A Biogeochemical Framework for Assessing Methylmercury Productivity and Expression in Aquatic Sediments

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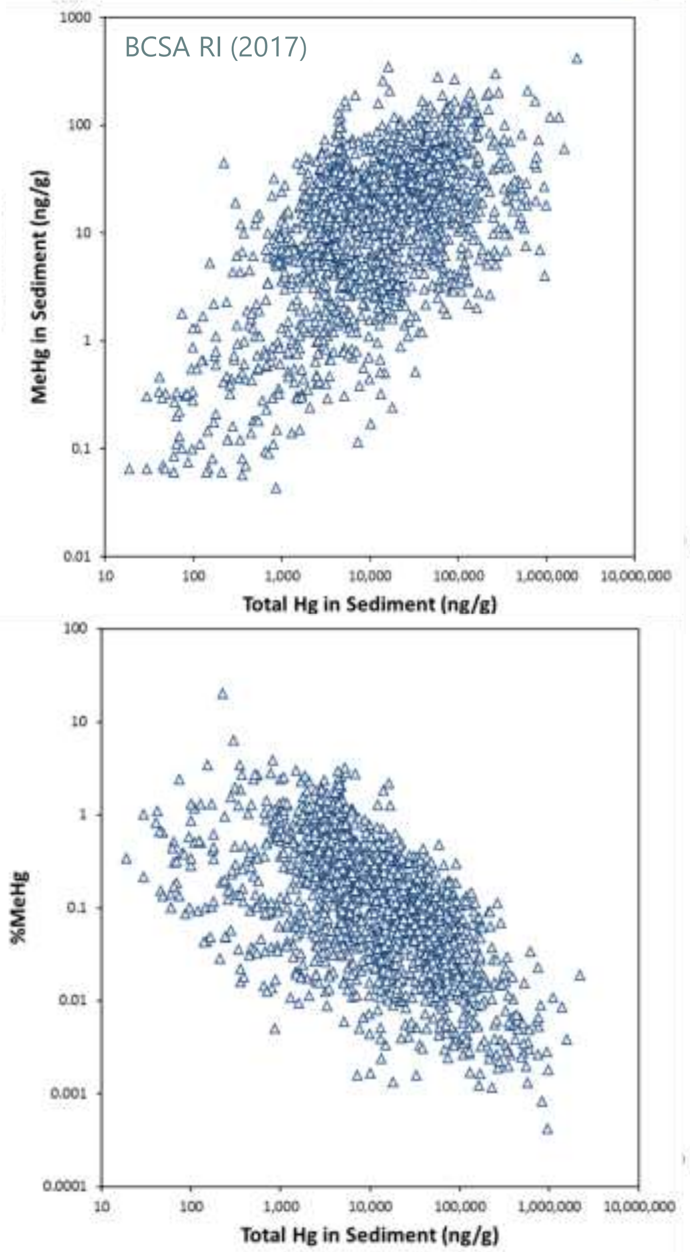
USGS

THE UNIVERSITY OF CALIFORNIA MERCED · LET THERE BE LIGHT · 2005

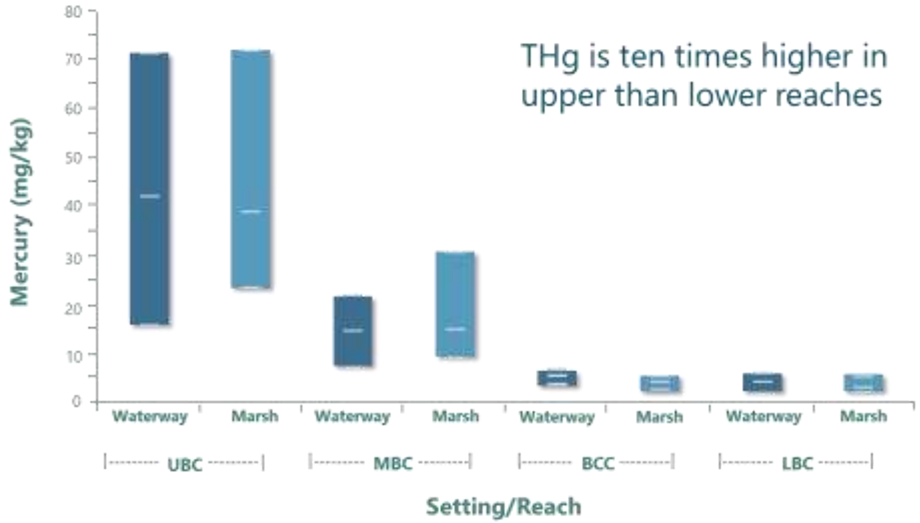
Smithsonian Environmental Research Center

