

SUMMARY REPORT

Quantitative Thermodynamic Exposure Assessment (QTEA) Supporting Resilient Contaminated Sediment Site Restoration

SERDP Project ER-2431

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Final Report

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TABLE OF CONTENTS

Executive Summary	1
1. Introduction.....	3
1.1. Background	3
1.2 Objective	8
2. New Bedford Harbor sediment mesocosm experiments - Methods	10
2.1. Site overview.....	10
2.2. Experimental sediments	10
2.3. Mesocosm experiment series	12
2.4. Mesocosms set-up, maintenance and experiment termination.....	13
2.5. Chemical analysis.....	20
3. New Bedford Harbor sediment mesocosm experiments – Remedy effectiveness	21
3.1. The effect of the presence of biota and baseline for evaluating treatments	21
3.2. Effectives of remedies in reducing bioaccumulation	24
3.3. Bioaccumulation of Highly Hydrophobic PCBs.....	29
3.4. “Mobile AC” Amendment to the Surface Water	32
3.5. Overall trends for treatment effectiveness for reducing the bioaccumulation of input PCBs	34
4. New Bedford Harbor sediment mesocosm experiments Cross validation of two polymer sampling approaches.....	36
5. New Bedford Harbor sediment mesocosm experiments –Thermodynamic exposure assessment (TEA)	39
6. Gould Island sediment mesocosm experiments.....	55
6.1. Remedy effectiveness assessment.....	55
6.2. Tier 1 TEA – A comparison of NBH and GI	58
7. Batch experiments evaluating the benefit of low-level activated carbon application	62
8. Food Web Model predictions for PCB uptake in functionally diverse aquatic organisms used in mesocosm experiments	65
9. RECOVERY 5.0: A contaminated sediment-water interaction model.....	74
9.1. Introduction	74
9.2. Model formulation.....	76
9.3. Modifications to allow upwelling of groundwater	77
9.4 RECOVERY Testing	80

9.5. Results	84
9.6. Summary	93
10. RECOVERY-NL A contaminated sediment-water interaction model	94
10.1 Introduction	94
10.2. Partitioning	97
10.3. RECOVERY Testing	97
10.4. No Action/Existing Conditions	97
10.5. Results	99
10.6. Summary	102
11. Conclusions.....	103
12. References.....	105
Appendix A – List of ER-2431 Peer-reviewed Publications and Dissertations	115
Appendix B – List of ER-2431-related Presentations.....	117
Appendix C: New Bedford Harbor RECOVERY Simulations Coupled with Food Web Model: Implementing Sediment Remediation.....	119

LIST OF TABLES

Table 1. Specifications on the New Bedford Harbor experimental sediment.....	11
Table 2. Specifications on the Bayou Lafourche experimental sediment.	12
Table 3. Brief description of the diversity in the experimental organisms selected to comprehensively assess sediment remediation efficacy across functionally distinct species.	14
Table 4. Contaminant parameters.....	80
Table 5. Contaminant Parameters	97
Table 6. Values Used in the RECOVERY Evaluation.....	98

LIST OF FIGURES

Figure 1. Conceptual model of contaminant pathways at a contaminated sediment site.....	4
Figure 2. Series of 6 New Bedford Harbor (NBH) sediment mesocosm experiments.	13
Figure 3. <i>Alitta virens</i> and <i>Mercenaria mercenaria</i> prior to being added to experimental mesocosms	15
Figure 4. Juvenile <i>Cyprinodon variegatus</i>	15
Figure 5. Mesh cage with partition for housing. <i>Cyprinodon variegatus</i> in experimental mesocosms.	16
Figure 6. General view of experimental mesocosms.	16
Figure 7. Schematic showing volume of contaminated sediment, volume of overlying water and number and mass of experimental organisms added to each experimental mesocosms.....	17

Figure 8. Input sediment being added as a slurry to an experimental mesocosm.....	18
Figure 9. Low density polyethylene (LDPE) passive sampler “strip” inserted into sediment bed at an angle (A.) and LDPE passive sampler “disc” suspended in the water column using aviation wire (B.)	19
Figure 10. Profiles of equilibrium concentrations of PCB 44 + 49 (native bed congeners) in LDPE located at different heights in the mesocosms for experiment 1 (E1, no biota) and E2 (with biota).	21
Figure 11. Freely-dissolved concentrations (C_{free}) of PCB 44 + 49 (native bed congeners) in the water column of mesocosms for experiments 1 and 2	22
Figure 12. Profiles for each mesocosm in E2 that received spiked influx. Stacked bars show lipid normalized bioaccumulation in biota with the scale at the top of the graphs.	23
Figure 13. Lipid normalized bioaccumulation in worms for the NBH series of experiments. Top row shows input congeners, bottom row shows native bed congeners. Low chlorinated congeners are on the left and highly chlorinated congeners are on the right.	25
Figure 14. Lipid normalized bioaccumulation in clams for the NBH series of experiments. Top row shows input congeners, bottom row shows native bed congeners. Low chlorinated congeners are on the left and highly chlorinated congeners are on the right.	26
Figure 15. Lipid normalized bioaccumulation in fish for the NBH series of experiments. Top row shows input congeners, bottom row shows native bed congeners. Low chlorinated congeners are on the left and highly chlorinated congeners are on the right.	28
Figure 16. Bioaccumulation in clams and fish for “highly hydrophobic” PCBs (ng PCBs/g lipid) for E2 (control), E3 (AC mix), and E4 (sand cap).	30
Figure 17. Bioaccumulation worms for “highly hydrophobic” PCBs (ng PCBs/g lipid) for E2 (control), E3 (AC mix), and E4 (sand cap). Bioaccumulation plots from Figure 18 are also shown for comparison.	31
Figure 18. The effect of “mobile” AC on fish bioaccumulation	32
Figure 19. The effect of “mobile” AC on clam bioaccumulation	33
Figure 20. The effect of “mobile” AC on worm bioaccumulation	34
Figure 21. Measurement of the total input PCBs in biota (ng PCB/g lipid; left y-axis) and bulk concentrations OC normalized prior of input sediment (ng PCB/g OC) sampled prior to addition to the mesocosms.	35
Figure 22. Relation between Dow Corning (DC) silicone: water partitioning (KDC:w) and octanol: water partitioning (KOW)	37
Figure 23. Comparison of the two polymer methods on the basis of C_{free} for all congeners in Experiments 1, 2, and 3.	38
Figure 24. PCB congener concentrations in silicone <i>Alitta virens</i> lipid from 90-day mesocosm experiments containing New Bedford Harbor sediment.	40
Figure 25. PCB congener silicone concentrations versus PCB congener clam (<i>Mercenaria mercenaria</i>) lipid concentration from 90-day mesocosm experiments containing New Bedford Harbor sediment.	41
Figure 26. PCB congener silicone concentrations versus PCB congener fish (<i>Cyprinodon variegatus</i>) lipid concentration from 90-day mesocosm experiments containing New Bedford Harbor sediment.	42

Figure 27. Measured lipid concentrations versus predicted (or the thermodynamic potential from the sediment). Here, silicone concentrations were converted to lipid concentration (using silicone:lipid partitioning from Gilbert et al. 2016).	44
Figure 28. Reference levels in lipid of native bedded PCB congeners in different media of the control (E2).	45
Figure 29. Concentrations in silicone and LDPE (surficial sediment sampled) plotted against worm lipid for clean and spiked input mesocosms of the control experiment. 2X and 10X bands are provided.	48
Figure 30. Thermodynamic potential from the sediment (or predicted lipid) versus measured concentrations in lipid (worms only, E2 and E3).	49
Figure 31. Thermodynamic potential from the sediment (or predicted lipid) versus measured concentrations in lipid (worms, clams, and fish, E2 and E3). Similar to Figure 30 above for worms only.	50
Figure 32. Comparing Fish to LDPE discs in the water column and LDPE strips in the sediment (both corrected for equilibrium using PRCs) for E2.	52
Figure 33. Comparing Fish to LDPE discs in the water column (corrected for equilibrium using PRCs) for E2, E3, E4, E5 and E6.	53
Figure 34. Fraction of PCB congeners remaining in lipid in equilibrium with the sediment determined from silicone coated jars	54
Figure 35. Matched congeners in LDPE and worms, or LDPE and clams. Each plot shows AC mix versus the control (clean input mesocosms).	56
Figure 36. Matched congeners in LDPE and worms, or LDPE and clams. Each plot shows AC mix versus the control (spiked input mesocosms).	57
Figure 37. Bioaccumulation in clams for the Gould Island experiments.	58
Figure 38. Equilibrium concentrations in silicone vs log K_{ow} for GI sediment amended with 0.026% AC by dry wt. (0.05% of the TOC)	60
Figure 39. Bioaccumulation of bed congeners in organisms vs. sediment LDPE strips (two sediments: GI and NBH).	61
Figure 40. Fraction of silicone uptake in treatment over the control for Ashtabula sediment (2.8% TOC) amended with low doses of AC.	63
Figure 41. Equilibrium silicone concentrations from Hunters Point sediment amended with low doses of activated carbon	64
Figure 42. Comparison of predicted and measured tissue concentration of PCB congeners in the benthic worm <i>Alitta virens</i> exposed to untreated NBH sediment in E2.	67
Figure 43. Comparison of predicted and measured tissue concentration of PCB congeners in the benthic worm <i>Alitta virens</i> exposed to untreated NBH sediment in E2.	68
Figure 44. Comparison of predicted and measured tissue concentration of PCB congeners in the benthic worm <i>Alitta virens</i> exposed to untreated NBH sediment in E2.	69
Figure 45. Comparison of predicted and measured tissue concentration of PCB congeners in the clam <i>Mercenaria mercenaria</i> exposed to untreated NBH sediment in E2.	70
Figure 46. Comparison of predicted and measured tissue concentration of PCB congeners in the clam <i>Mercenaria mercenaria</i> exposed to untreated NBH sediment in E2.	71

