

Passive dosing/sampling to measure PCB microbial dechlorination kinetics in sediments

Trevor Needham, Nathalie Lombard, and Upal Ghosh

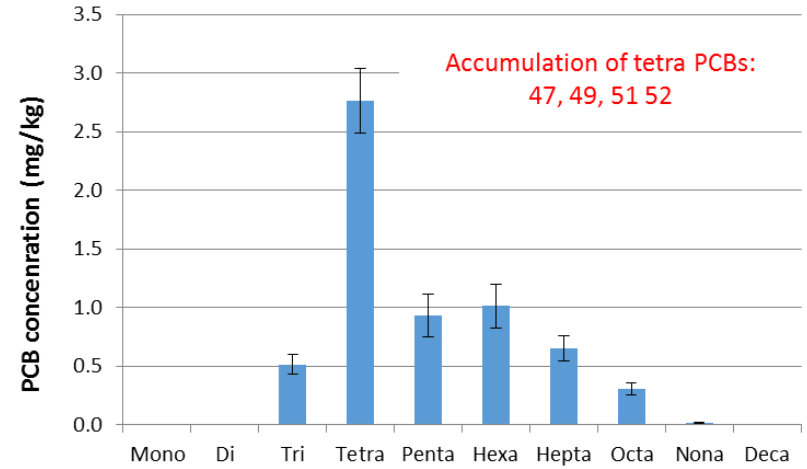
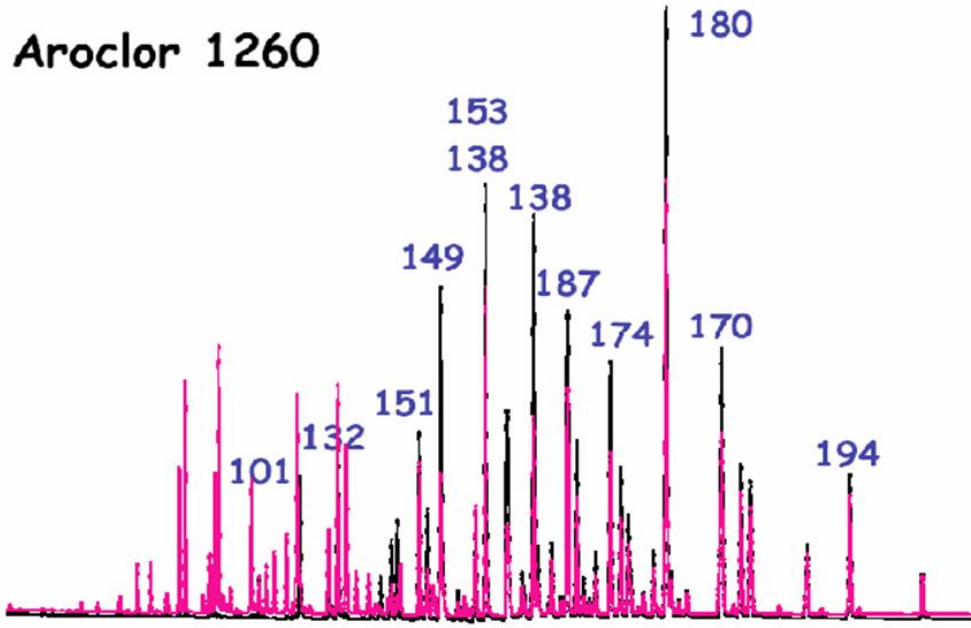
Department of Chemical, Biochemical, and Environmental Engineering

Kevin Sowers

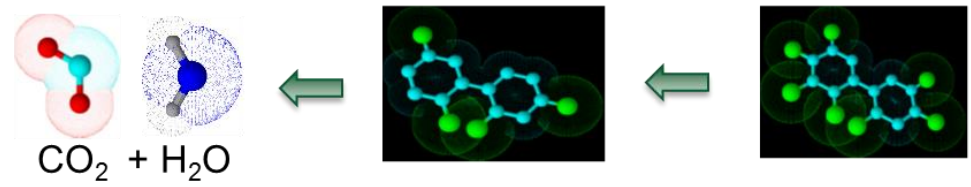
Institute of Marine and Environmental Technology

University of Maryland Baltimore County

How PCB Bioremediation Works



Aerobic Degradation
Anaerobic Dechlorination

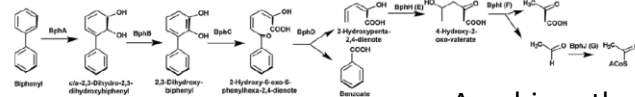
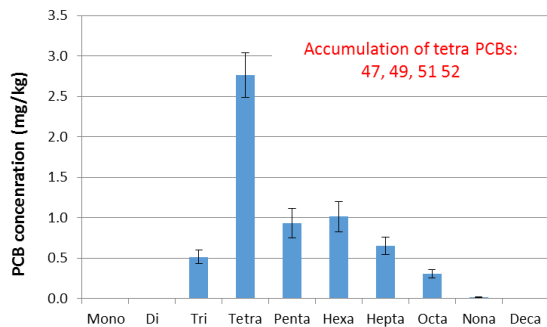


- Complementary activities of:
- 1) anaerobic halorespiring bacterium
 - 2) aerobic oxidizing/dechlorinating bacterium

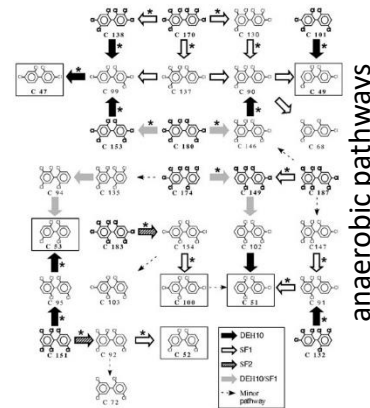
Microbial Biodegradation

- PCB aerobic degradation and anaerobic dechlorination observed 3 decades ago
- Aerobic transformation pathways reasonably well understood
- Dechlorination pathways identified; dechlorinators isolated and grown in the absence of sediments
- Biology reasonably well understood
- Anticipation of natural attenuation and engineering for remediation challenged by:

- poor mechanistic understanding of biotransformation kinetics
- issue of residuals after partial degradation



Aerobic pathway



anaerobic pathways

Polychlorinated Biphenyl Dechlorination in Aquatic Sediments

JOHN F. BROWN, JR., DONNA L. BEDARD, MICHAEL J. BRENNAN, JAMES C. CARNAHAN, HELEN FENG, ROBERT E. WAGNER

Science, 1987

In Situ Stimulation of Aerobic PCB Biodegradation in Hudson River Sediments

M. R. Harkness, J. B. McDermott, D. A. Abramowicz,* J. J. Salvo, W. P. Flanagan, M. L. Stephens, F. J. Mondello, R. J. May, J. H. Lobos, K. M. Carroll, M. J. Brennan, A. A. Bracco, K. M. Fish, G. L. Warner, P. R. Wilson, D. K. Dietrich, D. T. Lin, C. B. Morgan, W. L. Gately

Science, 1993

Long-Term Recovery of PCB-Contaminated Sediments at the Lake Hartwell Superfund Site: PCB Dechlorination. 1. End-Member Characterization

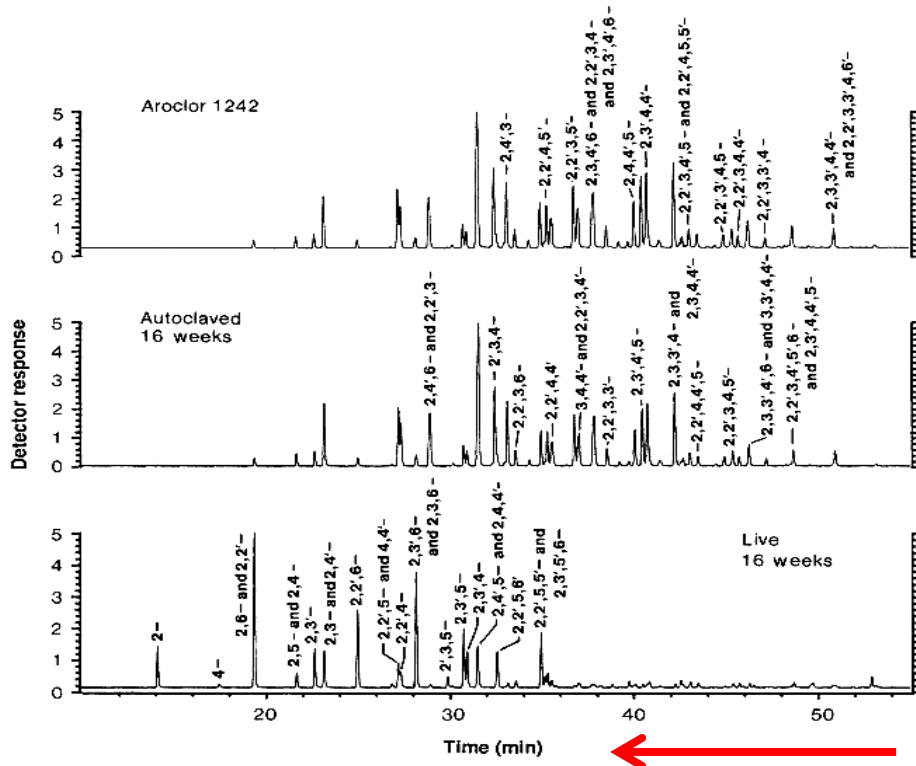
VICTOR S. MAGAR,*†
GLENN W. JOHNSON,‡
RICHARD C. BRENNER,§
JOHN F. QUENSEN, III,|| ERIC A. FOOTE,†
GREG DURELL,‡
JENNIFER A. ICKES,†,¶ AND
CAROLE PEVEN-MCCARTHY‡

U.S. Environmental Protection Agency, National Risk Management Research Laboratory, 26 West Martin Luther King Drive, Cincinnati, Ohio 45268, and Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio 43201

ES&T 2005



Microbial Biodegradation



Science, New Series, Vol. 242, No. 4879 (Nov. 4, 1988)

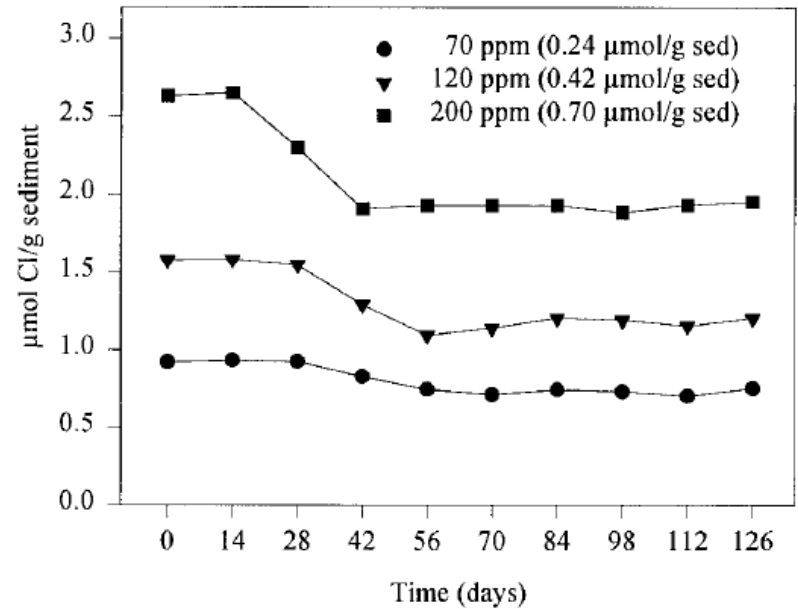


Fig. 3. The time course of dechlorination at various concentrations of Aroclor® 1248.

