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Recent Enhancements of Passive Sampling as a Decision-Making Tool for Sediment Sites

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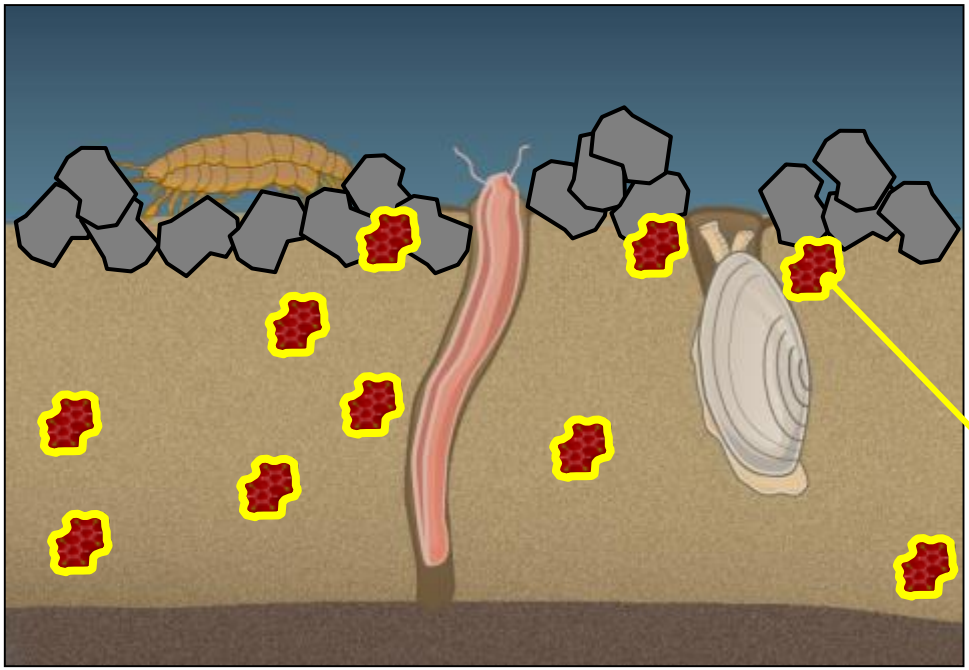

Sediment amendment added to surface of sediment

Organic/inorganic chemical

Introduction
Evaluating Sediment Amendments

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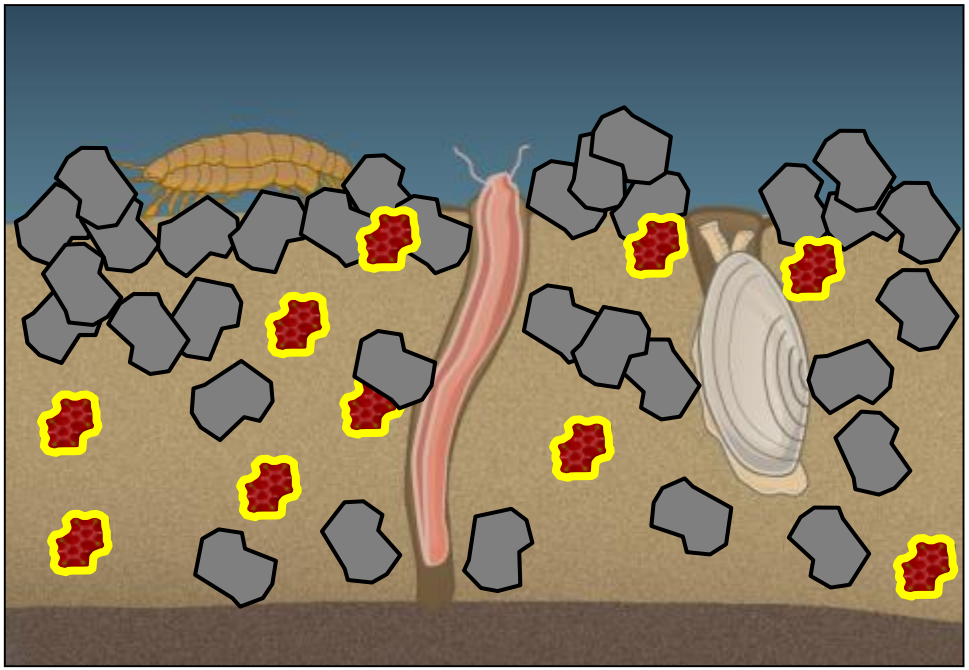
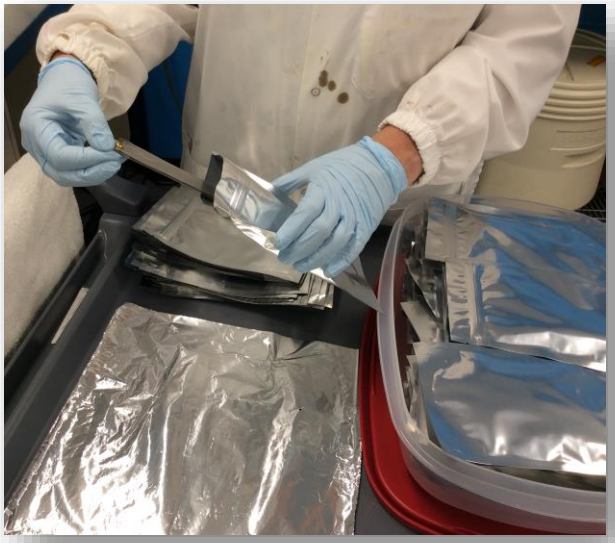


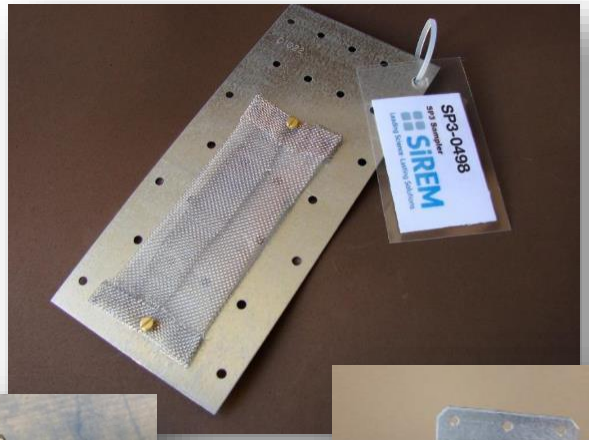
- Amendment mixes in and sorbs or dilutes freely-dissolved concentration (C_{free}) of chemicals, reducing availability
- Passive samplers the most convenient tools for measuring C_{free}