Figure 47. Comparison of predicted and measured tissue concentration of PCB congeners in the fish <i>Cyprinodon variegatus</i> exposed to untreated NBH sediment in E2.	72
Figure 48. Comparison of predicted and modeled uptake of total PCBs in functionally diverse aquatic organisms (<i>Mercenaria mercenaria</i> , <i>Alitta virens</i> , <i>Cyprinodon variegatus</i>) using the deconvoluted thermodynamic model or different treatment scenarios.	73
Figure 49. Schematic of the sediment-water system as modeled in RECOVERY.	75
Figure 50. No action/existing conditions scenario.	81
Figure 51. Sand cap scenario.	82
Figure 52. AC/sand cap scenario.	82
Figure 53. Mixed layer AC/sand cap scenario.	83
Figure 54. No action/existing conditions advective scenario.	84
Figure 55. No action/existing conditions (sediment, PW, and WC).	86
Figure 56. Sand cap scenario (sediment, PW, and WC).	87
Figure 57. AC/sand cap scenario (sediment, PW, and WC).	88
Figure 58. Mixed layer ac/sand cap scenario (sediment, PW, and WC).	89
Figure 59. Pyrene mixed layer ac/sand cap profile.	91
Figure 60. Pyrene sand cap profile.	91
Figure 61. Sediment profile for groundwater upwelling of 0 (a), 10(b), and 70(c) cm/yr.	92
Figure 62. Porewater mixed layer concentration for groundwater upwelling.	93
Figure 63. Schematic of the sediment-water system as modeled in RECOVERY-NL.	96
Figure 64. No Action/Existing Conditions Scenario.	98
Figure 65. No Action Scenario Water Column Compartment (RECOVERY-NL).	99
Figure 66. No Action Scenario Mixed Sediment Layer Concentration (RECOVERY-NL).	100
Figure 67. Anthracene Sediment Profile after 200 years (RECOVERY-NL).	100
Figure 68. No Action Scenario Water Column Compartment (RECOVERY).	101
Figure 69. No Action Scenario Mixed Sediment Layer Concentration (RECOVERY).	102
Figure 70. Anthracene Sediment Profile after 200 years (RECOVERY).	102

LIST OF ACRONYMS

C_{free}	freely-dissolved organic contaminant concentrations in sediment porewater
COC	contaminants of concern
DoD	Department of Defense
Dry weight	dw
ERDC	Engineer Research Development Center
GC	gas chromatography
HOC	hydrophobic organic contaminant
LOC	limit of detection
LDPE	Low density polyethylene
MNR	monitored natural recovery
NBH	New Bedford Harbor (NBH),
K_{ow}	octanol/water partition coefficient
f_{oc}	organic carbon fraction
K_{oc}	organic-carbon-normalized partitioning coefficient
PRC	performance reference compound
PCB	polychlorinated biphenyl
PAH	polycyclic aromatic hydrocarbon
PE	polyethylene
K_{PEW}	polyethylene-water partition coefficient
PW	pore water
QTEA	Quantitative Thermodynamic Exposure Assessment
SML	sediment mixed layer
CSP	sewer overflows
TEA	thermodynamic exposure assessment
TLC	thin layer cap
TOC	total organic carbon
USEPA	United States Environmental Protection Agency
WC	water column

Executive Summary

Objectives

The primary objective of this study was to develop an integrated, comprehensive capability for evaluating the effect of contaminant influx on the performance of *in situ* remedies, the Quantitative Thermodynamic Exposure Assessment (QTEA). Using *ex situ* equilibrium sampling, and *in situ* passive samplers with performance reference compounds (PRCs), in combination, exposure processes relevant to *in situ* remedy performance was assessed using experimental mesocosms. Using polymer sampling, tissue analysis, and modeling, QTEA was developed to guide and monitor site restoration through *in situ* remediation. Experiments were performed to reveal how activated carbon (AC) amendments can be most effectively applied to enhance the resilience of *in situ* sediment remedies challenged by ongoing sources of contamination. In addition, the modeling RECOVERY was improved to better simulate the addition of amendments, in particular activated carbon.

Technical Approach

The overarching hypothesis for the proposed work was that measured gradients in chemical activity can provide new information about the history and chemodynamics of contaminated sediments. A series of mesocosm experiments were conducted in which field-collected sediments contaminated with PCBs were employed. Both *ex situ* equilibrium samplers and *in situ* passive samplers were used in combination to evaluate changes in exposure produced by different forms of *in situ* remediation (e.g., thin-layer caps, amendment with activated carbon) under different chemical influx conditions (e.g., in the presence of ongoing inputs of clean or contaminated sediment). Polymer sampler data were used to quantify chemical processes and exposures to fish and benthic invertebrates included in the mesocosm experiments.

Results

- No remedy using AC or thin-layer capping was resilient (e.g. significant reduction >50%) to ongoing inputs of contamination. Therefore, the *in situ* remedies evaluated may only partially succeed under conditions of ongoing inputs at contaminated sites. Ongoing inputs must be controlled or at least minimized.
- Overall, thin sand capping outperformed AC mix with regard to native bedded congeners and input PCB 173. Sand cap was particularly effective in reducing superhydrophobic PCB accumulation in fish.
- Different polymer methods (*in situ* passive sampling with PRCs and *ex situ* equilibrium sampling with multiple polymer thicknesses) provided similar results.
- Comparisons of biota uptake and polymer equilibrium concentrations showed that AC caused reductions in polymer concentrations that were not always observed in tissue concentrations. the thermodynamic level of the sediment polymers was greater than the biota. Overall,

polymers were successful to monitor remediation as an important augmentation to bioaccumulation measurements.

- Fully successful remedy by AC was likely not achieved in the present study because of temporal factors. Sorption kinetics were slow from the sediment to the AC, especially for the most hydrophobic, highly chlorinated congeners (hepta- and higher). Within the three-month timeframe of the experiment, di-, tri-, tetra-, penta-, and hexa-chlorinated PCB congeners were treated effectively with AC, while the hept-, octa-, nona-chlorinated congeners were treated more effectively by the “layering effect” of the thin-layer caps.
- Reductions in bioavailability by AC (aside from continued inputs) required a dose equal to about half the natural total organic carbon (TOC) of the sediment. It is well established that in order to ensure effective treatment, the fundamental nature of the sediment TOC in the bioactive zone must be altered from labile (i.e., amorphous) to black carbon (e.g., AC). Although some sediments may be effectively treated at lower doses, our experiments indicated that effective reductions of PCB bioavailability occurred at a 50% the TOC.

The results of this work showed AC and thin-layer capping can provide value separately and in combination beyond what may be achievable by monitored natural recovery (MNR) alone. Thin-layer capping with AC should be considered as an early, first-step intervention at sites requiring enhanced MNR). Polymers can provide useful information for monitoring remedy performance.

While freely dissolved PCB concentration in sediment porewater provides one extreme boundary of thermodynamic potential for bioaccumulation in aquatic organisms, the actual steady state bioaccumulation are greatly impacted by the specific exposure conditions (e.g., differing contributions of sediment and water column exposures) and organism-specific biological attributes. Therefore, polymer sampling may not be able to completely replace the need to measure uptake by biota. However, in this study, uptake in mesocosm organisms was accurately predicted using a novel simplified model that captures the complexity of the aquatic food web, which may result in streamlined monitoring approaches.

Benefits

In situ remedies for contaminated sediments offer several potential advantages over remedies that predominately rely upon removal of contaminated sediments, among these benefits are risk reduction and reduced remedy costs. However, for these advantages to be fully realized, *in situ* remedies must provide effective risk reduction over the long-term. Achieving this objective requires the development of remedies that are resilient with respect to processes that can compromise or degrade the remedy’s ability to provide risk reduction benefits, e.g., through recontamination of surface sediments. This study provided insights needed to design resilient remedies while also producing the tools to evaluate and monitor management of *in situ* remedies to directly support remedial project managers other potential beneficiaries concerning remedy selection and monitoring at contaminated sediment sites.

1. Introduction

1.1. Background

One of the primary risk-drivers at Department of Defense (DoD) contaminated sediment sites is the concentration of polychlorinated biphenyl (PCB) in fish exceeding acceptable risk-based concentrations. The *a priori* assumption often used by risk managers at these sites is that chemical exposure to benthos and fish is primarily from PCBs in the sediment bed. However, in many urban and industrial environments, organisms are exposed to PCBs through numerous pathways, including urban runoff, storm sewers, municipal combined sewer overflows (CSOs), suspended sediments from upstream sources, groundwater discharge, atmospheric deposition (Figure 1, see Greenberg et al. 2014) and dissolved flux from sediment “hot spots” in other areas (Brown and Wagner 1990, Bergan et al. 1998, Rodenburg et al. 2011, Friedman et al. 2011). For example, Rodenburg et al. (2011) identified the Upper Hudson River, storm water runoff, CSOs, and wastewater effluents as input sources of PCBs to the New York/New Jersey Harbor (USA). Needham and Ghosh (2019) found that an old wastewater treatment plant in Baltimore, Maryland (USA) was still a source of PCBs, not just dissolved in the effluent, but also indirectly through land application of the sludge. Outside New Bedford Harbor (NBH), Massachusetts (USA), a sewage treatment plant was determined to be a source of PCBs (Bergan et al. 1998, Hofelt and Shea 1997), and inside NBH, CSOs have been a suspected source of ongoing PCB inputs (Bergan et al. 1998, Pruell et al. 1990). In Germany, and other urban areas in Europe, CSOs have also been identified as sources of PCBs to the sediment beds downstream (Schertzinger et al. 2019). PCBs in storm water sediments have been thoroughly identified and characterized in Maryland (USA) (Cao et al. 2019). Within the sediment bed of a waterbody, contaminated sediments are also re-suspended via storms (Latimer et al. 2003, Thibodeaux 2005, Bergan et al. 2005, Nelson and Bergan 2012), dredging activity (Bergan et al. 2005, Bridges et al. 2010), and ship traffic (e.g., prop wash, Kirtay et al. 2018, Karim et al. 2015). These sediments are then redistributed to other locations in the water body. Continuous inputs of PCBs also occur from the atmosphere (Praipipat et al. 2017, Naffrechoux et al. 2015, Melymuk et al. 2014) though overall there is probably a net loss of PCBs from contaminated sites and waterways to the atmosphere (Guo et al. 2017, Liu et al. 2016, Shen et al. 2012, Vorhees et al. 1997). All of these many ongoing inputs need to be included in the transport and exposure pathways of a good conceptual site model for sediment-associated contaminants at the macroscale (see Greenberg et al. 2014).

