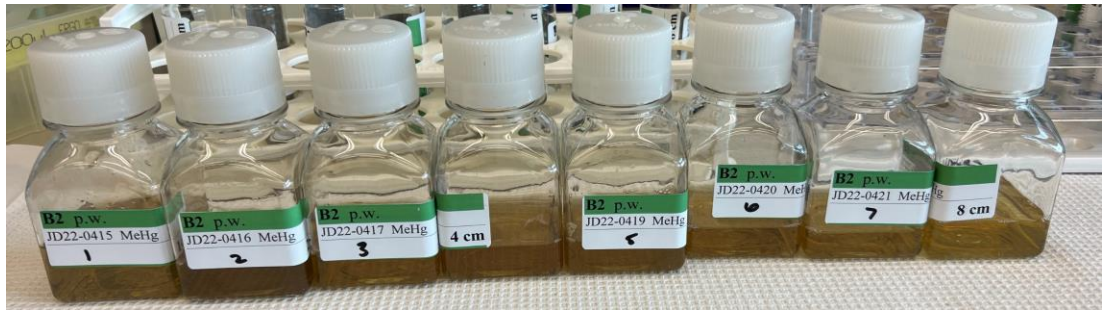
Profiling with ag+AC **PS**



- PS segmented (0.5 cm) after retrieval

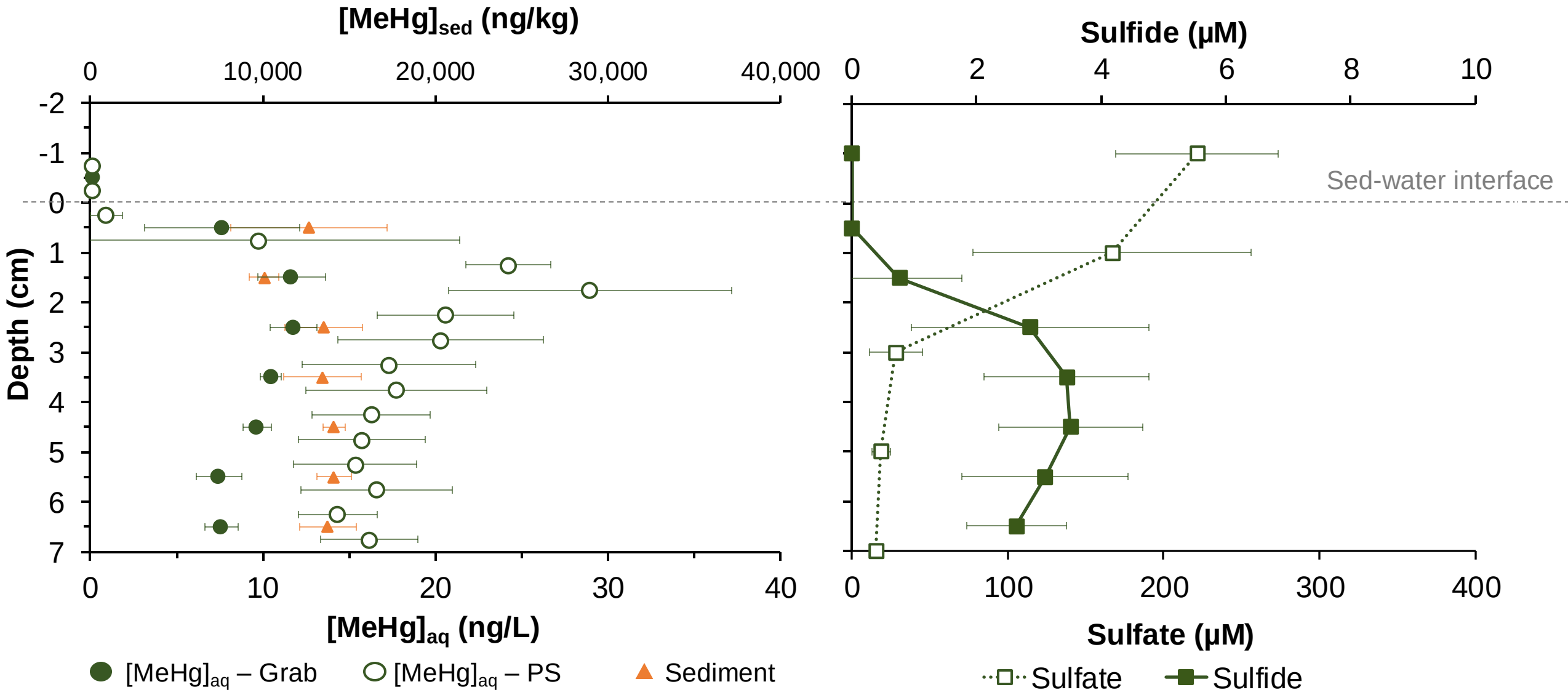
- vs -

Profiling with sediment cores & porewater **grab samples**

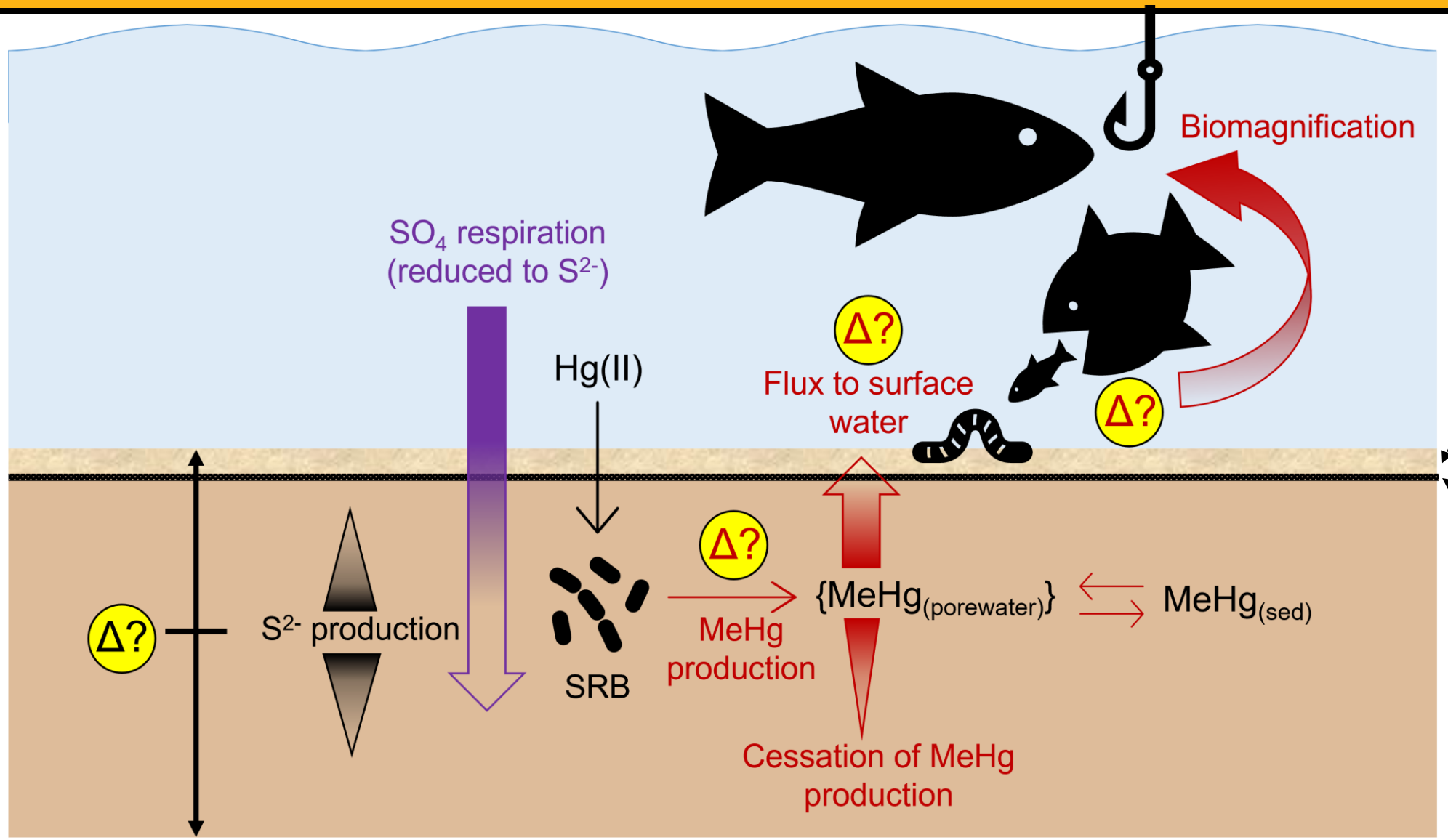


- *Several* cores collected from <u>each</u> microcosm
  - Needed to extract enough porewater for analyses
- Cores segmented (1 cm) in anaerobic glovebox
- Centrifugation extraction of porewater
  - Filtered to 0.45 µm

Porewater profiles provide great insight into biogeochemical effects



The goal for sediment treatment is to reduce MeHg bioavailability
i.e. by reducing surface porewater and surface water levels

