# *Thank you for signing in early*

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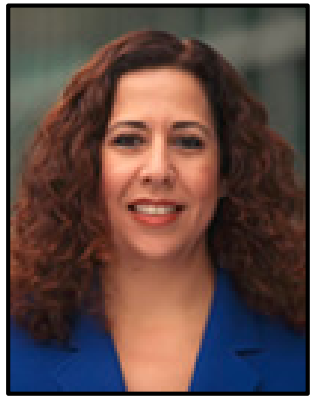
# Managing Contaminated Sediments: Passive Sampling Methods and In-Situ Treatment

April 11, 2019

SERDP DOD • EPA • DOE | ESTCP

# Welcome and Introductions



Rula A. Deeb, Ph.D.
Webinar Coordinator

SERDP DOD • EPA • DOE | ESTCP

# Webinar Agenda

- **Webinar Logistics** (5 minutes)
  **Dr. Rula Deeb**, Geosyntec Consultants
- **Overview of SERDP and ESTCP** (5 minutes)
  **Dr. Andrea Leeson, SERDP and ESTCP**
- **Passive Multi-Sampling Method to Measure Contaminant Bioavailability in Aquatic Sediments** (25 minutes + Q&A)
  **Dr. Rainer Lohmann**, University of Rhode Island
- **Evaluating the Efficacy of Bioaugmentation for In-Situ Treatment of PCB Impacted Sediments** (25 minutes + Q&A)
  **Dr. Kevin Sowers**, University of Maryland Baltimore County
- **Final Q&A session**

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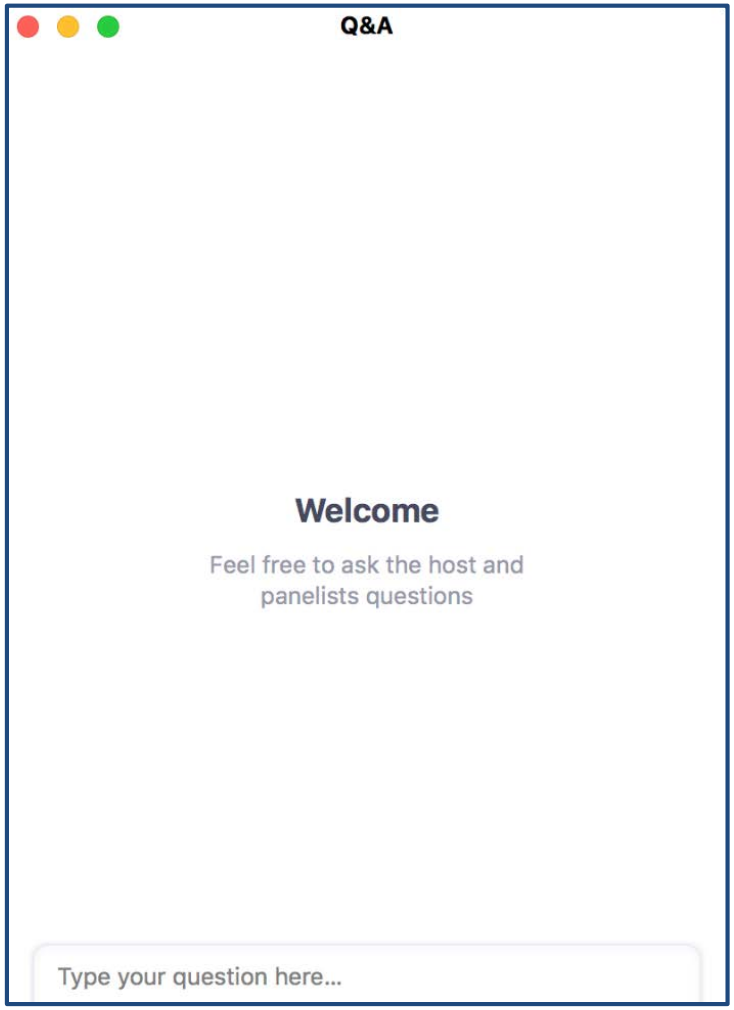


# SERDP and ESTCP Overview

Andrea Leeson, Ph.D.
SERDP and ESTCP

# DoD's Environmental Technology Programs

## Science and Technology

- Statutory program established 1991
- DoD, DOE, EPA partnership
  - Advanced technology development to address near-term needs
  - Fundamental research to impact real world environmental management

## Demonstration and Validation

- Demonstrate innovative cost-effective environmental and energy technologies
  - Transition technology out of the lab
  - Establish cost and performance
  - Partner with end user and regulator
  - Technology transfer
    - Accelerate commercialization or broader adoption
    - Direct technology insertion

# Environmental Drivers

## *Sustaining Ranges, Facilities and Operations*

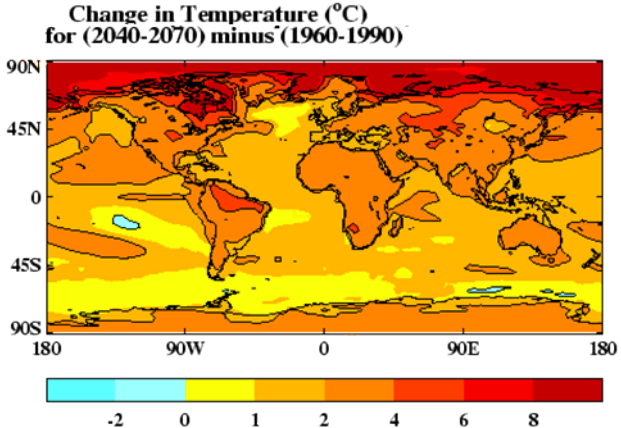
Maritime Sustainability
Threatened and Endangered Species

Toxic Air Emissions and Dust

UXO and Munitions Constituents

Noise

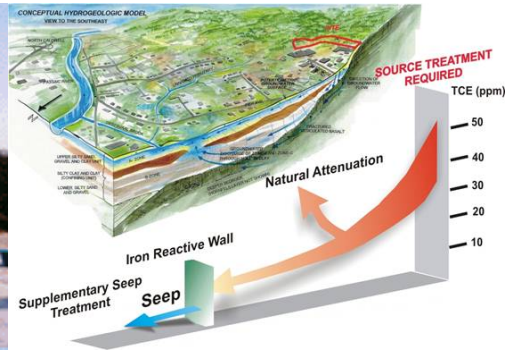
Sustainable FOB



# Environmental Drivers

## *Reducing Current and Future Liability*

### *Contamination from Past Practices*

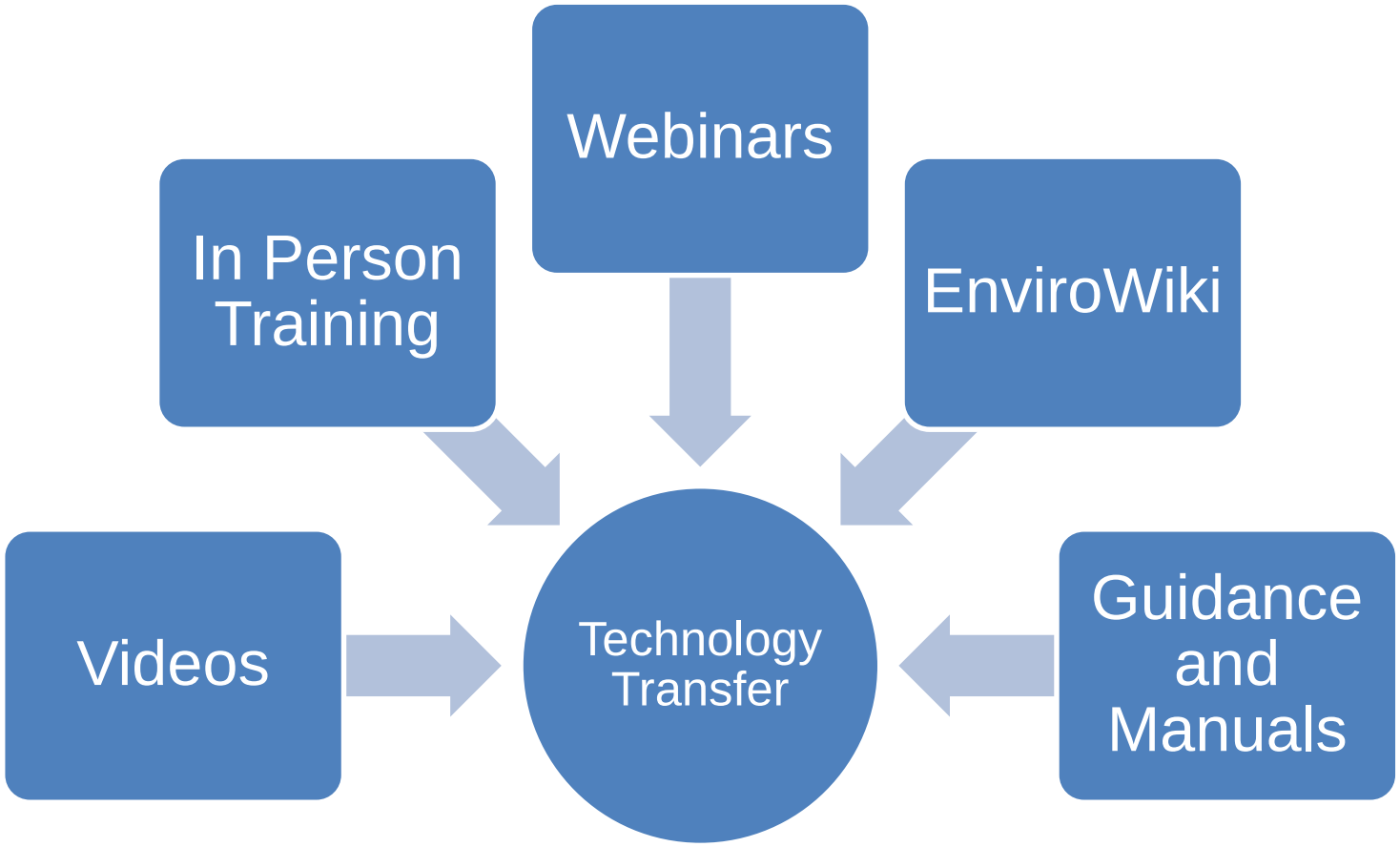



- Groundwater, soils and sediments
- Large UXO liability
- Emerging contaminants

### *Pollution Prevention to Control Life Cycle Costs*

- Elimination of pollutants and hazardous materials in manufacturing, maintenance, and operations
- Achieve compliance through pollution prevention

# www.serdp-estcp.org



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Technology Transfer

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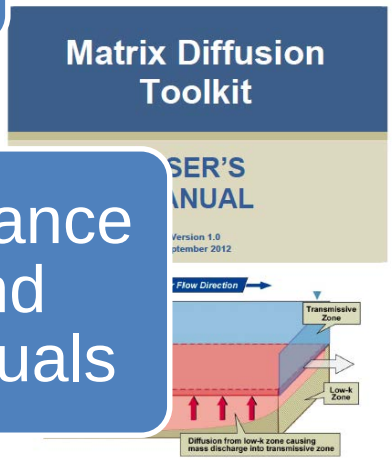

# SERDP and ESTCP Webinar Series

| Date | Topic |
|---|---|
| April 25, 2019 | Accelerated Corrosion and Ageing Studies |
| May 9, 2019 | Roles of Soil Microbial Communities in Ecosystem Restoration |
| May 23, 2019 | Treatment Options for the Emerging Contaminants 1,2,3-Trichloropropane and 1,2-Dibromoethane |
| June 6, 2019 | Developing and Demonstrating Non-Toxic and Sustainable Coating Systems for Military Platforms |
| June 20, 2019 | Developing Adaptation Strategies to Address Climate Change and Uncertainty |

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# Save the Date!

SERDP • ESTCP
SYMPOSIUM

A three-day symposium showcasing the latest technologies that enhance DoD's mission through improved environmental and energy performance

December 3-5, 2019
Washington Marriott Wardman Park

***Registration information available soon***

# Passive Multi-Sampling Method to Measure Contaminant Bioavailability in Aquatic Sediments

Rainer Lohmann, Ph.D.
University of Rhode Island

SERDP DOD • EPA • DOE | ESTCP

# Agenda

- Objective
- Test sampler in sediment
- Test sampler in water
- Ex-situ versus in-situ sampling
- Active versus passive sampling
- Spatial and temporal contaminant trends
- On-going work
- Key points and conclusions

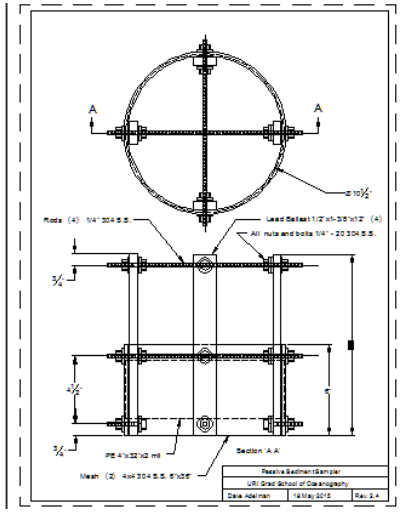
# Technical Objectives

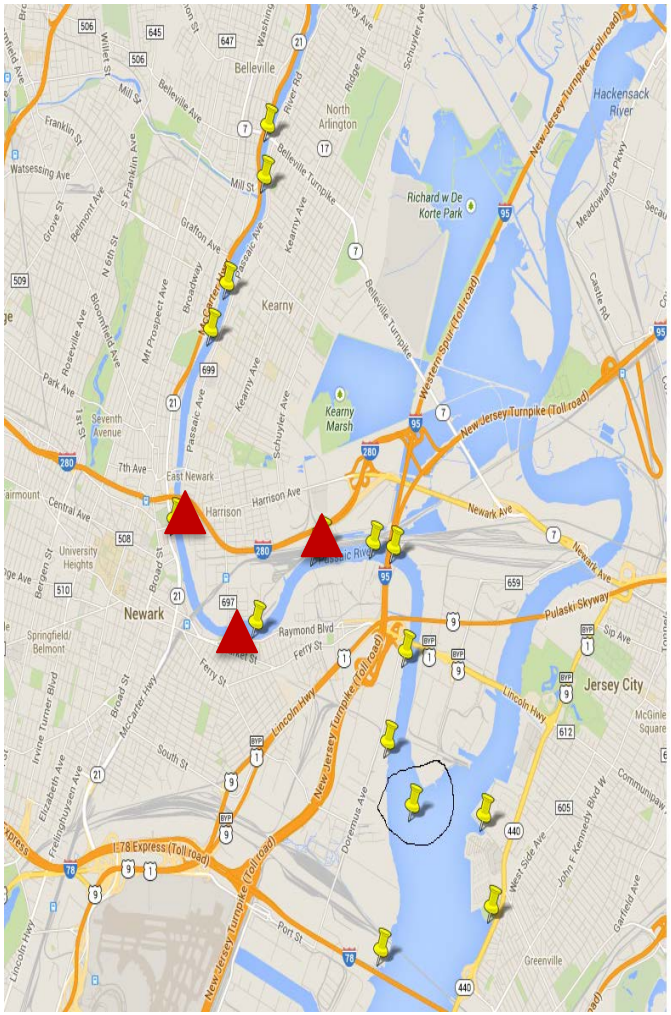
- Develop a passive sampling method with polyethylene samplers to sample organic contaminants in-situ
- Target a range of organic contaminants
  - Polychlorinated dioxins/furans
  - PAHs, PCBs, OCPs and PBDEs
- Compare ex-situ and in-situ sampling results
- Deploy the passive samplers without divers