Given that most of DoD’s contaminated sediment sites occur in urban and industrial environments, remedy selection, design, implementation, and monitoring should consider the full array of contaminant pathways that could affect remedy performance over both the short- and long-term. Developing tools to improve: (1) quantification of contaminant exposure, (2) prediction of bioaccumulation potential, and (3) remedy performance assessment, will support more reliable outcomes for site remediation and restoration projects.

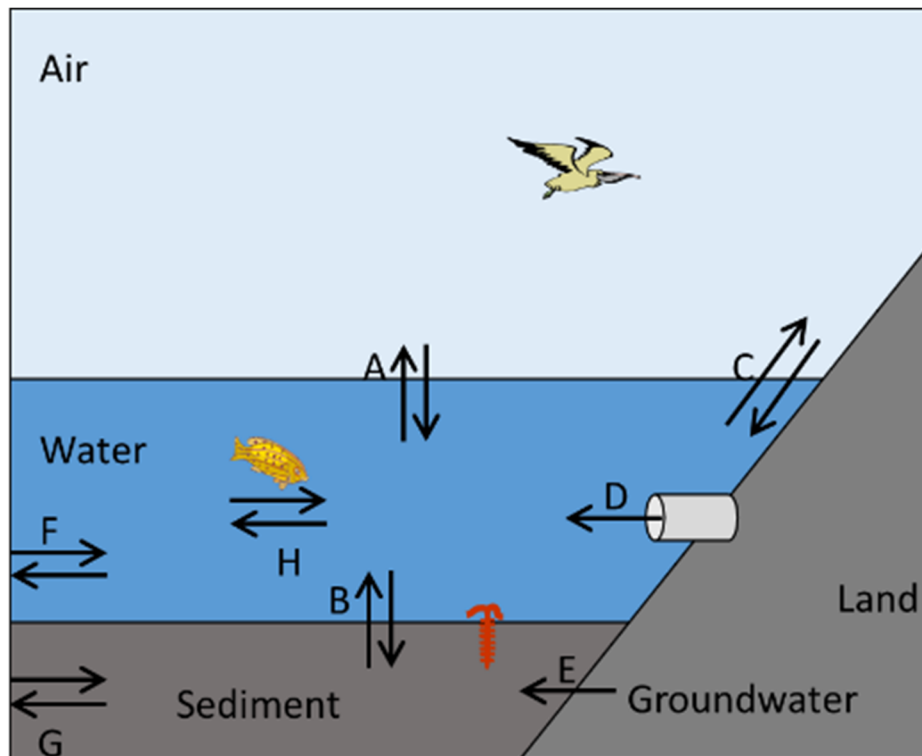


Figure 1. Conceptual model of contaminant pathways at a contaminated sediment site, including A, air-water exchange; B, sediment-water flux; C, land-water exchange; D, point-source inputs; E, groundwater discharge; F, surface water transport; G, sediment transport; H, resulting in bioaccumulation (from Greenberg et al. 2014).

All of the remedy approaches employed at contaminated sediment sites are vulnerable to the effects of relatively low levels of residual and on-going sources of contamination. This fact has been well established in the case of dredging (e.g., NRC 2007, Weston et al. 2002, Bridges et al. 2010) and is an increasing concern in regard to *in situ* remedies such as capping (SERDP 2012). For example, new deposition of contaminated particles reduced effectiveness of thin-layer capping in Trondheim Harbor (Cornelissen et al. 2011; Samuelsson et al. 2015), Grenlandfjords, and Frierfjord, Norway (Cornelissen et al. 2015; Cornelissen et al. 2012; Cornelissen et al. 2010). Failure to control contaminant sources occurred at an amended capping demonstration in the Anacostia River (Washington, DC, USA), and CSOs were a suspected source (Reible et al. 2006, Lampert et al. 2013). During any remediation activity “whirled-up” (Voie et al. 2002) sediment settles and can leave a thin “veneer” (Weston et al. 2002) of fine contaminated sediment often termed “residuals”. In a simulated resuspension event of field-aged sediment, an enrichment of PCBs occurred in the newly formed surface sediment (Chalhoub et al. 2013). The upper millimeters of sediment then often determine the magnitude of sediment to water fluxes of contaminants (Cornelissen et al. 2015). Contamination in new sediment deposits may be more bioavailable than contaminants in older, buried sediment contamination (Loonen et al. 1997),

though Cornelissen et al. (2010) found that recently settled particles had a higher organic-carbon-normalized partitioning coefficient (K_{oc}). Bergan et al (1993) noted that surface layers may contain algae and detritus (more organic matter) in the field compared to laboratory studies. It is clear that with regard to ongoing inputs, these surface-most layers have a strong link to ongoing inputs and these layers can be highly complex, site specific, and difficult to study.

While existing guidance makes it clear that controlling ongoing sources is a critical component of sediment remediation (USEPA 2005), the reality for urban and industrial sites is that complete control of ongoing sources cannot be achieved. Given this reality, the actions and technologies used to accomplish remediation should be employed to produce an overall remedy that is resilient to the influences of ongoing contaminant sources. The overarching need in this regard is to: 1) investigate how remedies are compromised by ongoing sources and then, 2) determine how to adjust or enhance remedies to make them more resilient.

The role of organic carbon in modifying the fate, transport, and exposure processes relevant to organic contaminants, like PCBs, point to opportunities to use carbonaceous geosorbents (e.g., activated carbon [AC] or biochar) to engineer more resilient sediment remedies. Rakowska et al. (2012) and Hilber and Bucheli (2010) reviewed numerous AC amendment studies performed in the laboratory and in the field. Many of these studies showed substantial reductions, often greater than 50%, in contaminant availabilities with AC amendment to sediment. However, the first pilot scale demonstration of AC amendment at Hunters Point in San Francisco Bay, CA, USA brought attention to the importance of contaminant pathways beyond the treated sediment bed (Zimmerman et al. 2004, Janssen et al. 2011, Ghosh et al. 2011). More literature reviews by Kupryianchyk et al. (2015) and Patmont et al. (2015) have described contaminated sediment remediation using AC in the context of accepted sediment remedies, such as MNR, capping, and environmental dredging. Patmont et al. 2015 considers AC amendment technologies to be another accepted technique ready for full-scale remedial application in a range of aquatic sites. While *in situ* carbon amendments are becoming more prominent as a remediation option for contaminated sediment sites (Ghosh et al. 2011, Jing et al. 2018, Abel et al. 2020), the primary objective of the present study was to determine how AC amendments can be most effectively employed to improve the resilience of sediment remedies regarding the influence of ongoing sources of contaminants.

Designing and implementing resilient remedies will require access to quantitative information about contaminant exposure processes in relation to remedies. Sampling techniques that utilize polymers have emerged as a powerful approach for collecting detailed information about contaminant partitioning, fluxes, and pathways at contaminated sediment sites (Parkerton et al. 2013). The sequestration of contaminants to carbonaceous geosorbents within sediment reduces freely dissolved contaminant concentrations (Cornelissen et al. 2005) or chemical activity (Reichenberg and Mayer, 2006), which can be considered the effective concentration determining organism exposure and uptake (Kraaij et al. 2003). Even before polymer sampling, freely dissolved concentrations were considered an important parameter in the investigation of PCB partitioning, leaching, and diffusive flux; and were either estimated or inferred (Brannan et al. 1991, Lin et al. 2003). This makes freely dissolved concentrations (C_{free}) a key parameter in

understanding the relationship between PCBs in water, sediment, and biota (Kraaij et al. 2003, Werner et al. 2010, Mayer et al. 2014). At NBH, early work by Hofelt and Shea (1997) used polyethylene (PE) tubing containing triolein (semipermeable membrane devices) as a site metric for hydrophobic organic contaminants (HOCs). Recent developments in measuring C_{free} have been made using a variety of polymer samplers. Currently, equilibrium (using polydimethylsiloxane and other silicones) (Reichenberg et al. 2008, Maruya et al. 2009, Jahnke et al. 2012) and pre-equilibrium (passive sampling using low density polyethylene [LDPE]) (Fernandez et al. 2009, 2012, Gschwend et al. 2011) samplers are being applied to obtain C_{free} or chemical activity. For example, glass vials thinly-coated with silicone represent a promising method for equilibrium sampling of PCBs in sediments, because they allow for relatively rapid achievement of equilibrium and have sufficient sensitivity (Reichenberg et al. 2008, Jahnke et al. 2012). Silicone coated jars with multiple coating thicknesses were introduced for analysis of polycyclic aromatic hydrocarbons (PAHs) in soil by Reichenberg et al (2008) and later applied to investigate PCBs in sediment by Mäenpää et al (2011 and 2015), Jahnke et al (2012, 2014a and 2014b), and Schäfer et al (2015). From equilibrium PCB concentrations in the silicone coating ($C_{\text{Sil}\rightleftharpoons\text{Sed}}$), freely dissolved concentrations can be determined via silicone-to-water partition ratios:

$$C_{\text{free}} \text{ (g/L)} = C_{\text{Sil}\rightleftharpoons\text{Sed}} \text{ (g/kg)} / K_{\text{Sil:water}} \text{ (L/kg)} \text{ (e.g., Gilbert et al. 2016).}$$

Likewise, equilibrium PCB concentrations in lipid ($C_{\text{Lip}\rightleftharpoons\text{Sed}}$) can be determined via lipid to silicone partition ratios:

$$C_{\text{Lip}\rightleftharpoons\text{Sed}} \text{ (g/kg)} = C_{\text{Sil}\rightleftharpoons\text{Sed}} \text{ (g/kg)} \times K_{\text{Lip:Sil}} \text{ (kg/kg)}$$

Those estimates can then be used to assess the thermodynamic potential for bioaccumulation (Jahnke et al 2014a, 2014b, Gilbert et al. 2016). Both equilibrium concentration in the polymer (in this case $C_{\text{Sil}\rightleftharpoons\text{Sed}}$) and C_{free} are directly related to chemical activity. However, C_{free} incorporates error associated with the independently determined polymer-to-water partitioning ratios, therefore, $C_{\text{Sil}\rightleftharpoons\text{Sed}}$ is the most precise and direct measurement of the sediment that is related to chemical activity. The major limitation of this method is that it designed only for *ex situ* application.