Rhee et al. ET&C 2001

- Began seeing shifts in PCB homolog distribution in historically contaminated sediments.
- Research investment by GE in the 80's and 90's.
- Initial successes in lab scale studies but unable to materialize significant results in field or pilot studies.

Traditional batch studies to measure microbial kinetics

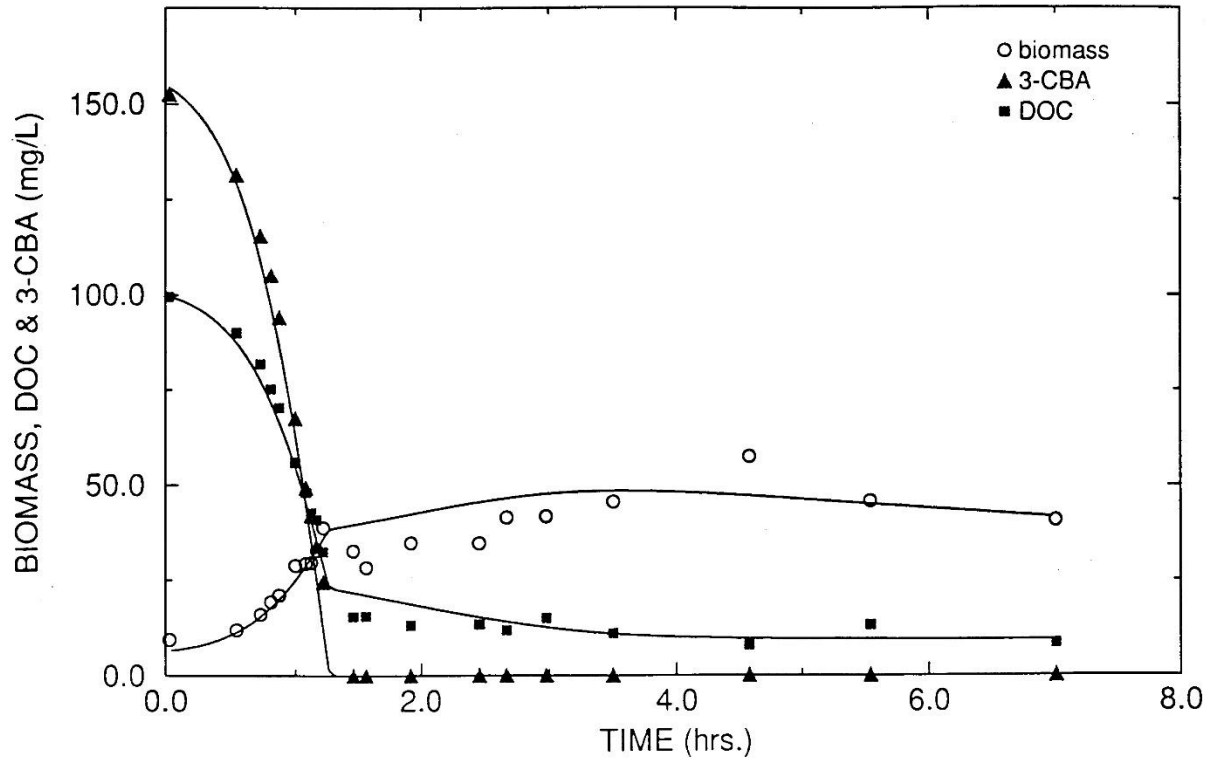


Figure 7.7. Batch from 3-day hydraulic detention time chemostat without replicate showing abnormally high biomass

Ghosh M.S. Thesis 1992

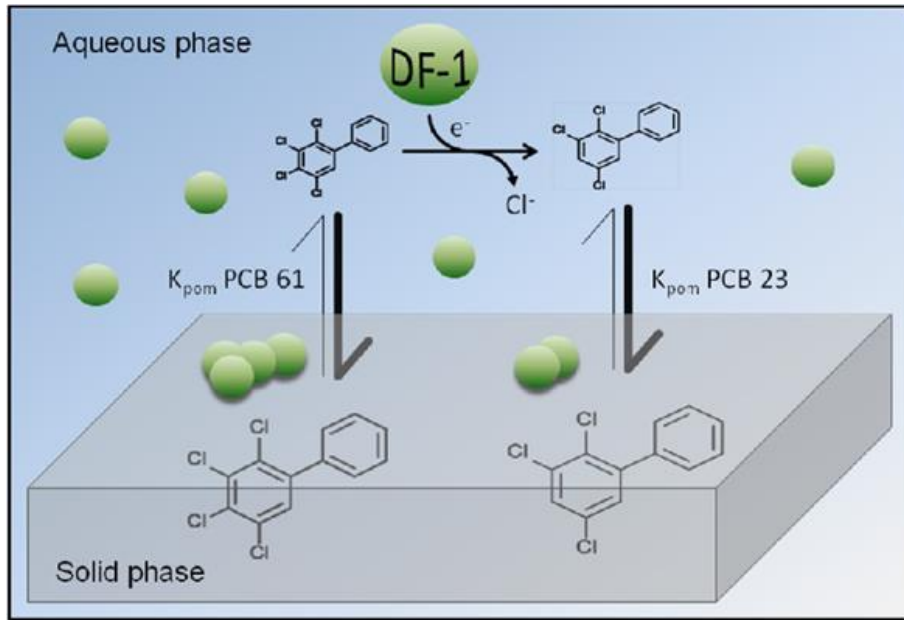
Challenges with measuring PCB dechlorination kinetics:

- 1) ultra low aqueous conc – sorption dominates
- 2) accurate quantification of the dechlorinators

New Understanding of PCB dechlorination kinetics

Kinetics and Threshold Level of 2,3,4,5-Tetrachlorobiphenyl Dechlorination by an Organohalide Respiring Bacterium

Nathalie J. Lombard,[†] Upal Ghosh,[‡] Birthe V. Kjellerup,[§] and Kevin R. Sowers^{*†}



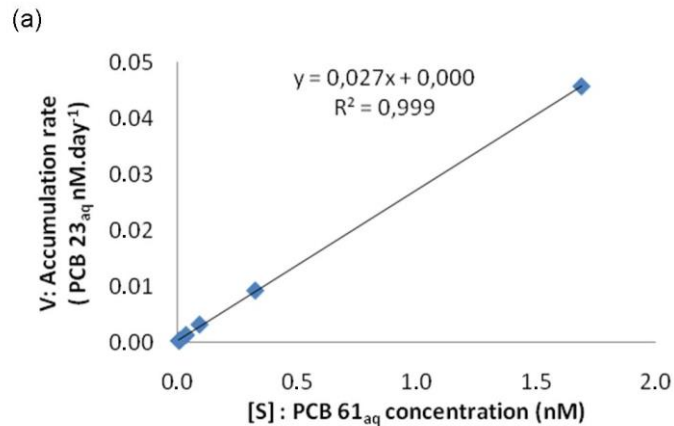
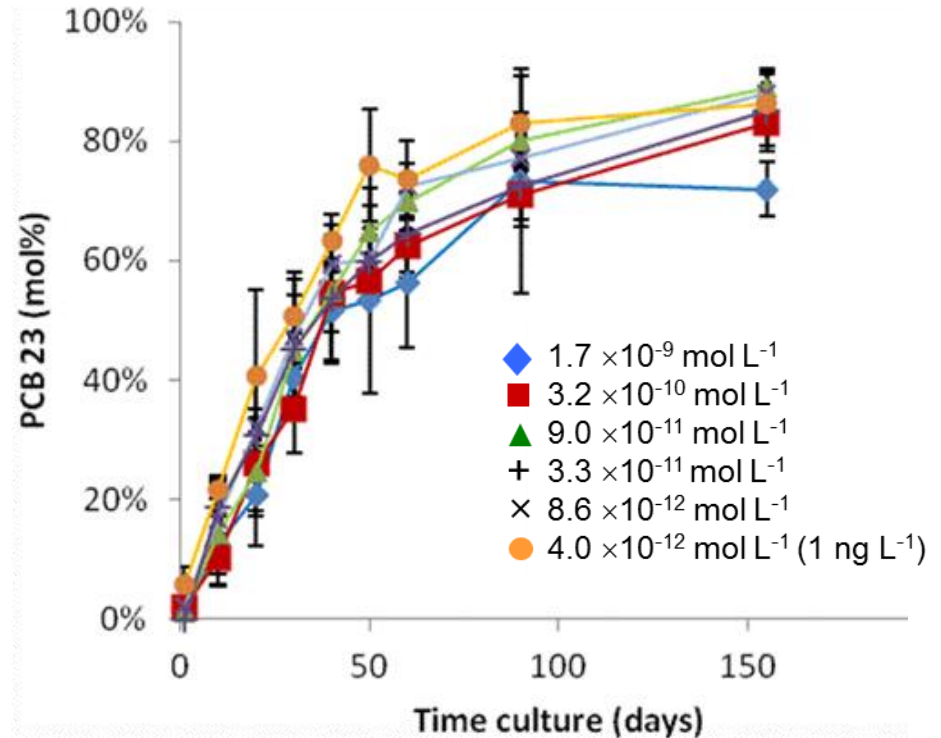
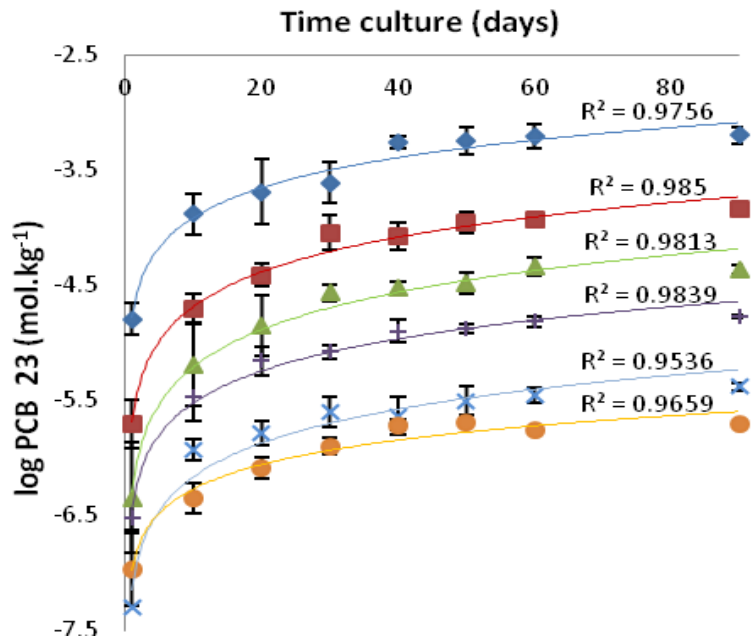
$$\frac{dC_w}{dt} \left(1 + \frac{m_s \cdot K_d}{V_w} \right) = C_w \cdot k_b$$

$$k'_b = \frac{k_b}{\left(1 + \frac{m_s \cdot K_d}{V_w} \right)}$$

The term in brackets in the denominator is the buffering capacity of the solid phase that attenuates the actual rate of degradation