Notes: PAHs = polycyclic aromatic hydrocarbons; PCBs = polychlorinated biphenyls; OCPs = organochlorine pesticides; PBDEs = polybrominated diphenyl ethers

# Prior Work and Results

- Sediment porewater multi-sampler
  - Construct, deploy, and validate
  - Dioxins/furans and other HOCs
- From double-rimmed to single tube






Notes: HOCs = hydrophobic organic contaminants

# Analytical Details

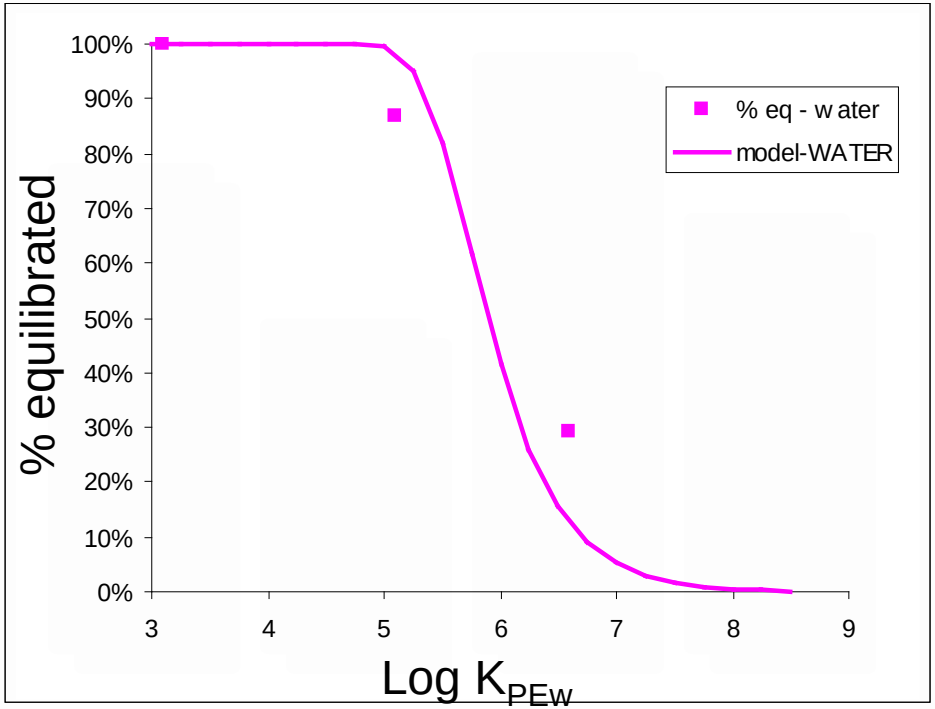
- Laboratory analysis
  - USEPA Method 1613B for dioxin/furans
- Instrument
  - Waters MICRO GC-MS/MS (gas chromatography tandem mass spectrometer)
- Agilent 6890 GC
- 2 parent/daughter mass transitions
- Detection limit
  - Approximately 10s pg on column (pg/L range)

Notes: pg = picogram

# Sampling Rate Approach

- Using 7 PRCs
  - 3 deuterated PAHs
  - 3 brominated biphenyls
  - Octachloronaphthalene
  - Polychlorinated dibenzodioxins (PCDD)
- $R_s$ in water
  - Average = 10 L/day
  - Range = 2-25 L/day

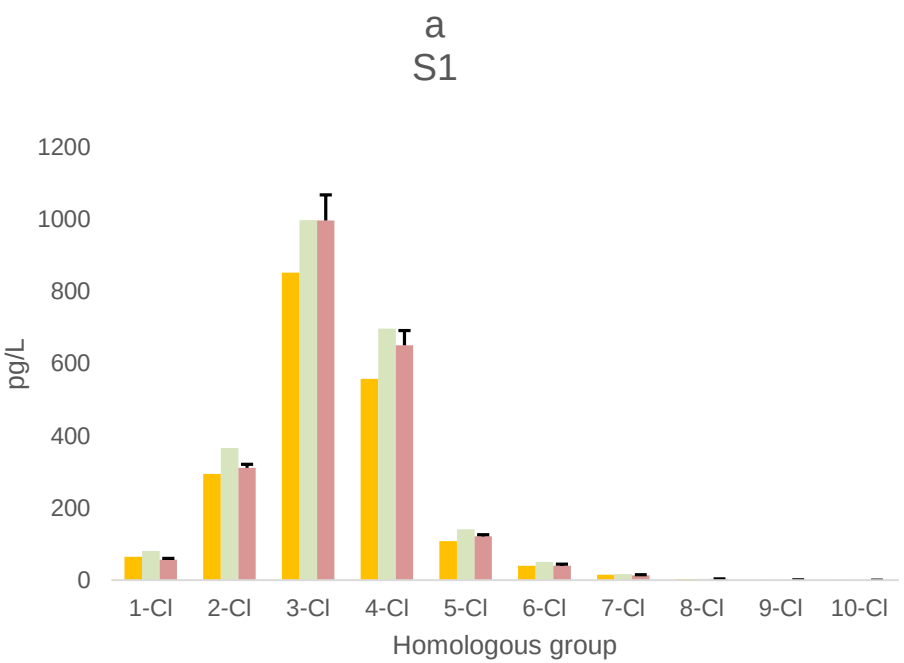
$$C_{a(w)} = \frac{C_{LDPE}}{K_{PEw\ (or\ PEa)} \times \left(1 - e^{-\frac{R_s \times t}{K_{PEw\ (or\ PEa)} \times m_{LDPE}}}\right)}$$

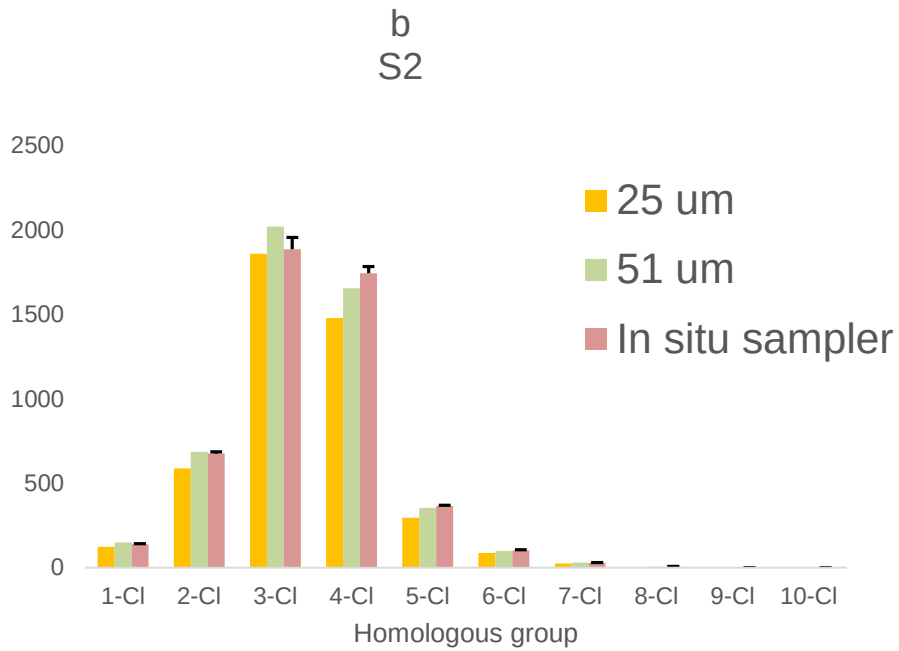



Notes: PRCs = performance reference compounds; Rs = sampling rate (L/day)

# Test Sampler in Sediment

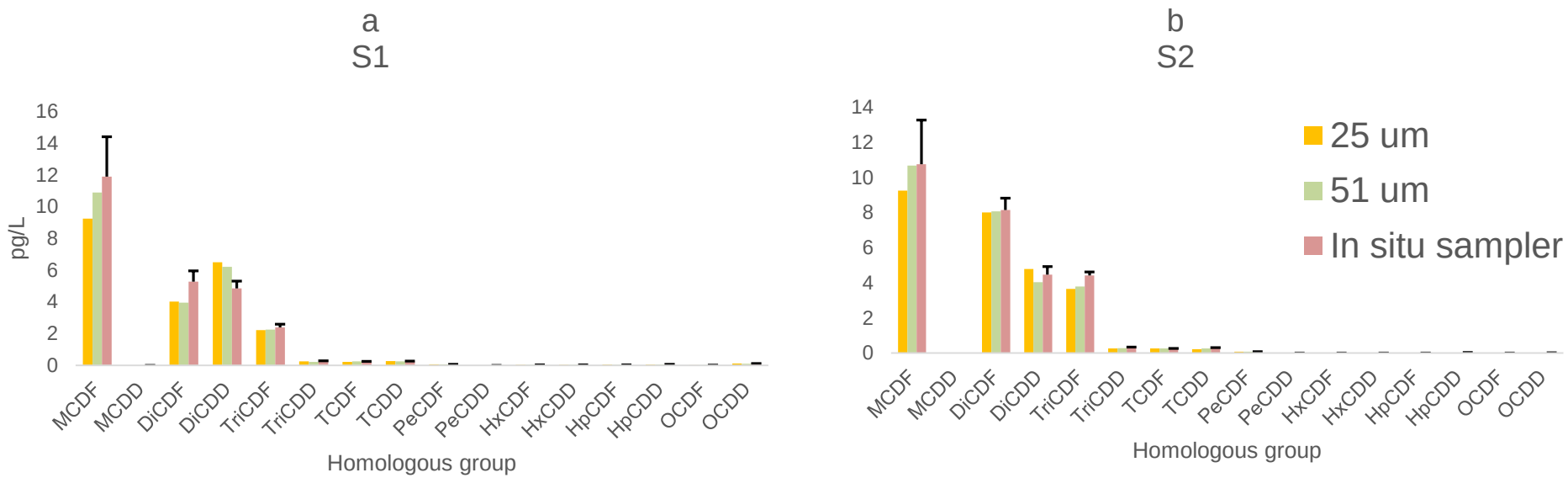
## *Compare Ex-situ and In-situ Porewaters: PCBs*



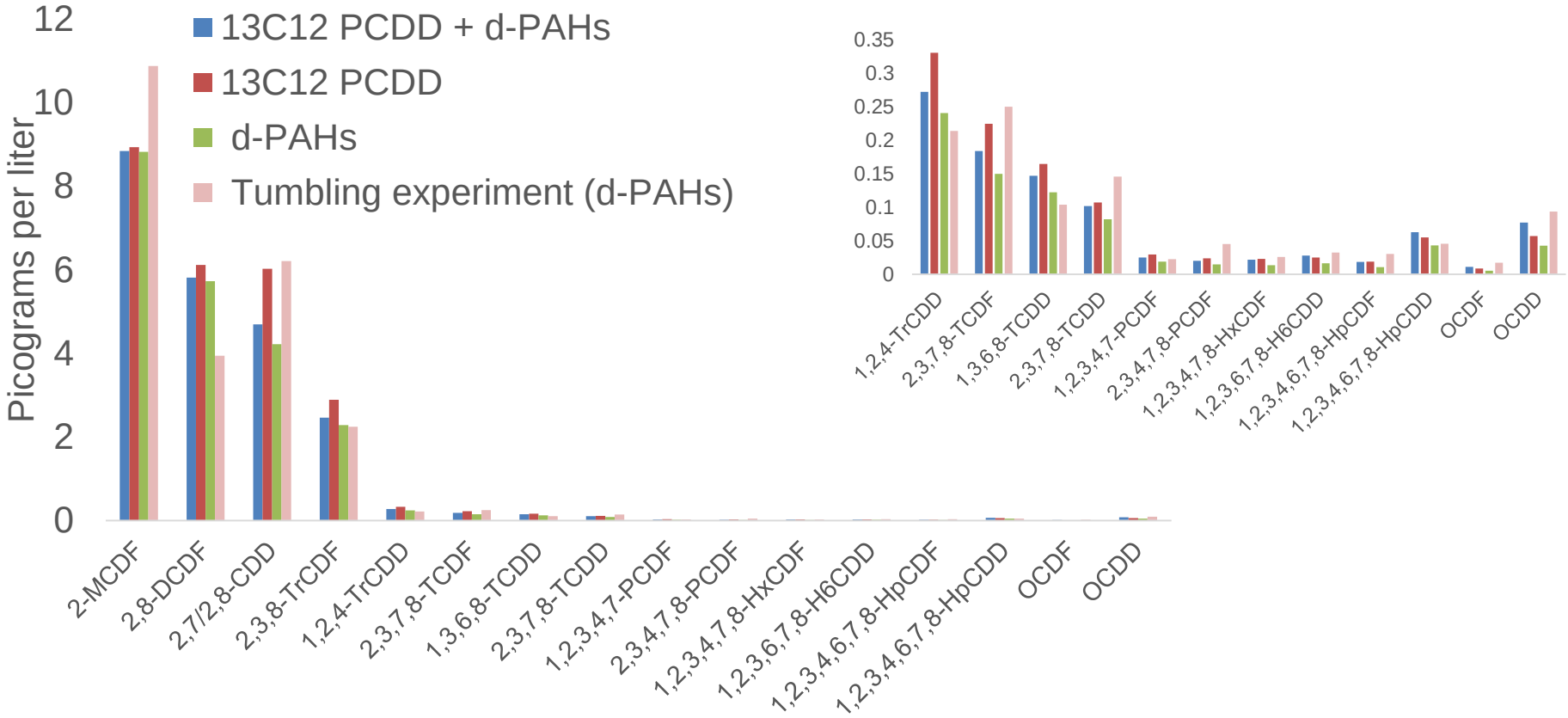
# Test Sampler in Sediment

## *Compare Ex-situ and In-situ Porewaters: PCDD/Fs*



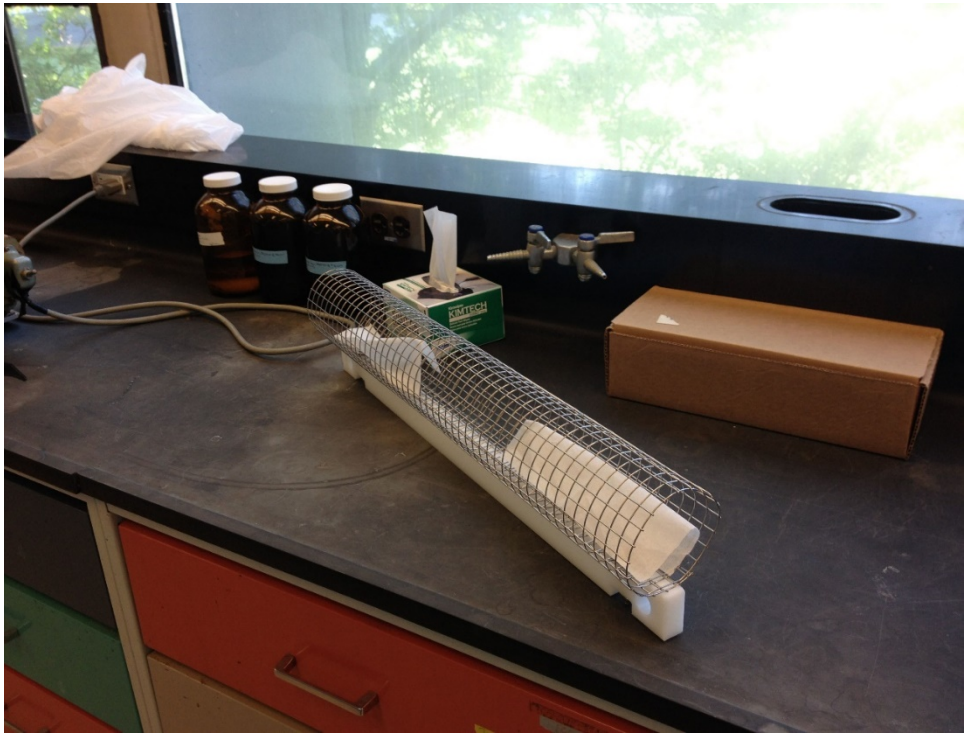
# Choice of PRCs for Sediment

- Better agreement with ex-situ results for PCDD/Fs using both d-PAHs and 13C-PCDDs