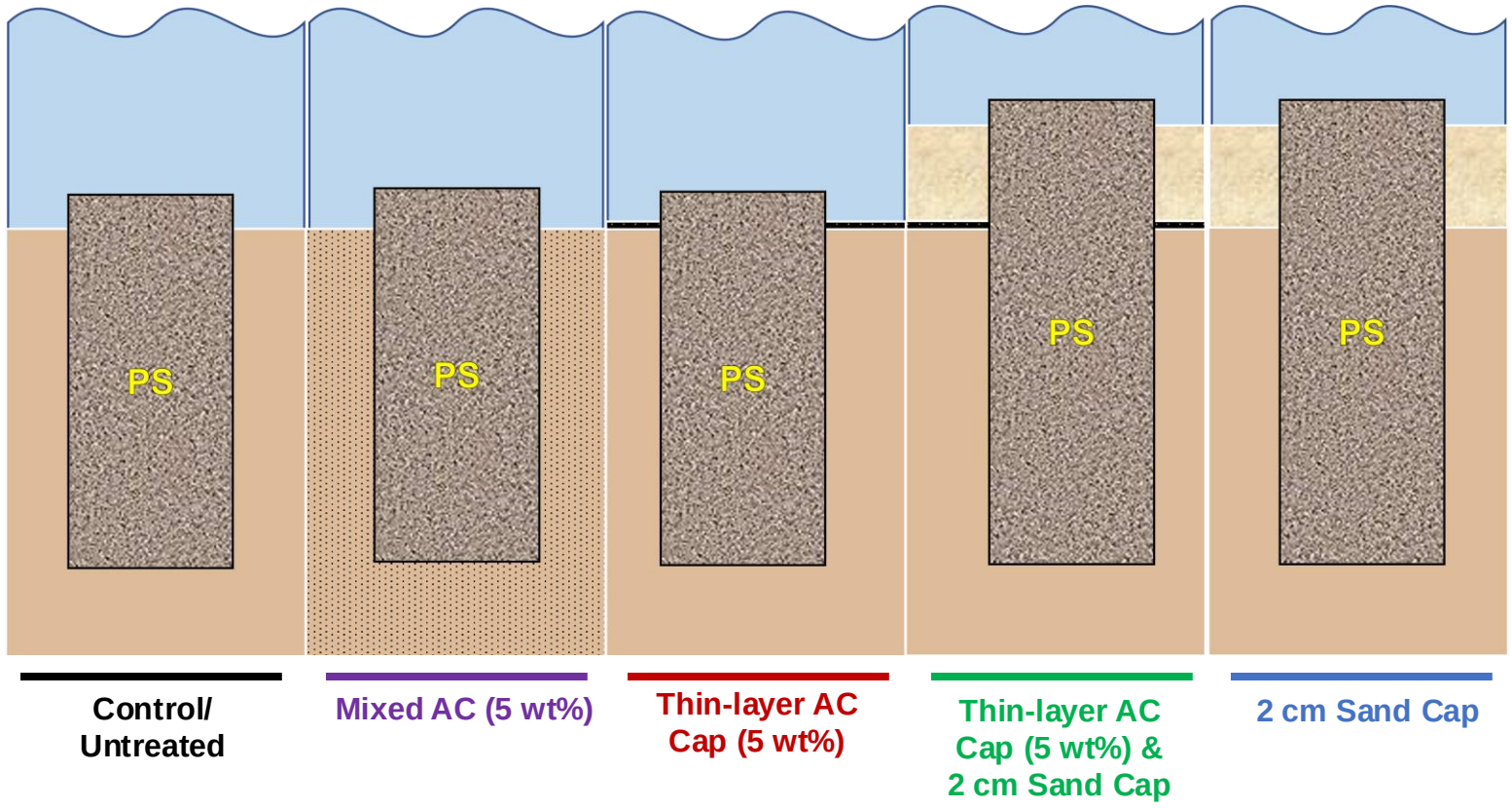


Scenario: Hg sourced from sediment

A Thick Sand Cap limits physical movement of aqueous MeHg to surface sediment porewater

Activated carbon AC adsorbs aqueous MeHg and iHg, lowering porewater concentrations

Demonstration 2: use PS-Derived MeHg aqueous profiles to compare performance of several amendment applications and their effect on Hg fate & transport