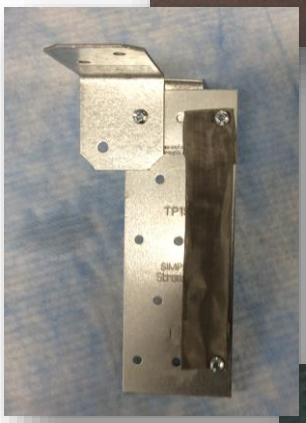
Outline

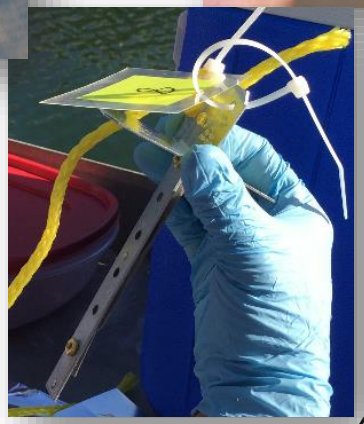
- Case studies for evaluating/comparing the performance of sediment amendments
- New passive sampling technology (internal research)

Introduction
SiREM Passive Sampling Services









- Off-the-shelf passive samplers ready for deployment:
  - Platform preparation for solid phase microextraction (SPME) and polyethylene (PE) samplers
  - Impregnating with performance reference compounds:10 rare PCBs (di- to octa- PCBs)*

* PCB-14, PCB-36, PCB-78, PCB-104, PCB-121, PCB-142, PCB-155, PCB-184, PCB-192, PCB-204

Introduction
SiREM Passive Sampling Services

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- All-inclusive sampling service including:
- Sampler and shipping to site
- Deployment and retrieval (if needed) using a push-pole system
- Processing of data into dissolved-phase
- Analytical report
- Internal R&D program to continually improve performance and lower costs

Push-pole system

Case 1: ***Assessment of Sediment Amendments***
Proposed Approach

- Lower Duwamish Waterway (LDW), Seattle, WA
- USEPA Superfund Site
- Does adding carbon to a sand layer make a difference in reducing PCB availability?
- Sand vs Sand+ Activated Carbon mix
- Passive sampling with SPME fibers:
  - Before and 1-, 2-, and 3-years' after amendment (2016-2020)

Case 1: ***Assessment of Sediment Amendments***
Study Design

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- Approximately 200 SPMEs for each monitoring event
- Deployed/retrieved manually or by the divers in three different locations
- Average deployment time: 42 days

Case 1: ***Assessment of Sediment Amendments***
Results

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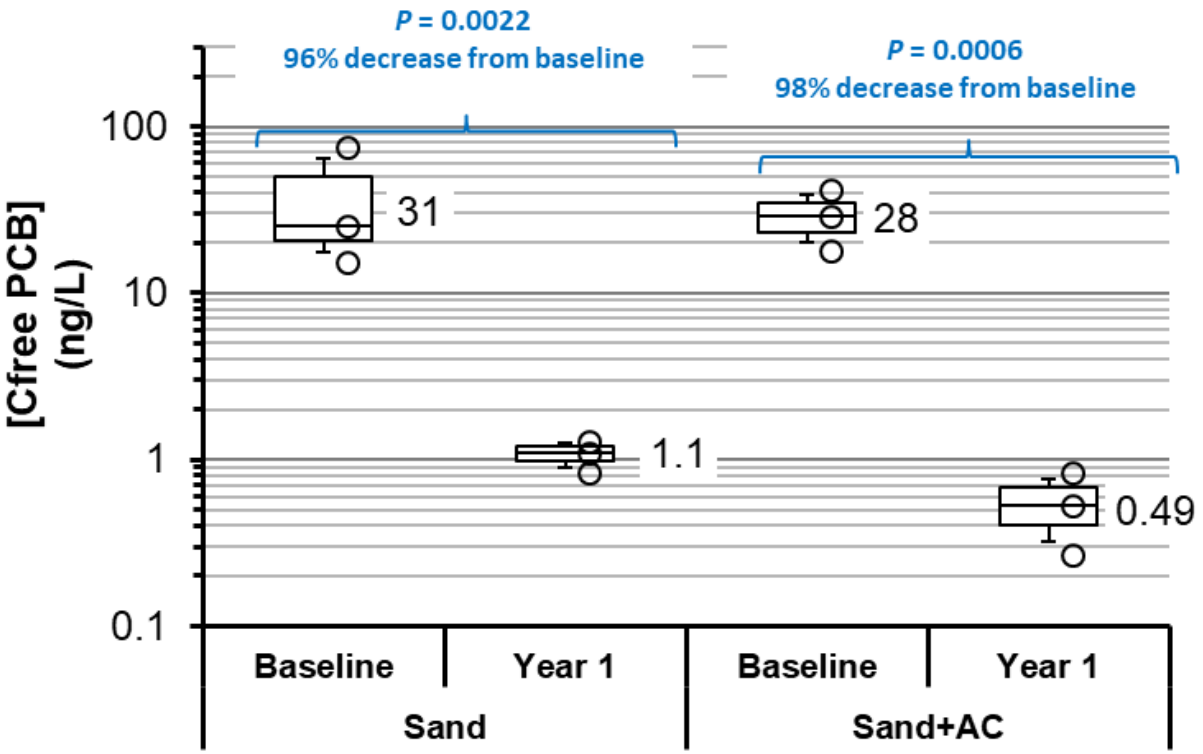

AC = Activated Carbon

Key
Circles – Raw data
Boxes – 25th to 75th percentiles
Whiskers – 10th and 90th percentiles
Values – Geometric means

- Both treatments reduced C_{free} of the total PCBs by 72%-98% after 1 year
- Lower C_{free} in the Sand+AC (compared to Sand) treatment plots in one location
- No statistical differences in C_{free} values between Sand+AC and Sand in two locations

Case 2: ***Assessment of Sediment Amendments***
Proposed Approach

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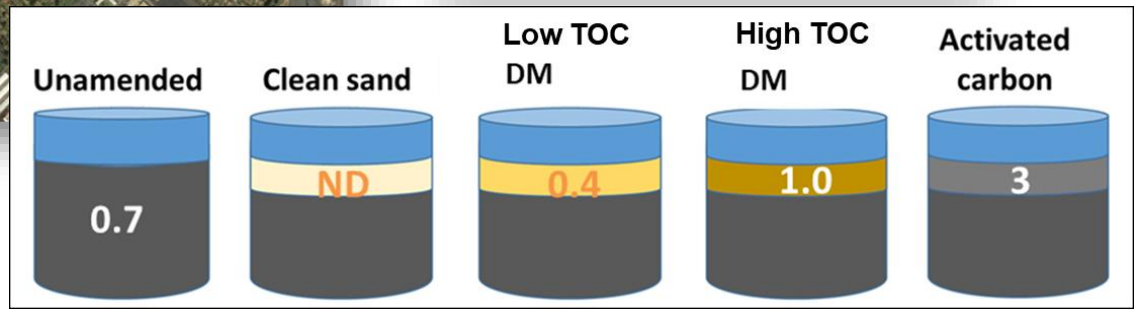
- Pearl Harbor Naval Shipyard, Hawaii (Navy site)
- Evaluate the potential for reuse of dredged material (DM)
- Clean dredge material as efficient as sand or activated carbon?
  - *In situ* evaluation with RARA*
  - Side project: *Ex situ* rapid assessment of the long-term success of remedy