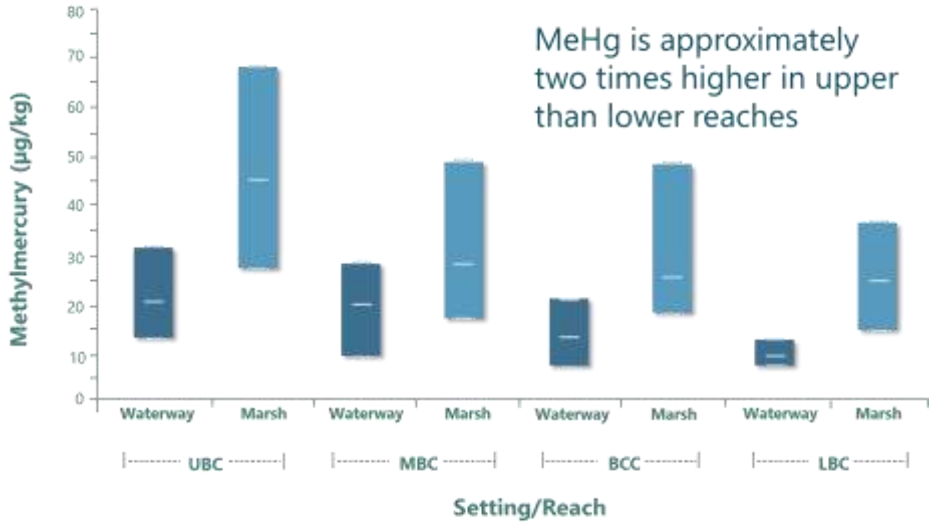
Background

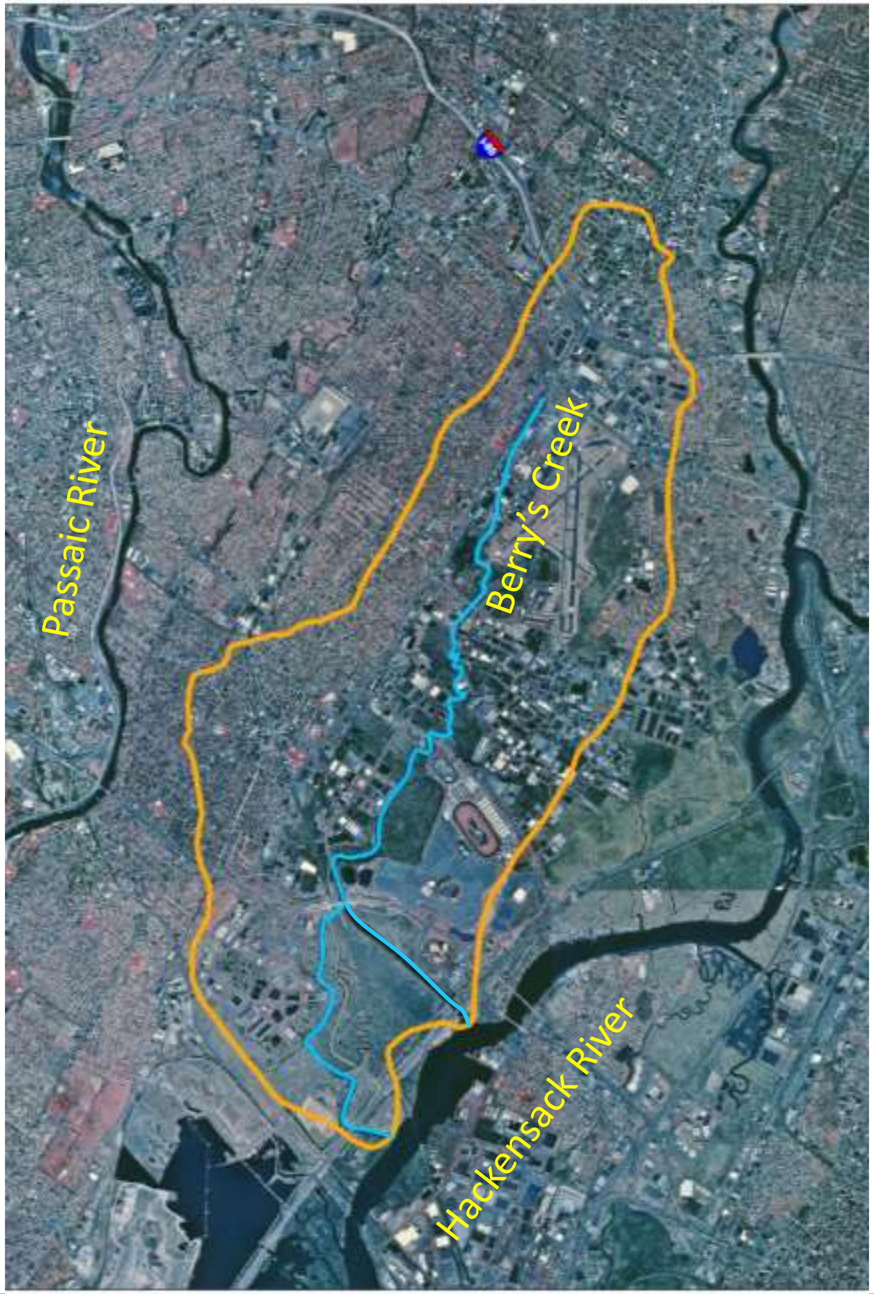
- Environmental risk in Hg contaminated sediments driven by methylmercury (MeHg) due to bioaccumulation and toxicity (ecological, human health – fish consumption)
- MeHg concentrations generally correlate with total mercury (THg) concentrations in sediment but relationship can be highly variable even a site
  - % MeHg/THg generally shows a decreasing trend with increasing THg
- Sediment cleanup standards and remedies traditionally set in terms of THg concentration
- Need for improved framework for assessing and ranking relative risk of Hg contaminated sediments