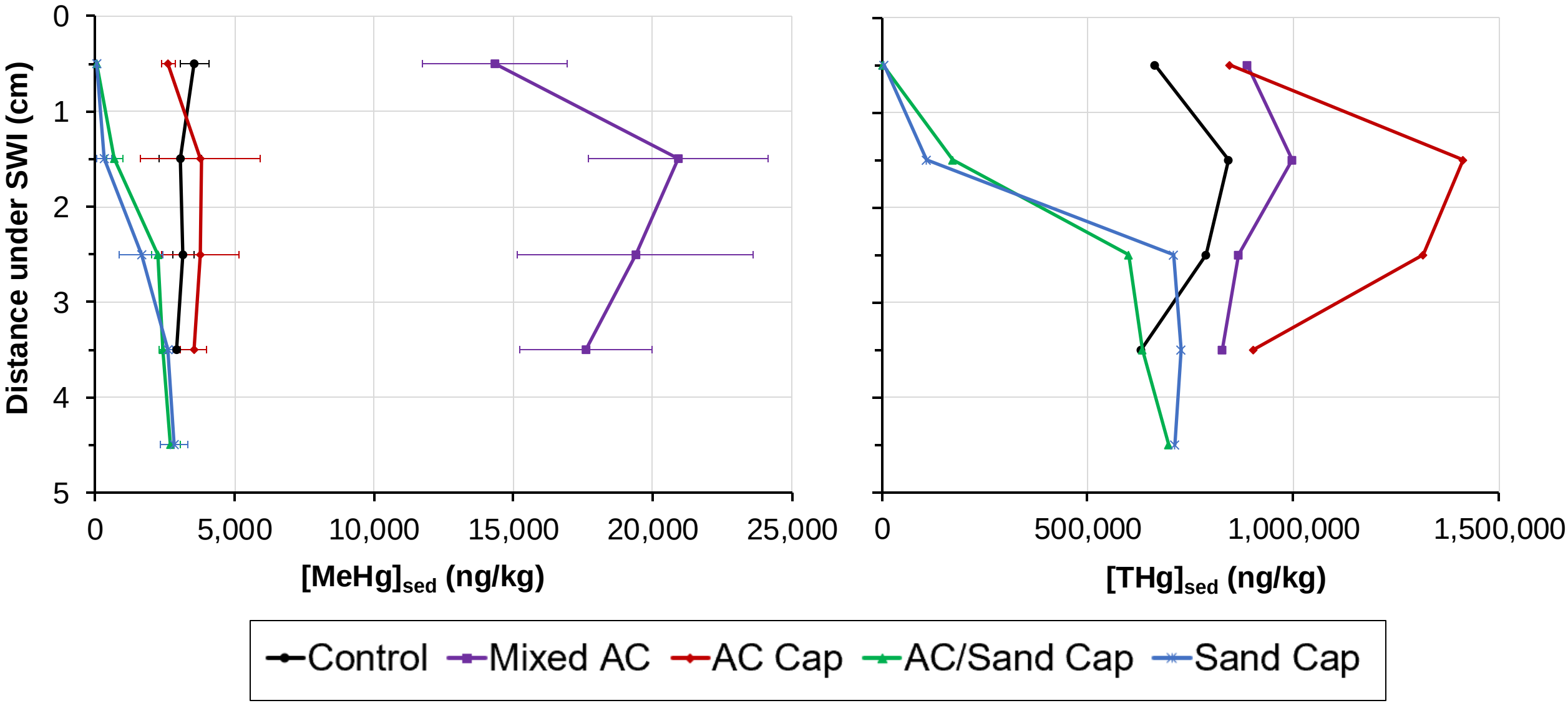


Core from 2 cm Sand Cap

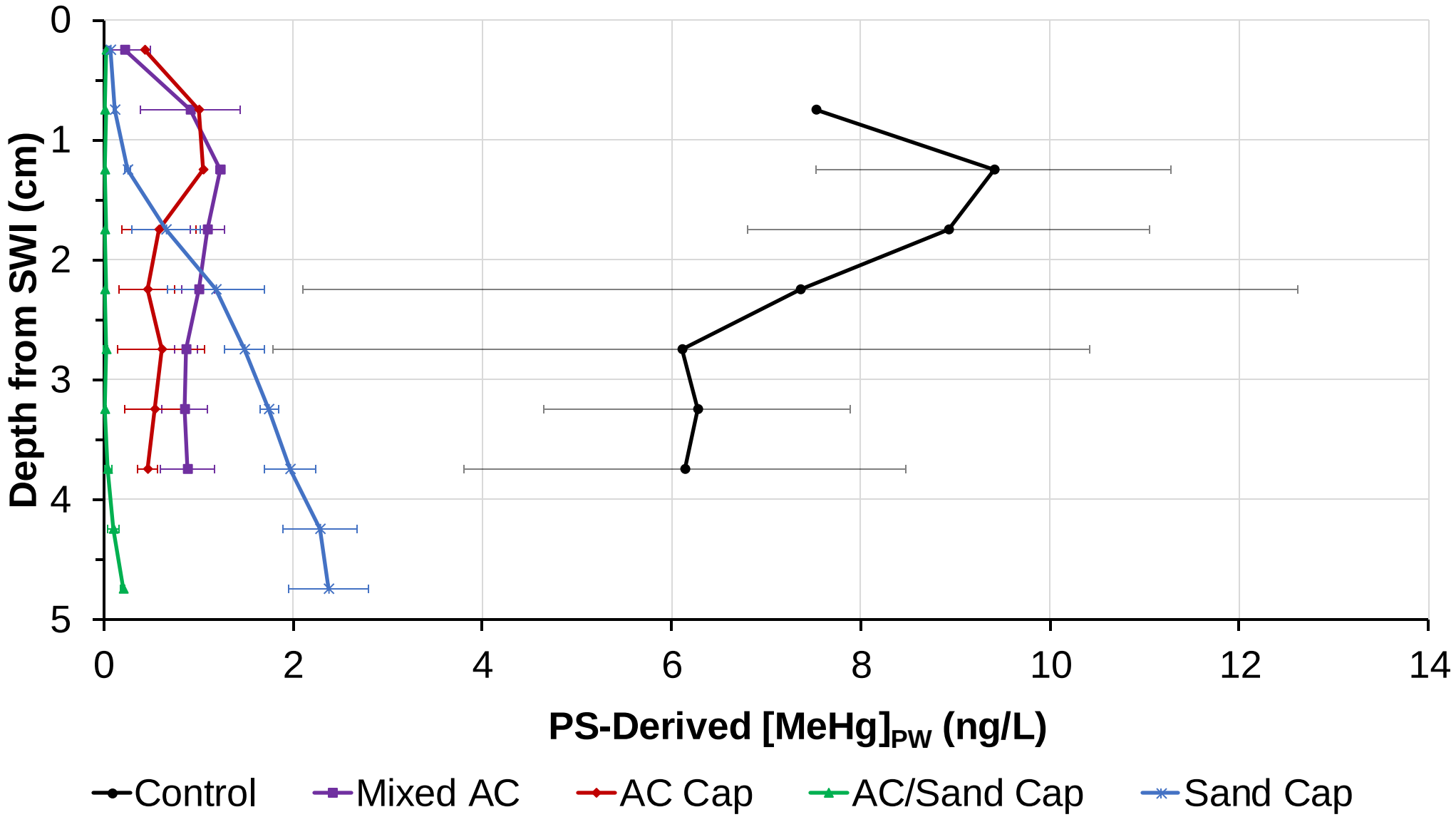
Core from Thin-layer AC Cap (5 wt%) & 2 cm Sand Cap