# Test Sampler in Water

- Validate polyethylene-based water column multi-sampler for various HOCs

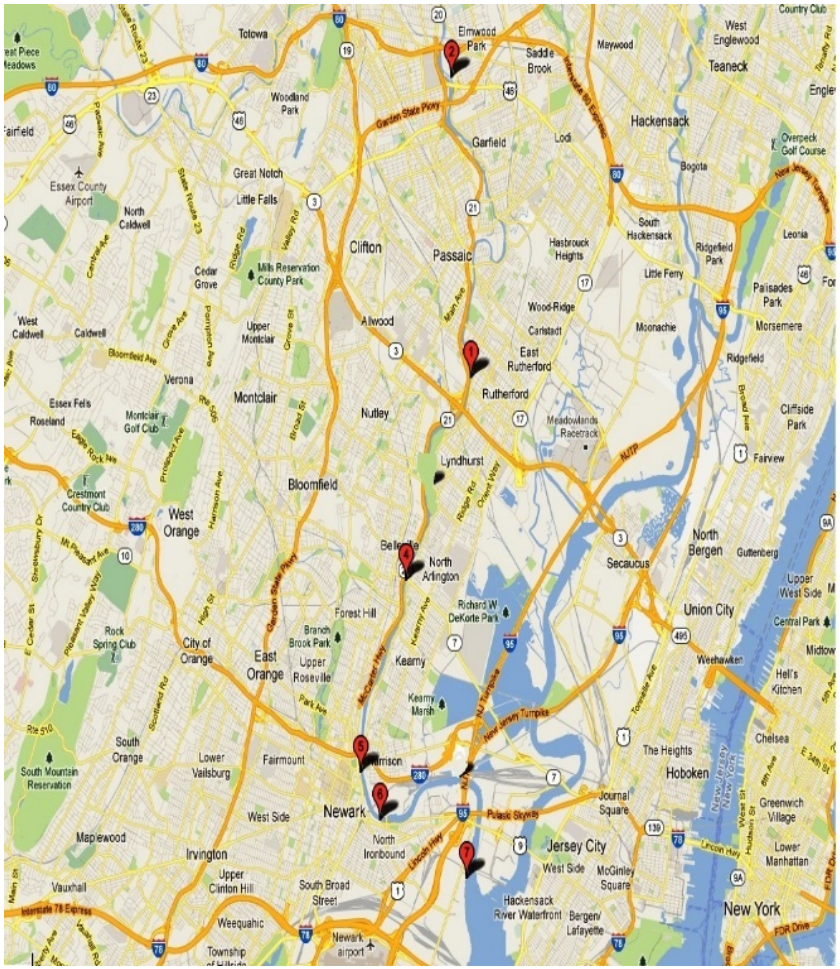


# Sorption of PBDEs in Water/Porewater

- Use of PRCs
  - (3 brominated biphenyls) for PBDEs
- $R_s$ from least square regression

$$C_{a(w)} = \frac{C_{LDPE}}{K_{PEw\ (or\ PEa)} \times \left(1 - e^{-\frac{R_s \times t}{K_{PEw\ (or\ PEa)} \times m_{LDPE}}}\right)}$$

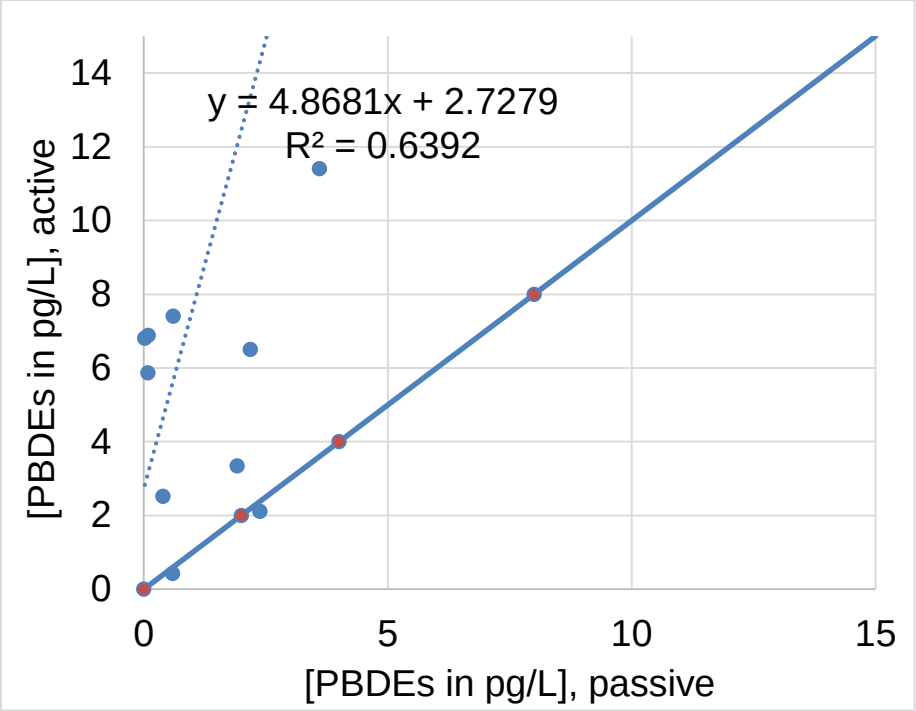
- Porewater concentrations from equilibration incubations

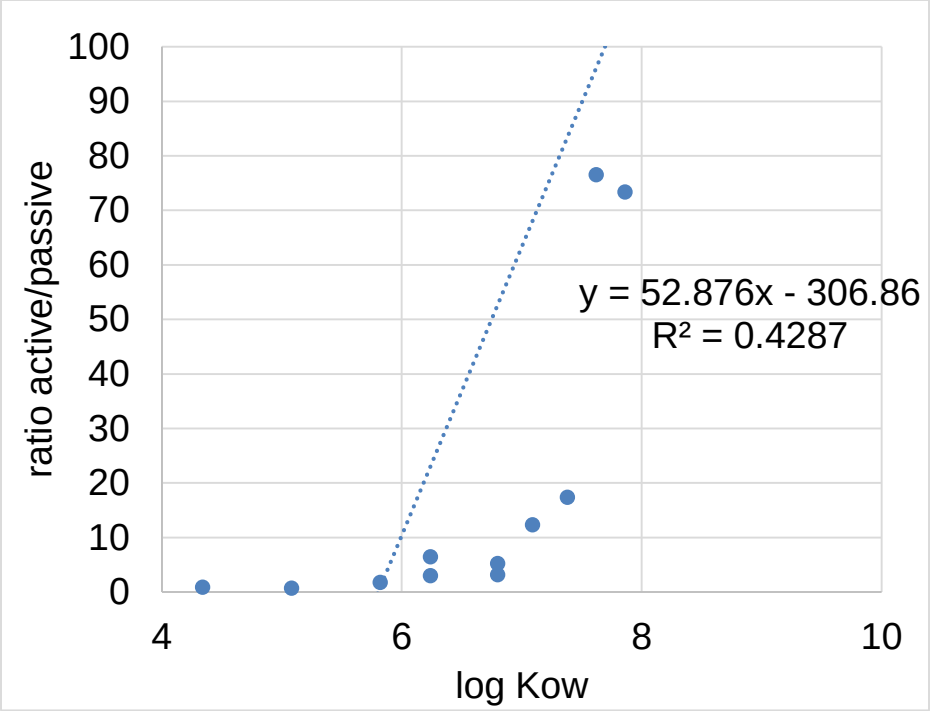



Source: Khairy and Lohmann, 2018

# Test Sampler in Water

## *Active vs. Passive Sampling - PBDEs*



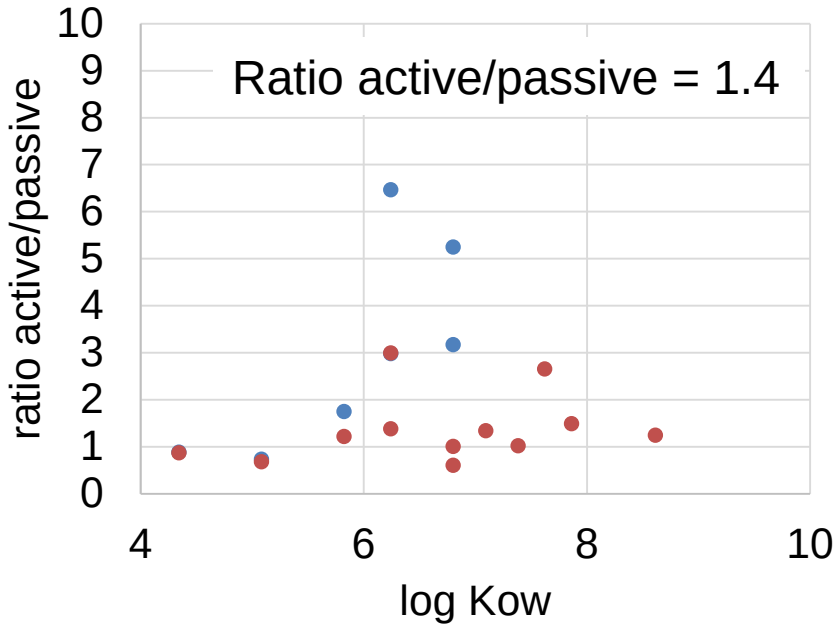

Ratio active/passive: 45

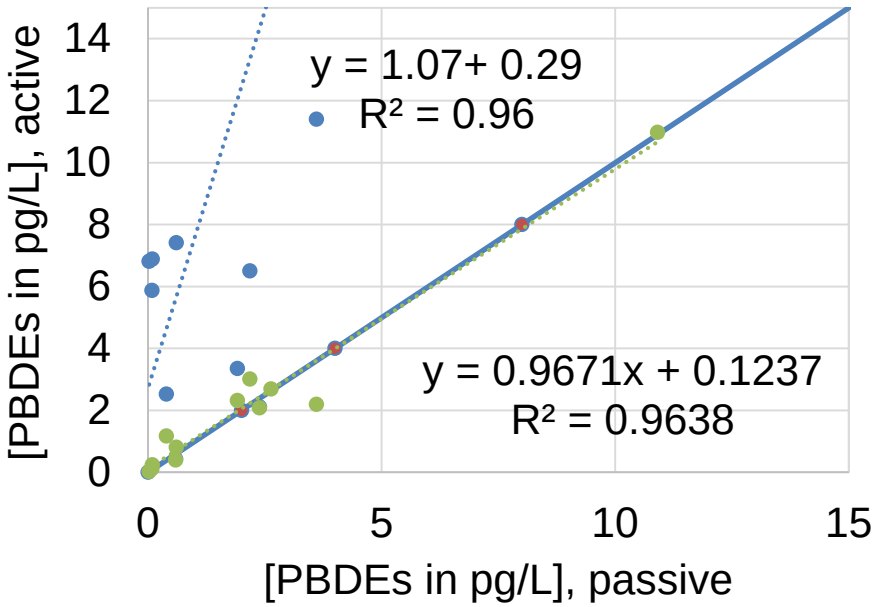
Notes: PBDEs = polybrominated diphenyl ethers; $K_{ow}$ = octanol-water partitioning coefficient
Sampling at Harrison, NJ; Active (March 2012); Passive (February – March 2012)

# Test Sampler in Water

## *DOC-Correction for PBDEs*

- DOC = 4.8 – 6.2 mg/L, average 5.3 mg/L
- Best fit: $K_{DOC} = 0.13 \times K_{ow}$