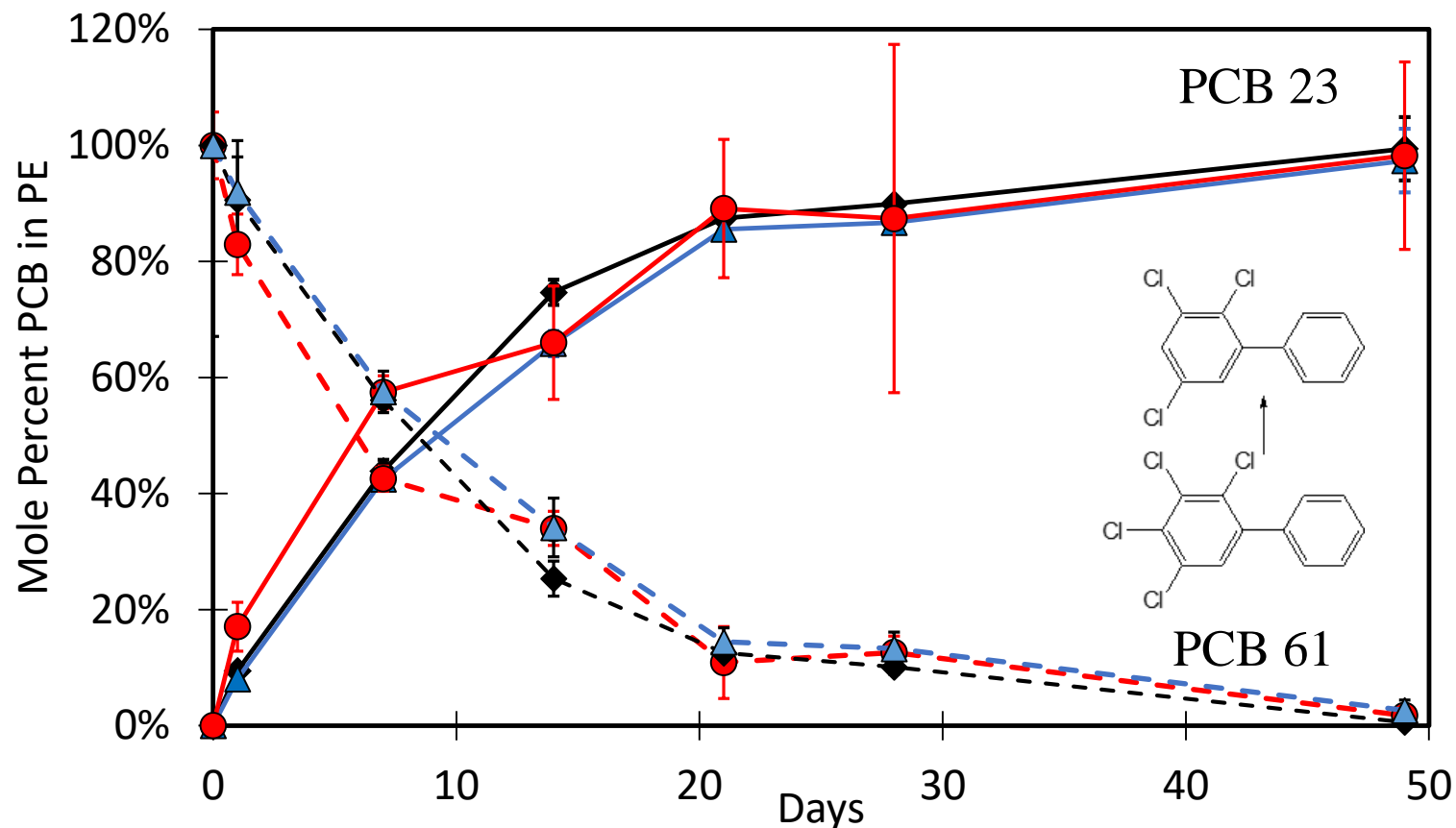
- PCB dechlorination rate at low aqueous concentration can be measured using passive dosing/sampling
- Mass transfer rate faster than dechlorination rate in well mixed batch

New Understanding of PCB dechlorination kinetics



- PCB dechlorination rate can be measured using passive dosing/sampling
- Rate of dechlorination linear function of PCB concentration
- Dechlorination observed down to 1 ng/L PCB concentration in water
- Rate constant same across 4 orders of magnitude

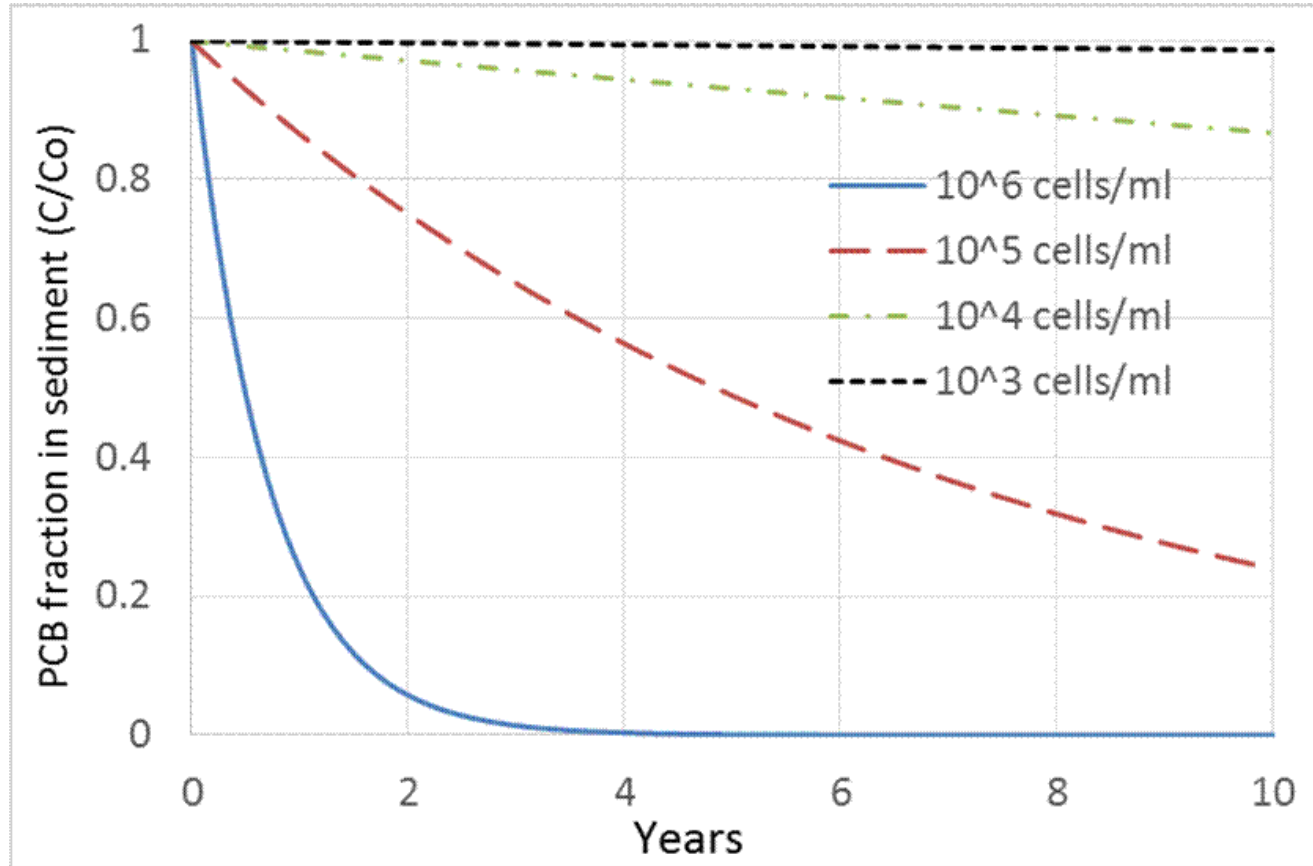
Validating work by Lombard et al. (2014)



Initial aqueous concentrations of PCB 61:

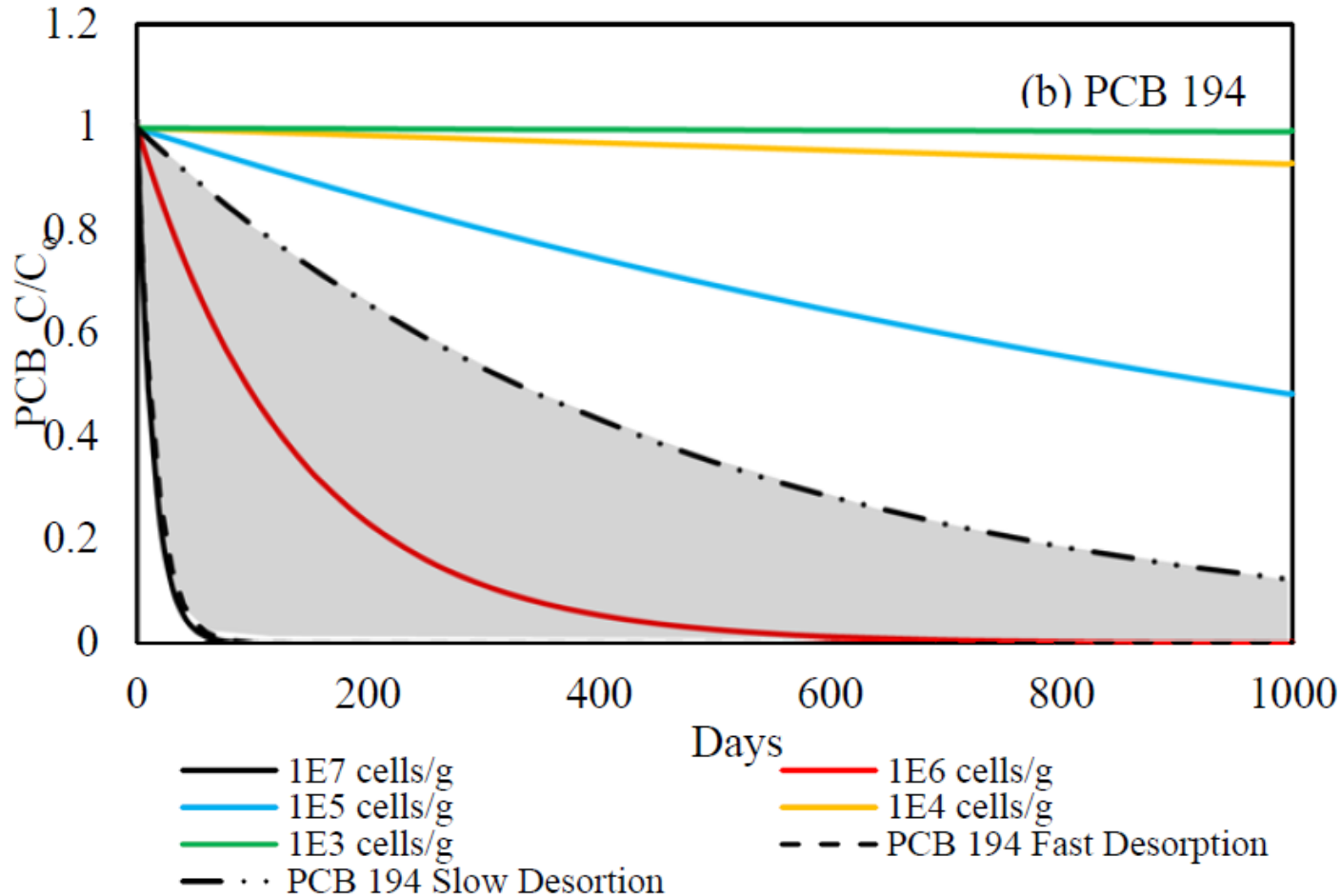
- 0.41 nM blue triangle
- 0.11 nM red circle
- 0.0043 nM black diamond