Berry's Creek Study Area NJ



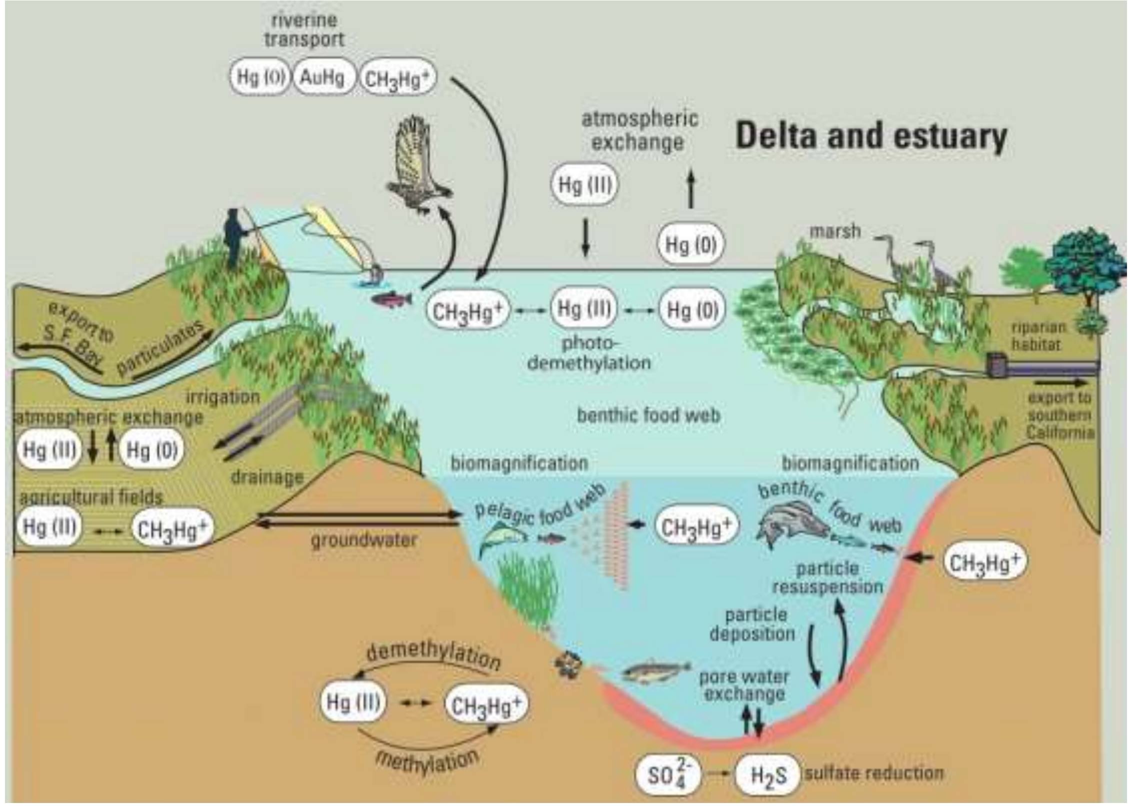




Factors Regulating Hg Methylation and Cycling in Sediments

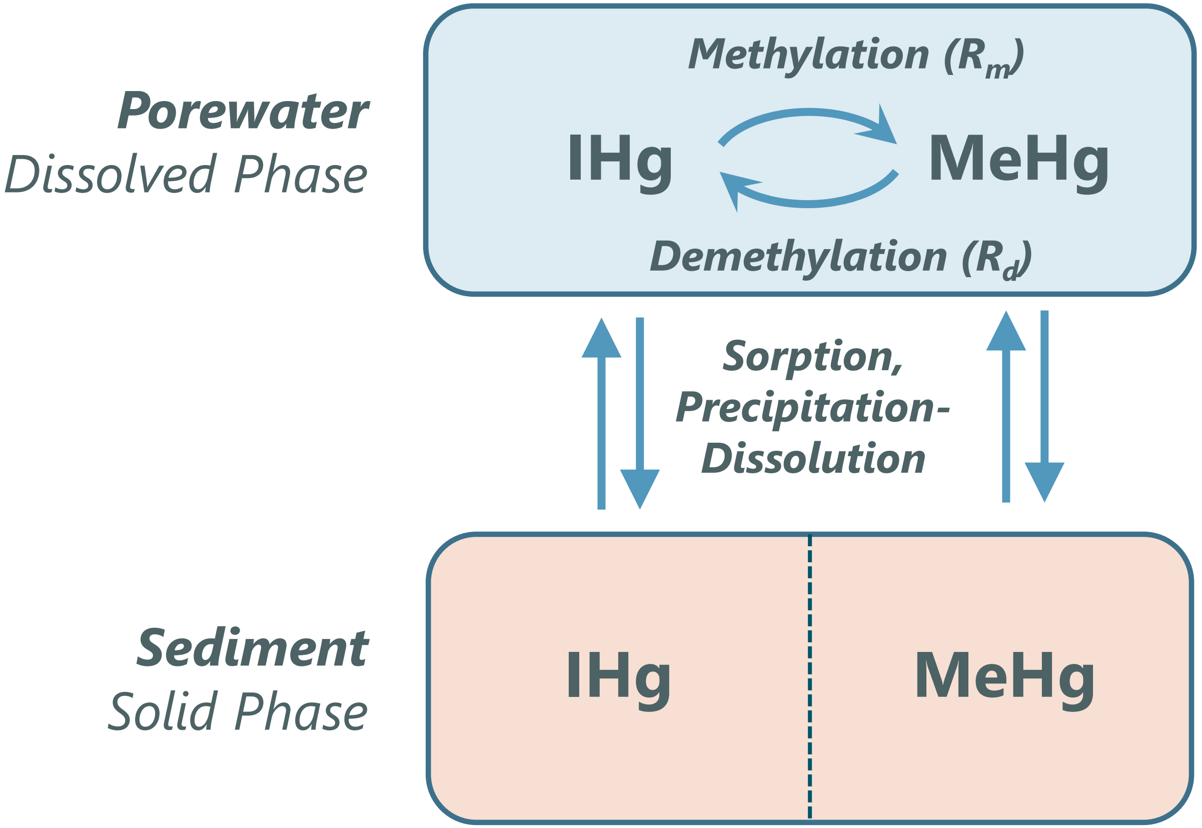
- Availability of inorganic Hg to methylating organisms
  - Partitioning to porewater – aqueous speciation, sorption (organic matter), solubility (HgS)
- Activity of microorganisms
  - Methylation linked to major redox cycles (sulfate and Fe(III) reducers)
  - Demethylation enhanced under both oxidizing and reducing conditions

[Hsu-Kim et al. 2013, ES&T]



Alpers et al (2005)

Biogeochemical Reaction Network for Hg Cycle in Sediments



THg = IHg + MeHg

R_m = *f*{IHg, TEAPs, DOM, H_2S, pH, etc.}

R_d = *f*{MeHg, TEAPs, etc.}

Sorption: Thiol groups in SOM, mineral surfaces

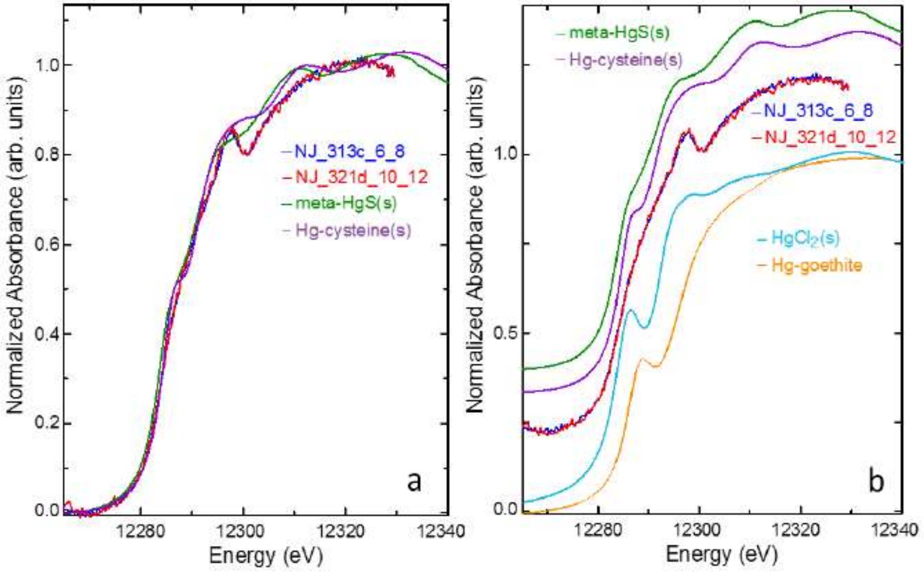
Solubility: HgS (metacinnabar, nano-HgS)

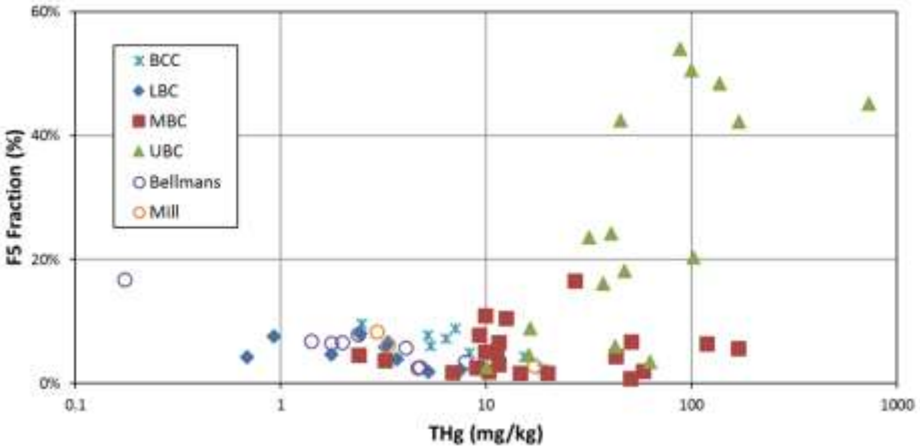
IHg = Inorganic Hg(II)
MeHg = Methylmercury

Modified after Olson et al. 2018 ES&T

Solid Phase Hg Speciation Reflects Hg Availability for Methylation

- BCSA case study
- **Sequential extraction**: Organic bound (F3) and HgS (F5) fractions important in all samples
  - F5 increases in importance with increasing THg concentration
- **Hg XANES**: spectra confirm presence of metacinnabar (β-HgS) and Hg-thiol complexes
- **S XANES**: confirms presence of organic sulfur groups and pyritic-S