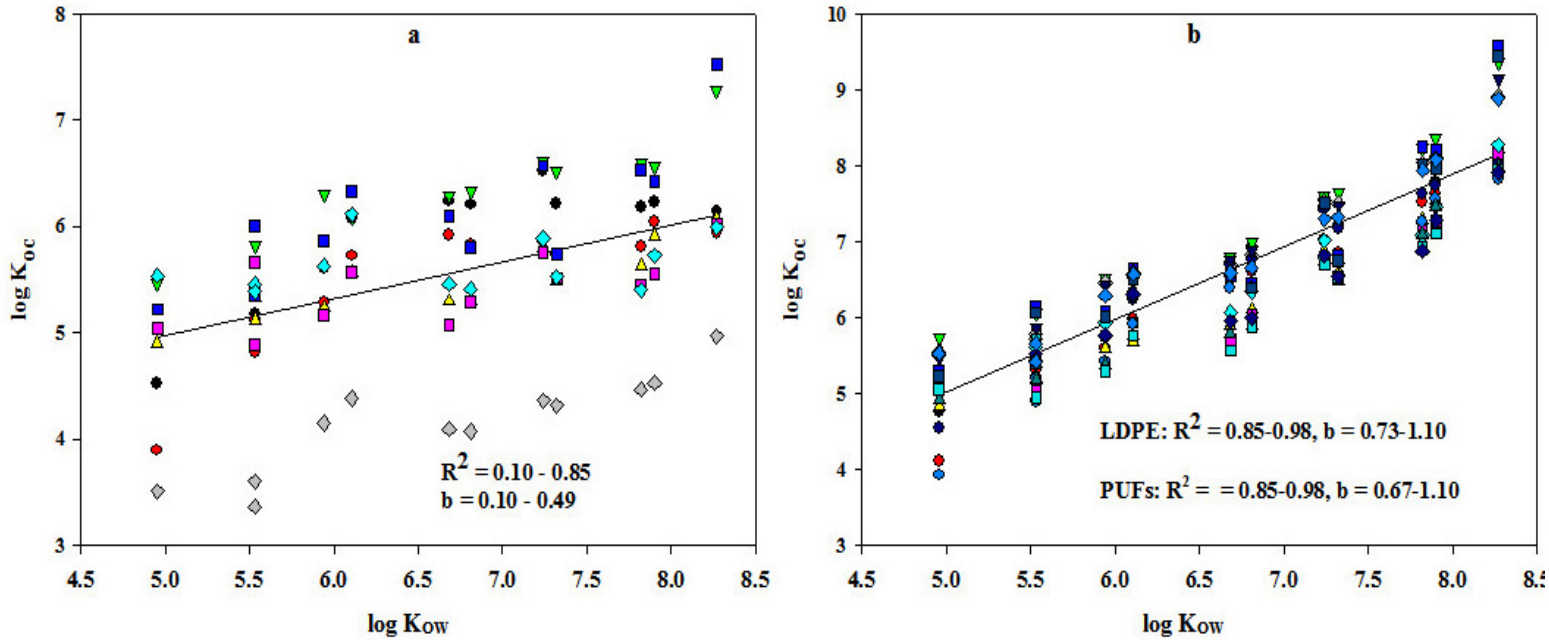

Notes: DOC = dissolved organic carbon; $K_{DOC}$ = DOC partitioning coefficient

# Passive vs. Active Sampling

- Affinity for DOC varies
  - PBDEs: 0.13 $K_{ow}$
  - PAHs: 0.50 $K_{ow}$
  - PCBs: 1.0 $K_{ow}$
  - PCDD/Fs: 1.0 $K_{ow}$
- Passive and active sampling results can be reconciled

# Sorption to Solids: PBDEs in Water

- Comparison active (PUF) vs. passive (PE) sampling
  - Correction for DOC ($K_{DOC}$ = 0.08 $K_{ow}$)

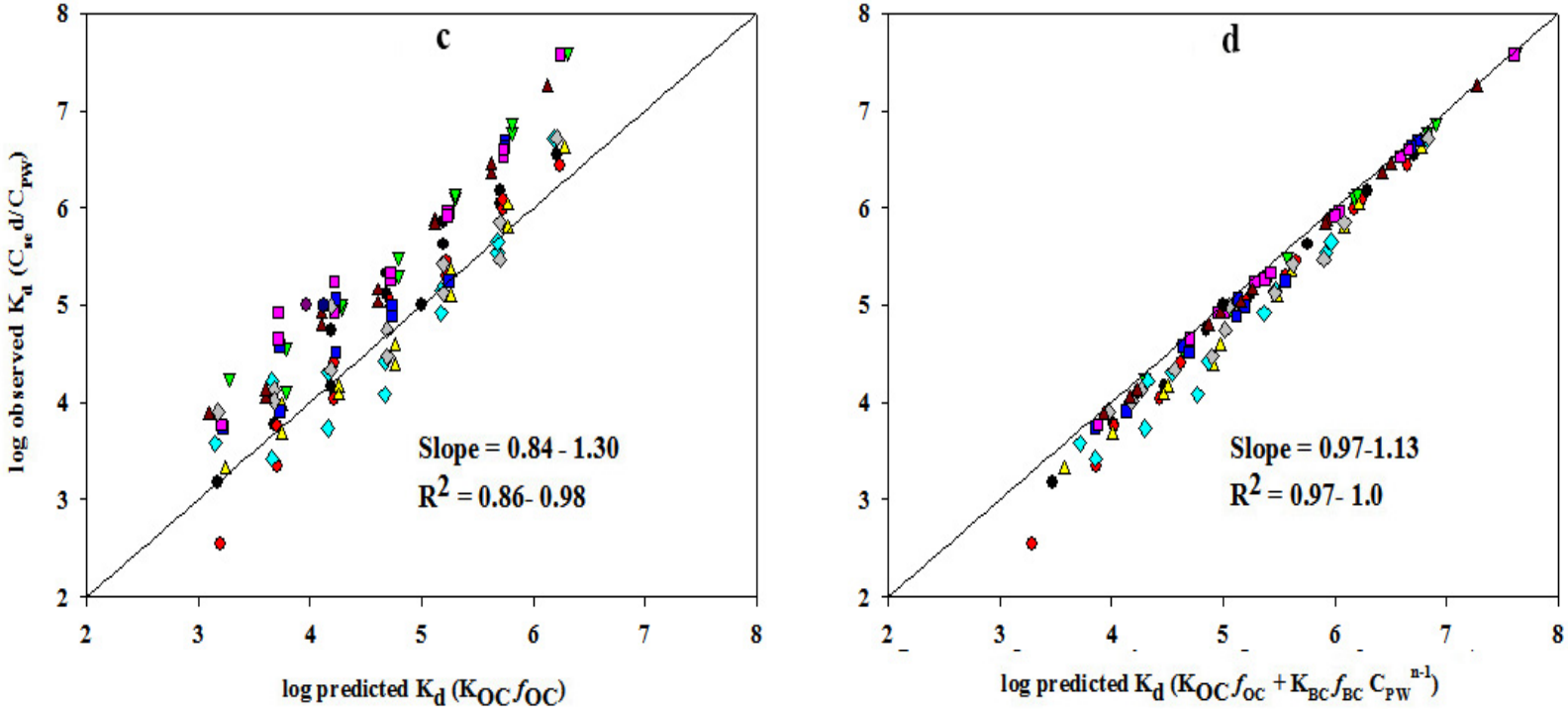



Notes: PE = polyethylene (passive sampler); PUF = polyurethane foam (active sampler)

Source: Khairy and Lohmann, 2018

# Sorption: PBDEs in Water Column

- $K_d = K_{OC} f_{OC} \; (+ f_{BC} K_{BC} C_{PW}^{n-1})$
  - Importance of dual BC + OC sorption

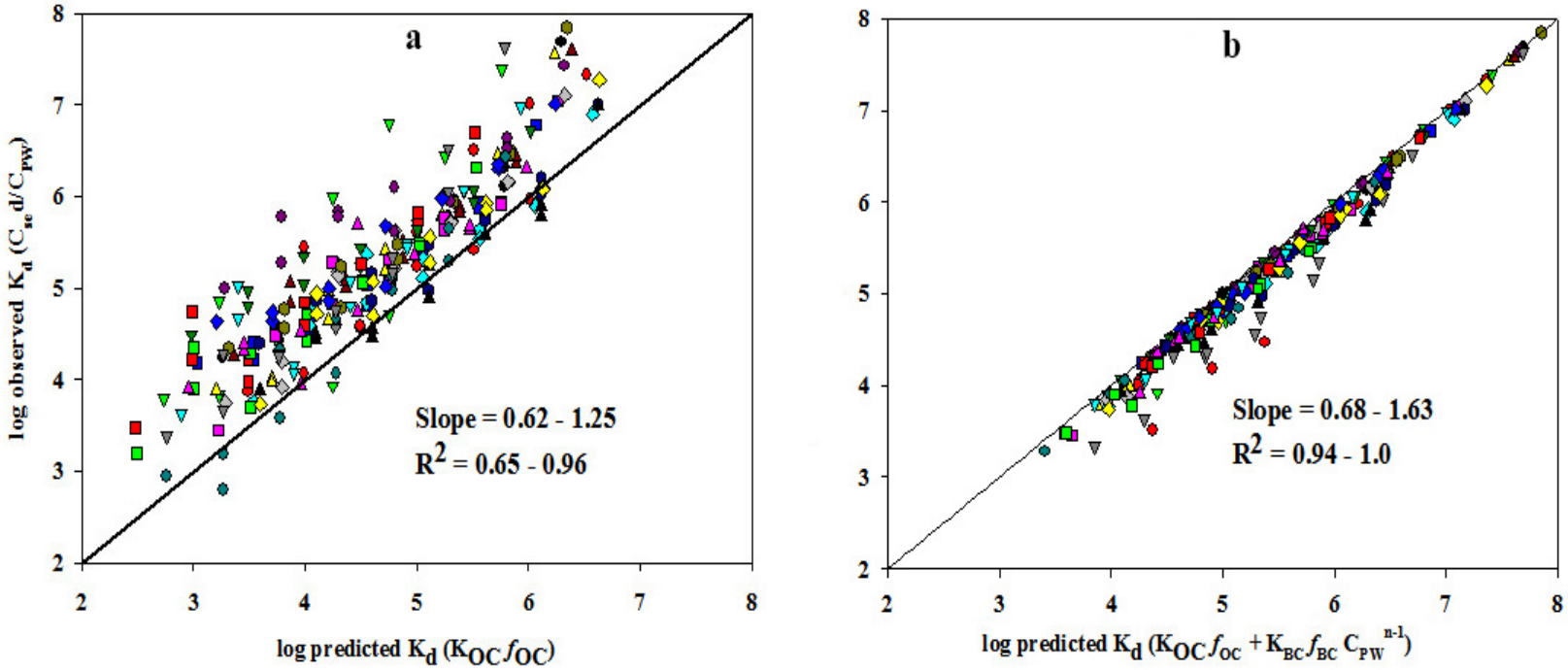



Notes: BC = black carbon; OC = organic carbon; n = Freundlich coefficient

Source: Khairy and Lohmann, 2018

# Sorption: PBDEs in Porewater

- $K_d = K_{OC} f_{OC} \ (+ f_{BC} K_{BC} C_{PW}^{n-1})$
  - Importance of dual BC + OC sorption

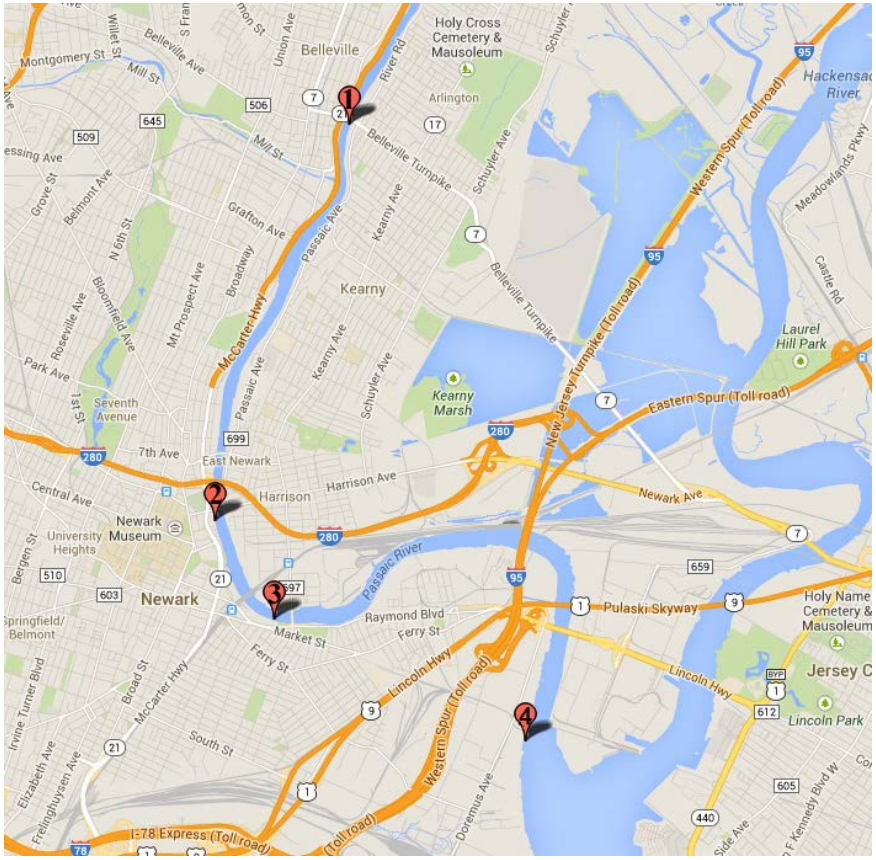



Notes: BC = black carbon; OC = organic carbon; n = Freundlich coefficient

Source: Khairy and Lohmann, 2018

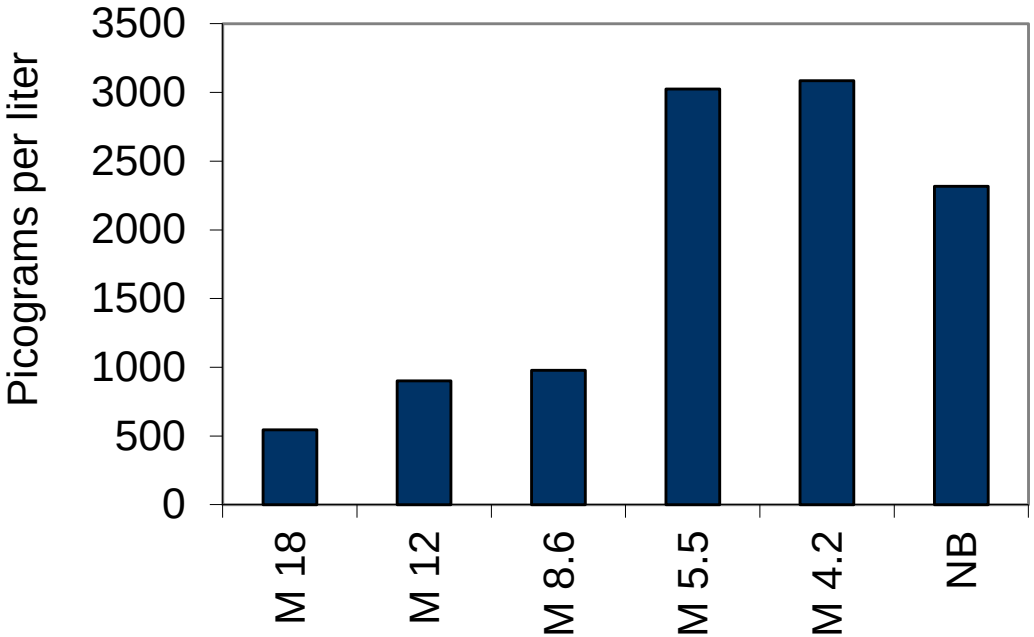
# Spatial and Temporal Trends

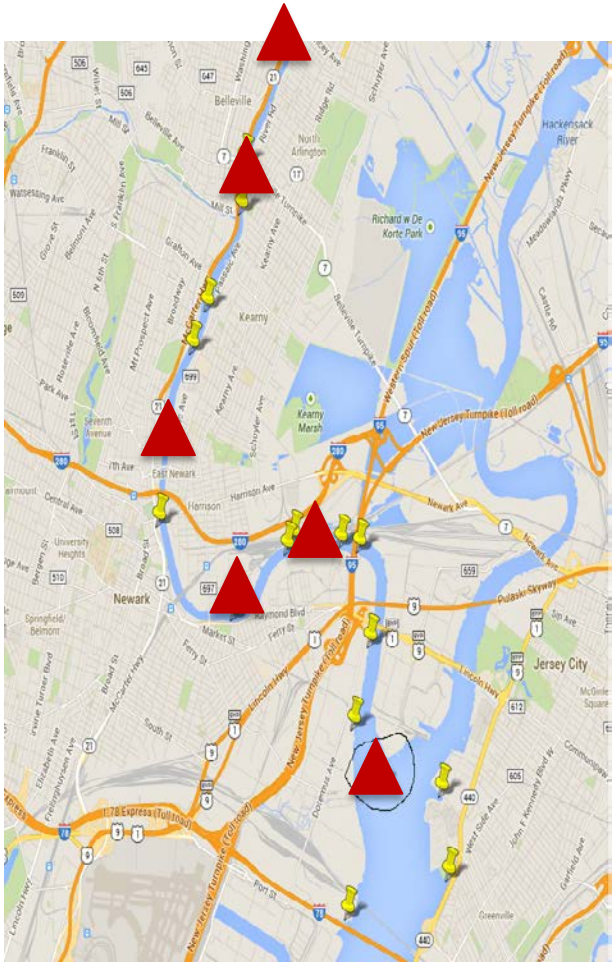
- Sediment, porewater and water column samples at several sites
- Dioxins/furans and other HOCs
- Derive and assess site-representative concentrations over time