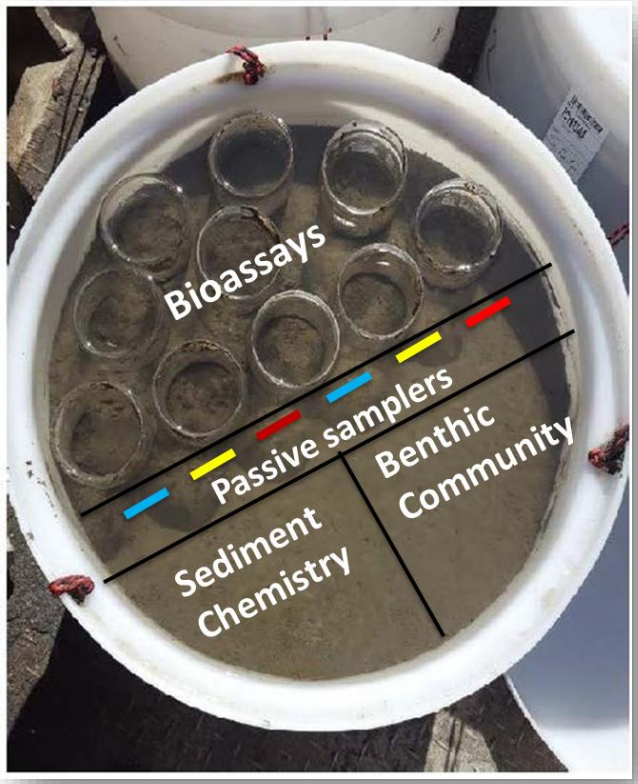
RARA



* Remedy & Recontamination Assessment array (Chadwick et al. 2017)

Study Design

RARA cell



RARA deployment: 2 & 10 months

Deployed arrays: ~40 feet deep

Rapid assessment of the long-term success of remedy

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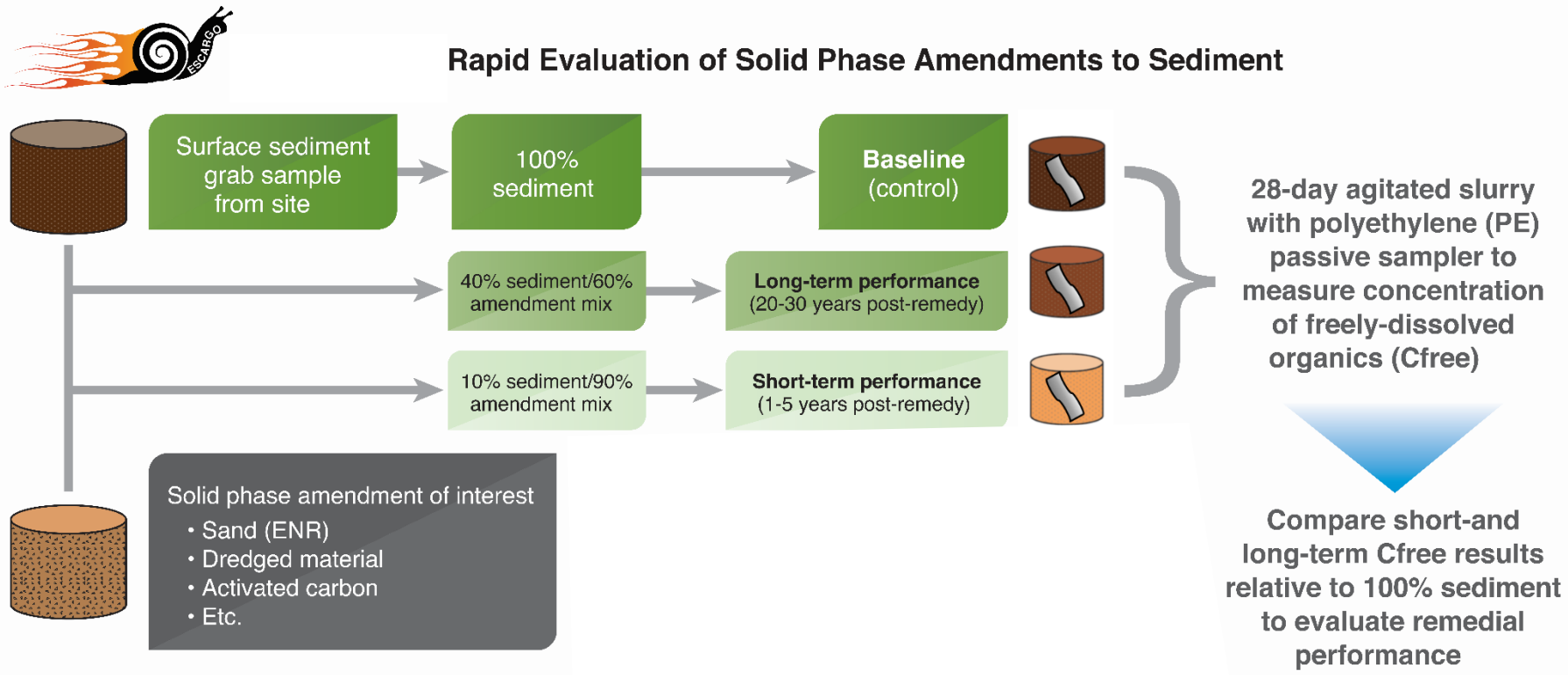