- Microcosms contain Hg-laden sediments (BCSA) diluted with pristine local freshwater sediments (SERC)
- Surface water collected from pristine local stream (SERC). Aerated throughout experiment
- 9 week incubation followed by 4 week PS deployment

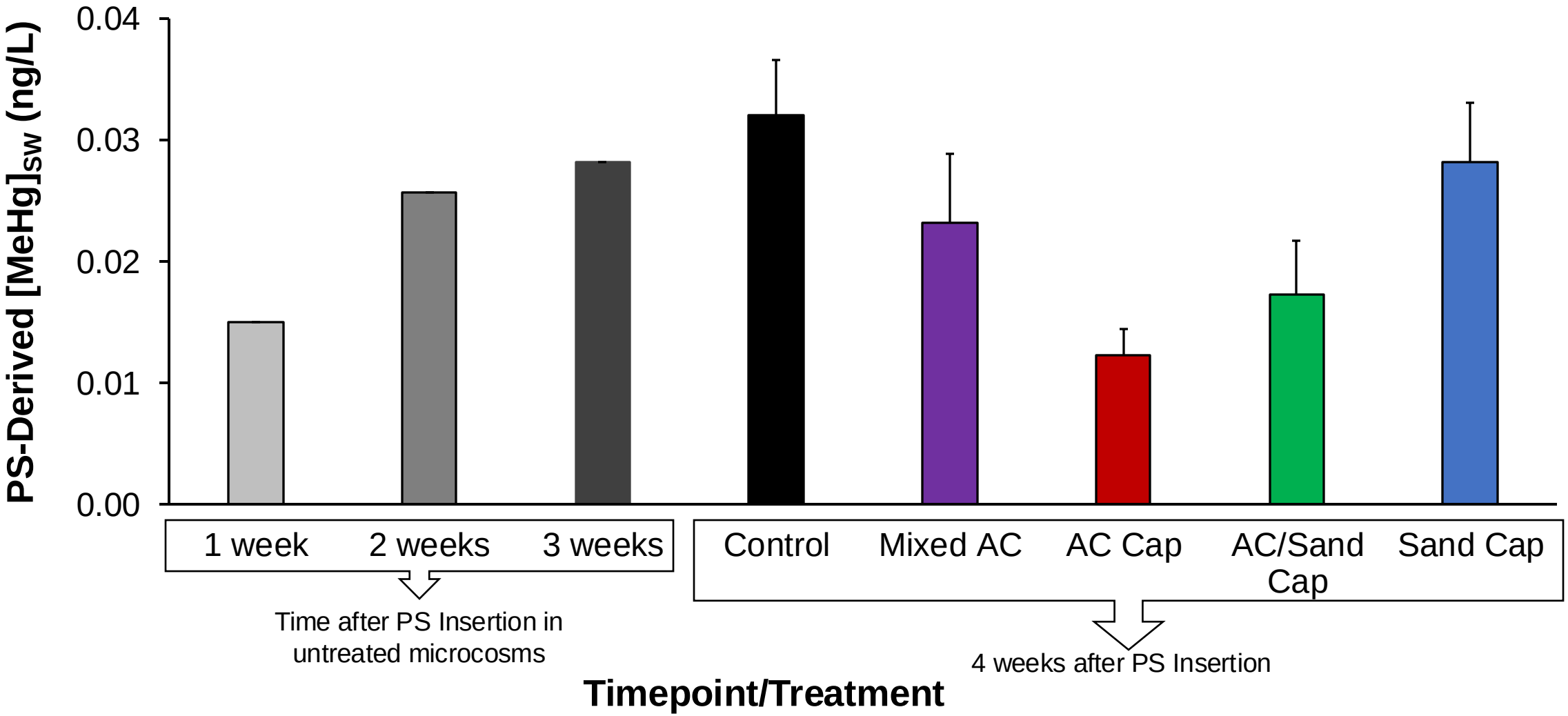
Preliminary Results: Sediment MeHg and THg profiles