# Spatial and Temporal Trends

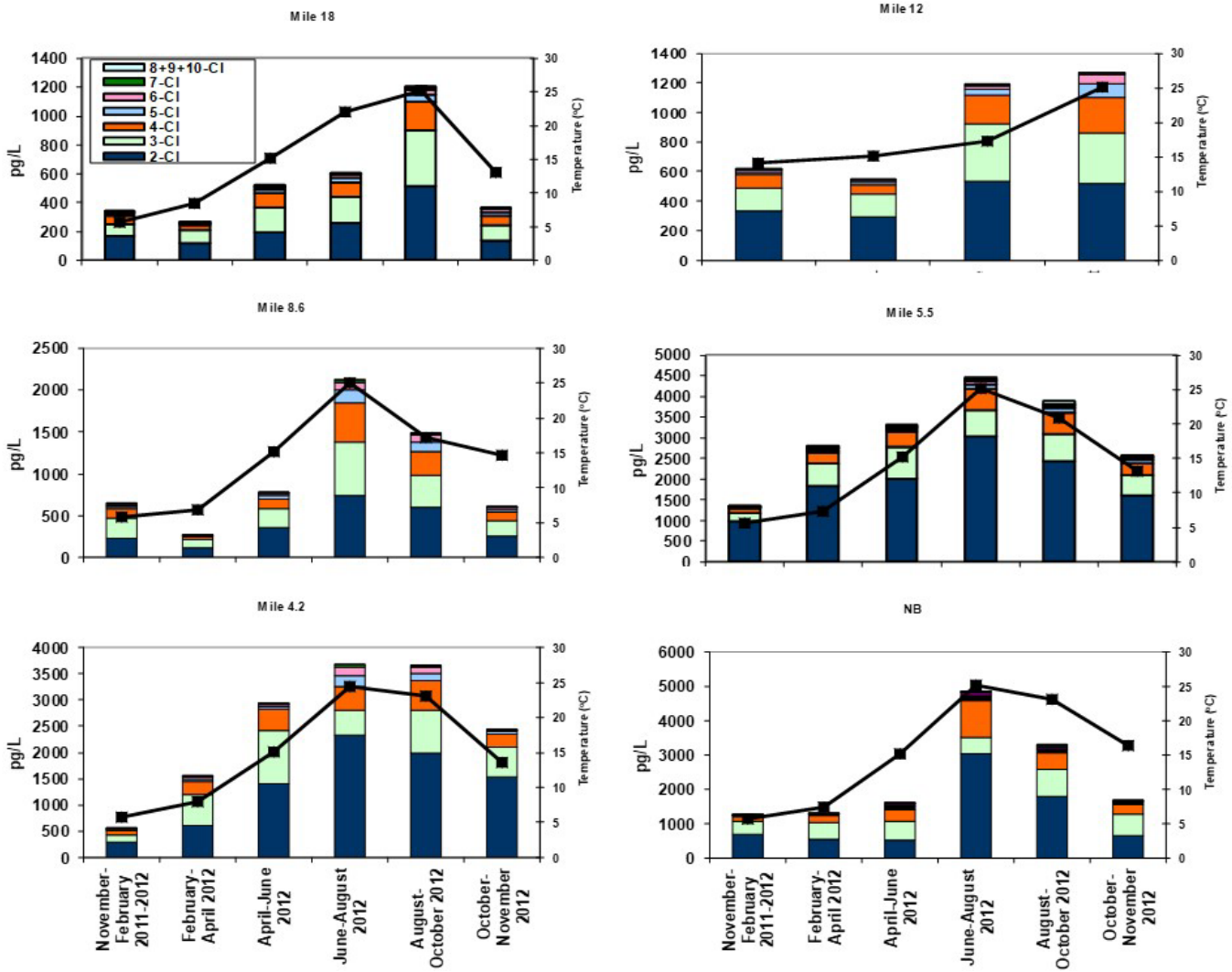
## *Water Column Results: Annual PCBs*



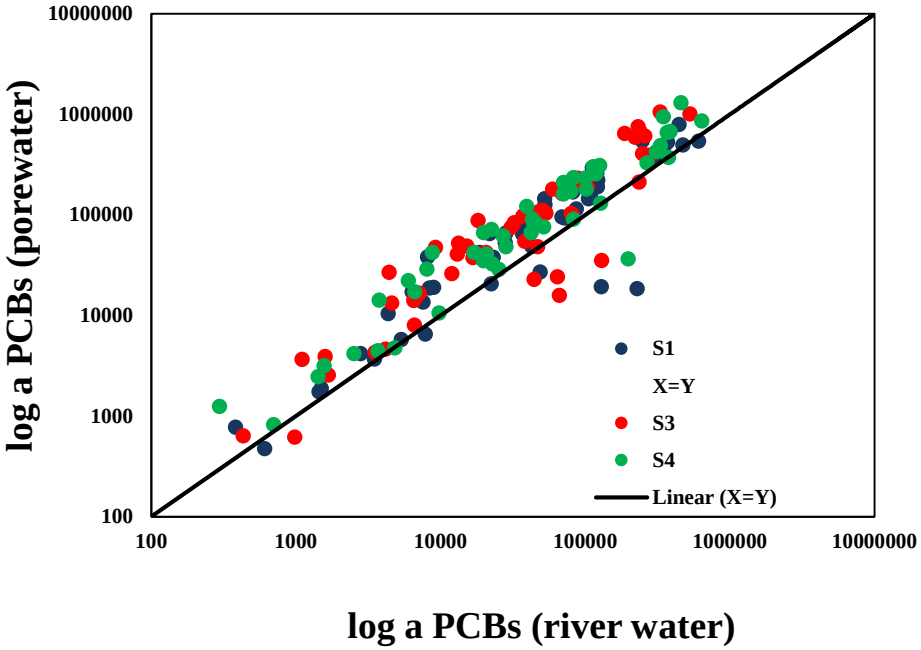
# Spatial and Temporal Trends

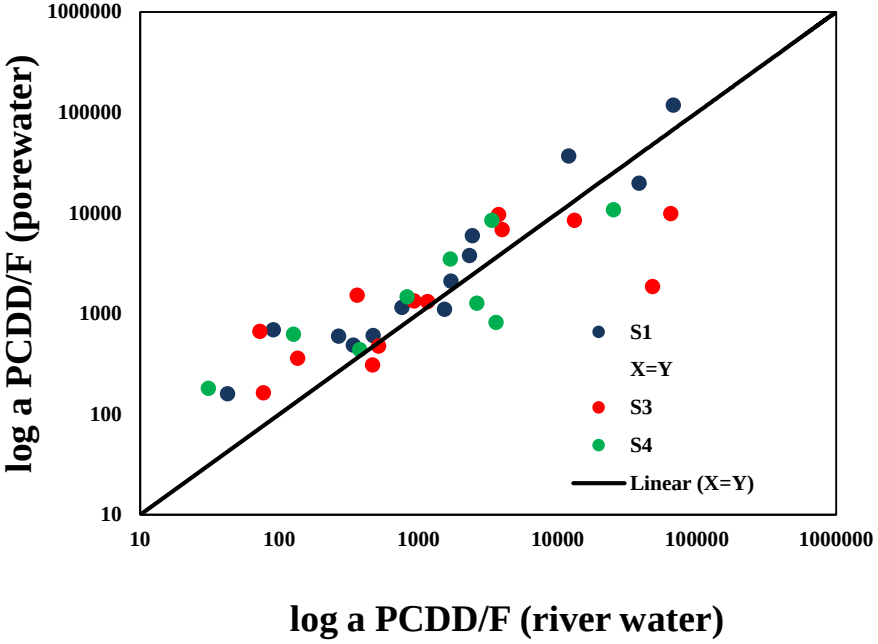
## *Water Column Results: PCBs*



# Chemical Activity Gradients

- Comparison porewater vs. water column
  - Porewater wins

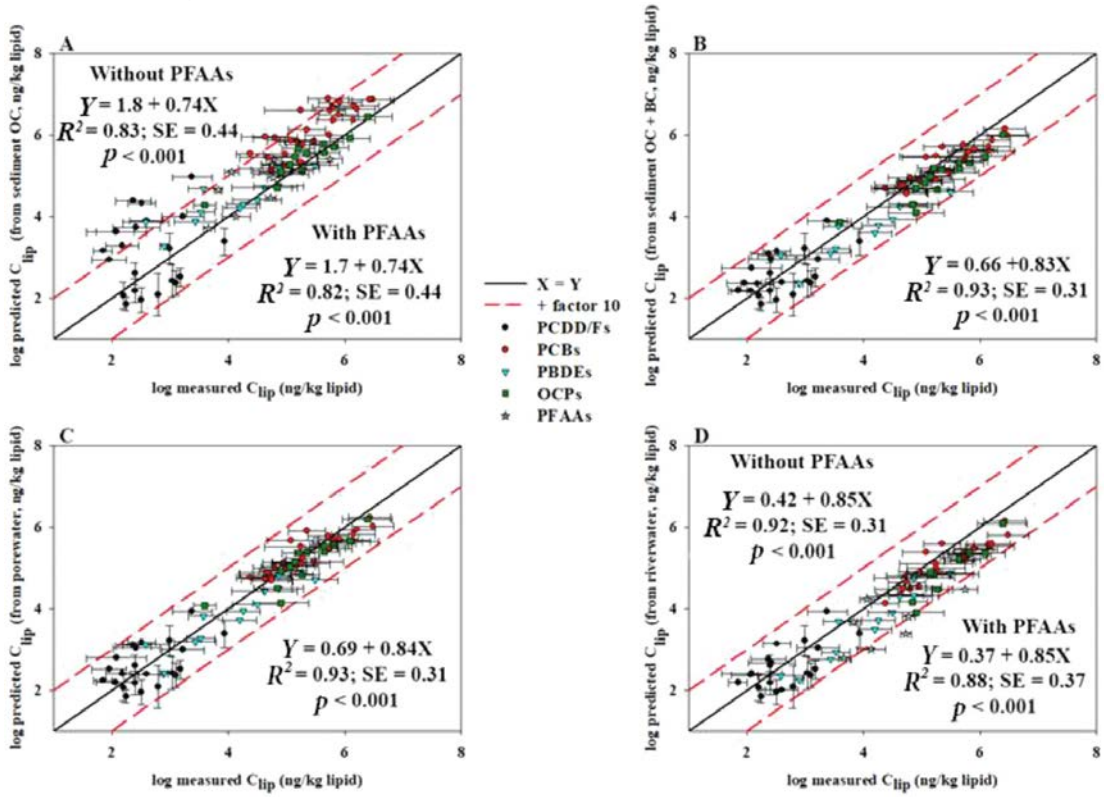


# What is Driving Bioaccumulation?

- PCBs, PCDD/Fs, PBDEs, OCPs in biota
  - Predicting bioaccumulation

OC




OC+BC

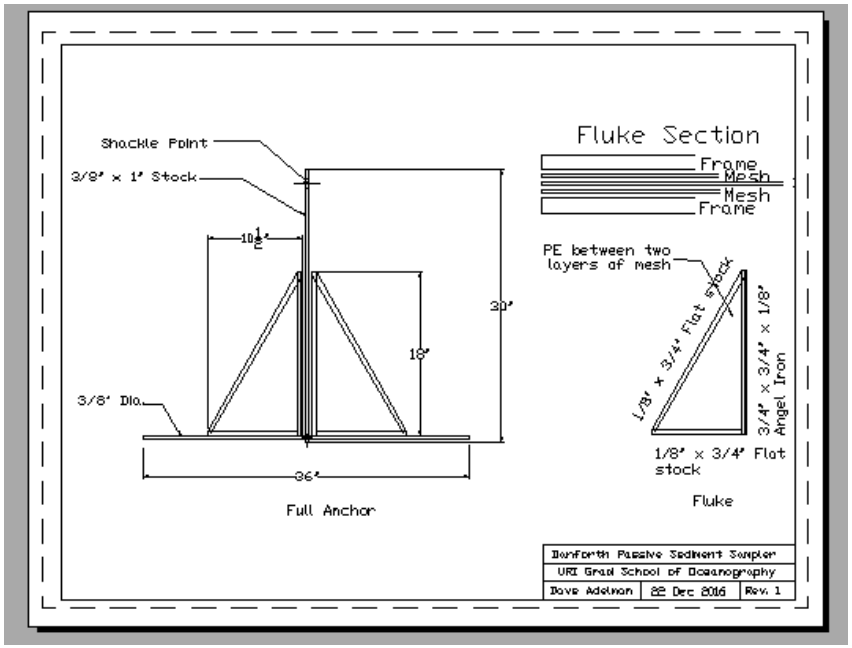
PW

River

Source: Khairy et al., 2019

# Ongoing Work

- Modify multi-sampler to be deployed (and retrieved) without divers



# Key Points

- Constructed sediment porewater and water column multi-sampler
  - For dioxin/furans and other HOCs
- Field-tested sampler without use of divers
- Yields PCBs, OCPs, PBDEs, PAHs and PCDD/Fs
- Compared performance ex-situ and in-situ
- Next steps: Comparison to benthic animals/ food-web