Low density polyethylene (LDPE) has been widely deployed in sediments and waters *in situ* as thin sheets loaded with performance reference compounds (PRCs) that allow for post-deployment determination of polymer equilibrium PCB concentrations (better known as “passive sampling” Jonker et al. 2020). Samplers made of LDPE and using PRCs have been used as *in situ* passive samplers where the fractional equilibration, f_{eq} , of each sampler is determined from the diffusive release of PRCs to surrounding media. The f_{eq} of LDPE in sediment can be calculated using available Matlab tools (Fernandez et al. 2009b, Gschwend et al. 2014). For samplers in water, a one-dimensional diffusion model that includes a water-side boundary layer (Thompson et al. 2015) was compared to a nonlinear least squares fitting of the sampling rate (Booij and Smedes, 2010) to determine f_{eq} . For the combinations of sampler thickness and target chemicals used in this work, the two methods were determined to give equivalent results. Equilibrium LDPE sampler concentrations can be calculated from those measured in the polyethylene (PE) following short-term exposure, $C_{\text{PE,t}}$, and the calculated f_{eq} :

$$C_{PE, \text{equil}} = C_{PE, t} / f_{eq}$$

Freely dissolved concentrations in water and sediment porewater, C_{free} , can then be calculated using polyethylene-water partition coefficients, K_{PEW}

$$C_{\text{free}} = C_{PE, \text{equil}} / K_{PEW}$$

where $\log K_{PEW}$ are derived from log octanol/water partition coefficient ($\log K_{ow}$) values (e.g., Hawker and Connell, 1988) by the following relation:

$$\log K_{PEW} = 0.97 \log K_{ow} - 0.07 \text{ (Fernandez et al. 2012)}$$

The calculated equilibrium concentrations in PE can be compared to the measured equilibrium concentrations in silicone using LDPE to silicone ($K_{LDPE, \text{silicone}}$) partitioning coefficients (Gilbert et al. 2016). Equilibrium PCB concentrations in lipid ($C_{Lip \rightleftharpoons Sed}$) can be determined via lipid to LDPE partition ratios:

$$C_{Lip \rightleftharpoons Sed} \text{ (g/kg)} = C_{LDPE \rightleftharpoons Sed} \text{ (g/kg)} \times K_{Lip:LDPE} \text{ (kg/kg)}$$

Those estimates can then be used to assess the thermodynamic potential for bioaccumulation (Smedes et al. 2017). C_{free} can also be compared between the two sampling methods (*ex situ* equilibrium sampling using silicone and *in situ* passive sampling using PE). However, it should be noted that the LDPE method can calculate C_{free} for all PCB congeners, because it extrapolates based on $\log K_{ow}$ for which all PCB congener $\log K_{ow}$ values are known (Hawker and Connell, 1988). Guidance on such an extrapolation for the silicone equilibrium sampling has not been found in the available literature, and instead, independent experimentally determined $K_{\text{sil:water}}$ have been used to calculate C_{free} for a limited (subset) number of congeners (Gilbert et al. 2016).

Mathematical modeling is increasingly used to inform risk assessments, engineering designs and the analyses of monitoring data at contaminated sediment sites (USEPA 2009). While the effective use of models within decision-making processes poses many technical challenges (e.g., Glaser and Bridges 2007), the complexity, variability, and diversity of processes contributing to risk management decisions necessitates their use. Developing modeling frameworks that represent the key processes relevant to *in situ* remedies, while also providing linkages to advancing passive sampling technologies, will support sound engineering designs and management strategies for *in situ* remediation. The RECOVERY modeling system is a framework that has been developed and used by U.S. Army Corps of Engineers and others to assess contaminant processes in sediment systems and develop engineering designs for *in situ* remedies (Ruiz et al. 2001). RECOVERY includes a well-mixed surface water layer underlain by a vertically stratified sediment column. The sediment column is segmented into layers that vary in thickness, porosity, and contaminant concentration. Processes incorporated into the model are sorption, decay, volatilization, burial, resuspension, settling, bioturbation, and pore-water diffusion. The model predicts the movement (i.e., flux) between specified sediment layers and the overlying water column and has been used extensively to assess natural recovery processes and capping designs at contaminated sediment sites. A reaction package to address sequential electron acceptor reactions and PCB degradation has been incorporated into

RECOVERY (Widdowson 2002, Mobile 2008). The capability of simulating multiple contaminants was extended in the release of RECOVERY 4.2 (Ruiz et al 2007).

In the present study, the bioaccumulation of PCBs was examined in aquarium experiments (“mesocosms”) using three co-exposed representative marine species: Sandworms (*Alitta virens*), hard clams (*Mercenaria mercenaria*), and sheepshead minnows (*Cyprinodon variegatus*). These organisms interact differently with the sediment and therefore provided insight to bioavailability and interactions of PCBs across a range of functionally distinct species. They were selected to represent distinct functional feeding and differing locations and interactions with the sediment, as detailed below. In addition to direct measures of bioaccumulation, bioaccumulation potential was also assessed using chemical activity measurements expressed as equilibrium concentrations in polymer samplers. LDPE were deployed in sediments and waters *in situ* as thin sheets loaded PRCs and silicone coated jars were used as an *ex situ* equilibrium sampling technique. The two polymer methods were compared based on C_{free} . Polymer sampling of hydrophobic organic contaminants (HOCs), including PCBs, has been used to predict whole-body bioaccumulation in aquatic organisms, in both laboratory and field exposures (reviewed in Joyce et al. 2016 and Schmidt and Burgess 2020). Finally, passive sampler and bioaccumulation data generated from multi-species mesocosms were used to develop a thermodynamics-driven bioaccumulation model.

1.2 Objective

The objective of the proposed effort was to develop the Quantitative Thermodynamic Exposure Assessment (QTEA) approach as an integrated, comprehensive capability for evaluating the effect of contaminant influx on the performance of *in situ* remedies. Using equilibrium samplers and passive samplers, in combination, exposure processes relevant to *in situ* remedy performance were assessed using experimental mesocosms. Using polymer sampling, bioaccumulation evaluation, and modeling, QTEA was developed to guide and monitor site restoration through *in situ* remediation. Experiments were performed to reveal how activated carbon amendments can be most effectively applied to enhance the resilience of *in situ* sediment remedies challenged by ongoing sources of contamination.

Specific objectives included:

1. Evaluation of the effect of contaminant influx on the performance of *in situ* remedies using experimental mesocosms.
2. Development of an approach for using equilibrium samplers and *in situ* passive samplers in combination to assess exposure reduction relevant to *in situ* remedy performance.
3. Integration of the use of passive sampling, bioaccumulation evaluation, and modeling to perform QTEA to support site restoration through exposure and risk reduction.
4. Determining how activated carbon amendments can be most effectively applied to enhance the resilience of sediment remedies challenged by ongoing sources of contamination.

5. Improve modeling frameworks to support the design and evaluation of resilient *in situ* remedies
6. Develop and evaluate a simplified model that captures the complexity of biota functional feeding and differing interactions with the sediment and water column to allow clearer assessments of the role of thermodynamic drivers from the sediment and surface water phases.

2. New Bedford Harbor sediment mesocosm experiments - Methods

2.1. Site overview

The superfund site in NBH has been studied for over 40 years, is recognized for PCB (Weaver G, 1984; Gidley PT, 1984) contaminated sediments, and contains heavy metals (Stoffers et al. 1977; Gidley PT, 1984). Therefore, the use of NBH sediment in this research allowed the project team to leverage on past research conducted before polymer sampling or AC amendment became of interest. For example, the history of contaminated sediments at New Bedford follows the history of: 1) contaminated sediments in general (Brannon et al. 1991, Bergen et al. 1993, Burgess et al. 1996, Latimer et al. 2003), 2) the environmental forensics of PCBs using gas chromatography with electron capture detector or mass spectrometric studies (Farrington et al. 1986, Pruell et al. 1990, Brown and Wagner, 1990, Lake et al. 1992), 3) our understanding of microbial degradation (Brown and Wagner, 1990, Lake et al. 1992), toxicity (Brown and Wagner, 1990) and bioaccumulation of PCBs (Connally 1991, Lake et al. 1995), and 4) PCB concentrations in air during dredging (Vorhees et al. 1997). A Google Scholar search for “New Bedford Harbor PCBs” results in 4070 results. Remedial dredging and residuals (Bergen et al. 2005; Karim et al. 2015) have been investigated at NBH, and some of the project team members have previously investigated the use of AC with NBH sediment (Bridges et al. 2017). Bioavailability at NBH was studied early-on by Hofelt and Shea (1997) using semi-permeable membrane devices, and has continued with LDPE (Friedman et al. 2009, 2011; Burgess et al. 2015; Joyce and Burgess, 2018). Innovative sampling techniques using NBH sediment has also continued (Coleman et al. 2014; Sinche et al. 2019; Vitale et al. 2019). Site monitoring of NBH continues to show no significant decreases in mussel bioaccumulation of PCBs and remediation is planned to continue for another 20 years (Nelson and Bergen, 2012; Subedi et al. 2014).