Explanation of slow PCB dechlorination kinetics in sediments



- Low rates in environment due to low cell numbers, not bioavailability thresholds
- Bioaugmentation increases rate of degradation
- Predictive models possible based on PCB porewater concentration, number of dechlorinating microorganisms, and sediment buffering capacity

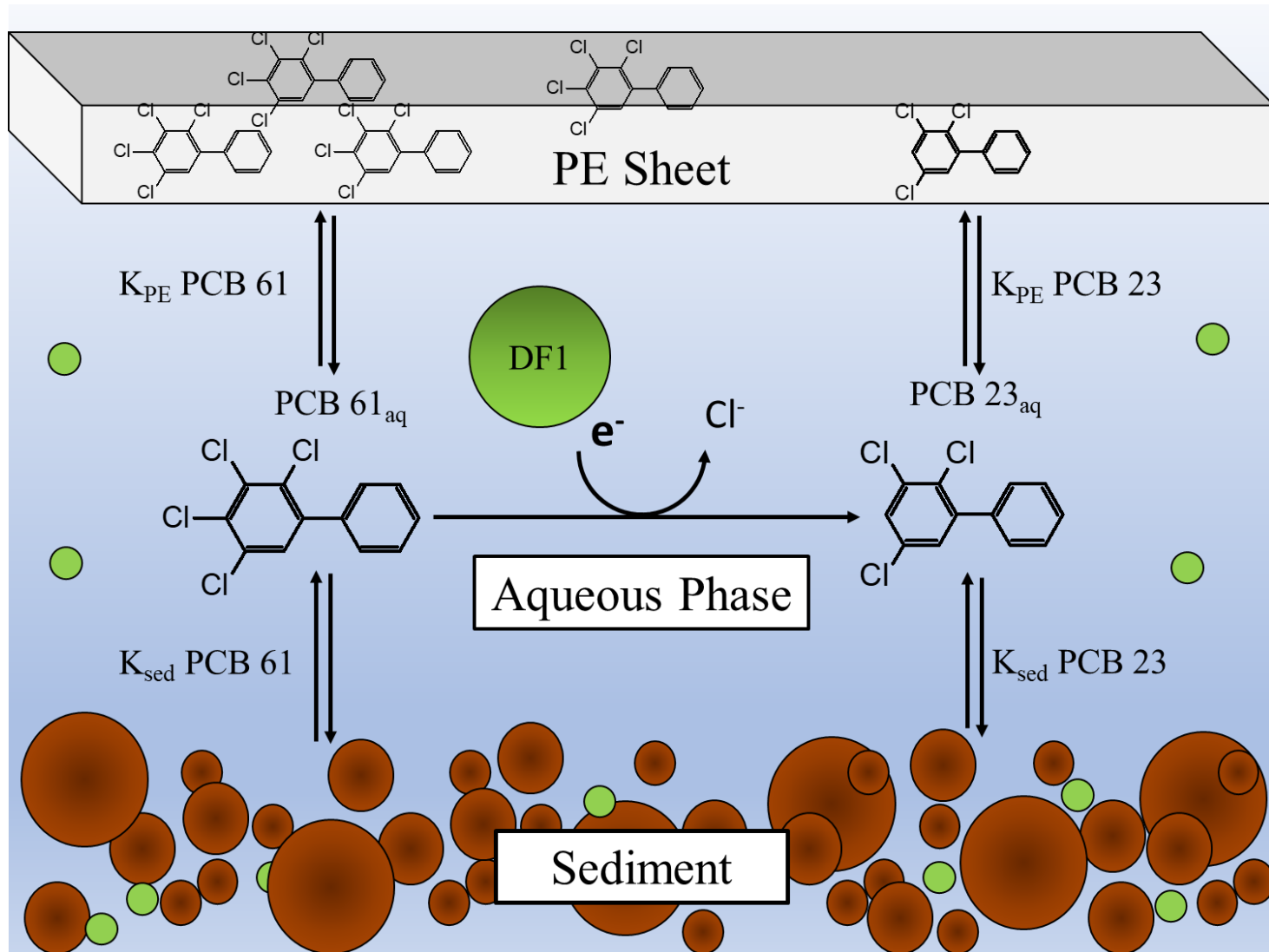
Desorption Rate vs Dechlorination Rate



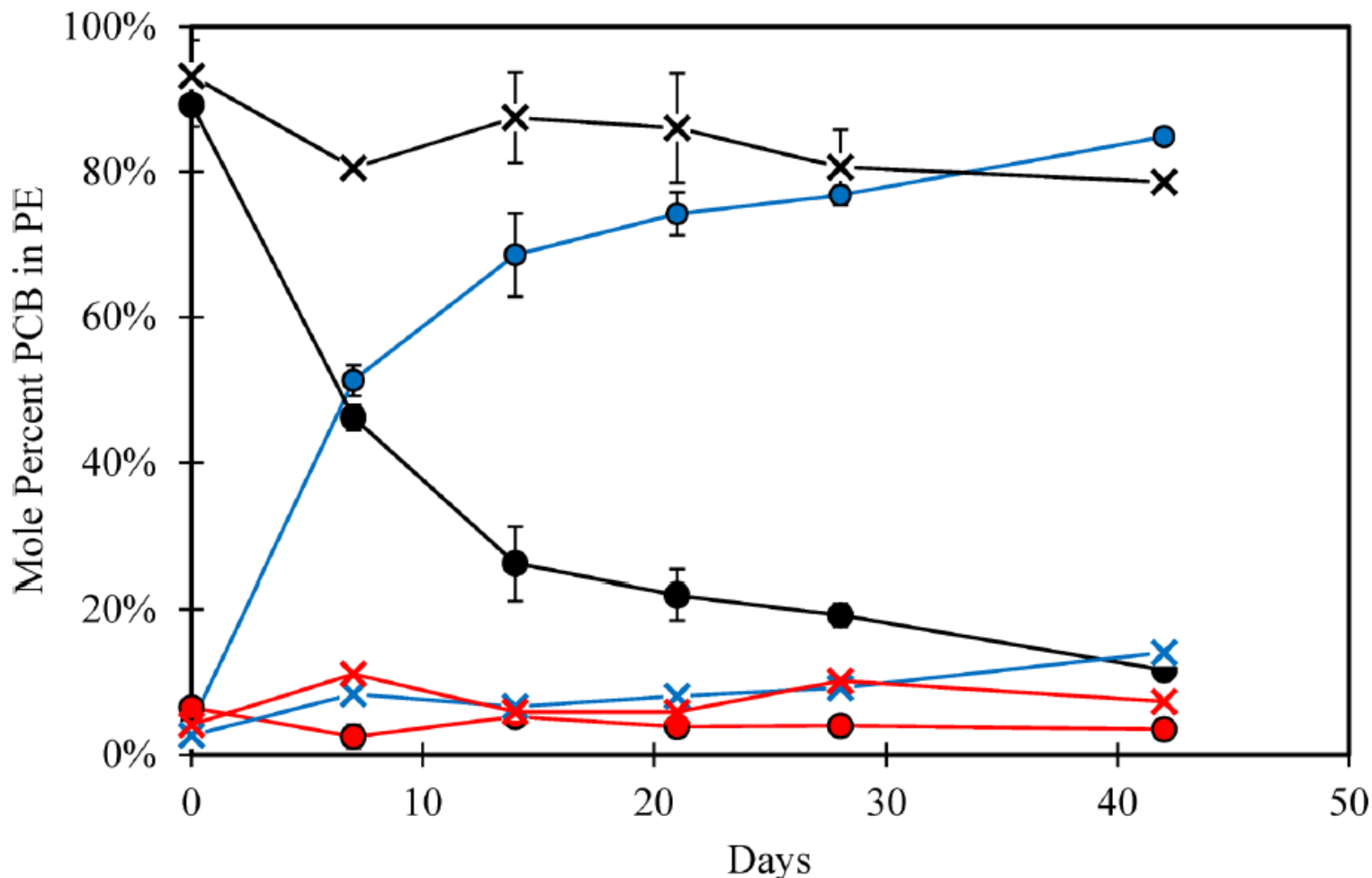
- PCB Desorption rates exceed dechlorination rates of indigenous halo-respiring populations
- Bioremediation increases dechlorination at rates similar to desorption rates