*Case 2:**Side Project***
Rapid assessment of the long-term success of remedy

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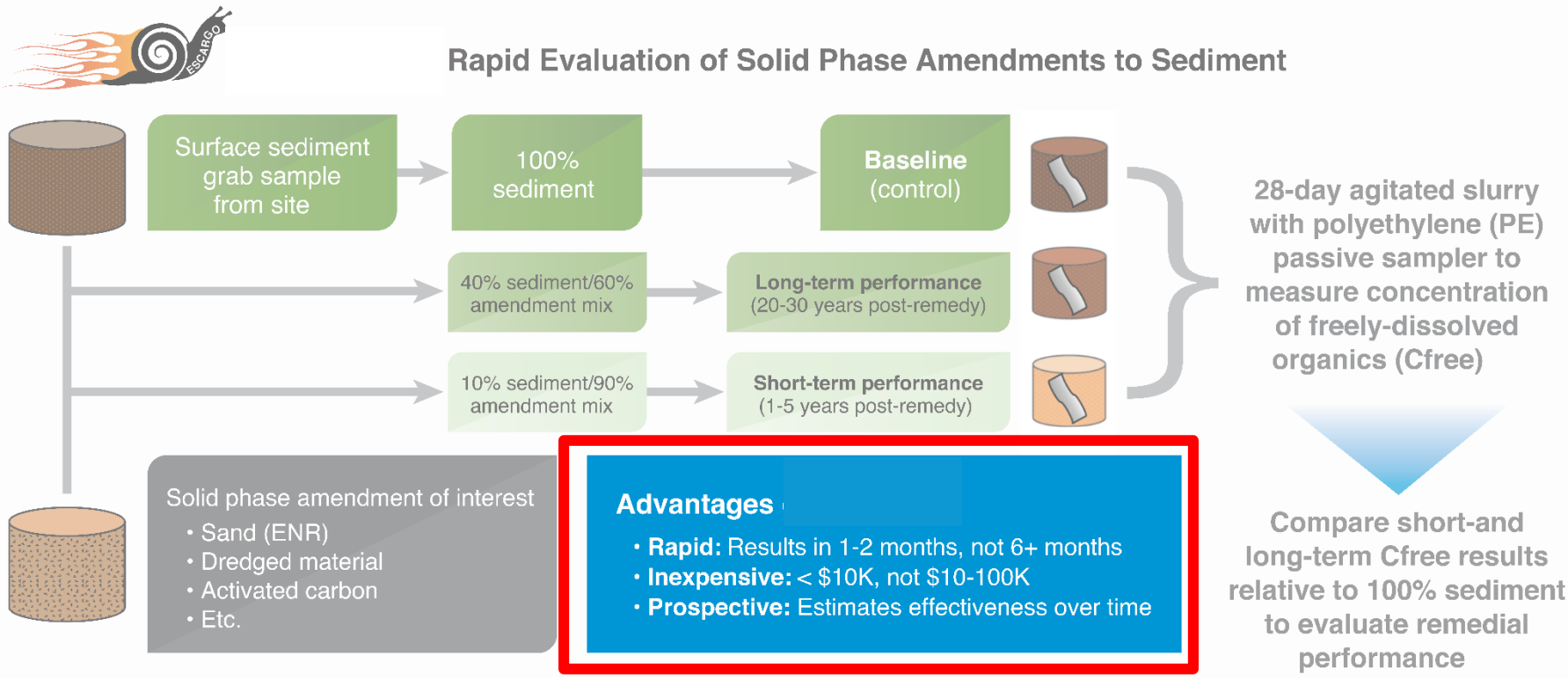
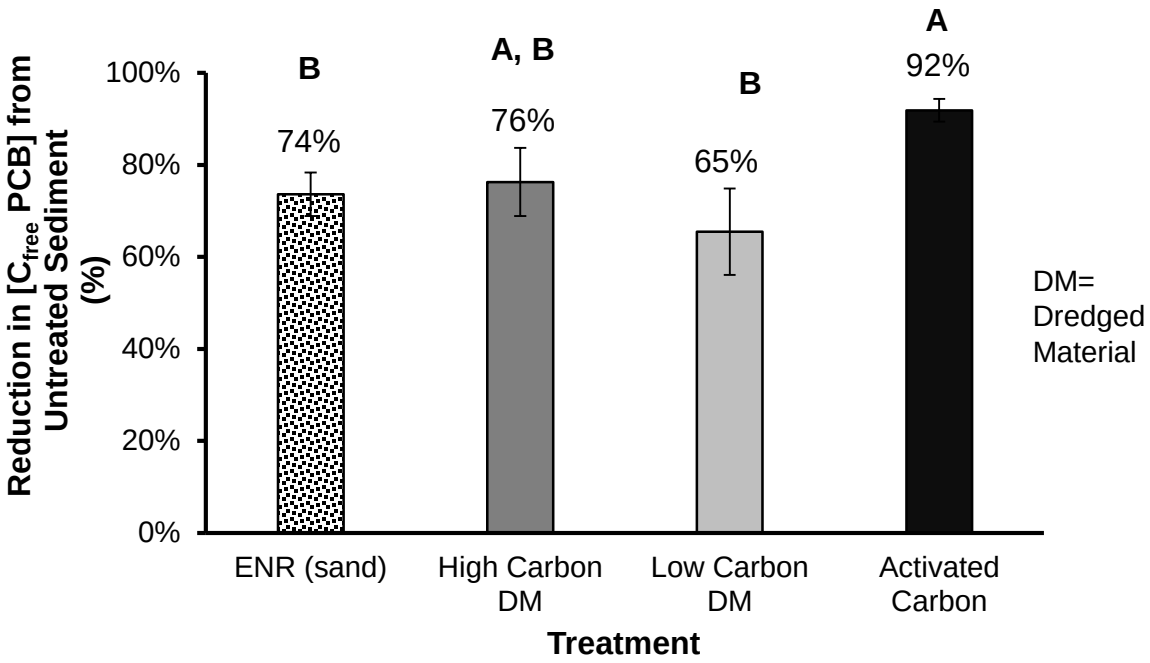
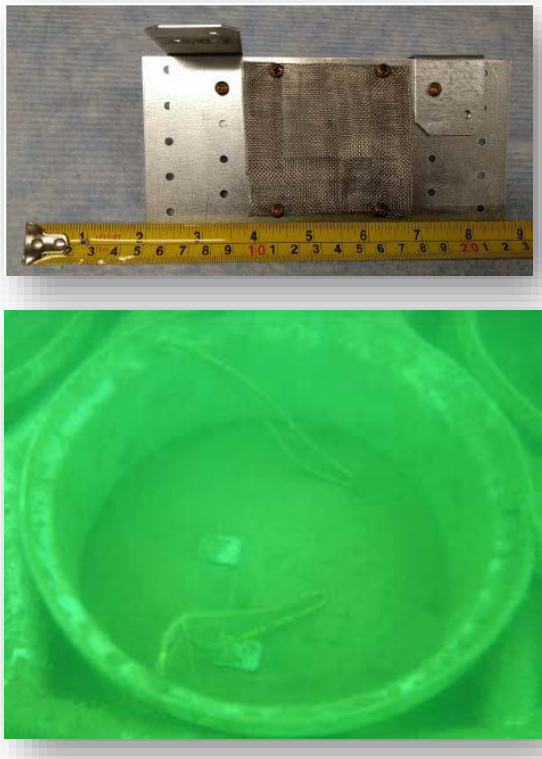