At NBH, the primary sources of PCBs were historic industrial discharges directly, or through CSOs (Pruell et al. 1990, Bergen et al. 1998) and a primary sewage outfall was a source near the outer harbor (Hofelt and Shea, 1997, Bergen et al. 1998). NBH is about 440 ha and has had total PCB concentrations in the range of a few ppm to over 100,000 ppm (Weaver 1984, Bergen et al. 1993, Subedi et al. 2014), while the worst “hot spots” have been removed (Bergen et al. 2005), elevated levels remain, and our study used sediment at approximately 30 mg/kg-dry wt total PCBs.

2.2. Experimental sediments

Sediment was collected from NBH on June 14 and September 25, 2014. The sediment was transported to the U.S. Army Engineer Research Development Center (ERDC) and then stored in steel drums at 2.8-4.0°C for about a year. Sediment from three drums was carefully homogenized (1:1:1) for 30 min using a propeller mixer (Lightnin Vari-Mix portable mixer, Mixing Equipment Co., Inc., USA), and then stored for a short time (<24 hrs) before use.

Characterization of the experimental, *i.e.*, the homogenized, sediment included (1) determination of total solids, (2) a particle size analysis, (3) determination of the TOC content, and (4) determination of total extractable concentrations of oil/grease, PCBs, and PAHs, as summarized in Table 1. The particle size analysis was performed following the ASTM protocol D422 (ASTM 2007). The TOC content was determined following the Lloyd Kahn Method (USEPA 1988). To perform the chemical characterization, the experimental sediment was first extracted by pressurized fluid extraction using hexane and acetone following the US EPA Method 3545A and then cleaned with H₂SO₄ following a modified US EPA Method 3665A. After extraction and clean-up, the hexane extracts were analyzed by dual column gas chromatography (GC) combined with electron capture detection (ECD), as described in detail below.

Table 1. Specifications on the New Bedford Harbor experimental sediment.

Total solids	47.7%
Sand*	37%
Silt*	56%
Clay*	7%
TOC	4.5% (dw)
Oil and grease*	657 mg/kg (dw)
ΣPCBs	31.5 mg/kg (dw)
Σ18 PAHs*	10 mg/kg (dw)

*value determined from two of the three portions of NBH sediment going into the experiment sediment. “Oil and grease” are total hexane extractables. The sediment was analyzed for the 16 US EPA PAHs plus 1-methylnaphthalene and 2-methylnaphthalene.

As described in detail below, mesocosms received sediment input PCB-spiked or un-spiked. The sediment used for this purpose was collected from a relatively clean area in Bayou Lafourche near the town of Leeville (LA, USA). The sediment was wet sieved to 2 mm, and mostly woody material was removed. Further, the d₁₅ value was 2.9 μm and the d₈₅ value was 63.1 μm. Sediment characteristics are presented in Table 2.

Table 2. Specifications on the Bayou Lafourche experimental sediment.

Total solids	27%
Sand	4%
Silt	76%
Clay	20%
TOC	5.6% (dw)
Σ PCBs	ND
Σ 16 PAHs	0.068 mg/kg (dw)
Total solids	27%

ND: non detect

As described in detail below, six mesocosms contained sediment amended with AC in Experiment 3, twelve mesocosms total were capped with sand mixed with AC in Experiments 5 and 6, and six mesocosms received AC amendment applied to surface water after contaminated sediment inputs. The AC was a coal-based powdered product from Calgon Carbon Corporation (USA, “TOG LF 80X325”). Using a Beckman Coulter Counter (LS 13 320 Dry Powder System), the mean particle size was determined to be 111 μm . Further, the d10 value was 32 μm , the d50 (median) value was 112 μm , and the d90 value was 184 μm . This AC product was selected because the partitioning of PCBs to this carbon in the presence of sediment and dissolved organic matter has been previously published (Hale et al. 2010; McDonough et al. 2010). Additionally, this AC has been used in numerous other amendment studies mixed in sediment (Sun et al. 2008), soil (Paul and Ghosh 2011), and sand for use as caps (Gidley et al. 2012).

2.3. Mesocosm experiment series

The overall experimental design for the New Bedford Harbor series of experiments is depicted in Figure 2. There were six experiments ranging from a simple sediment bed and no biota to complex systems with biota and AC applied in various ways. Mesocosms were prepared in standard aquaria, and ongoing inputs of sediment were always applied to generically represent ongoing deposition, such as from nearby dredging activity or storm water/CSO runoff. Half of the mesocosms received ongoing input of sediment spiked with PCB congeners 13, 54, and 173. Experiments were run for a total of 90 days, but fish were only exposed to the systems for a period of 60 days. Experiment 1 (E1) was a control (i.e., no remedy) with no biota, E2 was a control with biota, E3 was similar to E2 but had AC pre-mixed into the bed (hereafter, denoted “AC mix”), E4 was similar to E2 but had a very thin 2-3 cm fine sand cap (“Sand Cap”), E5 was similar to E4 but had AC incorporated into the sand cap (“AC-sand Cap”), and E6 was similar to

E5 but had AC repeatedly applied to the surface water which then settled with input sediment (“AC-sand Cap + Mobile AC”) (Figure 2).

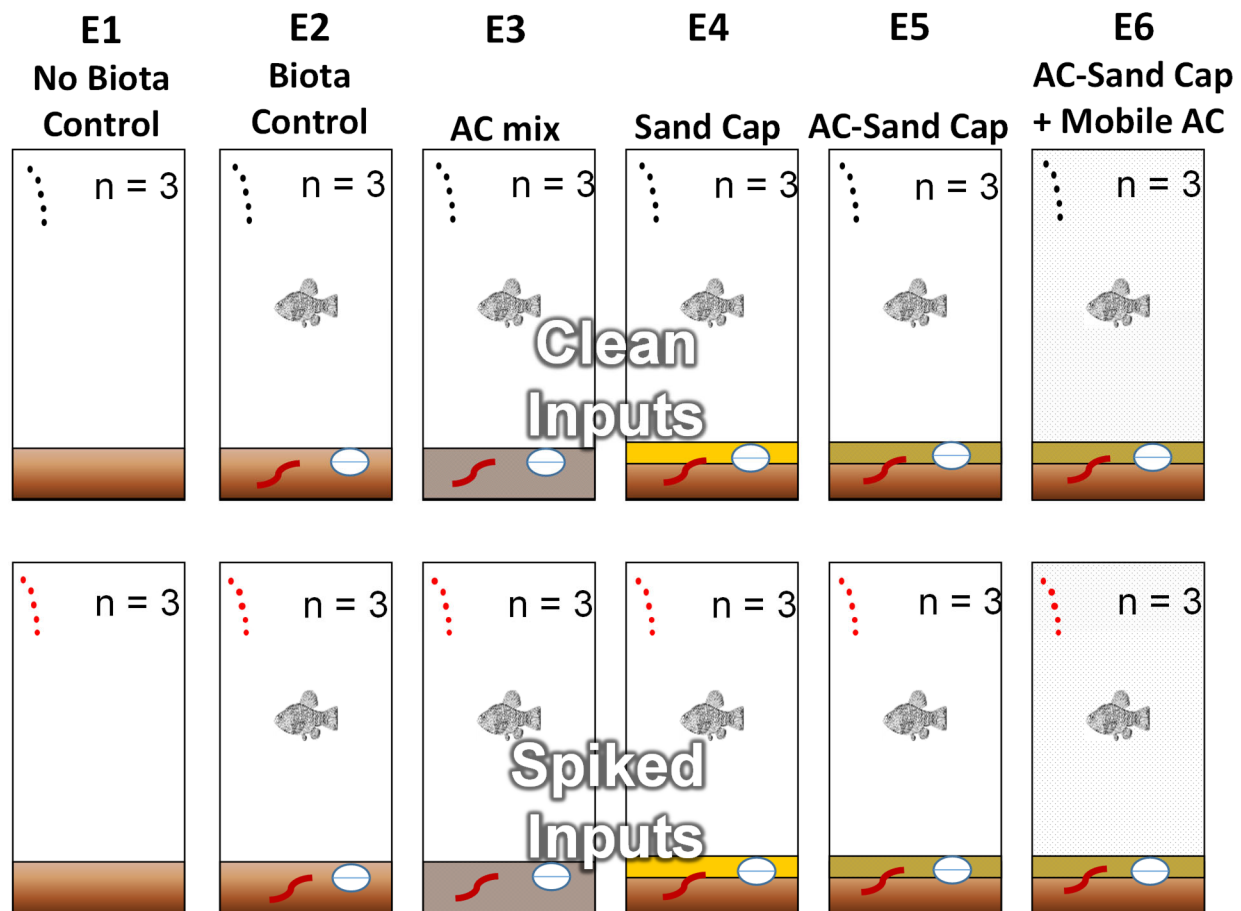


Figure 2. Series of 6 New Bedford Harbor (NBH) sediment mesocosm experiments. Each box above represents 3 replicates of a particular condition. Each experiment consisted of 6 mesocosms; 3 with clean input sediment and 3 with spiked input sediment. Experiment 1 (E1) was a control with no biota, E2 was a control with biota, E3 had activated carbon (AC) pre-mixed into the bed, E4 had a thin (2-3 cm) sand cap, E5 had a similar sand cap amended with AC, and E6 was the same as E5, but with ongoing “mobile” AC added to the surface water (chasing inputs).