Preliminary Results: PS-Derived porewater Profiles



Preliminary Results: PS-Derived Surface Water Measurements



Conclusions, Implications & Next Steps

- Demonstrated successful application of ag+AC PS for fine-scale (0.5 cm resolution) $[MeHg]_{aq}$ profiling
- In demonstration 1, the porewater profile showed that peak $[MeHg]_{PW}$ corresponded, spatially, to where sulfate reduction and sulfate production was observed.
  - *Suggestive of where the biological activity responsible for Hg methylation takes place, providing a target for treatment*
  - *Locating peak $[MeHg]_{PW}$ can be indicative of exposure to sediment dwelling organisms*
- In demonstration 2, the depletion of $[MeHg]_{PW}$ and $[MeHg]_{sed}$ in treatments with a 2 cm sand cap indicated limited MeHg transport in surficial sediments
  - *Low porewater recovery in sand layers, porewater profiling with PS can be crucial for assessing cap performance and breakthrough*
- In demonstration 2, significant increase in $[MeHg]_{sed}$ when 5 wt% AC was mixed into bulk sediments, opposed to cap with same AC mass, although $[MeHg]_{PW}$ in the two treatments were comparable
  - *treatment application method does impact performance and Hg F&T.*

Next Steps:

- additional chemical profiling in remediation study to study biogeochemical impact of treatment applications
- use data to build quantitative relationships to describe Hg F&T

Thanks for Listening!

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Environmental Research Center

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Let's Connect!

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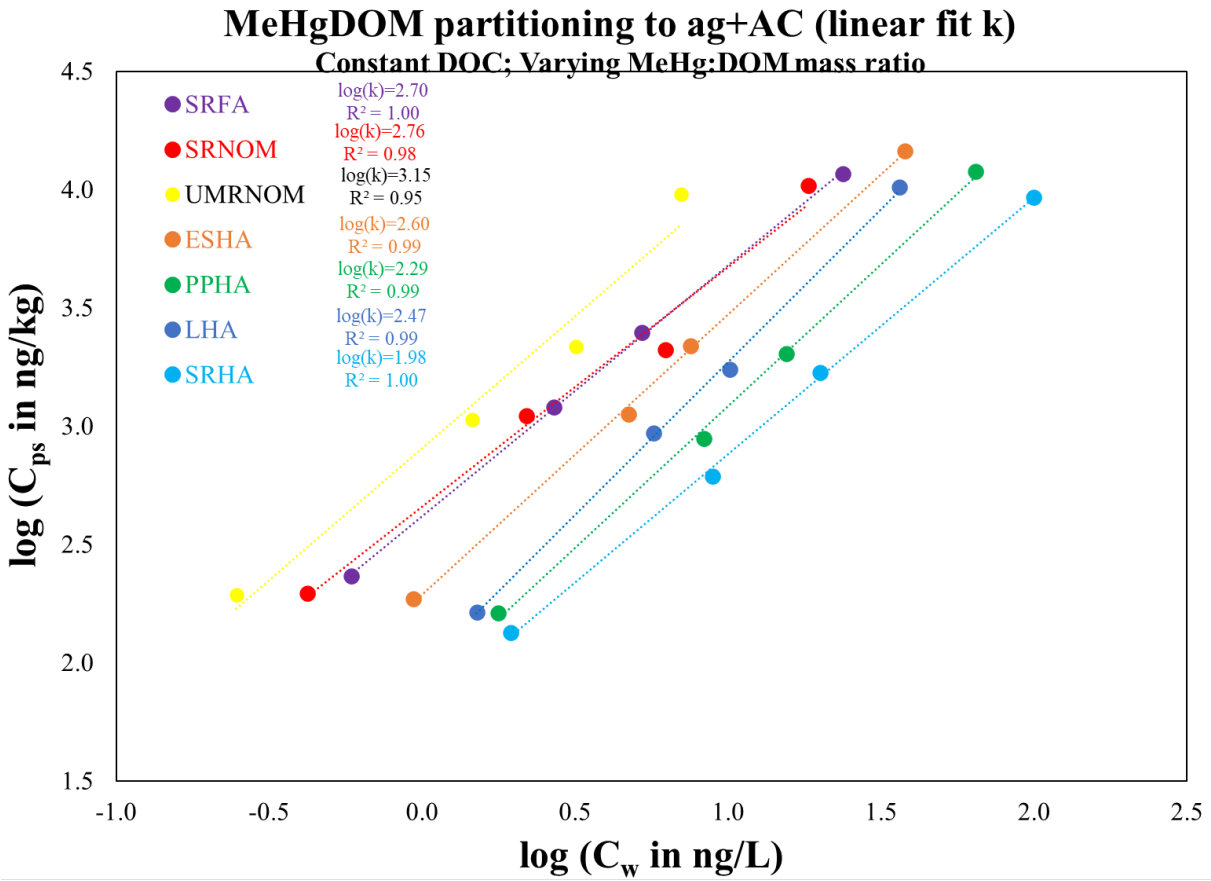
Supplement Slides

ag+AC PS Characterization & Development



- **Tight K_{PS} range** for aquatic, unfractionated HMW and LMW DOM species
- **Detectable Measurements** ($K_{PS} \cong 10^3$)
  Using average K_{PS} from DOM isotherms
- ag+AC **equilibrium reached after 14 days**