Case 2: ***Assessment of Sediment Amendments***
Results

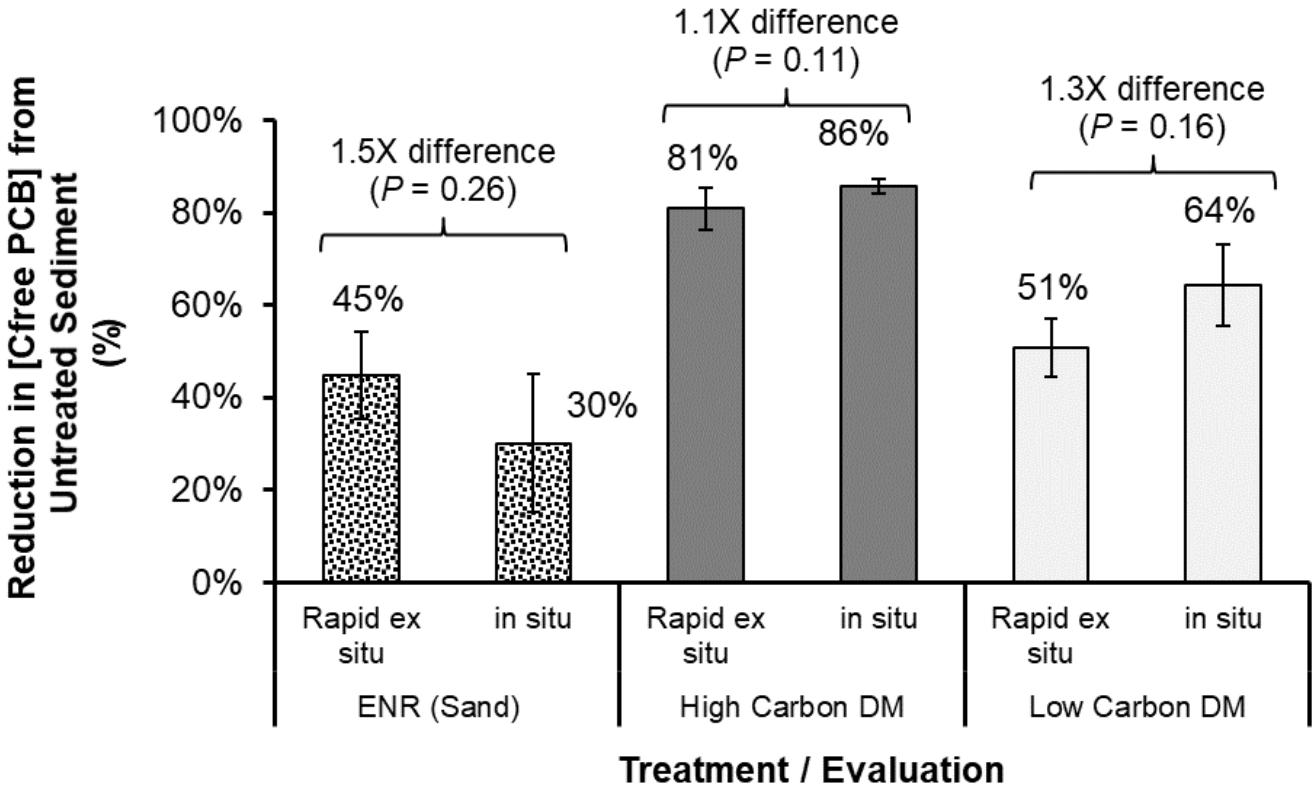


SP3 sampler



- Activated carbon performance is as expected (i.e., a 80-90% reduction in availability) after 10 months
- High TOC is as efficient as activated carbon in reducing PCB availability, and both are better than Low TOC and clean sand

Case 2: ***Assessment of Sediment Amendments***
Results



DM= Dredged Material

- Agreement between field and rapid ex situ study when results expressed as % reduction in availability
- Both approaches identify HC dredged material as best remedy (no surprise due to highest TOC)

Case 3: ***In Situ Monitoring of AC Performance***
Proposed Approach

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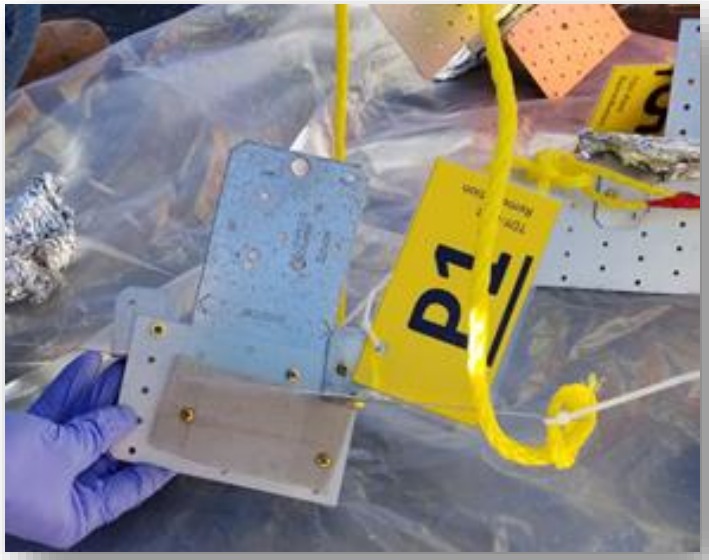
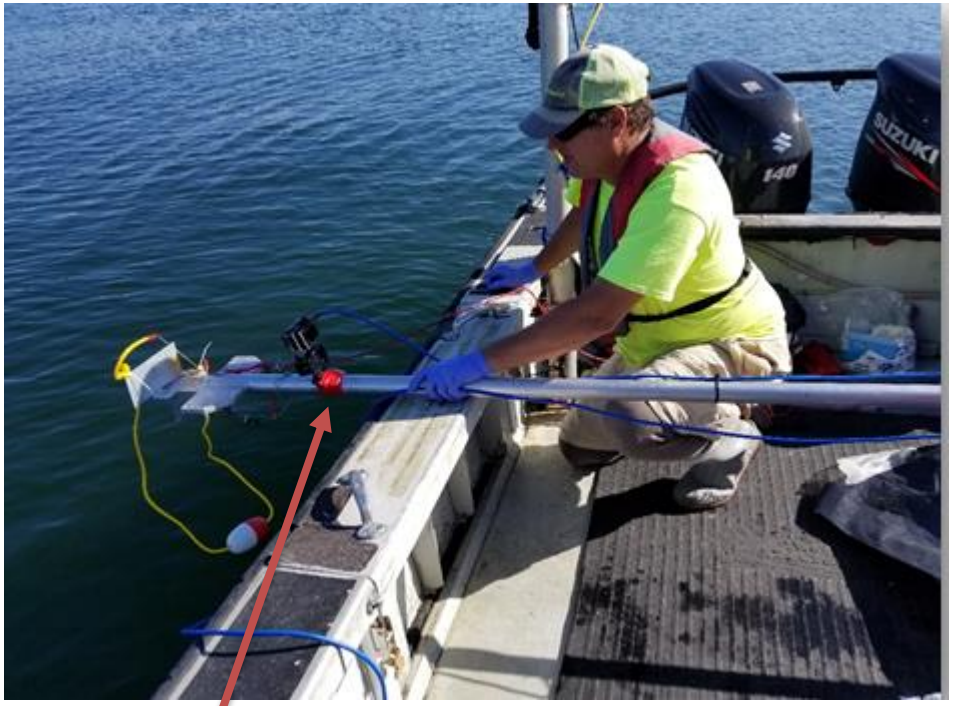
- PCB contaminated site in South of San Diego, CA
- Pilot study to evaluate the effectiveness of a sand cap amended with AC after 1 year
  - C_{free} PCBs measured with polyethylene passive samplers
  - C_{free} values compared before and one year after treatment