2.4. Mesocosms set-up, maintenance and experiment termination

Sandworms (*Alitta virens*), hard clams (*Mercenaria mercenaria*), and sheepshead minnows (*Cyprinodon variegatus*), hereafter denoted as worms, clams, and fish, respectively, were selected as test species. These organisms interact differently with the sediment and therefore allowed for an evaluation of remediation effectiveness across a range of representative functionally distinct species (Table 3). They were selected to satisfy the following criteria: 1) phylogenetic diversity, 2) distinct functional feeding, 3) differing locations and interactions with

the sediment, and 4) common use in ecotoxicological and environmental risk assessment research and management decisions. Worms and clams (Figure 3) were field-collected and acquired from Aquatic Research Organisms, and fish were laboratory-cultured and obtained from Aquatic Biosystems. The worms and clams were allowed to acclimate to laboratory conditions for at least 24 h before addition to experiments, whereas the fish were permitted at least 1 week to acclimate. Fish (<90 d old) (Figure 4) were all males to reduce the variability in lipid content among individuals during maturation. Because preliminary experiments resulted in the fish resuspending large amounts of bed sediment that would have altered the release of PCBs into the water column beyond what would be realistic in the field, fish were restricted to the water column using stainless steel cages (Figure 5). Stainless steel dividers and fish refuges (either stainless steel or Teflon) were placed inside the cages to reduce aggressive fish interactions. Fish were periodically moved to the opposite side of the divider to disrupt social dominance hierarchies.

Table 3. Brief description of the diversity in the experimental organisms selected to comprehensively assess sediment remediation efficacy across functionally distinct species.

Organism	Common name	Phylum	Feeding	Habit (behavior, sediment interactions)
<i>Alitta virens</i>	Sandworm	Annelida	Deposit-feeders	Infaunal, deep sediment burrowers
<i>Mercenaria mercenaria</i>	Hard clam	Mollusca	Filter-feeders (at water-sediment interface)	Epifaunal, shallow sediment burrowers
<i>Cyprinodon variegatus</i>	Sheepshead minnow	Chordata	Predators	Pelagic, water column and epibenthic swimmers

Experimental mesocosms were prepared in 52-L glass aquaria measuring 51×25×41 cm (length×width×height, Glasscages.com, USA), and 13-14 kg of wet sediment was added to each of six aquaria used in each experiment (36 aquaria in total using NBH sediment) (Figure 6). Reconstituted seawater (30‰) was prepared by dissolving Instant Ocean® in water treated by reverse osmosis filtration and then slowly added to fill the aquaria. The mesocosms were kept at 20°C using a water bath, covered by acrylic lids, and left to consolidate for 8-14 d before the experiments started. After consolidation, but prior to capping (if present), the sediment layer was approximately 6 cm thick.



Figure 3. *Alitta virens* and *Mercenaria mercenaria* prior to being added to experimental mesocosms



Figure 4. Juvenile *Cyprinodon variegatus*



Figure 5. Mesh cage with partition for housing *Cyprinodon variegatus* in experimental mesocosms.

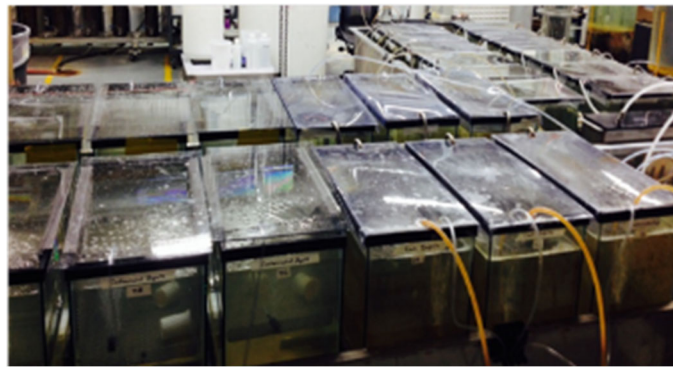


Figure 6. General view of experimental mesocosms.

In Experiments 2 to 6, five worms, 15 clams, and five male fish were added to each mesocosm (Figure 7). During the 90-d experiments, diffused air was continuously supplied (via an aquarium air stone) to aerate the surface water. Gravel bed treatment systems were operated to maintain low ammonia levels, and the surface water was re-circulated with an overall flow rate of $14.9 \pm 8.7 \text{ L h}^{-1}$ (range: $5.6 - 46.1 \text{ L h}^{-1}$, $n = 79$) in the 36 mesocosms across all NBH experiments. When E1 is excluded, the flow rate was $11.8 \pm 3.1 \text{ L h}^{-1}$ (range: $5.6 - 18.7 \text{ L h}^{-1}$, $n = 64$). Water quality (temperature, pH, dissolved oxygen, and salinity) was monitored daily, and ammonia levels were monitored at least once a week and were within acceptable range. The mesocosm experiments were conducted with a photoperiod of 16 h light and 8 h dark.

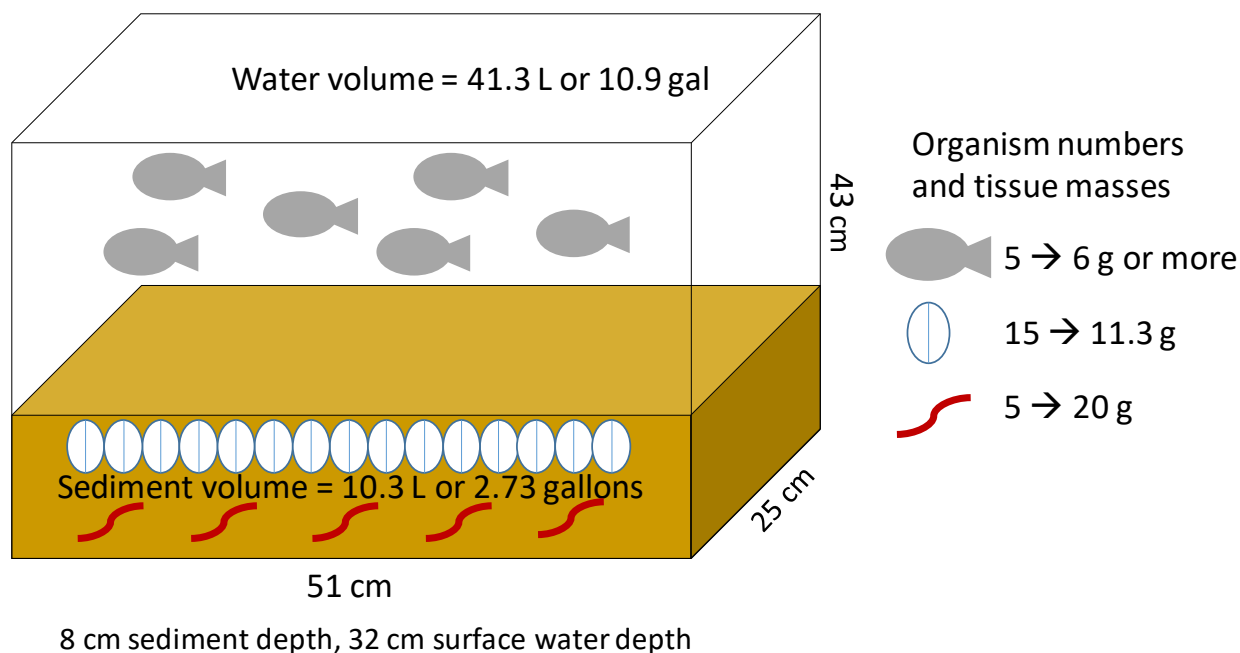


Figure 7. Schematic showing volume of contaminated sediment, volume of overlying water and number and mass of experimental organisms added to each experimental mesocosms.

In each experiment, three replicate mesocosms received PCB-spiked sediment input three times a week for the full period of 90 d to simulate on-going PCB contamination of the sediment. Correspondingly, three replicate mesocosms received unspiked sediment. Sediment from Bayou Lafourche with no detectable contamination with PCBs were spiked with “input” PCB congeners 13, 54, and 173 (Ultra Scientific, USA). The spiking was performed following the shell coating method described by Northcott and Jones (2000) and Lotufo et al (2001). For each of the three congeners, an acetone solution was prepared and pipetted into the same 2-L glass jar. The jar was rolled horizontally (5.5 rpm) with no lid until complete evaporation of the acetone, leaving the compounds coated on the inner jar surface. Then, 700 g of wet sediment was added, the jar sealed and left to roll horizontally at 5.5 rpm for two weeks before use as PCB-spiked input sediment. Sediment from Bayou Lafourche where sediment was also rolled horizontally alongside the spiked inputs was used as clean input sediment. The sediment inputs were introduced to the 36 mesocosms manually by pre-mixing 5 mL sediment (containing approximately 1.35 g dry sediment particles) with water from the respective mesocosm to form a uniform and dispersible plume in the mesocosm surface water (Figure 8). Water circulation through the treatment systems was stopped just before adding the input material and switched off for 7 h to allow the introduced sediment to settle.