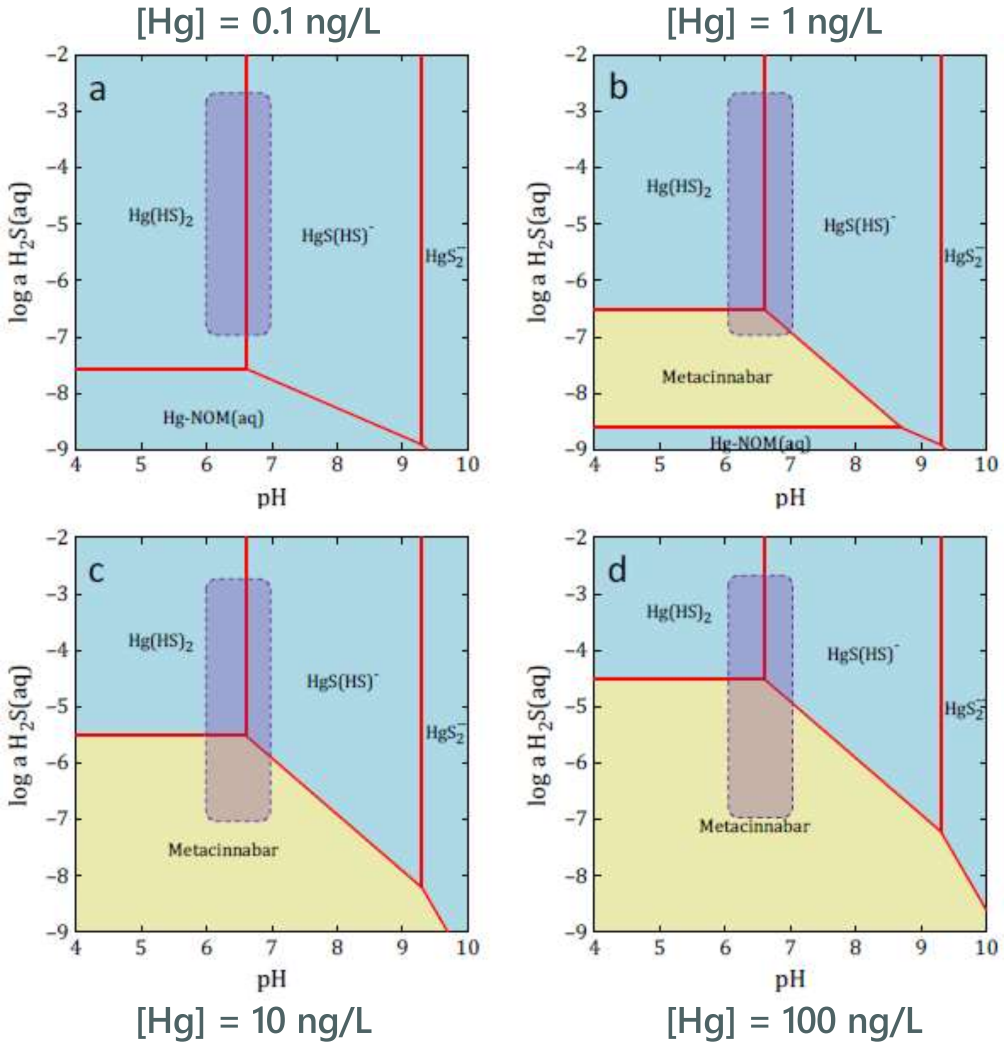




ANCHOR QEA

Thermodynamic Stability of Metacinnabar (HgS) in Sulfidic Sediments

- Metacinnabar stability field expands with increasing Hg concentration
- Solubility increases with increasing pH and ΣH_2S
- Nano-HgS expected to behave similarly although effective solubility may be higher due to surface energy effects
- SOM sorption sites and HgS are main Hg pools in sediment



In all diagrams, [Cl-] = 0.3 M, [NOM] = 20 mg/L

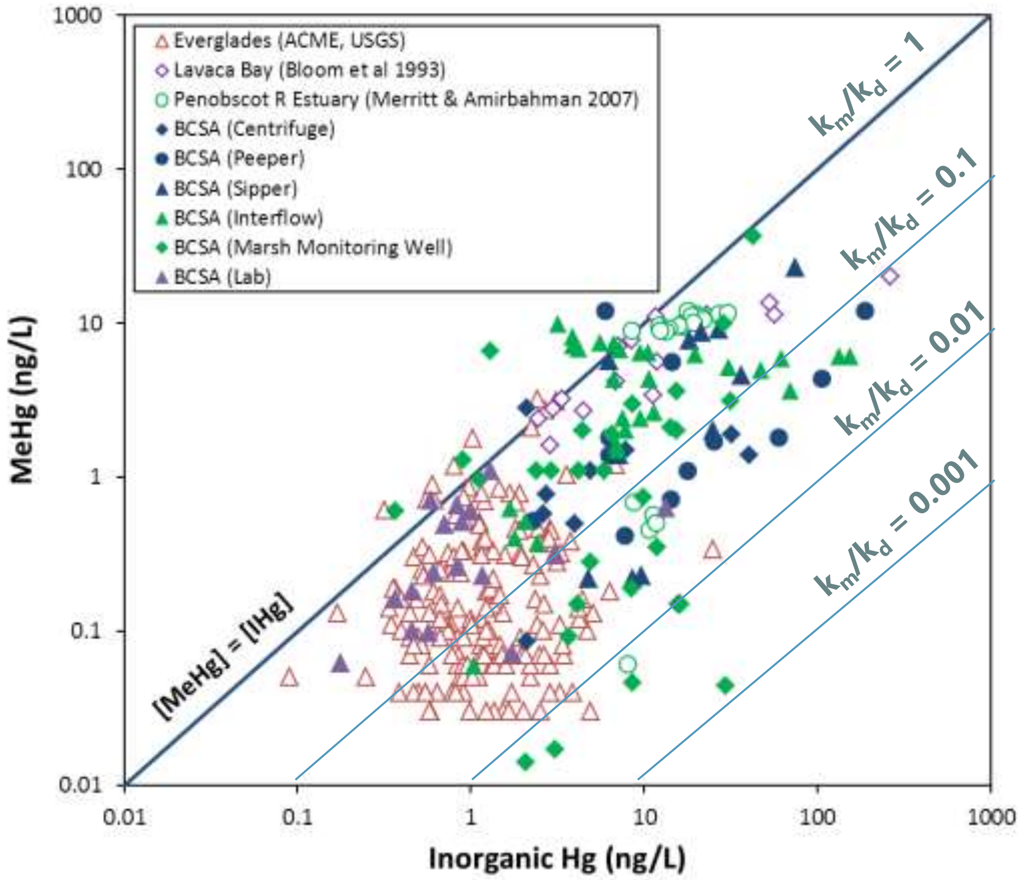
MeHg-IHg Relationship in Porewater Reflects Microbial Activity