# Conclusions

- Validated porewater multi-sampler for PCDD/Fs and PCBs
- Field-tested water column multi-sampler for PBDEs and HOCs
- Important for contaminated site assessment
- Relevant for remediation monitoring

# Benefits to DoD

- Many DoD sites have multiple contaminants
- PE samplers can be used to target many HOCs
- Sampling in water column and sediment
- In-situ passive PE results match other approaches
- Determine spatial and temporal trends

# Publications


- Khairy, M., Barrett, K., and Lohmann, R. The changing sources of polychlorinated dibenzo-p-dioxins and furans in sediments from the lower Passaic River and Newark Bay, New Jersey, USA. Environ Toxicol Chem 2016, 35, 550-562, DOI: 10.1002/etc.3223
- Khairy, M. and Lohmann, R. Partitioning, fluxes and bioaccumulation of PBDEs in an urban river. Environ Sci Technol 2017, 2017, 51, 9062−9071. http://dx.doi.org/10.1021/acs.est.7b02418
- Michiel T.O., Jonker, S.A. van der Heijden, D. Adelman, J.N. Apell, R.M. Burgess, Y. Choi, L.A. Fernandez, G.M. Flavetta, U. Ghosh, P.M. Gschwend, S.E. Hale, M. Jalalizadeh, M. Khairy, M.A. Lampi, W. Lao, R. Lohmann, M.J. Lydy, K.A. Maruya, S.A. Nutile, A.M.P. Oen, M.I. Rakowska, D. Reible, T.P. Rusina, F. Smedes, and Y. Wu. Advancing the use of passive sampling in risk assessment and management of contaminated sediments: Results of an international passive sampling inter-laboratory comparison. Environ Sci Technol 2018, 52, 3574−3582
- Khairy, M., Gregory O. Noonan, and Lohmann, R. Contrasting uptake and bioaccumulation of legacy and emerging contaminants in the aquatic food web of the Lower Passaic River: OCPs, PBDEs and PFAAs. Environ Tox Chem (in press)

# For additional information, please visit

https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Sediments/Bioavailability/ER-2538

## Speaker Contact Information

rlohmann@uri.edu; 401-874-6612

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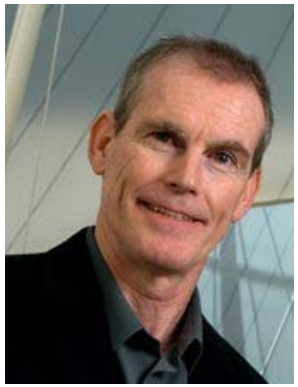
# Q&A Session 1

SERDP DOD • EPA • DOE | ESTCP

# Evaluating the Efficacy of Bioaugmentation for In-Situ Treatment of PCB Impacted Sediments



Kevin R. Sowers, Ph.D.
University of Maryland Baltimore County

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# Agenda

- Objective
- Background
- Description of the technology
- Site description
- Treatability study
- Field study
- Summary

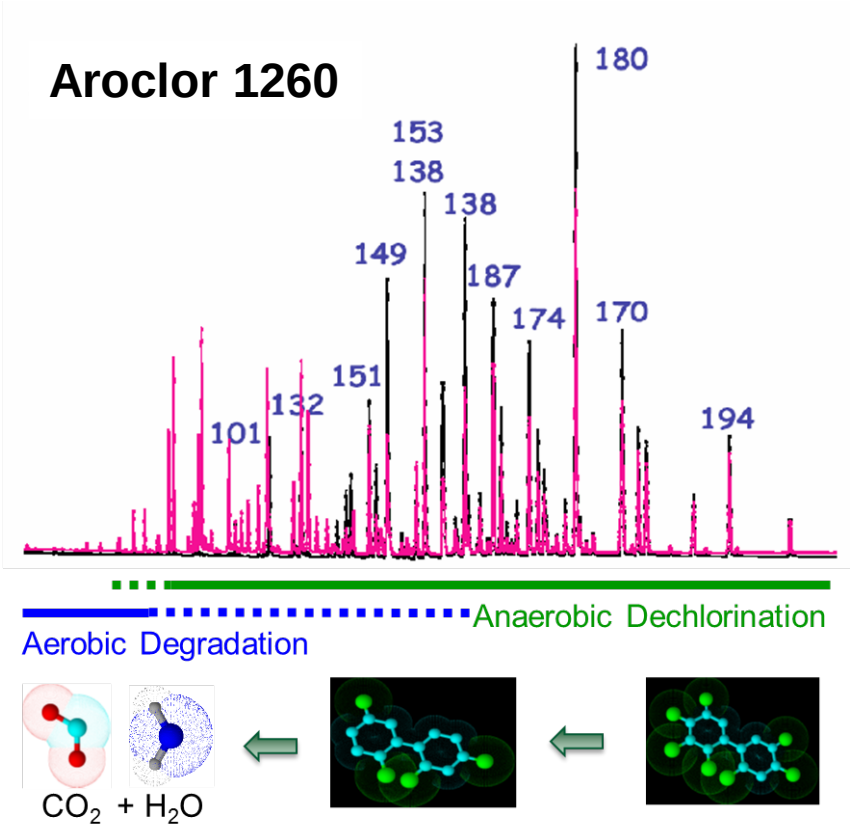
# Benefits to DoD

- Many DoD sites impacted with PCBs
- Dredging and capping
  - Destructive to environmentally sensitive areas
  - May not reduce risk sufficiently
- In-situ treatment with Bioamended Activated Carbon
  - Lower cost than dredging
  - Both sequesters and degrades PCBs
  - Rapidly deployed and minimally invasive
  - Reduces health risks associated with sediment disruption
  - Reduced carbon footprint
  - No extensive waste management and habitat restoration

# Technical Objectives

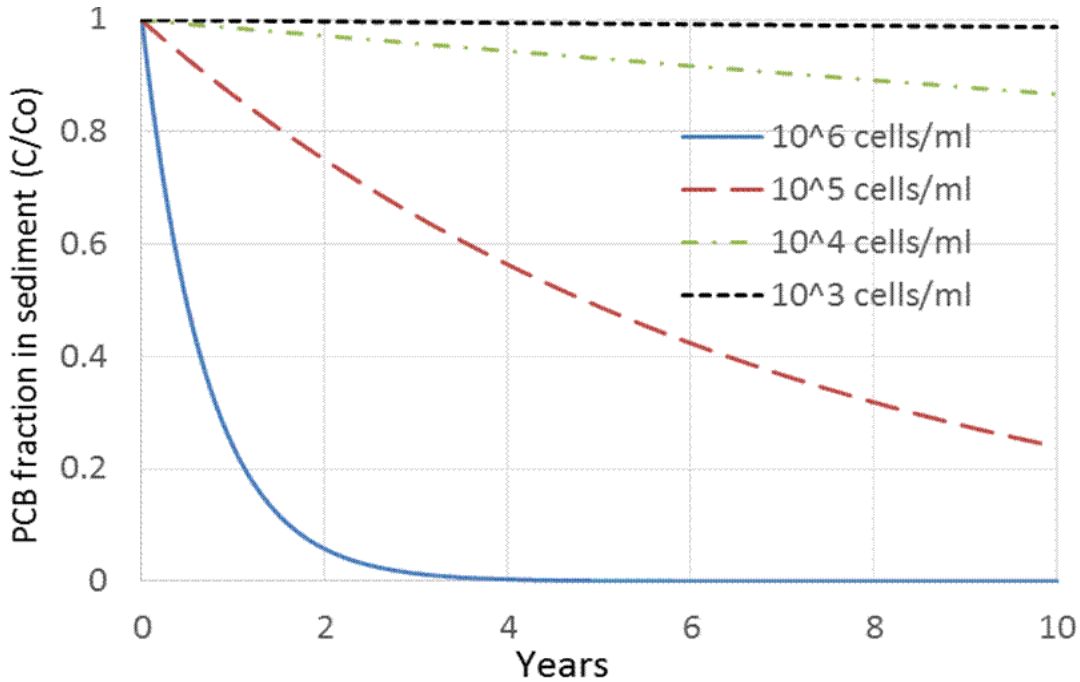
- Demonstrate and validate bioamended activated carbon (AC) for in-situ treatment of PCB impacted sediments
- Specific goals are to demonstrate the following:
  - Mass culture bioamendment, transport to site and deliver to sediments without loss of viability
  - Treatment with bioamended AC reduces the total and aqueous concentrations of PCBs
  - Treatment has minimal effect on the indigenous microbial community

# How Bioremediation of PCBs Works




- Complementary activities
  - Anaerobic halorespiring bacterium
  - Aerobic oxidizing/dechlorinating bacterium

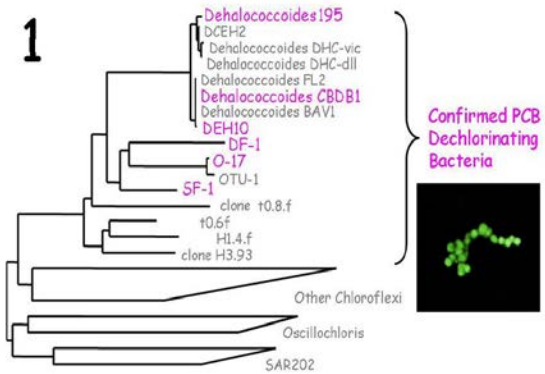
# Natural Attenuation of PCBs is Slow



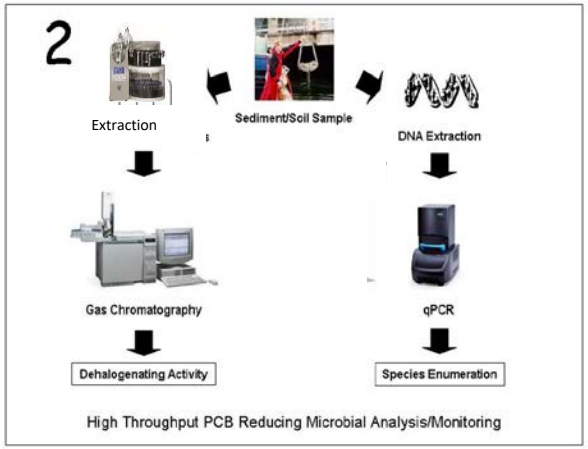

- PCB dechlorination follows first order rate kinetics
- Low cell numbers due to high $k_{ow}$ of PCBs
- Increasing cell numbers increases the dechlorination rates

# Technology/Methodology Description

1




2

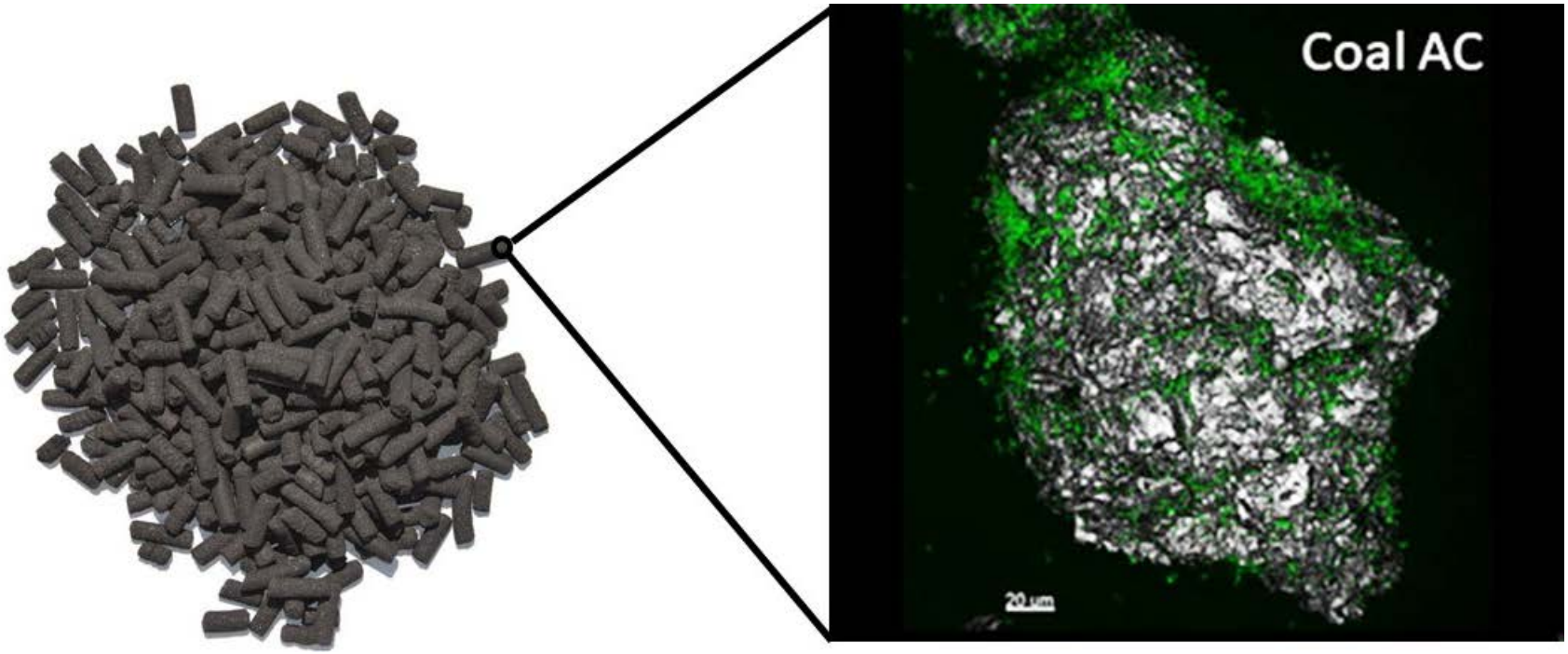



3

4

1. PCB transforming anaerobic halorespirer and aerobic degrader available
2. Assays developed for monitoring treatment and bioamendments
3. Methods developed for biomass scale-up of bioamendments
4. System developed for in-situ deployment of bioamendments on activated carbon agglomerate (SediMite)