Needham *et al.*, submitted

Buffering due to sorption to solids

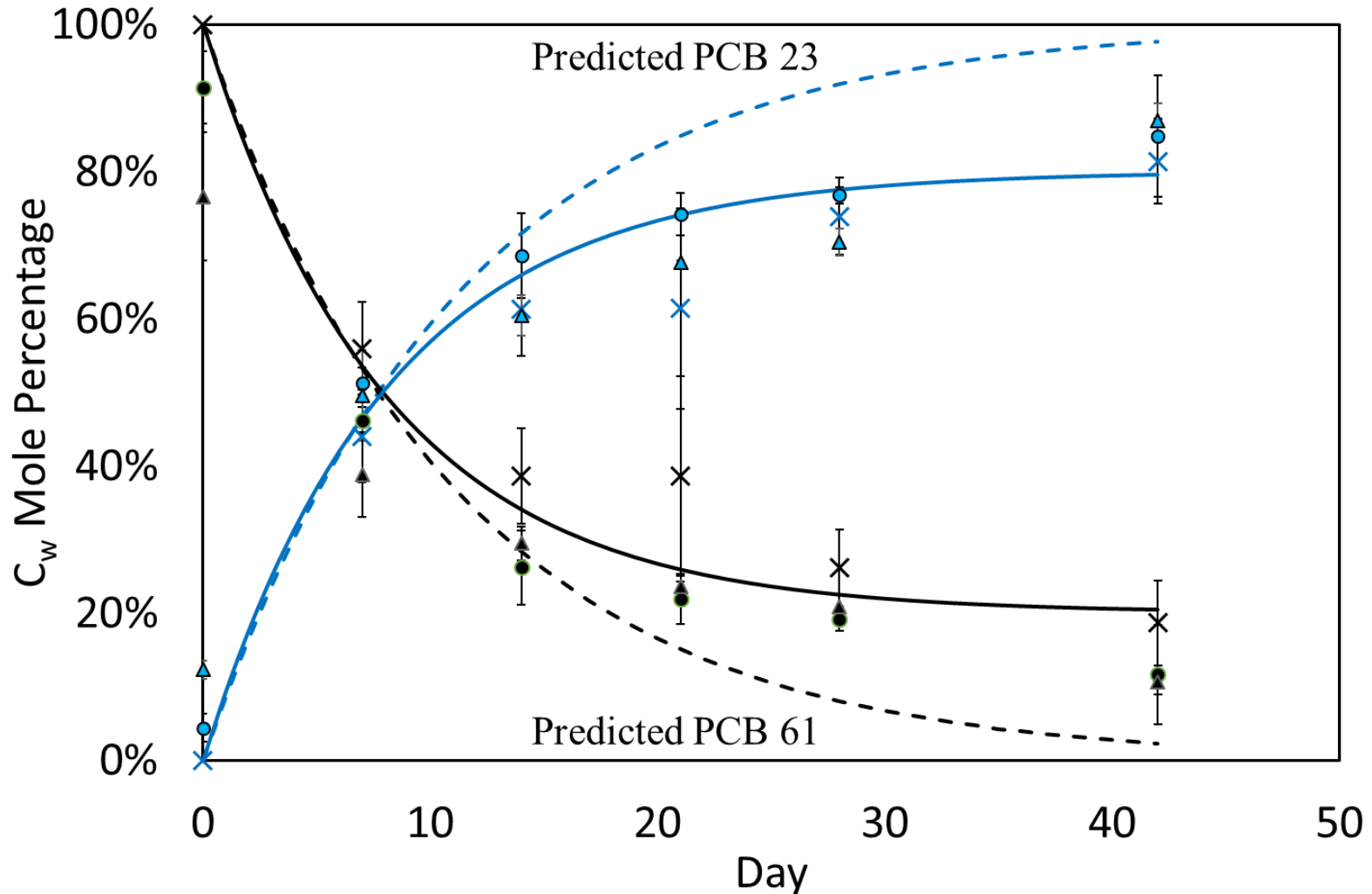


Dechlorination in sediment mecosoms



Comparison of PCB 61 dechlorination measured in unamended control sediment (x) containing a native microbial community and in DF-1-bioamended sediment (●): PCB 61 (black), PCB 23 (blue), and PCB 29 (red).

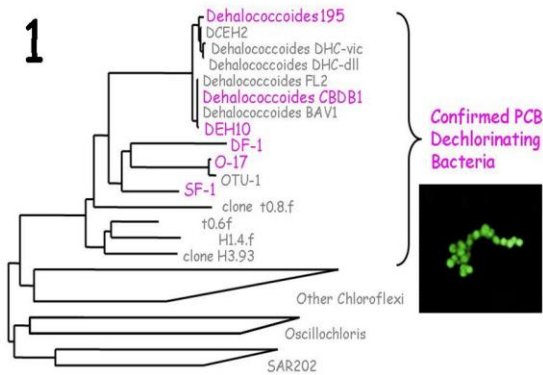
Predicting Dechlorination in Sediment Slurries



- Dechlorination in sediment explained by kinetics measured in sediment-free system
- About 20% residual PCB desorbs slower than microbial dechlorination

Technology Scaleup and Translation

1



3

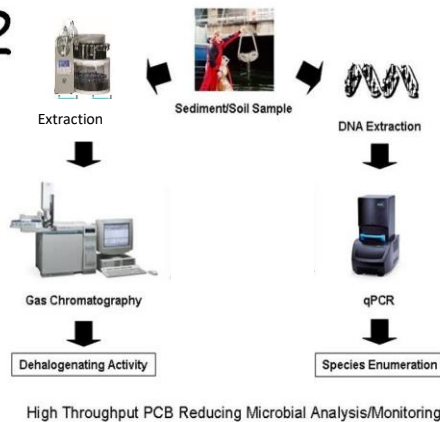


1) PCB anaerobic halo-respirer and aerobic degrader available

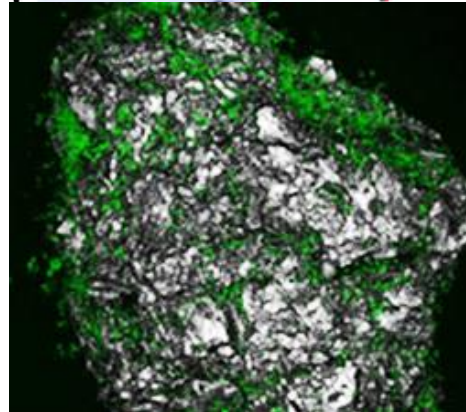
2) Assays developed for monitoring treatment and bioamendments

3) Methods developed for biomass scale-up of bioamendments w/o PCB

2

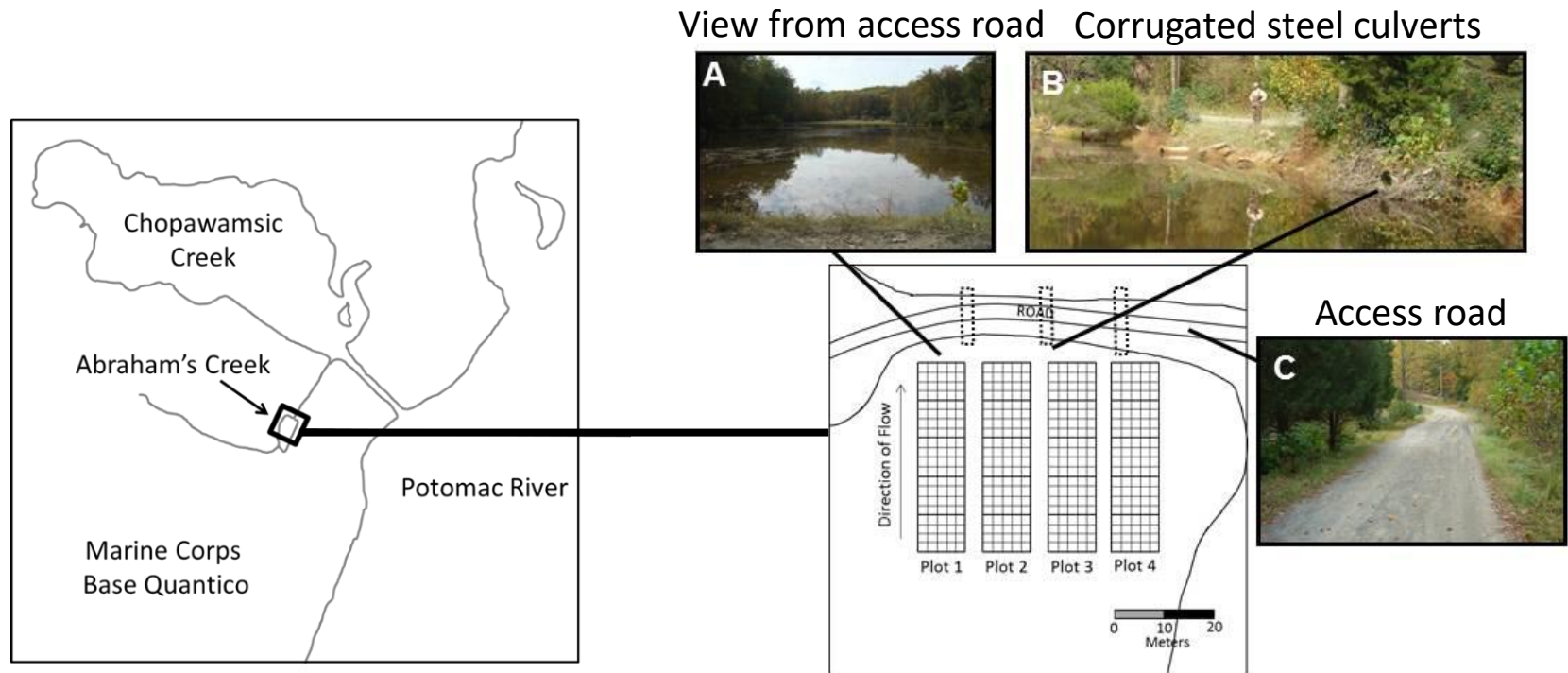


4



4) System developed for *in situ* deployment of bioamendments on activated carbon agglomerate

Abraham's Creek VA – April 2015



- Abraham's Creek MCBQ is an 8 acre/32,000 m² watershed outflow
- Original contaminant likely A1260
- Currently contaminated with an average 5 ppm PCB
- Treatments in four 400 sq. m plots
- Load rate = 1 ton SediMite + 10¹² cells/400 m²

Treatability Study-Experimental Design

Treatment	SediMite™	Cellulose	Cells g ⁻¹ sediment	Anaerobic Dechlorinator	Aerobic Degrader
1	-	-	-	-	-
2	3%	-	-	-	-
3	3%	0.03%	-	-	-
4	3%	0.03%	5×10^3	DF-1	LB400
5	3%	0.03%	5×10^4	DF-1	LB400
6	3%	0.03%	5×10^5	DF-1	LB400
7	3%	-	5×10^5	DF-1	LB400
8	3%	0.03%	5×10^5	SF1+DEH10	LB400
9	3%	0.03%	5×10^5	o-17	LB400
10	3%	0.03%	5×10^5	DF1+SF1+DEH 10+ o-17	LB400