- Simple bioreactor analogy:

$$R_m = \frac{d[MeHg]}{dt} = k_m[IHg] - k_d[MeHg]$$

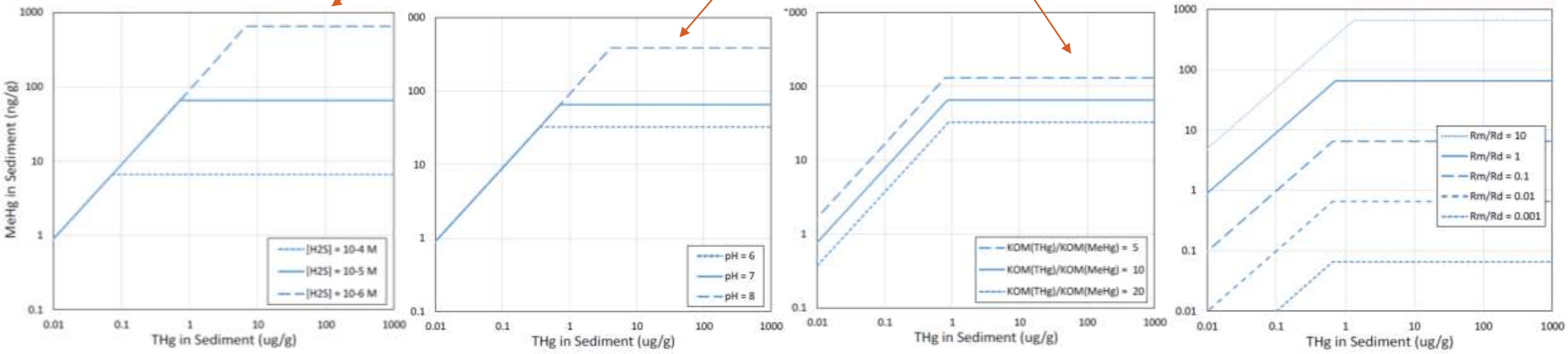
$$R_d = \frac{d[IHg]}{dt} = -k_m[IHg] + k_d[MeHg]$$

- At steady state (R_m=R_d), [MeHg]/[IHg] = k_m/k_d
- k_m/k_d is a methylation intensity index, related to activity of methylating microorganisms relative to demethylation processes
- [MeHg]/[IHg] ≅ 1 defines upper limit to "supported" [MeHg] (closed system)