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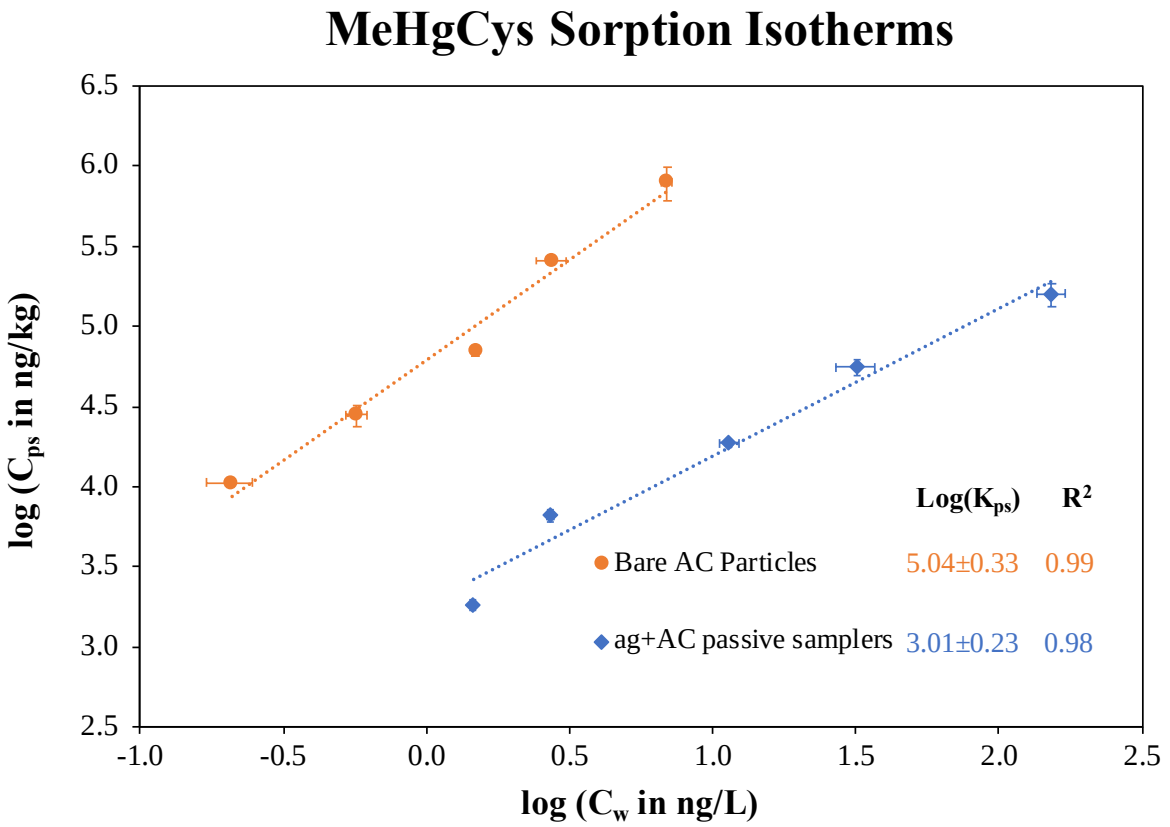
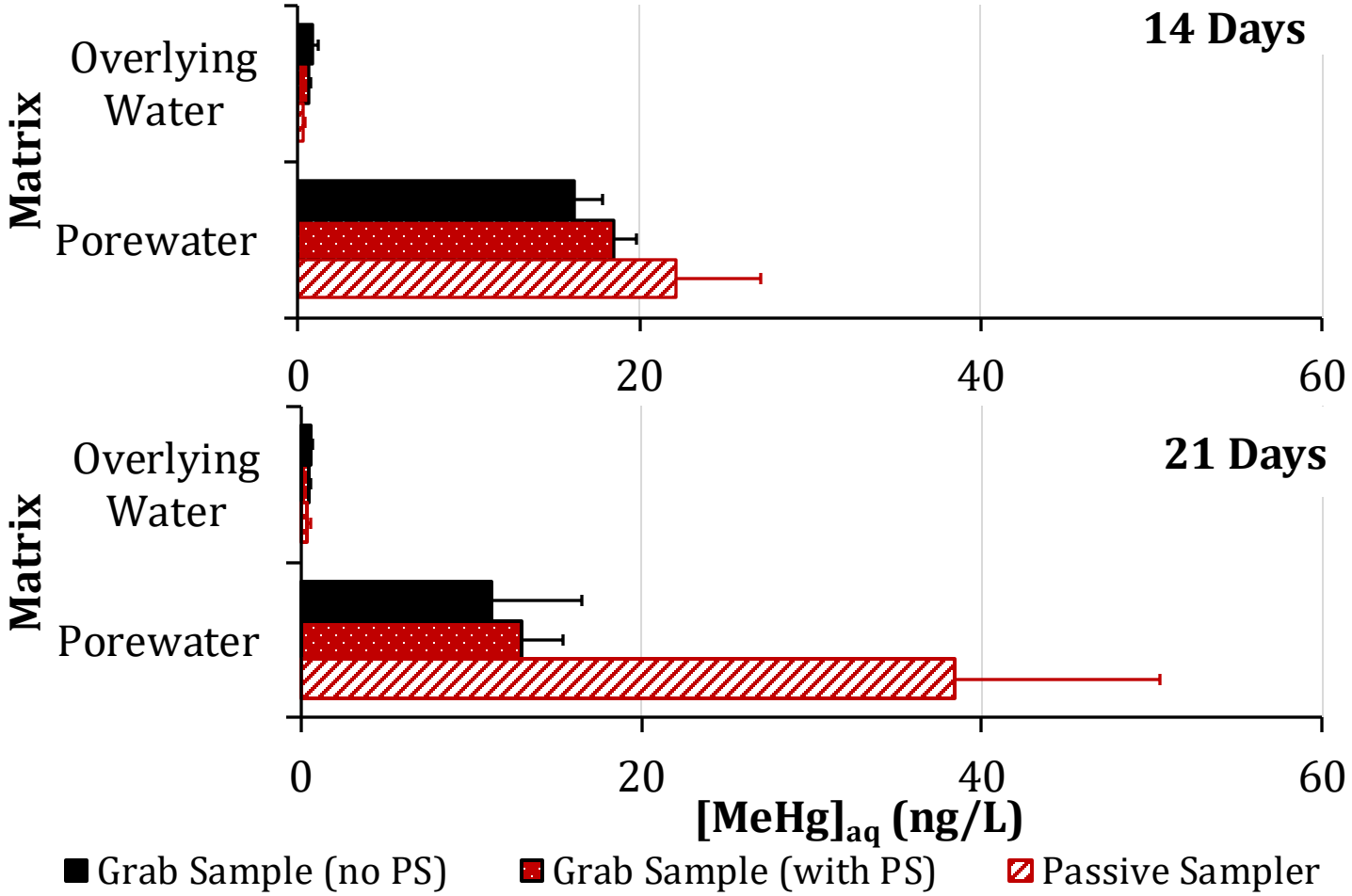
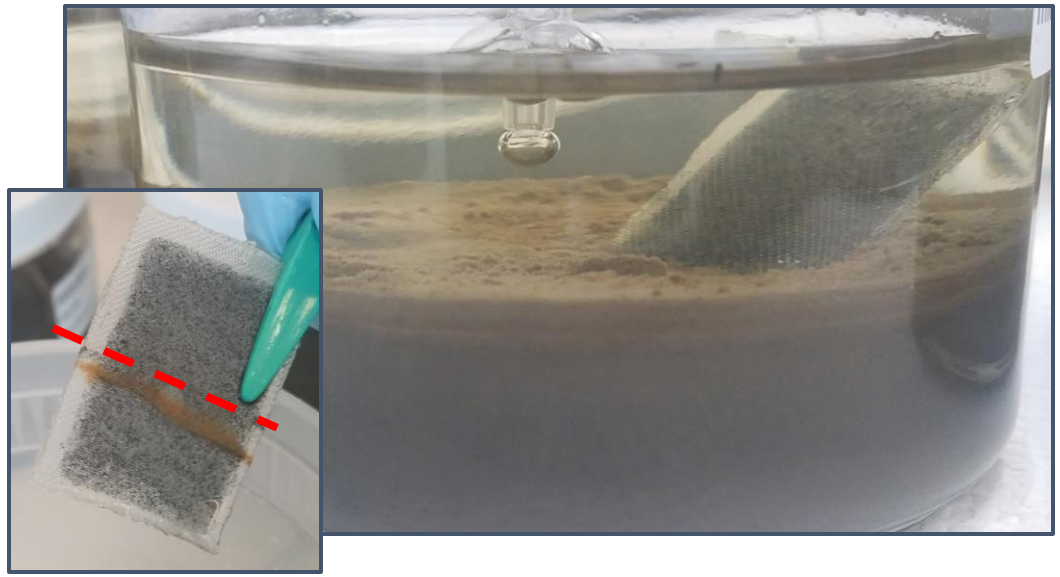


ag+AC PS successfully measured time-integrated $[MeHg]_{aq}$ across sed-water interface



$$[MeHg]_{aq} = \frac{[MeHg]_{PS}}{K_{PS}\ (= 10^3)}$$



- PS-Derived measurements **within a factor of 4** of grab sample measurements
- PS had minimal effects on sediment and porewater conc.