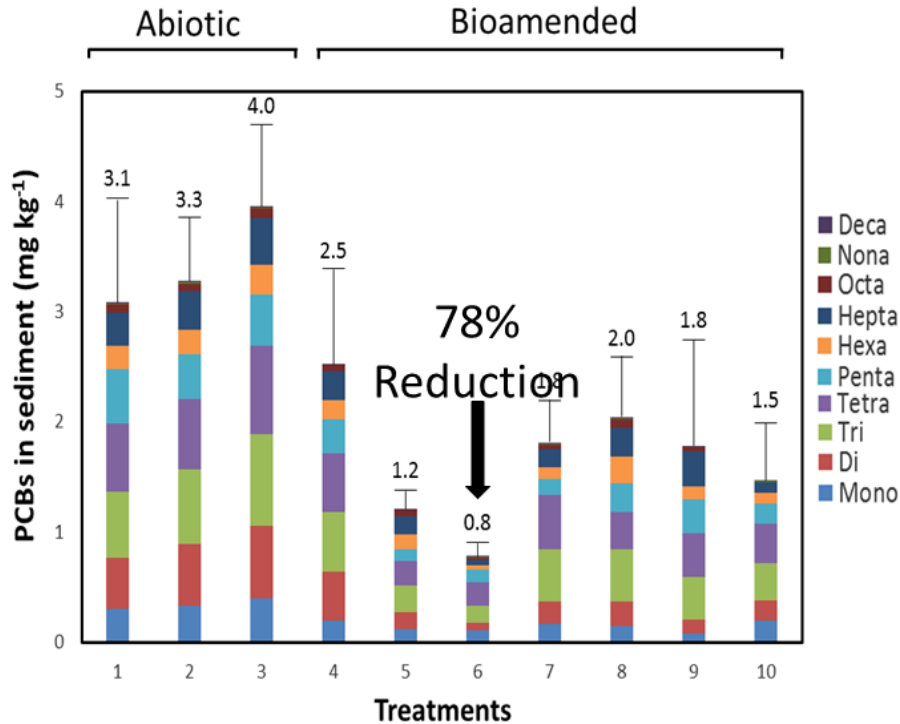


- Abiotic controls
- Bioamendment titer
- Bioamendment, no cellulose
- Different halorespirers

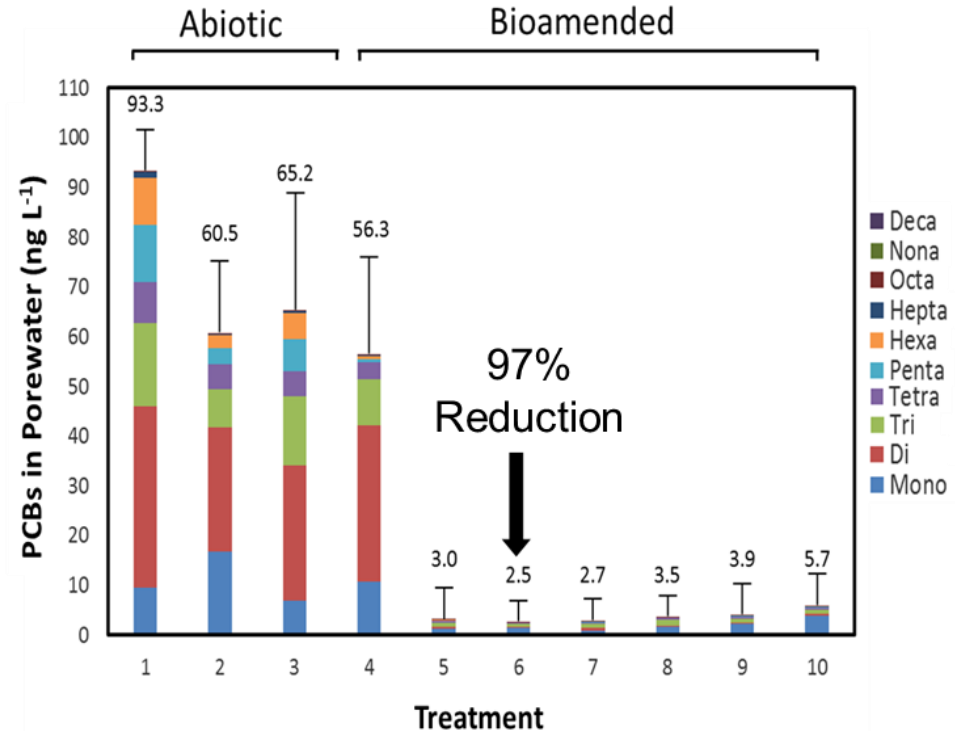
- 2 L recirculating mesocosms mimic *in situ* conditions
- Water is aerated to 6.8 mg/L and returned to system
- Tops sealed to minimize loss of PCBs from vapor phase
- XAD-2 resin to prevent build up of PCB products in water

Treatability Study-Results

PCBs in Sediment



Freely Dissolved PCBs

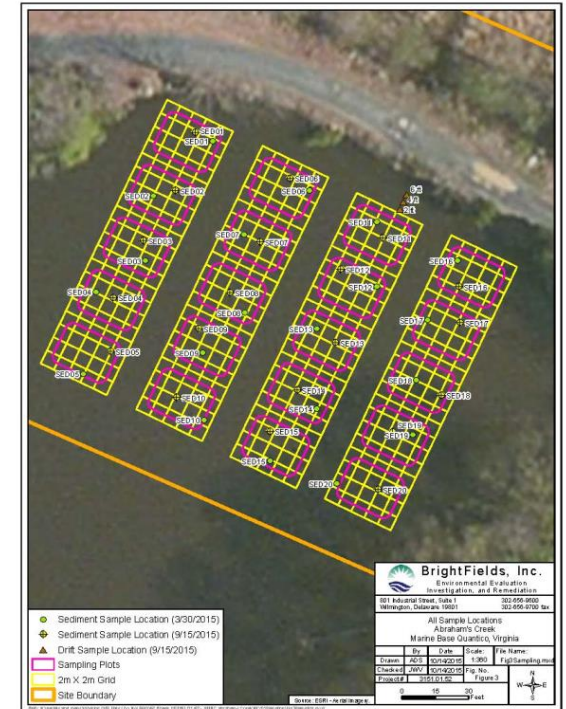
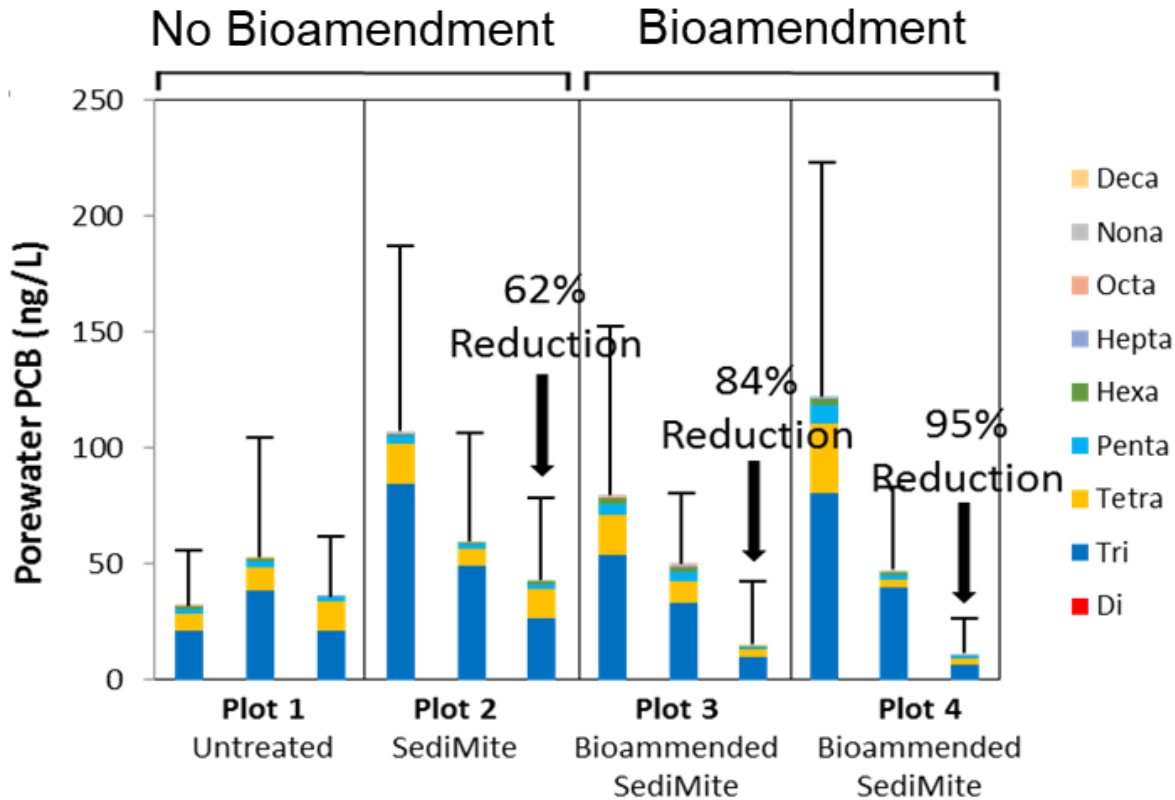


- Bioamending with 10⁵ cell/g yielded greatest reduction of PCBs after 375 days
- DF1 and LB400 were most robust bioamendments
- Addition of carbon source only slightly stimulated PCB degradation
- Mono- to nona-chlorobiphenyls were reduced = anaerobic & aerobic activity

Field Test-Deployment



Performance Assessment-Dissolved PCBs



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



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A Pilot-Scale Field Study: In Situ Treatment of PCB-Impacted Sediments with Bioamended Activated Carbon

Rayford B. Payne,[†] Upal Ghosh,[‡] Harold D. May,[§] Christopher W. Marshall,^{||,⊙} and Kevin R. Sowers^{*,†,⊙}



Full-Scale Applications

South Wilmington Wetland Park
Mouth of drainage outlet (14,150 sf)
Scheduled Apr 2019



Anne Arundel Co. former Formica
plant cooling pond (32,336 sf)
Tentatively Scheduled June 2019