Geochemical Reaction Path Model

Upper Limit to MeHg due to HgS Solubility

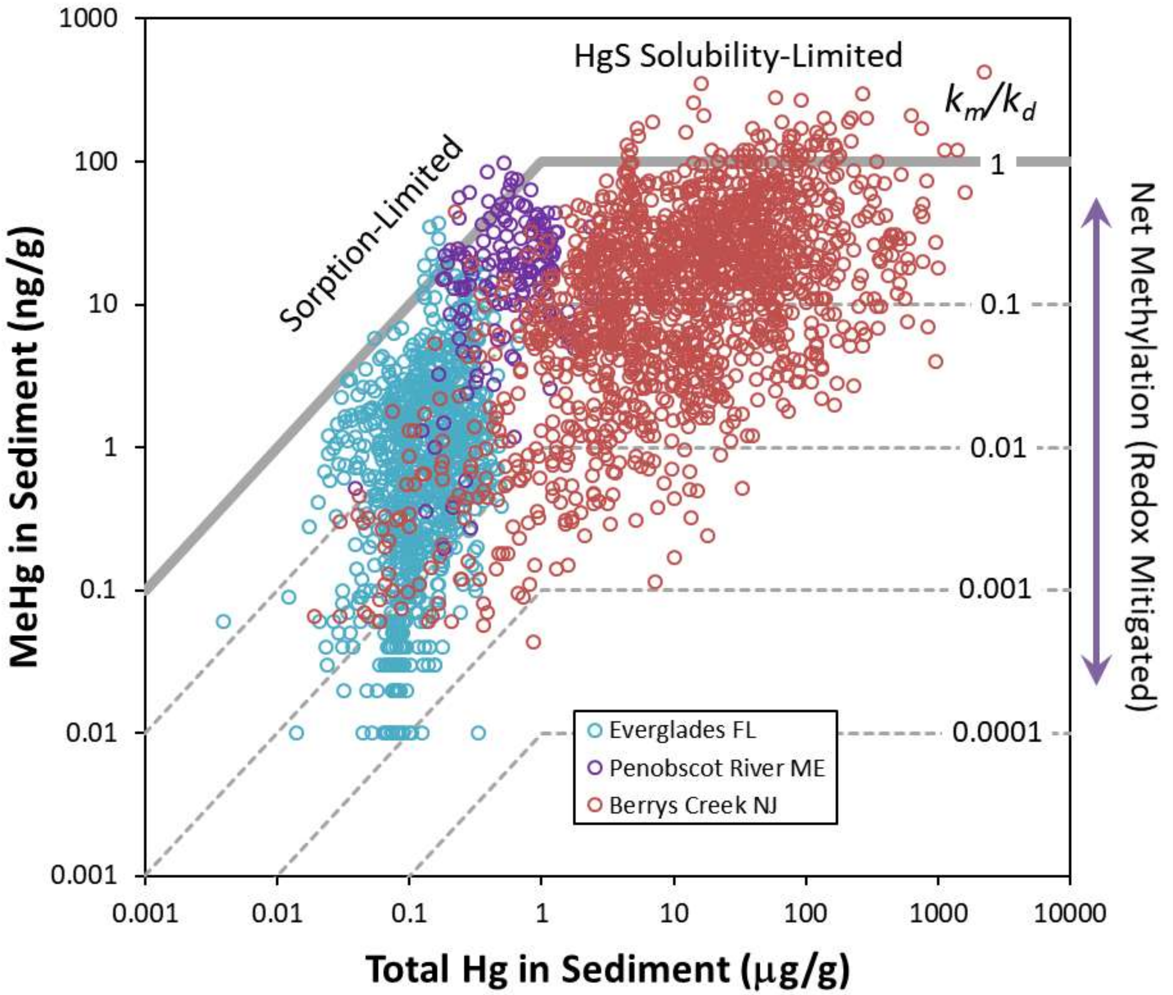


Variable: $[H_2S]$ | pH | $K_{SOM(IHg)}/K_{SOM(MeHg)}$ | k_m/k_d

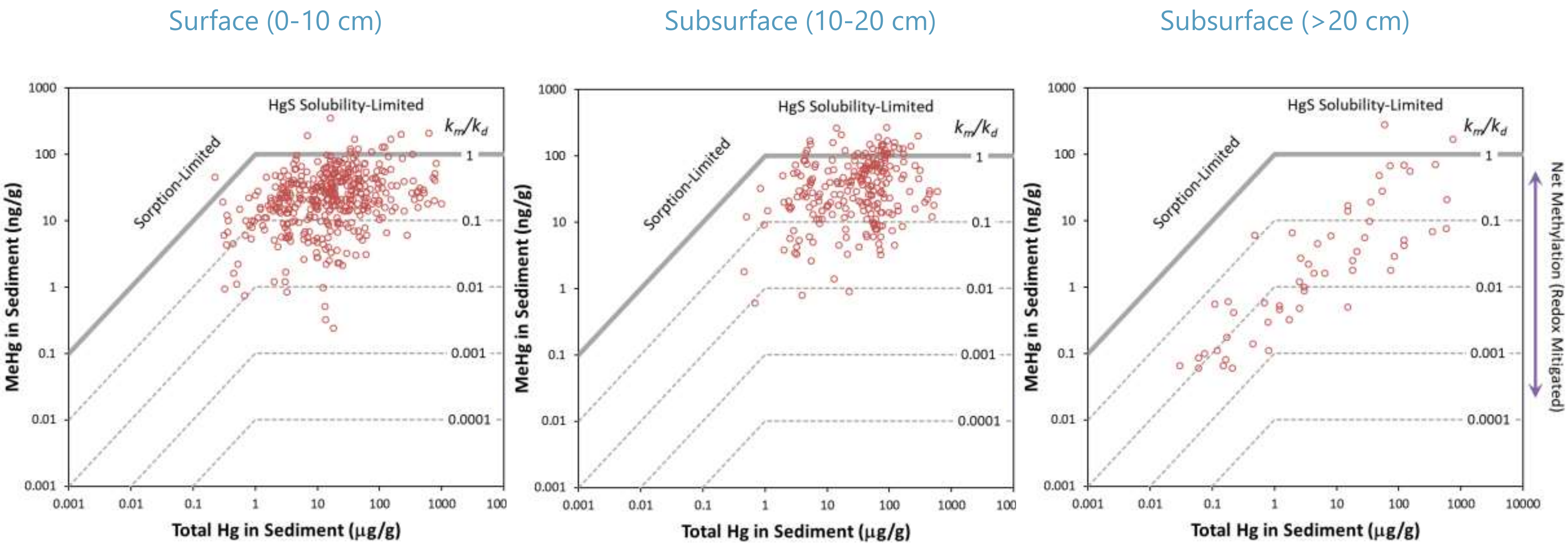
Unless varied, $[H_2S]=10^{-5}$M, pH=7, $K_{OM(IHg)}/K_{OM(MeHg)}=10$, $k_m/k_d=1$

Upper Bound Limits to MeHg in Aquatic Sediments

- Model framework tested against large marsh sediment datasets (BCSA, Penobscot River, Everglades)
- k_m/k_d=1 defines upper limit to MeHg as function of THg across systems
- MeHg ranges from 1 to 3 orders of magnitude below upper bound at different locations within each system
- Mapping k_m/k_d could be used to identify methylation hotspots and moments

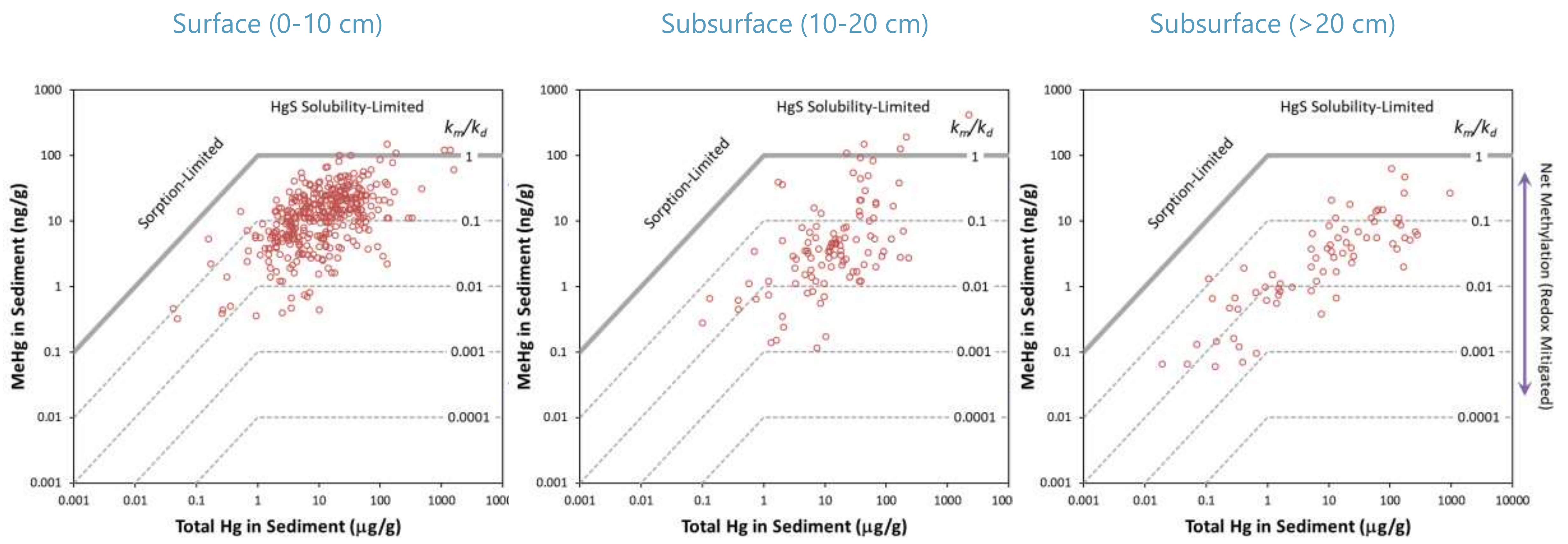


Effect of Sample Depth (Burial) on k_m/k_d in BCSA Marshes



BCSA Remedial Investigation Report (2017)