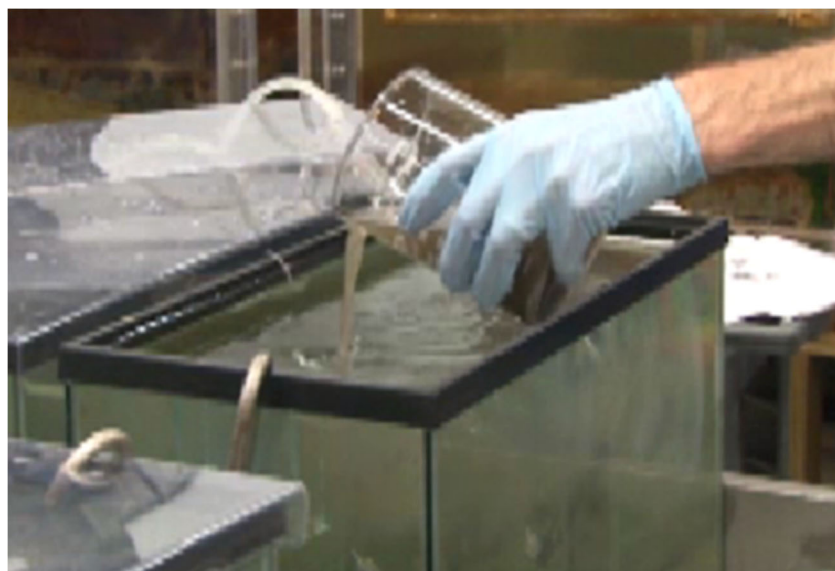


Figure 8. Input sediment being added as a slurry to an experimental mesocosm.

For *in situ* pre-equilibrium sampling with LDPE, strips prepared from a LDPE sheet with a thickness of $25.4\ \mu\text{m}$ (ACE Hardware Corp., U.S.A.) and measuring $2.5 \times 15.2\ \text{cm}^2$ were used. Uptake in LDPE was corrected for equilibrium using PRCs. LDPE passive samplers in the sediment were supported by stainless-steel frames, expanded vertically across the sediment-water interface, and deployed for the full 90 days of the mesocosm experiments. Sediment samplers were inserted at a 45° angle in experiments 2 to 4 (Figure 9A) due to limited sediment depth, but vertically (90°) in experiments 5 and 6 after it was decided that the vertical orientation was preferred and the cap over sediment provided plenty of support for the vertical orientation. After the deployments were completed, samplers were recovered and divided into two sections at the sediment-water interface line (a “sediment side” and “water side” strip). Surface water passive samplers were deployed using stainless steel aviation wire attached to the side of the mesocosm (Figure 9B) over two time intervals (0-45 and 45-90 days) of the 90-day experiments. The passive sampling methodology with LDPE, including determination of equilibrium concentrations, is described in detail in Schmidt et al. (2017).

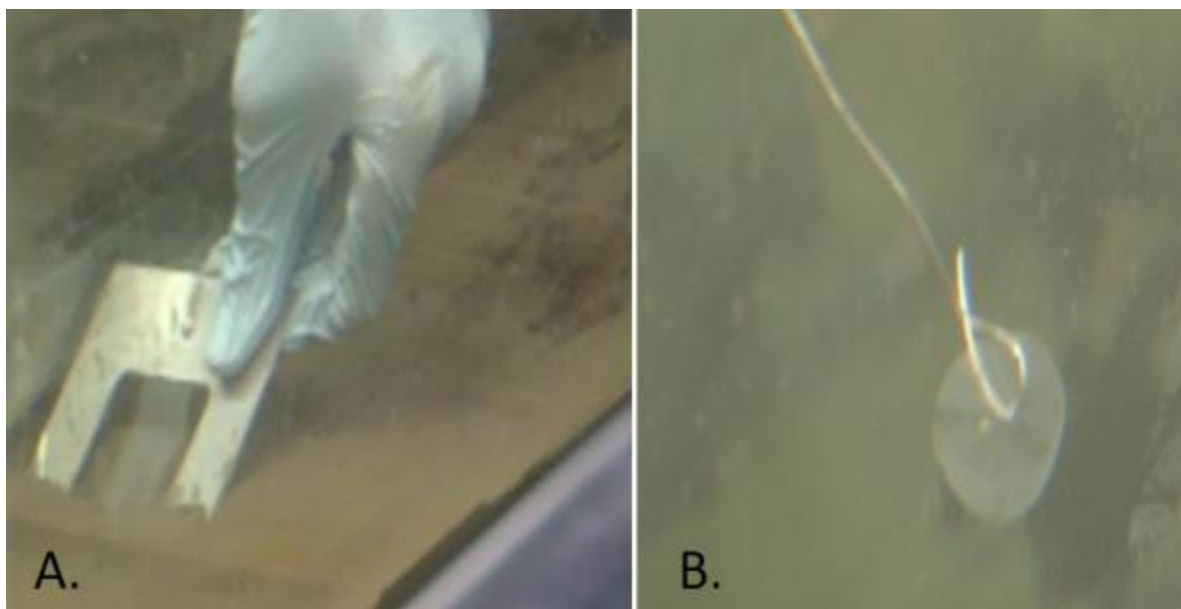


Figure 9. Low density polyethylene (LDPE) passive sampler “strip” inserted into sediment bed at an angle (A.) and LDPE passive sampler “disc” suspended in the water column using aviation wire (B.)

For nondepletive *ex situ* equilibrium sampling with silicone, sampling was conducted in silicone coated jars with multiple coating thickness. Target thickness were 1, 2, and 4 μm , but the exact mass of each jar was recorded. The mass of PCB congener (ng) was plotted versus the silicone mass (g) to determine the quality of the data, and the concentrations of each PCB congener in silicone (ng/g) as the slope of the regression forced through the origin. Details of the methodology and QA/QC criteria are provided in Schmidt et al. (2017).

The fish were not fed at the same time as the addition of ongoing input sediment to reduce PCB sorption to feed, thus minimizing dietary exposure. Because the clams were previously reported to close their valves and presumably reduce their filtering rate when suspended food sources were limited (Bridges et al. 2017), they were fed an algae mix (PhytoPlex®; Kent Marine) ration of approximately 10 000 cells/mL 3 times per week. Clam food was added immediately after adding ongoing input sediment. Even though no specific supplemental food was provided, worms likely ingested bed sediment organic matter enriched with unconsumed feed and feces.

At the termination of the experiments, the surface water was siphoned off, sediment core samples were taken for equilibrium sampling, and passive samplers were retrieved as detailed in Schmidt et al. (2017). For each mesocosm, recovered organisms were separated by species, and placed into clean seawater to allow purging of their gut contents for 24 h. The fish were euthanized with tricaine methanesulfonate (MS-222; 3 g/L in clean seawater buffered with 2.1 g/L NaHCO_3). Clams were further dissected to remove remaining sediment from the gut as described by Kennedy et al. (2010). All tissues were frozen until homogenization, extraction, and analysis.

2.5. Chemical analysis

Without further cleanup, hexane extracts from LDPE strip segments and silicone in the ESDs were analyzed by dual column gas chromatography (GC) combined with electron capture detection (ECD) according to EPA SW 846 Method 8082A.26. The HP 6890 GC was equipped with a SPB-octyl column (Sigma-Aldrich, U.S.A.) and an RTX-5MS column (Restek, U.S.A.). Both columns were 30 m long, had an inner diameter of 0.25 mm, and a film thickness of 0.25 μm . Two μL of extract was injected in splitless mode, the carrier gas was helium, and operated at a flow rate of 1.8 mL min^{-1} . The following temperature program was used: $120\text{ }^{\circ}\text{C}$ held for 2 min, temperature ramped to $255\text{ }^{\circ}\text{C}$ at $1.4\text{ }^{\circ}\text{C min}^{-1}$, and finally temperature ramped to $265\text{ }^{\circ}\text{C}$ at $18\text{ }^{\circ}\text{C min}^{-1}$. The peaks were integrated using MSD Chem Station E.02.02.1431 software (Agilent, U.S.A.), then checked, and integrated manually (if needed). Finally, the peaks were quantified using internal calibration with pentachloronitrobenzene and PCB 204 (Ultra Scientific, U.S.A.) as internal standards added at injection, which adjusted peak areas based on standard responses. Using this method, each hexane extract was analyzed for about 130 PCB congeners with a limit of detection (LOD) of $0.25\text{--}0.33\text{ ng/mL}$ and a limit of quantification (LOQ) of 1 ng/mL . Data $> \text{LOD}$ was included in the data treatments. Before the experiments started, NBH sediment was screened to select appropriate internal standards and PCB congeners to be used as PRCs and ongoing input congeners. These compounds were selected to avoid interference with native PCBs in the sediment in terms of presence and analytical separation.

3. New Bedford Harbor sediment mesocosm experiments – Remedy effectiveness

3.1. The effect of the presence of biota and baseline for evaluating treatments

An examination of E1 (no organisms) and E2 (biota added) provides an understanding of the effect of the presence of biota in mesocosms. LDPE was compared between these two experiments. Profiles for the sum of PCBs 44 and 49 are shown in Figure 10. PCBs 44 and 49 were selected because they were the only native bedded congeners detected in the surface water LDPE discs in all reps at late times (45-90 days). Biota increased the levels of native bed PCBs in the surface water as measured by uptake in LDPE corrected for equilibrium using PRCs. These indicate that the biota influenced the fate and transport of PCBs in the systems via bioturbation (which includes bioirrigation).