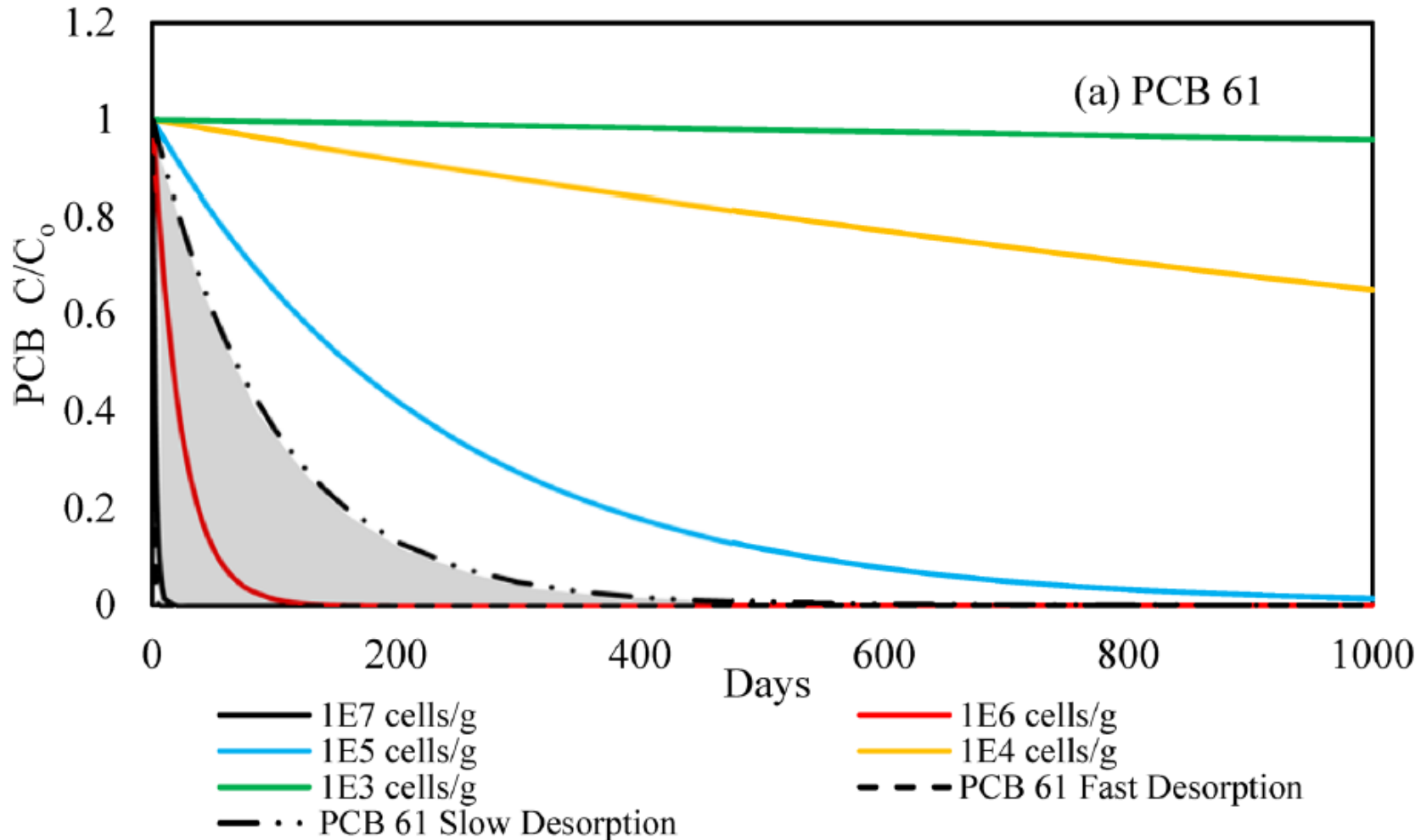
Contributors, Collaborators, Funding Source

- **Kevin R. Sowers & Ray Payne**
University of Maryland Baltimore County, IMET
- **Upal Ghosh and Trevor Needham**
University of Maryland Baltimore County, CBEE
- **Hal May**
Medical University of So. Carolina

Funding: SERDP, ESTCP, NIEHS, ONR

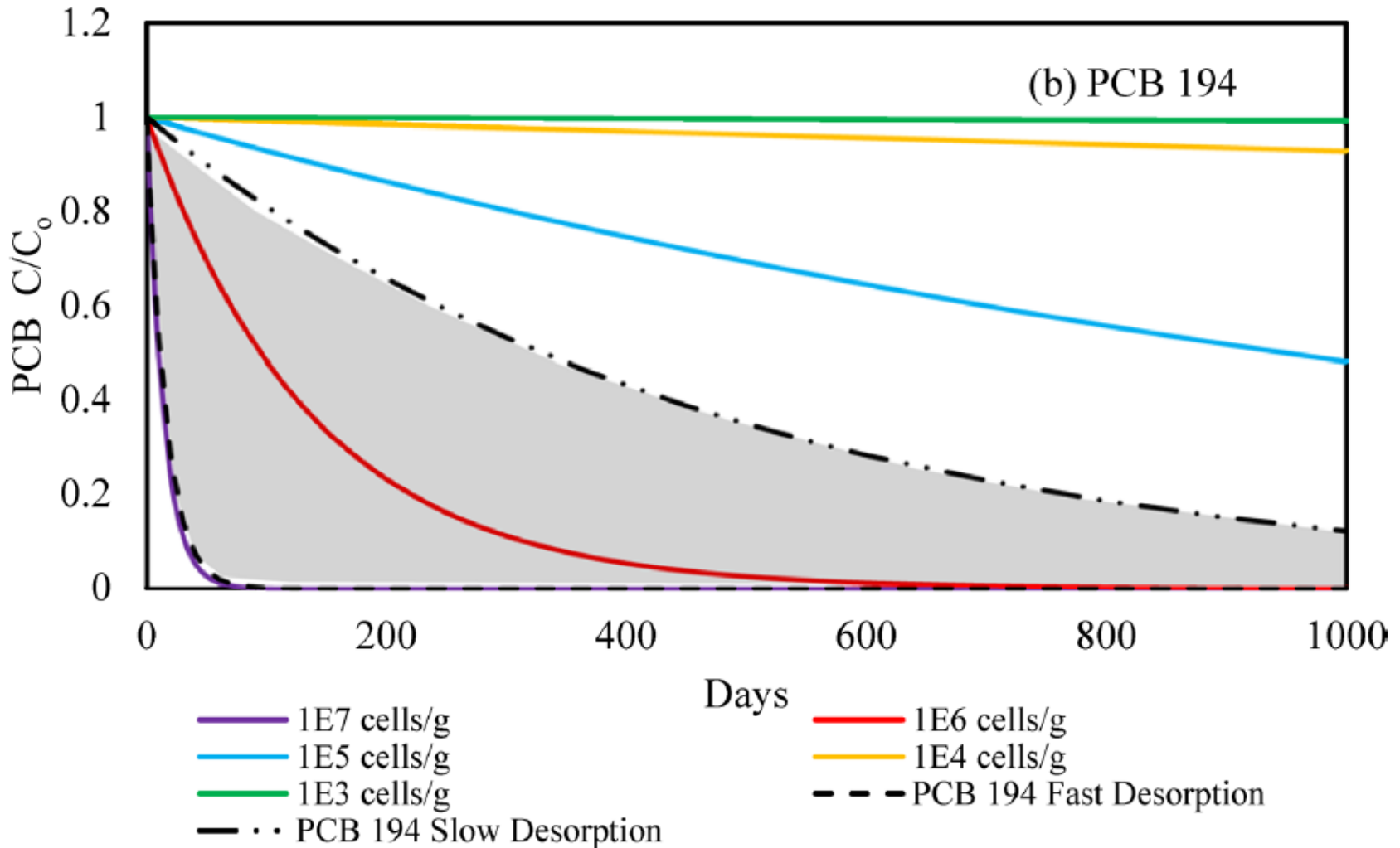


Predicting Dechlorination in Sediment Slurries



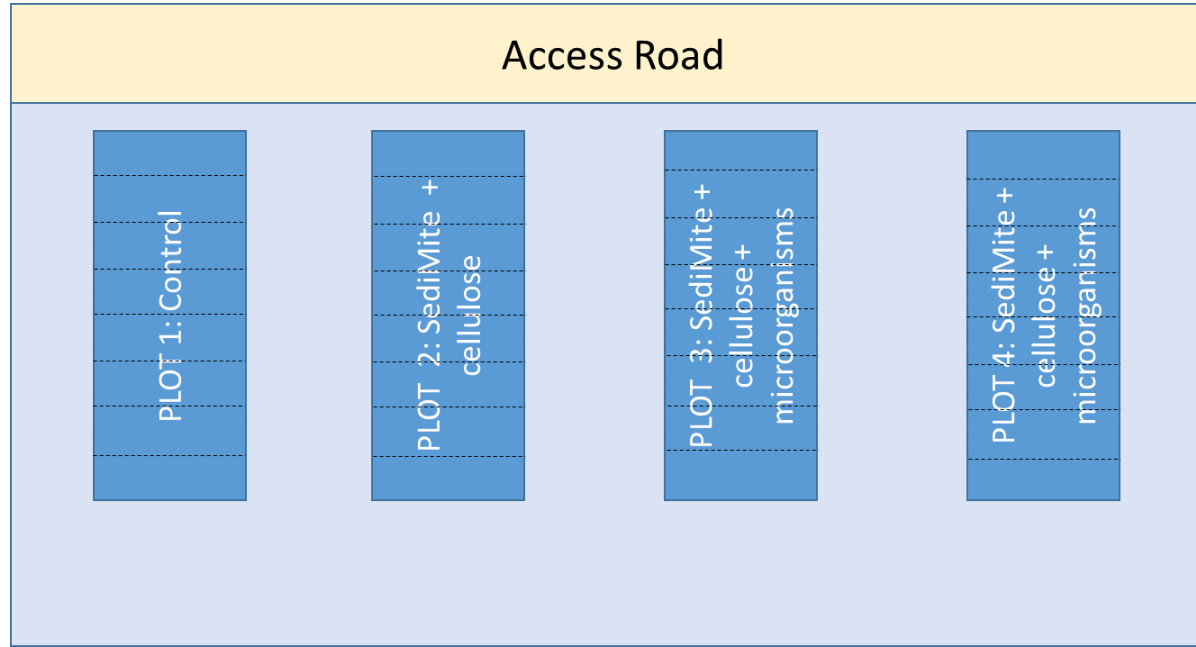
Effect of cell density of DF-1 on dechlorination rate compared with the rate of desorption of PCB 61. The shaded region depicts the range between fast and slow desorption rates estimated for Grasse River sediment.

Predicting Dechlorination in Sediment Slurries



Effect of cell density of DF-1 on dechlorination rate compared with the rate of desorption of PCB 194. The shaded region depicts the range between fast and slow desorption rates estimated for Grasse River sediment.