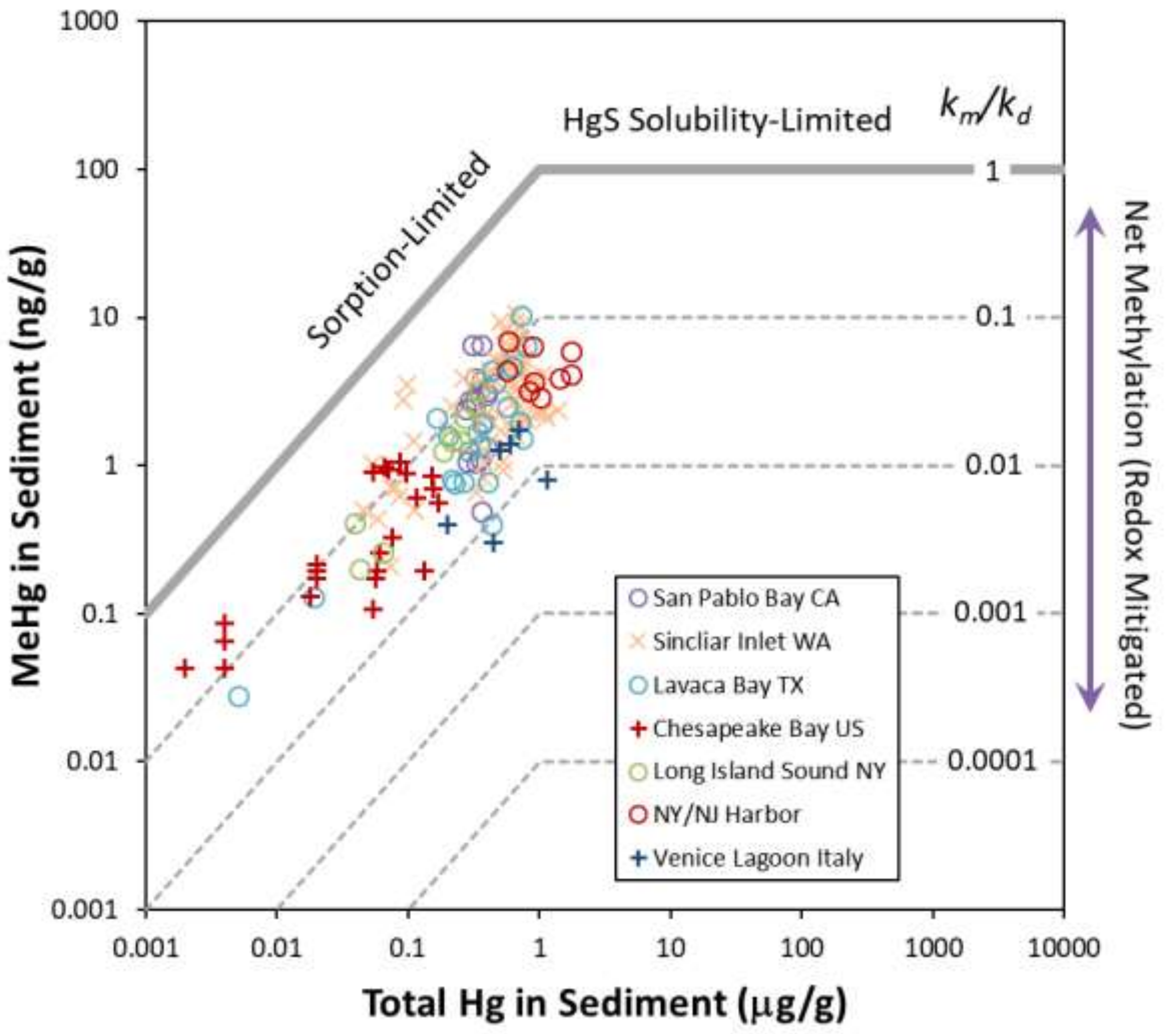
Effect of Sample Depth (Burial) on k_m/k_d in BCSA Waterways



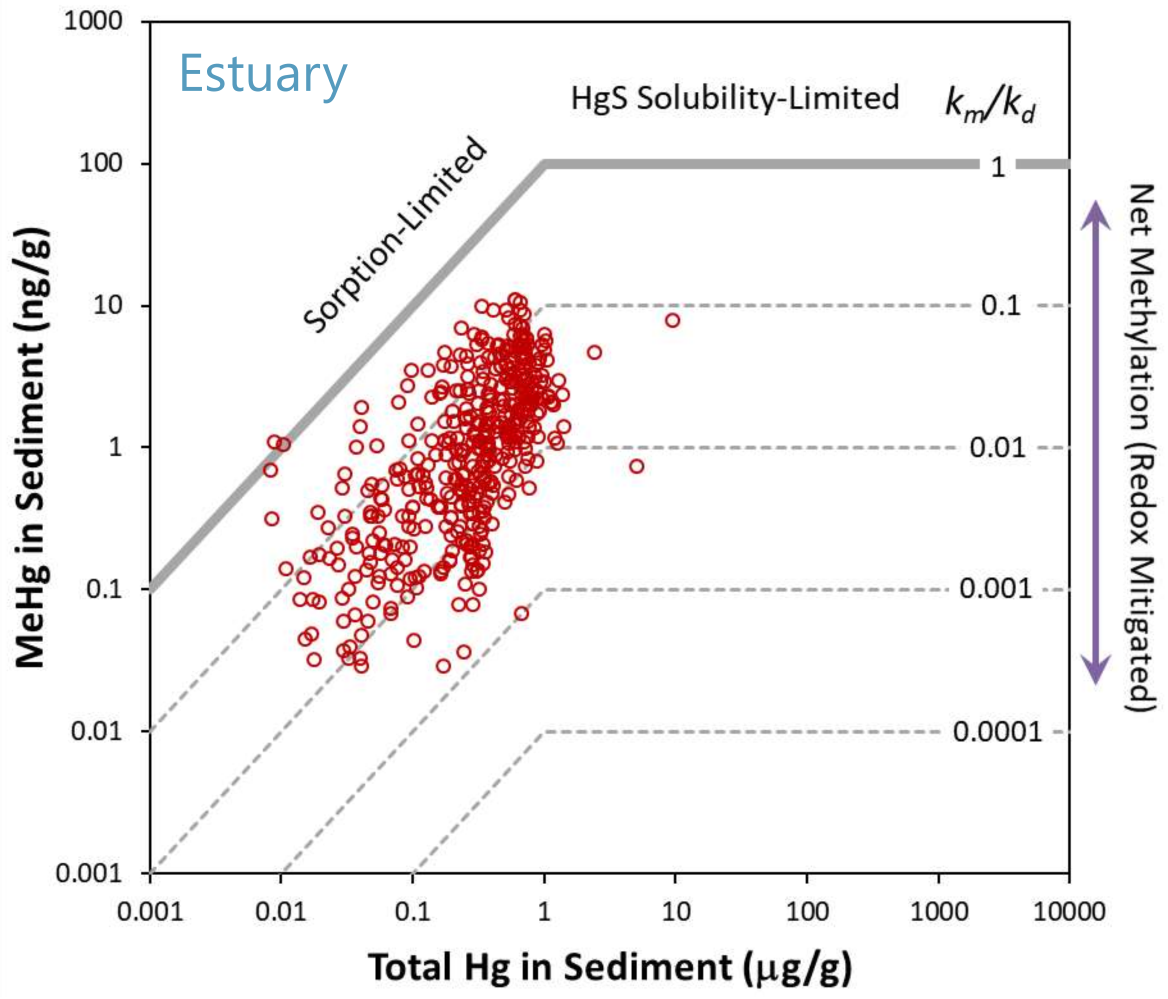
BCSA Remedial Investigation Report (2017)