PE samplers were deployed with a push-pole system and retrieved by divers after 44 days



Push-pole system

Case 3: ***In Situ Monitoring of AC Performance***
Results

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- Average C_{free} pre treatment: 2,200 pg/L
- Average C_{free} one year after treatment: 142 pg/L
- Percent Reduction of C_{free}: 93.5%
- PCB C_{free} reduced by a factor of 10 to 23
- Benthic diversity score unchanged 1 year

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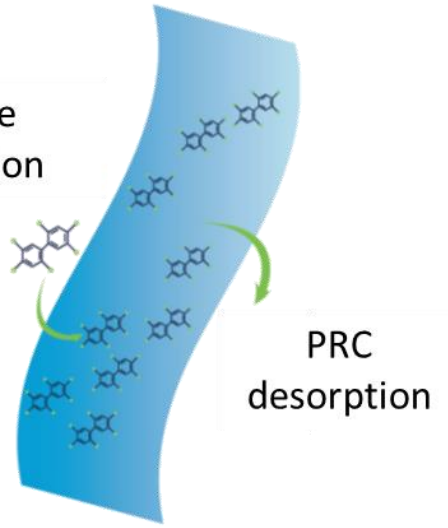
$$C_{free} = \frac{C_{sampler}}{\left(1 - e^{-k_e t}\right) \times K_{sampler}}$$

$$k_e = \ln\left(\frac{C_{PRCi}}{C_{PRCf}}\right) \times \frac{1}{t}$$

$$COC_D = \frac{COC_{PS}}{K_{PS-D}} * 1000$$



- Equilibrium is slow for strongly hydrophobic compounds
  - Performance Reference Compounds (PRCs) are used to predict equilibrium
  - Desorption kinetics of PRCs are used to correct for non-equilibrium

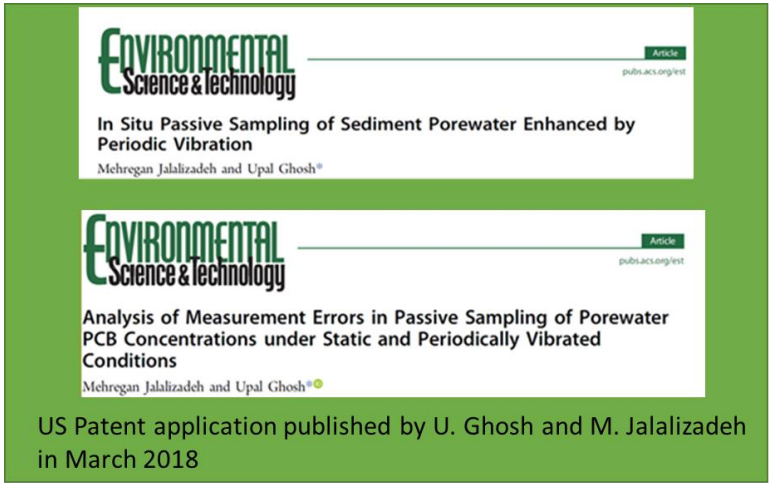
Proposed Approach

In situ measurements of C_{free} of high K_{ow} compounds are challenged by extremely slow mass transfer rates

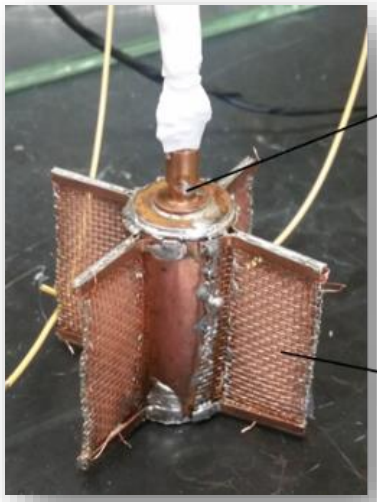
Proposed Approach:

Periodic vibration of passive samplers during deployment

Shaking the thermometer
Faster reading!



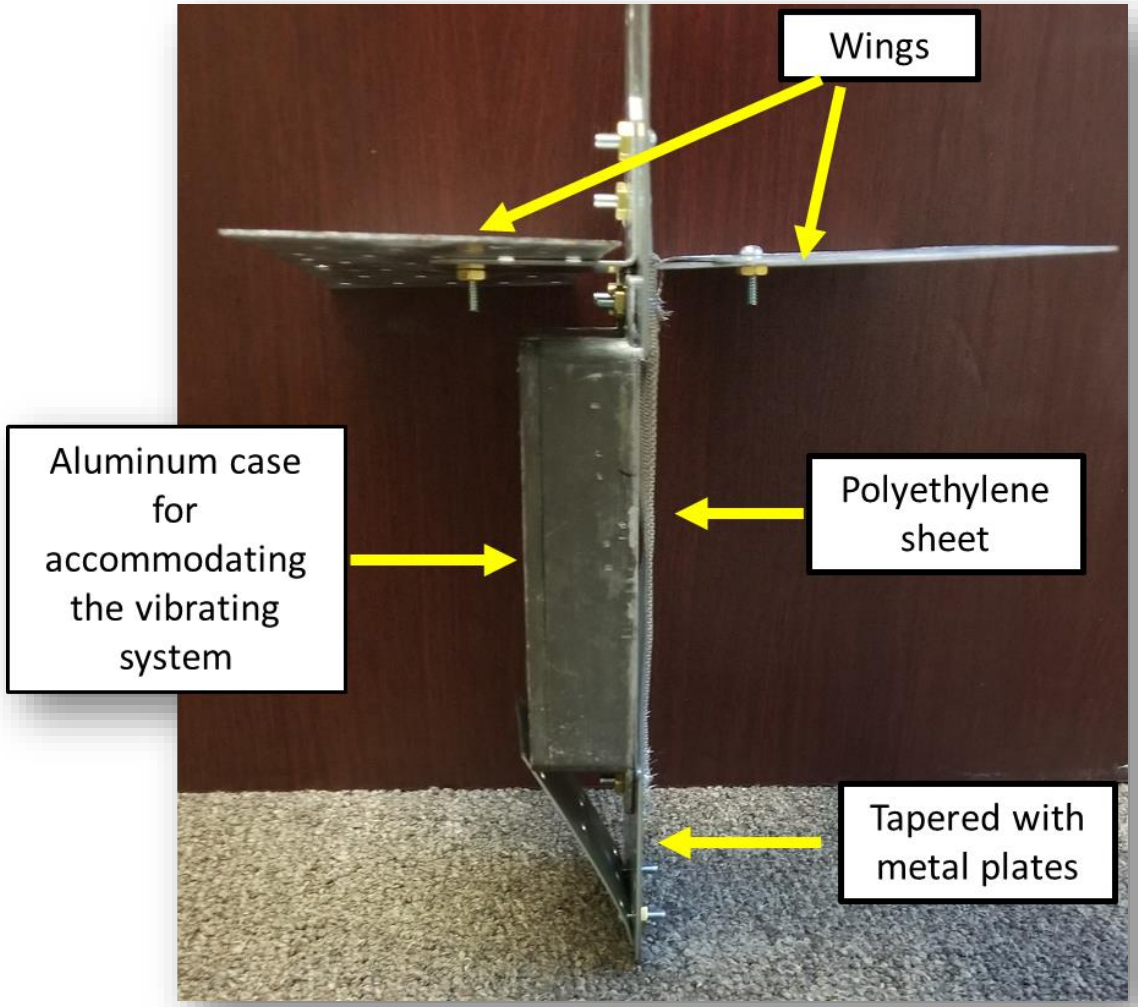
US Patent application published by U. Ghosh and M. Jalalizadeh in March 2018