Field Test Design

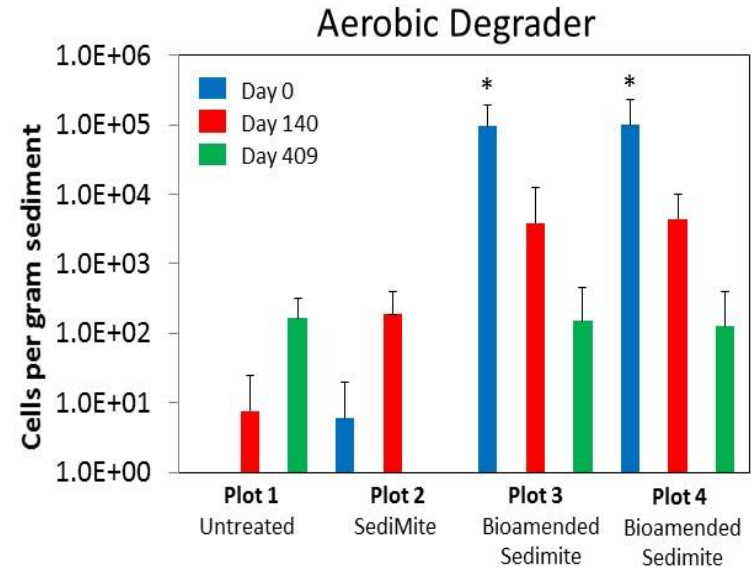
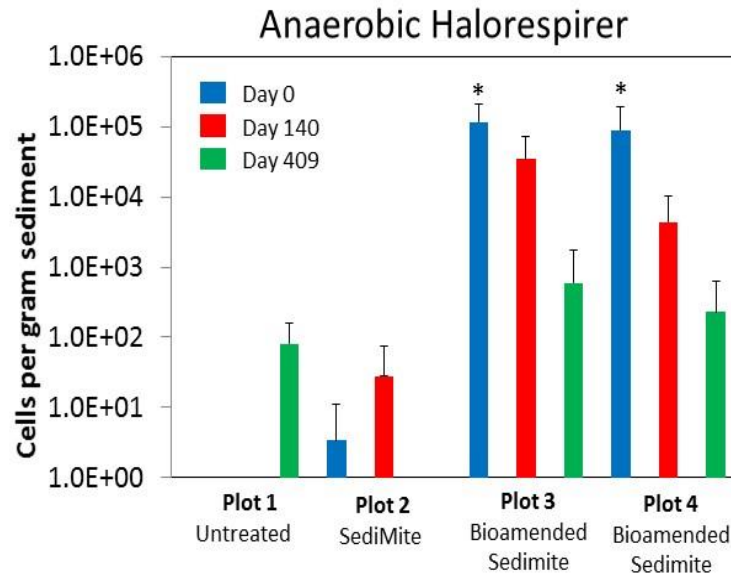


- Layout of four treatment plots each 400 m² in area
- Plot 1 – no treatment
- Plot 2 – SediMite containing cellulose as a slow release carbon source
- Plot 3/4 – SediMite/cellulose amended with anaerobic PCB dechlorinating DF1 and aerobic dechlorinating/oxidizing LB400

Field Test-Deployment

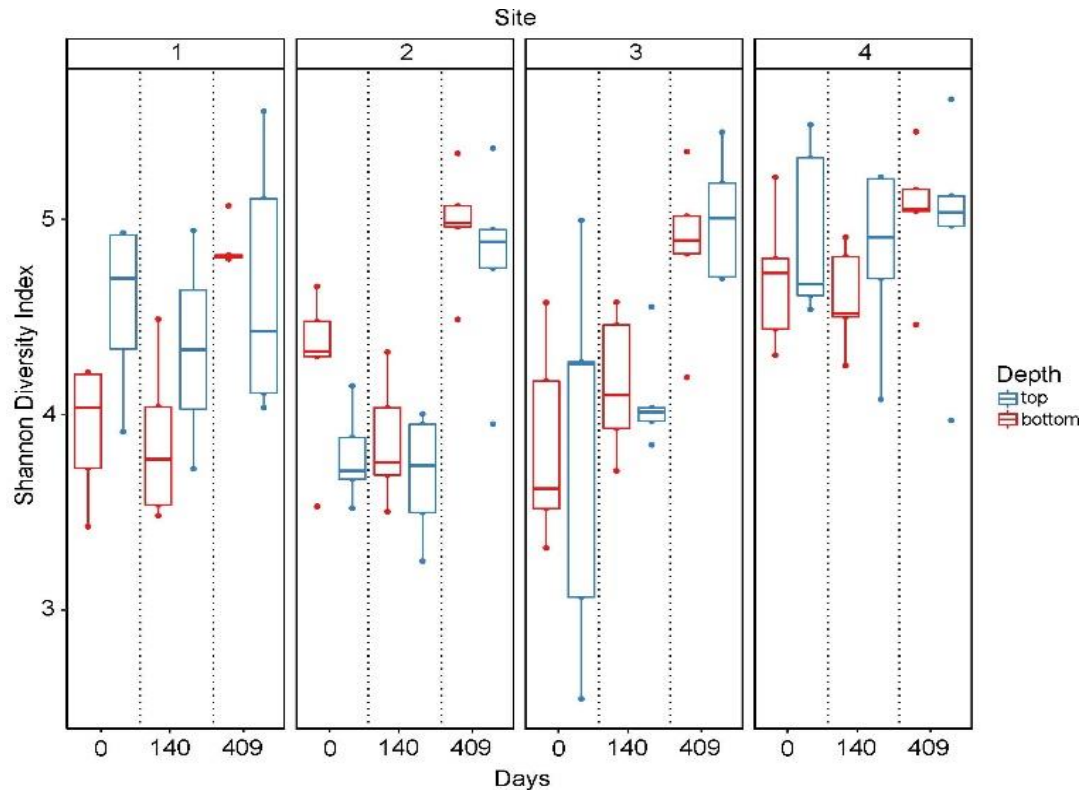


Fate of Bioamendments



- Halorespirer and aerobic degrader decreased by 2 to 3 orders of magnitude after 409 days in plots 3 and 4
- Similar decrease in cell numbers observed in the mesocosm treatability study after a similar period of time
- Despite the decrease the titer was 2-3 orders of magnitude greater than background levels after 409 days

Effect of Treatments on Indigenous Bacteria

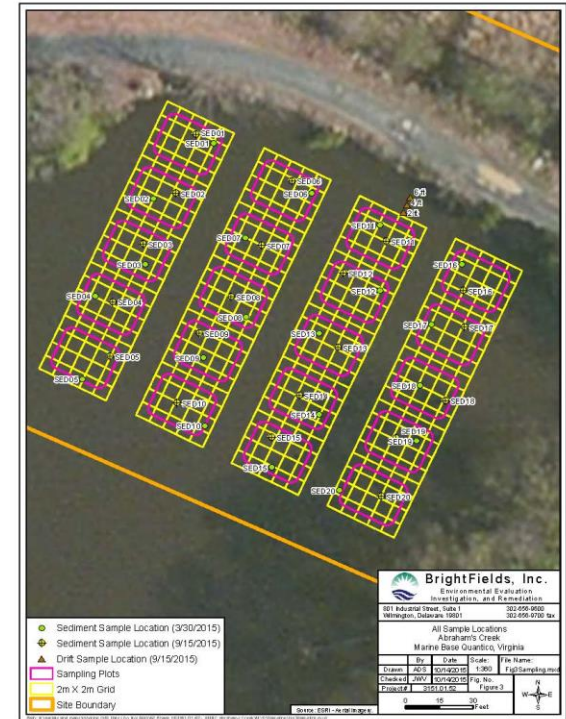
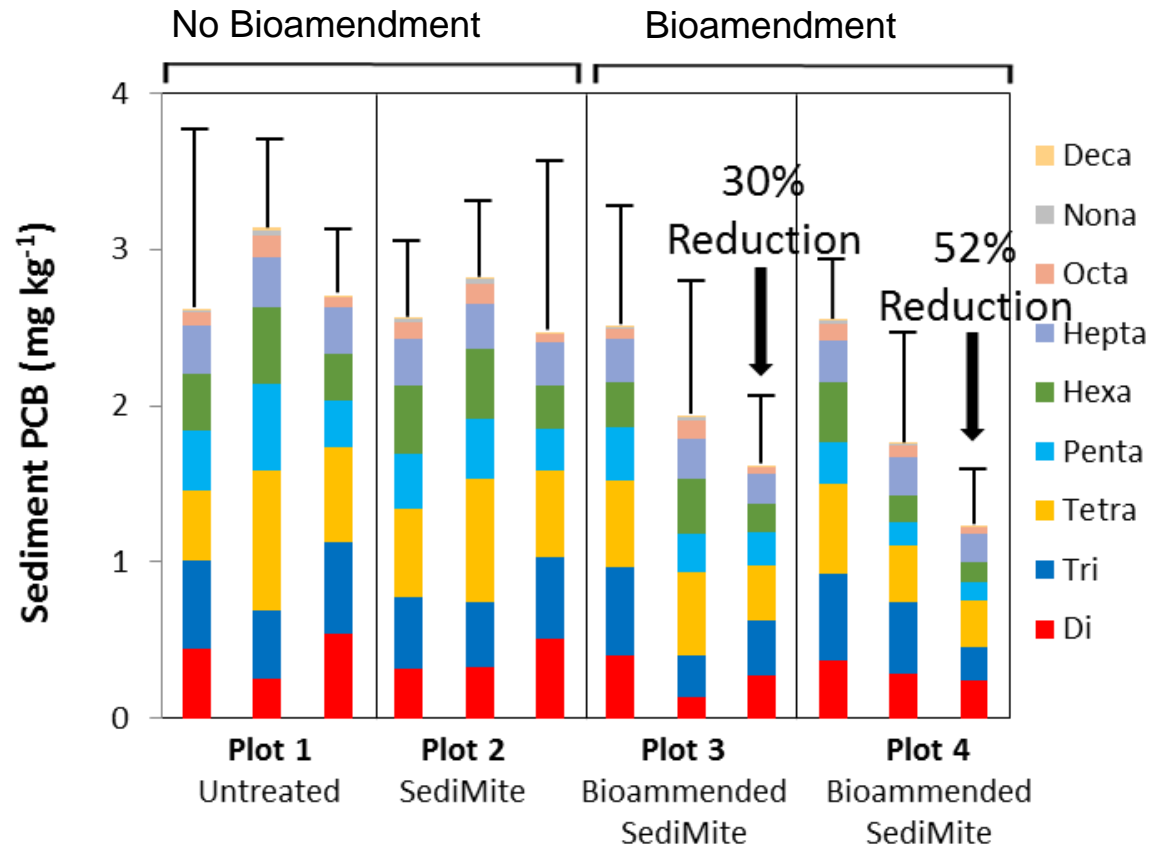


- Plot 4 began the experiment significantly more diverse than all other sites and remained significantly more diverse over 140 days
- The microbial diversity was not significantly different between any other sites, time points, or depths.
- Therefore, bioaugmentation and the addition of activated carbon did not significantly alter total microbial diversity on a macroscale.

Performance Summary

- The bioamended effectively reduces both the total mass and soluble fractions of PCBs and the AC serves as a delivery system, a solid substrate for maintaining the bioamendments and a strong adsorbent for soluble PCBs
- There was a direct relationship between the extent of degradation and the amount of bioamended AC applied indicating that uniform application is required to achieve consistent degradation throughout the site
- The treatment rapidly degrades the soluble and rapidly desorbing PCBs, then the process continues at a slower rate for the remaining slow desorbing PCBs
- The bioamendment was stable and did not migrate downstream of application in a stream with intermittent flow during rains and spring melts
- The treatment is well suited for environmentally sensitive sites, difficult to reach areas such as under piers, water margins, dredged materials and sites where dredging or capping are not options

Performance Assessment-Total PCBs



- Decrease in bioamended plots after 409 days
- 80% reduction in total mass of coplanar PCBs
- No significant change in untreated plots and below benthic zone
- Difference observed between Plots 3 & 4



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