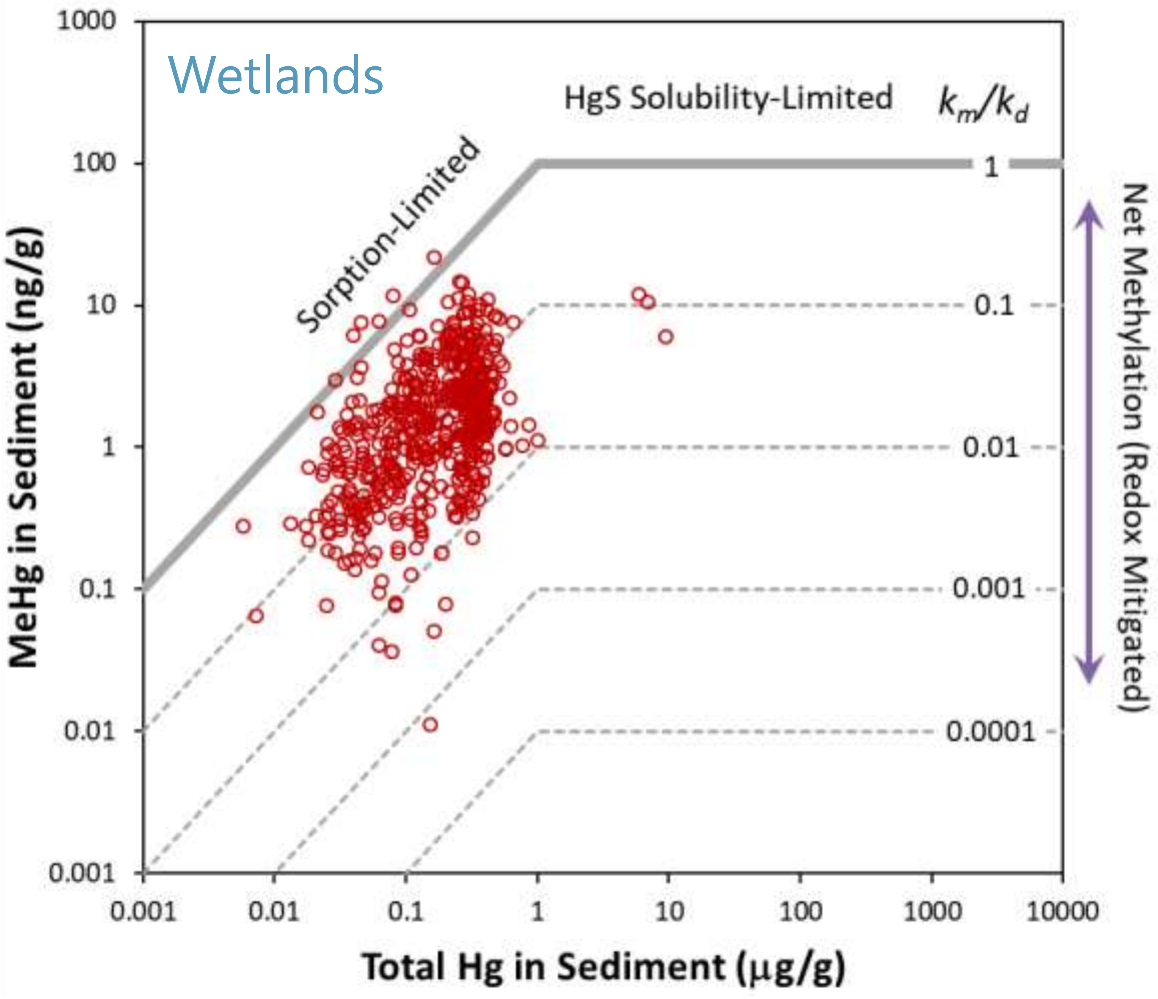
Open Water/Marine Sediment Environments

- US east coast, west coast, Gulf coast and Venice Lagoon
- Hg partitioning dominantly via sorption processes
- Net methylation appears to be relatively uniform across systems and less than upper bound (k_m/k_d ~ 0.1-0.01)



Western North America (USGS Data)





Fleck et al. 2016 STOTEN 568:727-738

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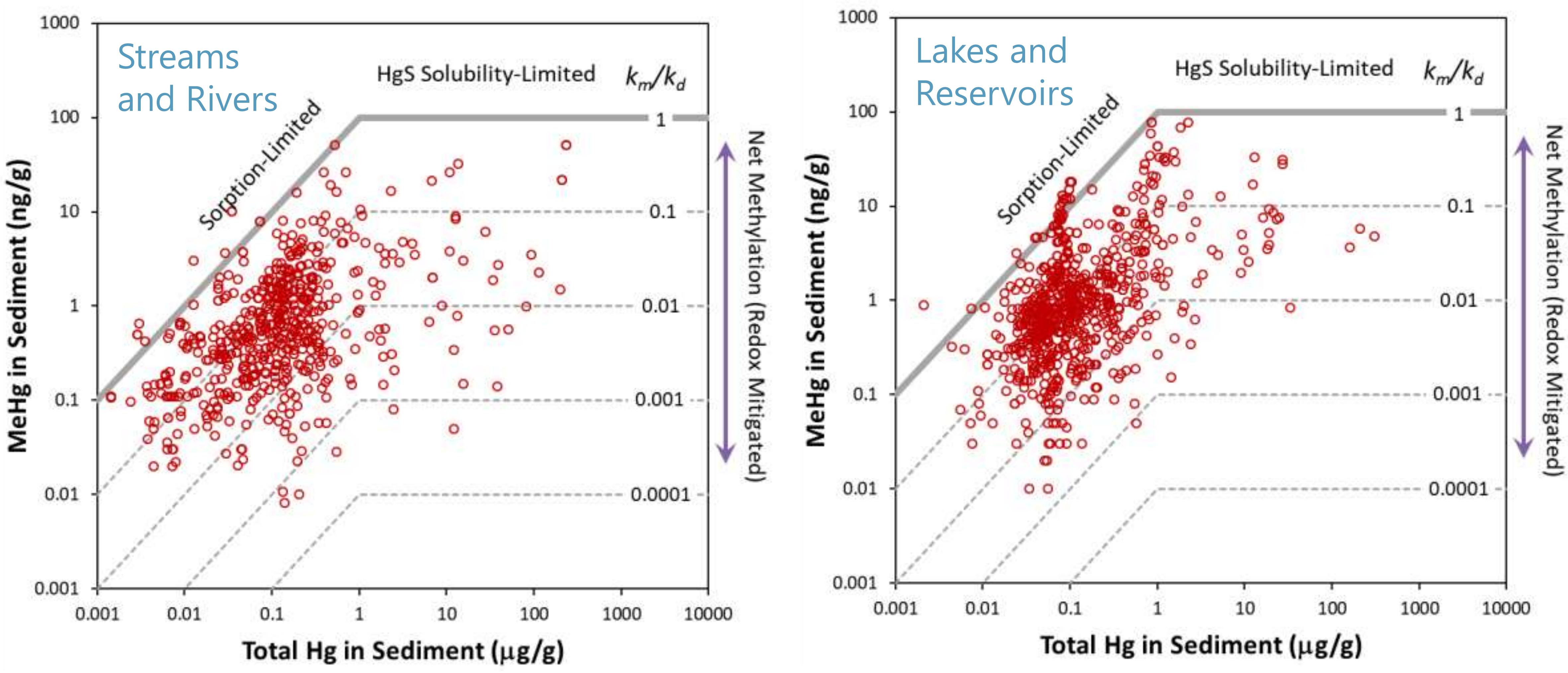

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Summary

- Simplified thermodynamic biogeochemical model provides a systematic framework for assessing Hg methylation status of aquatic sediments based on THg and MeHg measurements
- Sediment-porewater partitioning controlled by two mechanisms: sorption to SOM and precipitation of HgS (metacinnabar, nano-HgS)
- Semi-empirical approach to methylation-demethylation processes in terms of ratio of rate constants (k_m/k_d)
- Model defines thermodynamic limit for sediment MeHg concentrations, verified by comparison to data from multiple field sites
- Potential applications to contaminated sediment management for mapping areas where net Hg methylation is high as targets for remediation
- Ongoing work (Helmrich) to incorporate mechanistic model of (de)methylation linked to speciation, biogeochemical redox processes and microbial activity