25mm vibration motor from Precision Microdrive

20 mg polyethylene

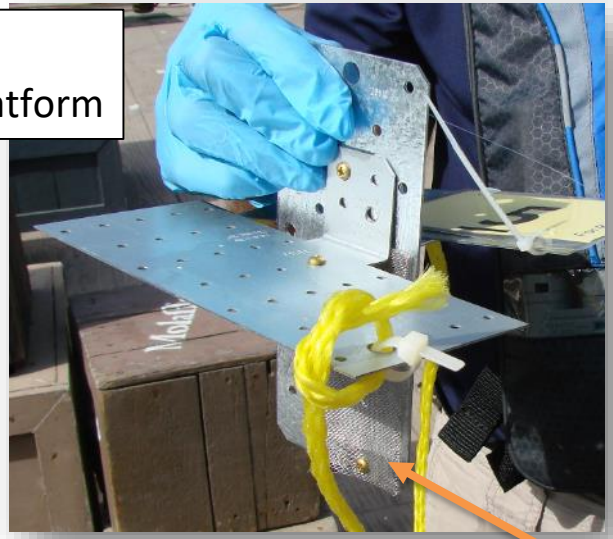
- Gentle vibration for 5 seconds, every 4 hours:
- Mixes up the sediment adjacent to the sampler
- Enhances the mass transfer of the contaminant from sediment into the sampler
- We are not changing the results. Just speed up the sampling



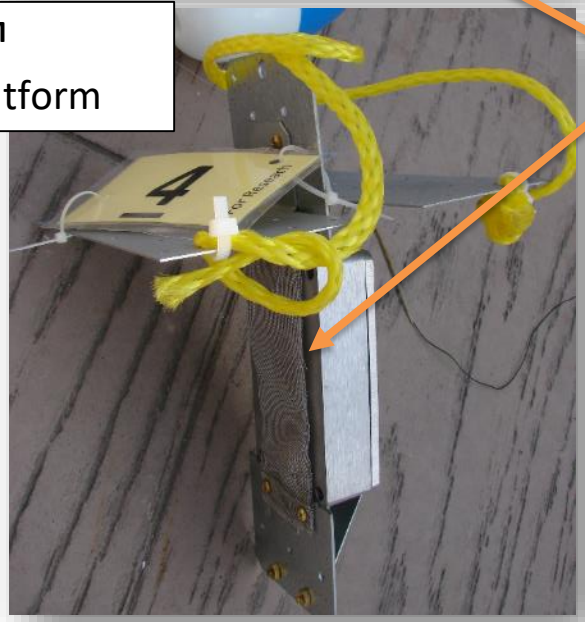
Study Design

- Platforms deployed in a marine sediment (10-15 ft water depth) in a harbor
  - Static platforms
  - Vibrating platforms (5 sec vibration every 4 hours)
- Deployment times: 7 and 14 days
- 10 rare PCB PRCs in each sampler (di- to octa- PCBs)
  - % losses of PRCs (% to equilibrium) from static and vibrating deployment modes compared