# Bioamended Activated Carbon

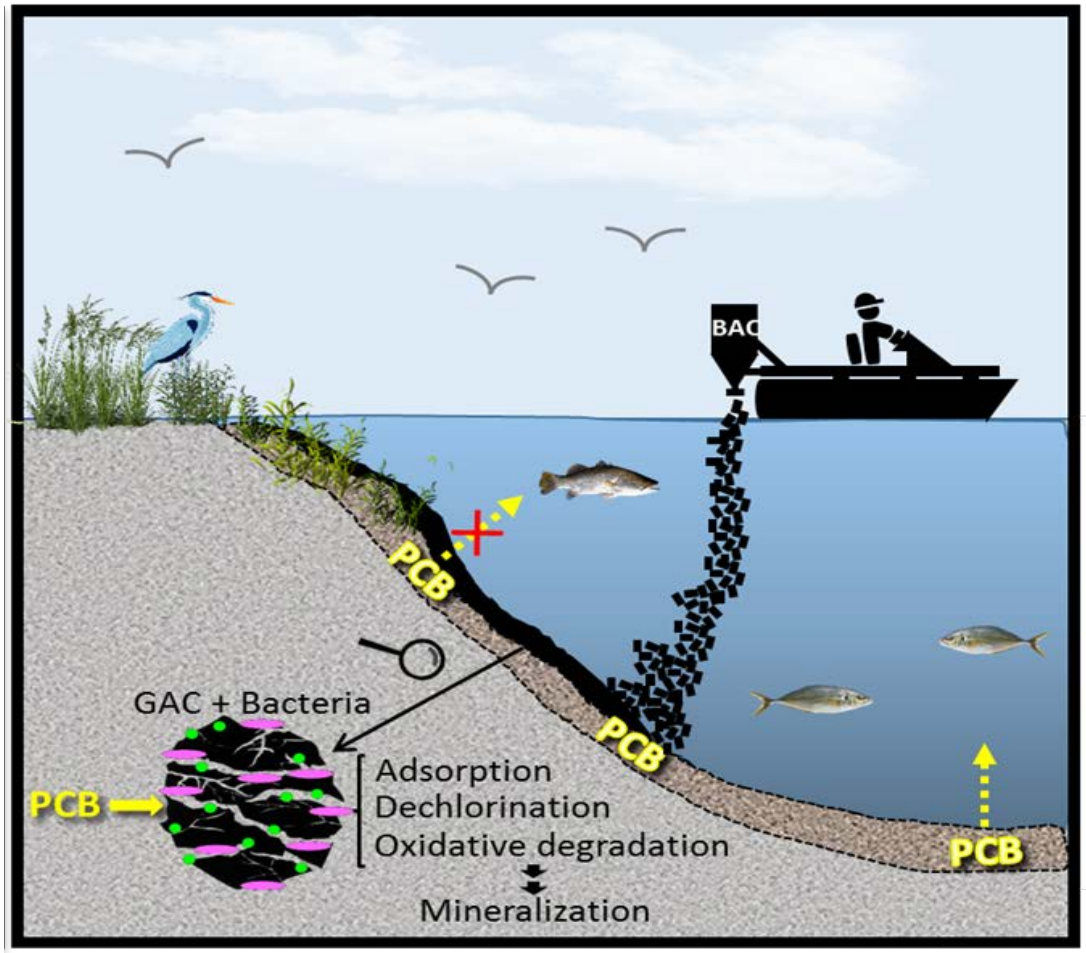



***SediMite™ with biofilm of PCB transforming microorganisms***



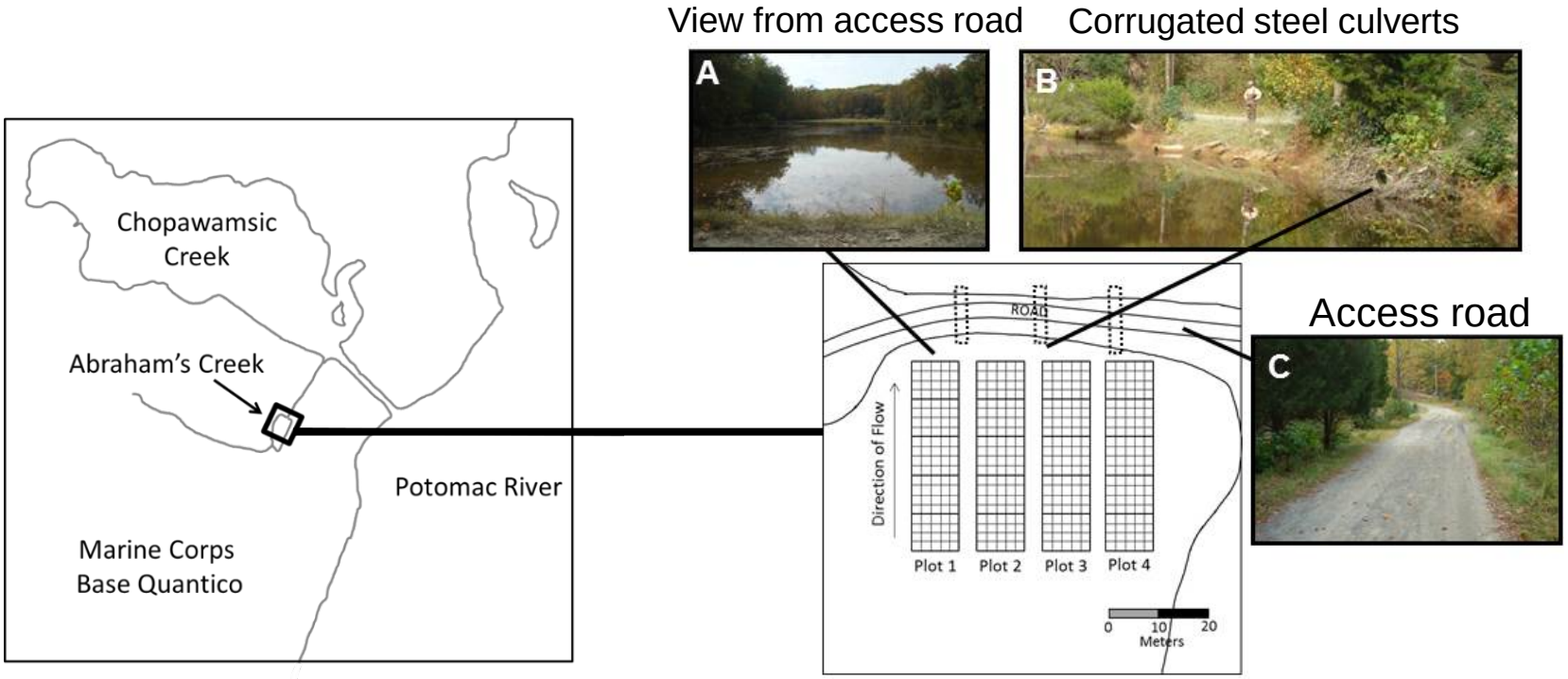
Capozzi et al., 2018. Biofouling: 10.1080/08927014.2018.1563892

# Application of Bioamended AC




***SediMite™ with biofilm of PCB transforming microorganisms***

# Site Description



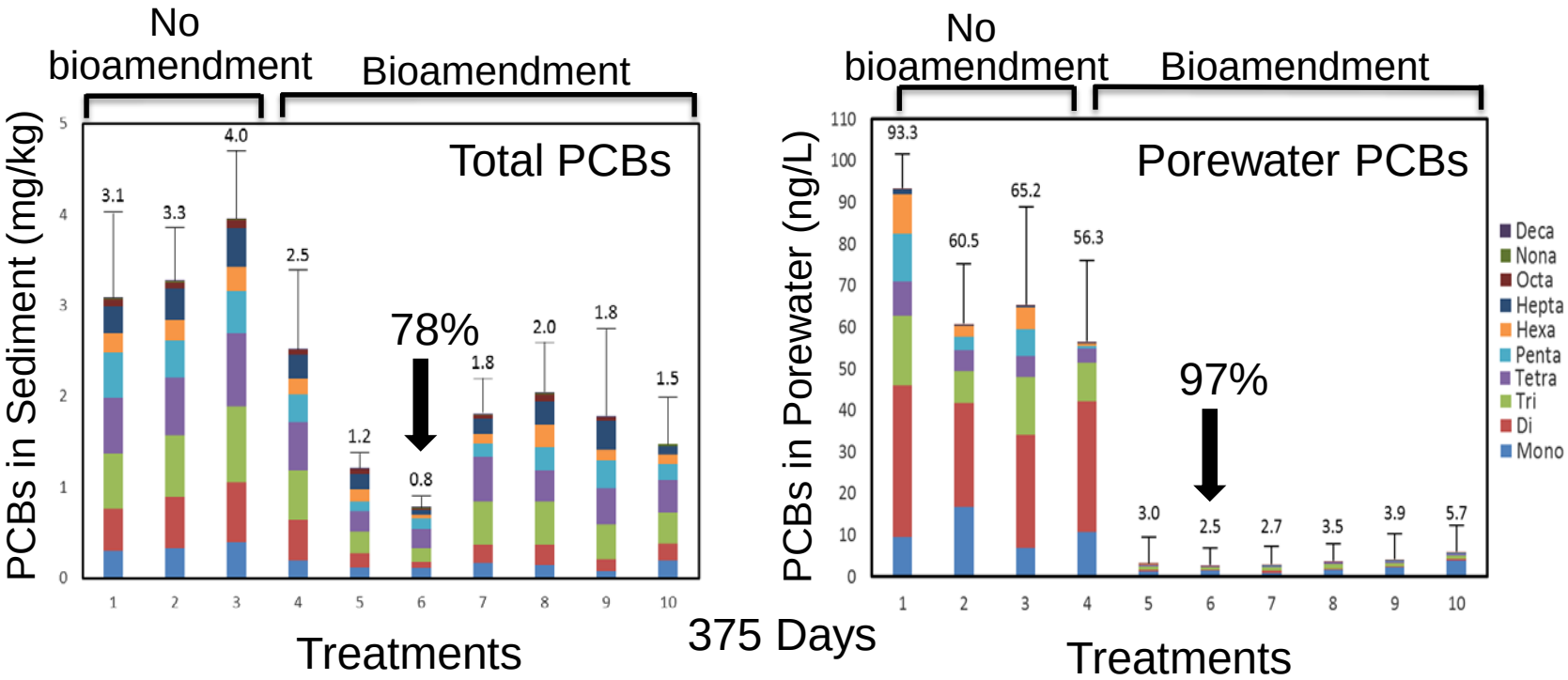

- Abraham's Creek MCBQ is an 8 acre/32,000 $m^2$ watershed outflow
- Original contaminant likely aroclor 1260
- Currently contaminated with average 5 ppm PCB
- Treatments in four 400 $m^2$ plots
- Load rate = 1 ton SediMite + $10^{12}$ cells/400 $m^2$

# Mesocosm Treatability Study

| Treatment | SediMite™ | Cellulose | Cells $g^{-1}$ sediment | Anaerobic Dechlorinator | Aerobic Degrader |
|---|---|---|---|---|---|
| 1 | - | - | - | - | - |
| 2 | 3% | - | - | - | - |
| 3 | 3% | 0.03% | - | - | - |
| 4 | 3% | 0.03% | $5 \times 10^3$ | DF-1 | LB400 |
| 5 | 3% | 0.03% | $5 \times 10^4$ | DF-1 | LB400 |
| 6 | 3% | 0.03% | $5 \times 10^5$ | DF-1 | LB400 |
| 7 | 3% | - | $5 \times 10^5$ | DF-1 | LB400 |
| 8 | 3% | 0.03% | $5 \times 10^5$ | SF1+DEH10 | LB400 |
| 9 | 3% | 0.03% | $5 \times 10^5$ | o-17 | LB400 |
| 10 | 3% | 0.03% | $5 \times 10^5$ | DF1+SF1+DEH10+ o-17 | LB400 |

- Abiotic controls
- Bioamendment titer
- Bioamendment without cellulose
- Different halorespirers

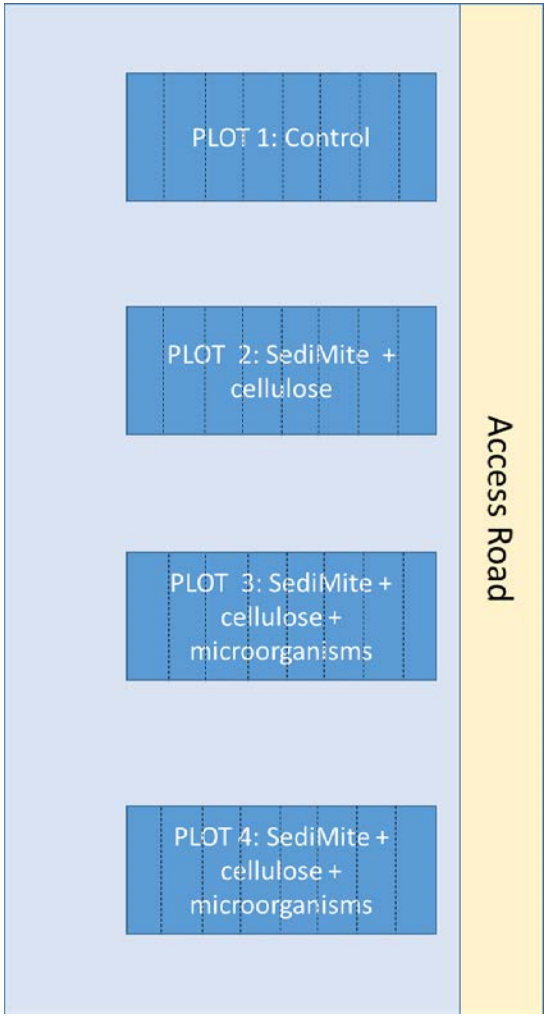
# Mesocosm Treatability Study




- *No significant reduction in PCB mass without bioamendment*
- *78% reduction in total PCB/97% reduction in soluble PCB with $10^5$ cell/g*
- *Dioxin-like congeners reduced 90%*
- *DF1/LB400 combination catalyzed greatest reduction in mass*
- *Reduction in concentration of both total and soluble mono- to nona-chlorobiphenyls*

# Field Study Design

- Layout of four treatment plots each 400 $m^2$ in area
- Plot 1 – no treatment
- Plot 2 – SediMite and cellulose as a slow release carbon source
- Plot 3 and 4 – SediMite/cellulose amended with anaerobic PCB dechlorinating DF1 and aerobic dechlorinating/oxidizing LB400



# Field Study Design

*Production of SediMite*

- 2,700 kg
  - 50% activated carbon
  - 30% sand
  - 20% clay binder
  - 0.1% cellulose by dry weight
- SediMite was loaded in 500 kg bulk bags and shipped on standard pallets loaded two bags per pallet

# Field Study Design

*Production of Bioamendments*

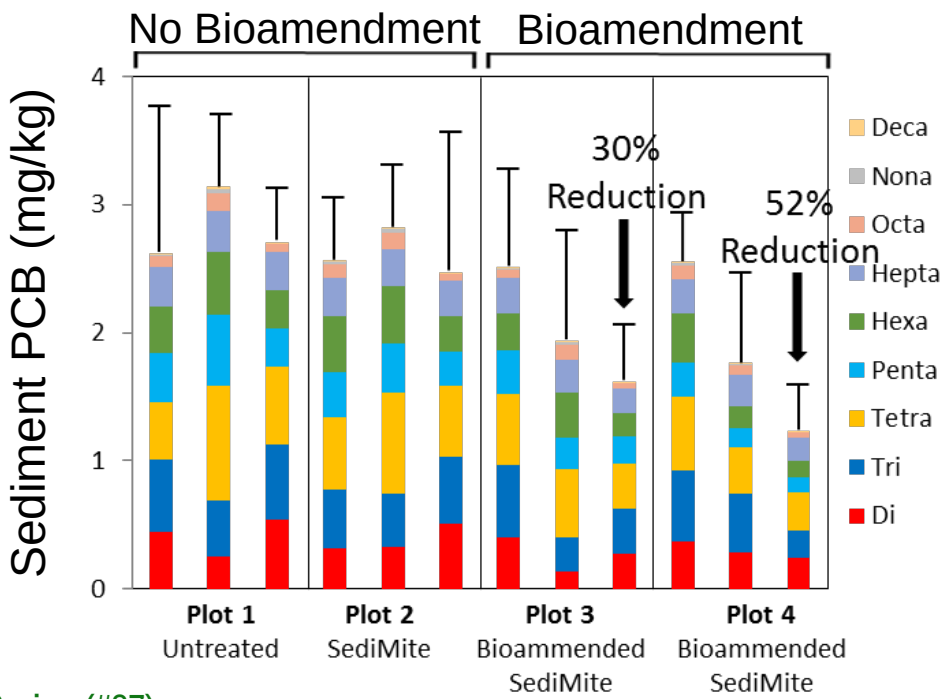
- Anaerobe
  - Scaled up using a 250 liter pilot-scale bioreactor
- Aerobe
  - Scaled up using a 20 liter bioreactor
- Cells were shipped in 20 liter Cornelius flasks

# Field Study Deployment

- 3,000 kg bioamended SediMite deployed with air horn
- Final SediMite concentration = 0.3g/10g sediment
- Final bioamendment concentration = $10^6$ cells/10g sediment
- Sediments sampled 0, 140 and 409 days post-treatment

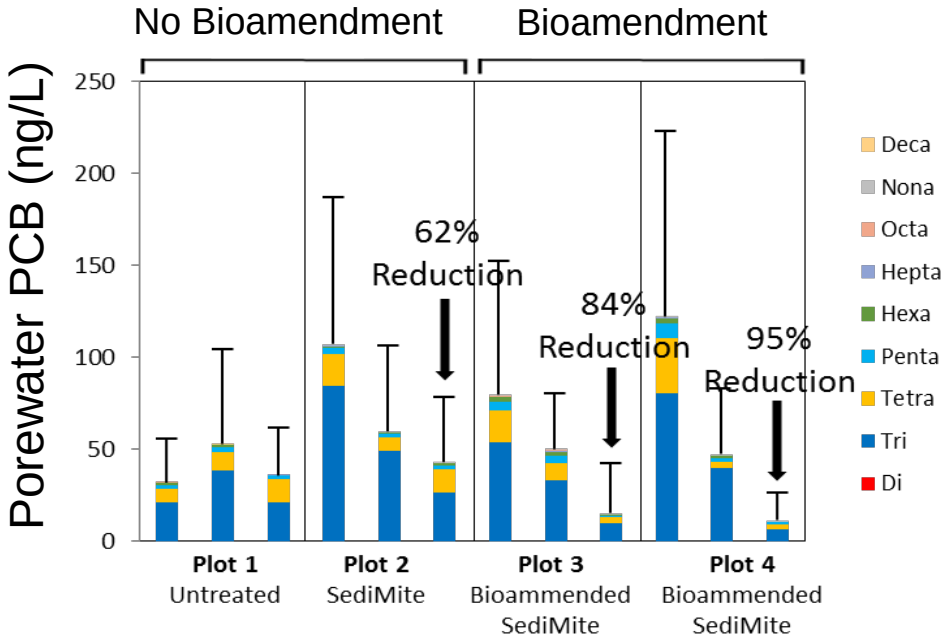
# Field Study Results: Total PCBs

- 80% reduction in coplanar PCBs in bioamended plot 4 after 409 days
- No significant change in untreated plots and below 7.5 cm



# Field Study Results: Dissolved PCBs

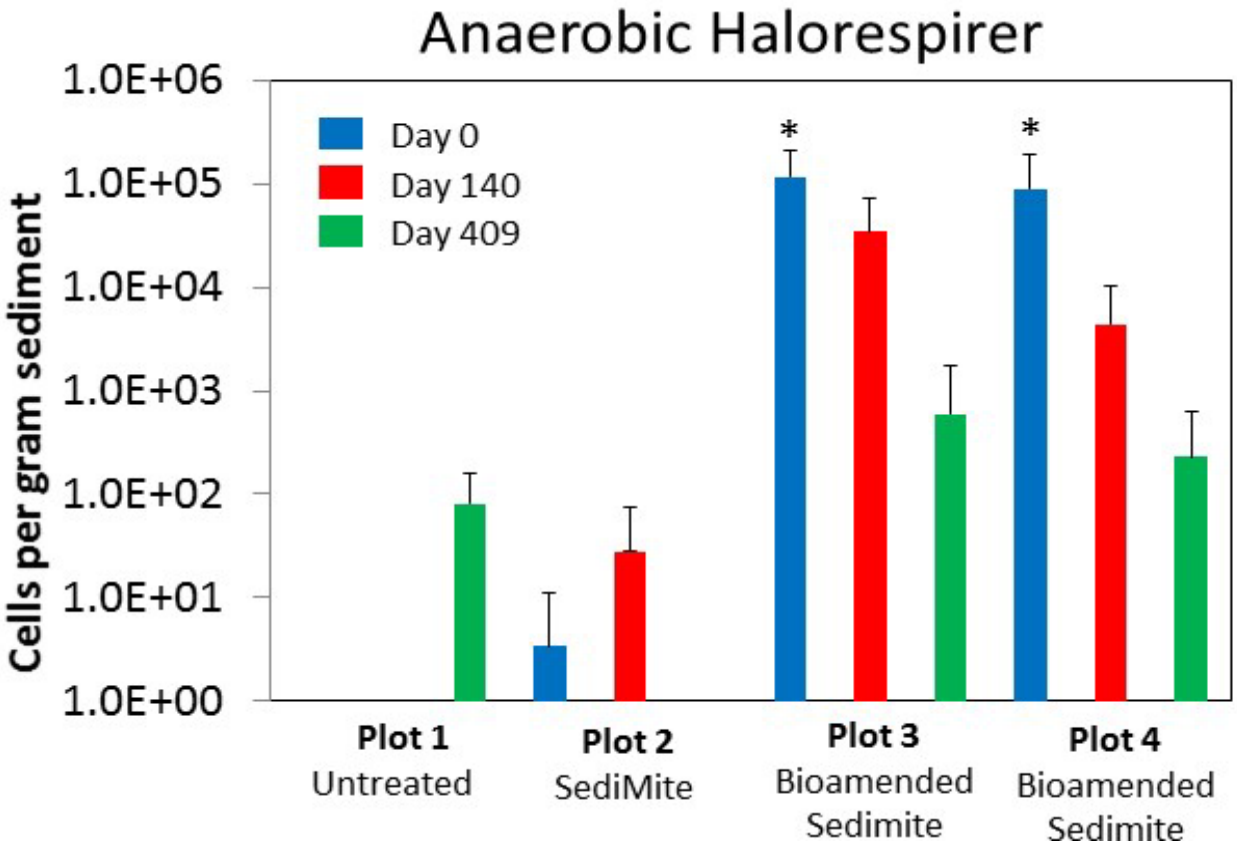
- PCB decrease in bioamended plots after 409 days
- Some decrease with AC due to adsorption
  - Significantly less decrease than bioamended plots
- No significant change in untreated plot and below benthic zone



# Field Study Results

## *Bioamendment Titer*

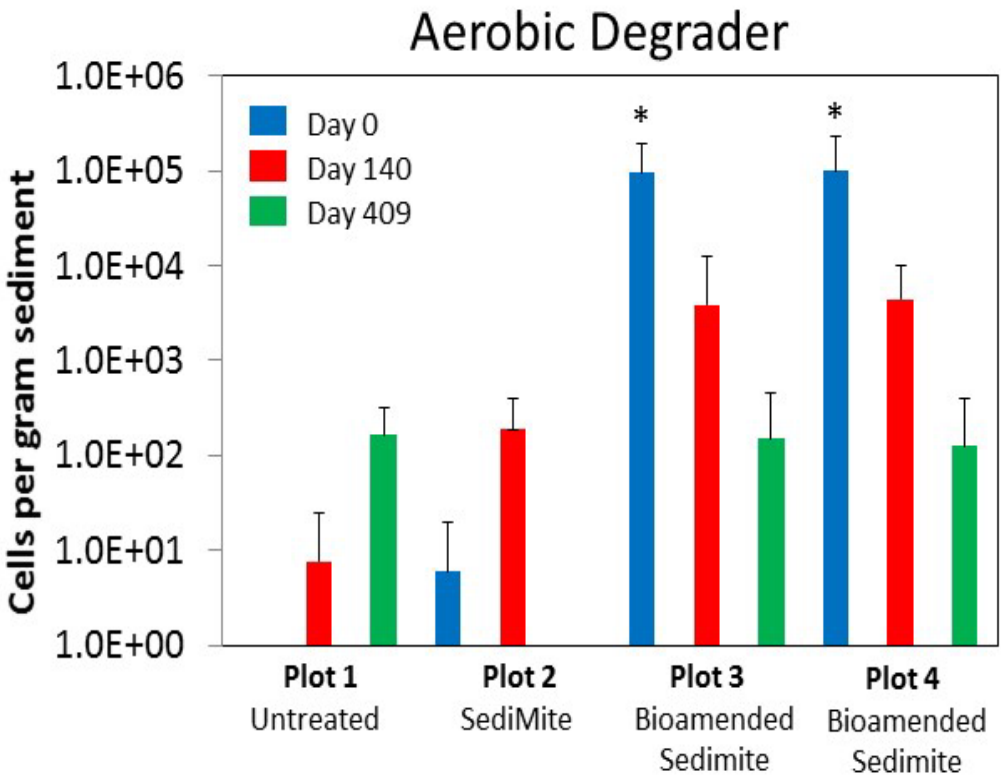
- Halorespirer and aerobic degrader decreased by 2-3 orders of magnitude after 409 days in plots 3 and 4



# Field Study Results

## *Bioamendment Titer*

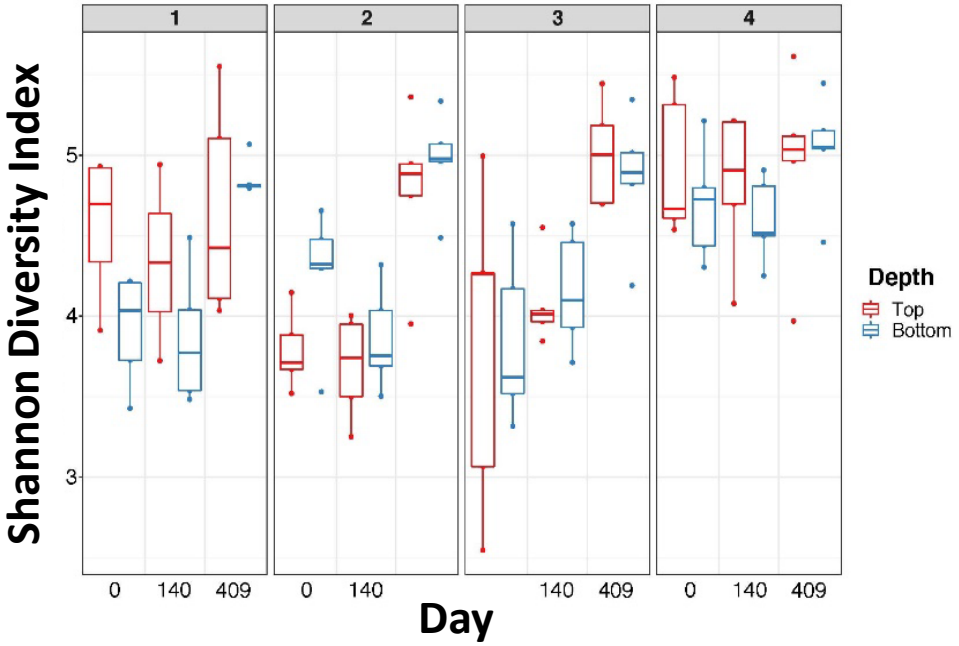
- Expected decrease due to low bioavailability of PCBs
- Despite the decrease the titer was 2-3 orders of magnitude greater than background levels after 409 days



# Effect of Treatments

## *Indigenous Bacteria*

- Microbial diversity
  - Not significantly different within plots, time points, or depths
  - Plot 4 significantly more diverse throughout study than other plots




*Bioaugmentation and the addition of activated carbon did not significantly alter total microbial diversity on a macroscale*

# Cost Assessment

***Comparison of total capital costs of implementation of remediation technologies for 7.8 acre pond in Abraham's Creek***

| Treatment Alternative | Total Capital Cost (2017 dollars) | O and M Cost | Total Annualized cost ($/acre) |
|---|---|---|---|
| **Alt 1: No further action** | 0 | 0 | 0 |
| **Alt 2: Monitored Natural Attenuation** | 130,000 | 520,000 | 83,333 |
| **Alt 3: Isolation cap** | 4,030,000 | 910,000 | 633,333 |
| **Alt 4: Excavation and on-site CDF** | 17,030,000 | 910,000 | 2,300,000 |
| **Alt 5: Excavate and off-site disposal** | 25,090,000 | 0 | 3,216,000 |
| **Alt 6: Partial excavation and off-site disposal** | 11,570,000 | 260,000 | 1,516,666 |
| **Alt 7: Capping and wetland creation** | 5,850,000 | 910,000 | 866,666 |
| **Alt 8: Reactive cap** | 4,030,000 | 910,000 | 633,333 |
| **Alt 9: Bioamended SediMite™ (present study)** | 1,767,920 | 910,000 | 343,323 |
| **Alt 10: SediMite™ only** | 1,096,720 | 910,000 | 250,840 |

*Costs for Alt 1-8 are based on 2008 Feasibility Study for the site (Battelle, 2008)*

# Summary

- Bioamendments were mass cultured, transported to site, delivered to sediments without significant loss of viability
- Significant reduction in total and soluble PCBs in bioamended plots
- Significant reduction in toxic equivalency (TEQ) of coplanar PCBs in bioamended plot 4
- No significant effect on indigenous bacterial community
- Long-term effects of treatment to be determined

# Acknowledgments


- Upal Ghosh
  - Sediment Solutions, LLC
- Harold D. May
  - Medical University of South Carolina, Marine Biomedicine and Environmental Science Center
- Jeff Vance
  - Brightfields, Inc.

# For additional information, please visit

https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Sediments/In-place-Remediation/ER-201215

## Speaker Contact Information

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# Q&A Session 2

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# The next webinar is on April 25, 2019

## *Accelerated Corrosion and Ageing Studies*

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# Survey Reminder

*Please take a moment to complete the survey that will pop up on your screen when the webinar ends*

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