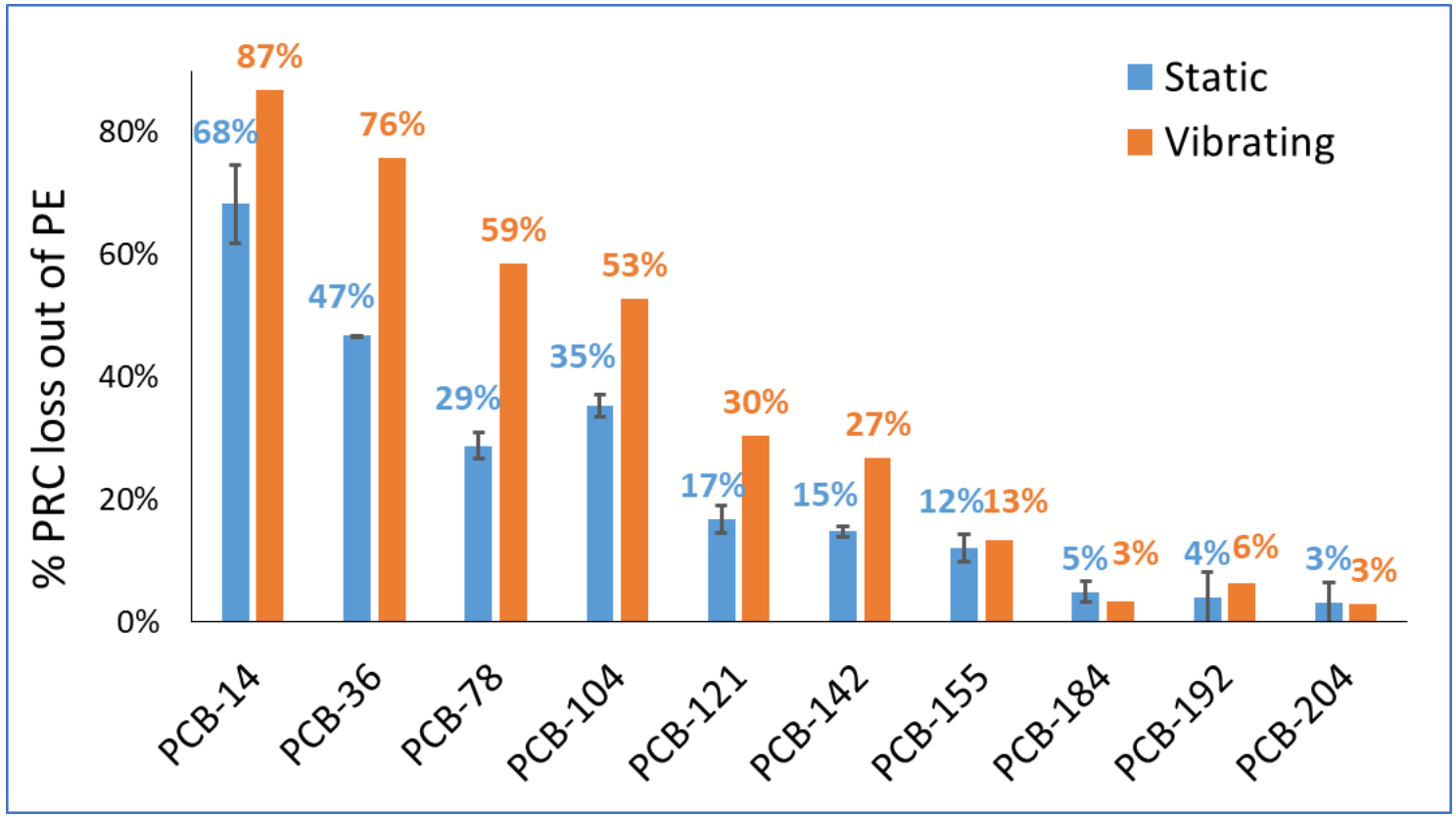
SP3™
Static Platform



VibraSP3™
Vibrating Platform



PE sheet impregnated with PRCs



Only 1 Vibra sampler used in the 7-day evaluation (limited number of prototypes), 3 static samplers

- % losses of most PRCs improved by a maximum factor of 2

Research: ***Actively Shaken In Situ Deployment***
Results (14 d Deployment)

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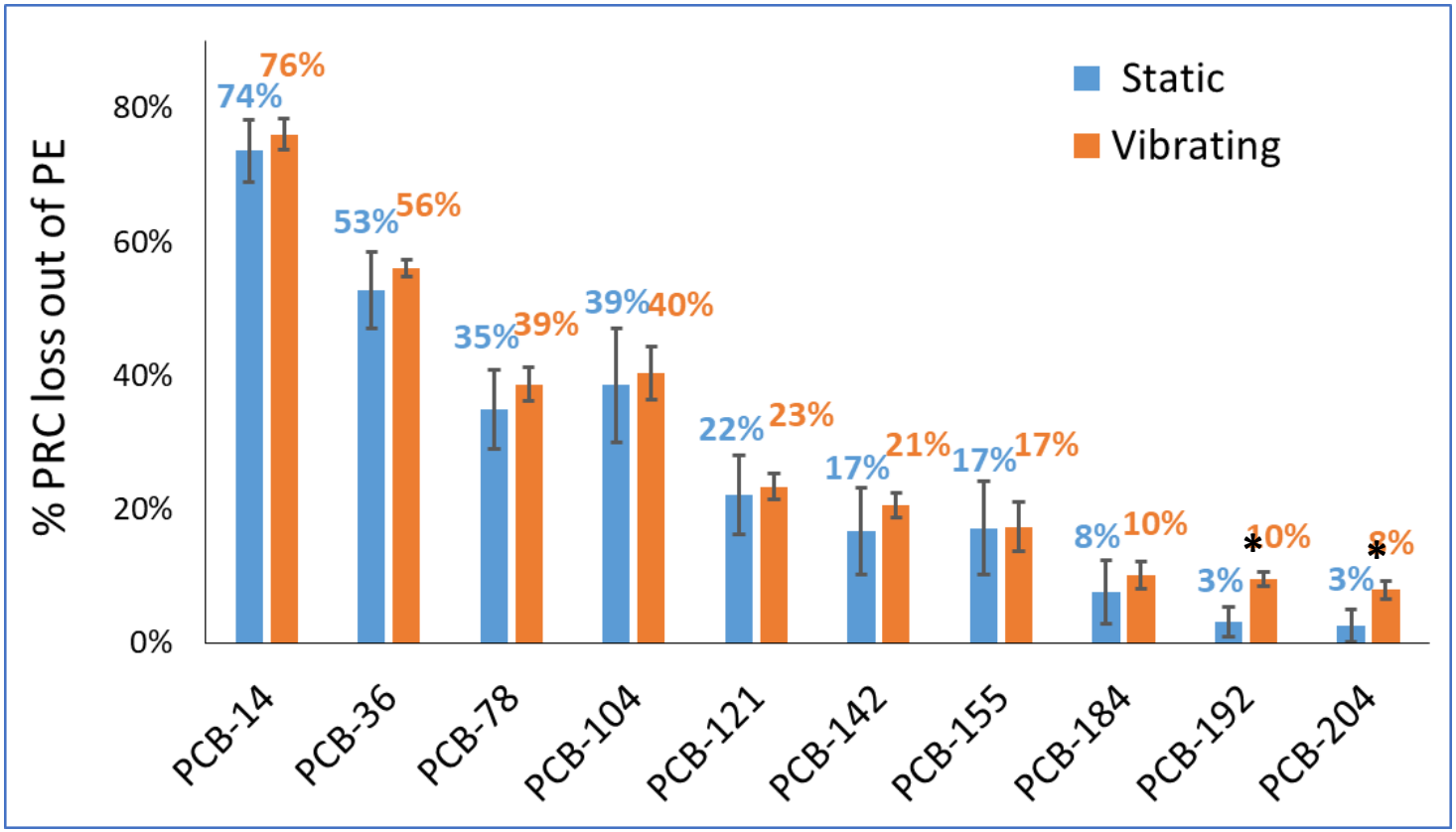

3 Vibra and 3 static samplers used in the 14-day evaluation

- % loss of the lower molecular weight PRCs were not statistically-different
- % loss of PCB-192 and PCB-204 improved by a factor of 3 (*statistically different) and achieved a 10% level of equilibration
- Can turn up the vibrational frequency and power to improve equilibration

Summary

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Past/Ongoing Passive Sampling Projects

- Passive sampling accomplished with lower cost, time, health & safety risk
  - Driverless deployment
  - *Ex situ* rapid assessment of the amendment
    - Great tool for smaller projects, or before conducting large pilot scale/complicated lab evaluations

New Upcoming Technology

- Vibrating platform (saves money & time)
  - Remained waterproof & functional in marine sediment field conditions for 14 d
  - Increased sampling rates for hepta- & octa- PCBs to acceptable levels within 14 d
  - Further increases in sampling rates possible with adjustment to design

Acknowledgement

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  - Jeff Roberts
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  - Professor Upal Ghosh
  - Nathalie Lombard
  - Actively Shaken In-Situ Passive Sampler Platform for Methylmercury and Organics (SERDP Project ER-2540)

Thank You For Listening

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