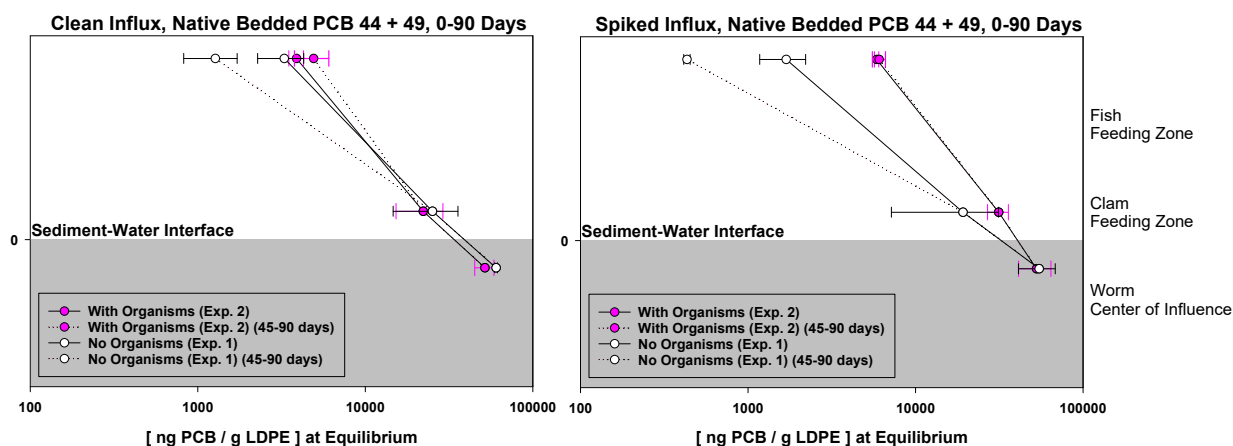


Figure 10. Profiles of equilibrium concentrations of PCB 44 + 49 (native bed congeners) in LDPE located at different heights in the mesocosms for experiment 1 (E1, no biota) and E2 (with biota). The plot on the left shows clean influx mesocosms and the plot on the right shows spiked influx mesocosms. The data above and below the sediment-water interface are derived from a single LDPE sediment strip sectioned above and below that interface. Data high in the water column are derived from separate LDPE discs (sampled over two time periods).

The influence of the biota and the nature of the input sediment (clean or spiked) on native bed PCBs concentrations in the water column is shown in Figure 11. The sum of PCBs 44 and 49 were converted to C_{free} from the surface water LDPE discs and presented as bar plots (showing E1 and E2, clean and spiked influx, and 0-45 days and 45-90 days). The presence of biota increased the chemical activity of native bed PCBs in the water column, more so for the spiked influx mesocosms. In the mesocosms without biota, C_{free} for native bed PCBs decreased over time, but when biota was present C_{free} remained relatively constant. The depletion in E1 may also be due to the “layering effect” of input sediment overtime. In E2 the presence of PCBs in the input sediment increased the water-column concentration of native bed congeners.

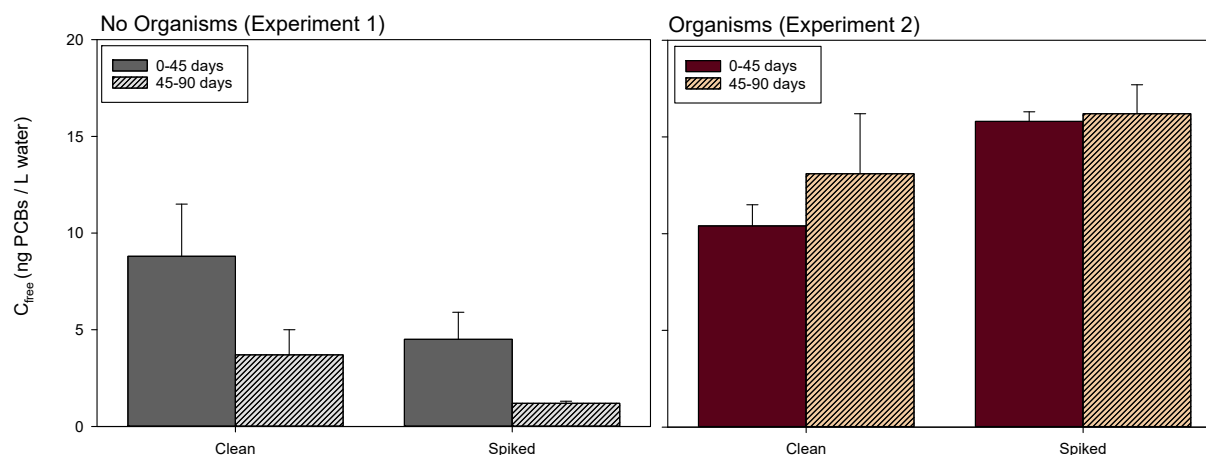


Figure 11. Freely-dissolved concentrations (C_{free}) of PCB 44 + 49 (native bed congeners) in the water column of mesocosms for experiment 1 (E1, no biota, gray bars) and E2 (with biota, brown bars). Within each plot the left grouping shows clean influx mesocosms and the right grouping shows spiked influx mesocosms. Dark solid bars show the 0-45 day period, and light hatched bars show the 45-90 day period.

The bioaccumulation and uptake in LDPE of PCBs for each replicate mesocosm in E2 is shown in Figure 12. Here, input PCB 54 was compared to similar native bed congeners (i.e., sum of tri- and tetra- chlorinated PCBs). For PCB 54 in the LDPE strips, an average of the sediment portion and water portion was presented because combined they represent the entire sediment layer enriched with PCB 54. For the native bed PCBs, the sediment portion of the LDPE strip was used as it more conservatively represented that compartment. The location of the bars was chosen to represent the feeding locations of each species: worms feeding primarily in the bed sediment, clams feeding at the sediment-water interface, and fish feeding in the surface water. The lipid content of the organisms from each mesocosm is provided along the y-axis on the right side of each plot as the tissue concentrations are lipid normalized. Bioaccumulation in clams was similar across the three replicates (2A, 2B, and 2C). Accumulation in surface water LDPE also consistent across the three mesocosms for native bed tri- and tetra- PCBs and input PCB 54. The concentration of PCB 54 in LDPE across the sediment-water interface was also similar across replicates. The bioaccumulation and uptake in LDPE of native bed PCBs varied widely across replicates. However, the worms and LDPE were matching well in each mesocosm. The log scale of these plots should also be noted. The mesocosm with the highest average flow rate (2A) had the lowest sediment concentrations (as shown by LDPE and worms). The depleted sediments might have had more PCBs passing through in the surface water for bioaccumulation. There could have been depletion of the native bed sediment PCBs in 3 months, or there was heterogeneity in the bed sediments. The PCBs in LDPE in the surface water depleted over time; 0-45 days, solid lines, compared to 45-90 days, dotted lines, but this was not a drastic depletion relative to the difference between surface water and porewater. These results highlight the importance of matching polymers to bioaccumulation within each replicate for illustrating the relation between polymer and biota data.

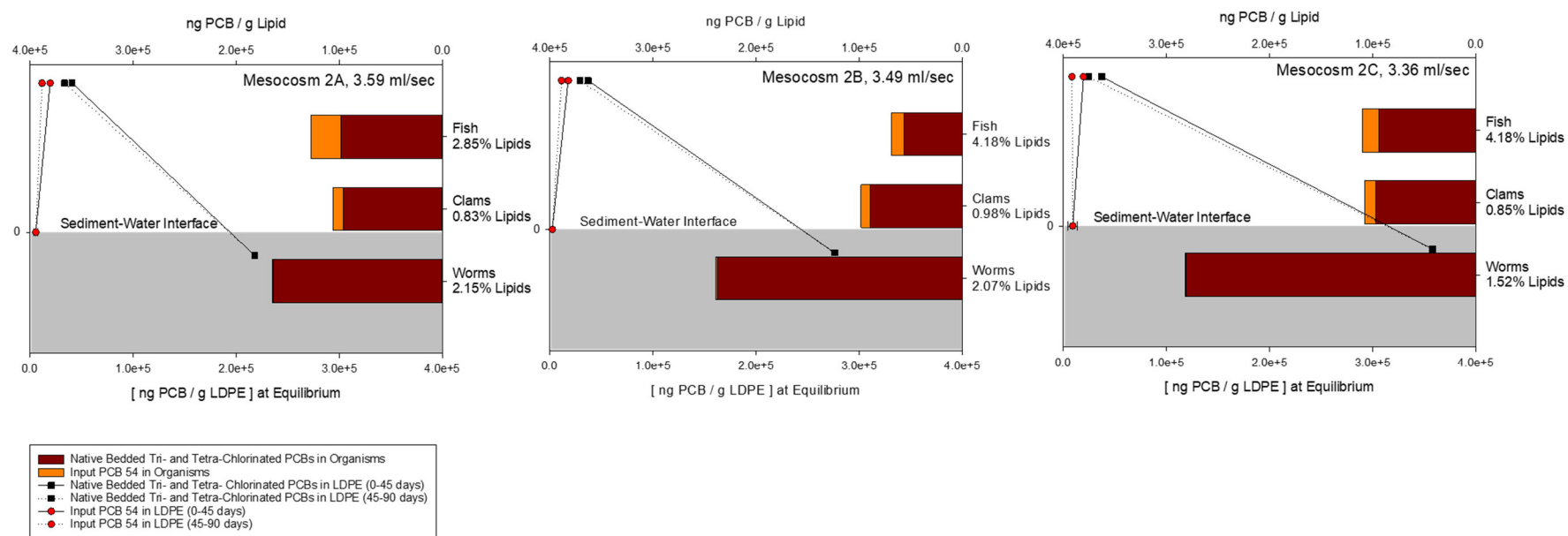


Figure 12. Profiles for each mesocosm in E2 that received spiked influx. Stacked bars show lipid normalized bioaccumulation in biota with the scale at the top of the graphs.

3.2. Effectives of remedies in reducing bioaccumulation

The effects of remedies investigated across a series of mesocosms experiments (Figure 2) can be compared using bioaccumulation in the three experimental organisms used in the present study (Figures 13-15). For those comparisons, the bed congeners were split in terms of di- and tri-chlorinated congeners, tetra- and penta- chlorinated congeners, and hexa- to nona-chlorinated congeners. The corresponding input congeners (of similar chlorination) are in the plots directly above those for bed congeners. The native bed congeners dominated the bioaccumulation in worms (Figure 13). For the light to medium (di- to penta-chlorinated congeners) the control (E2) and the AC mix (E3) show two extremes of high and low bioaccumulation. The various capping remedies (E4 though E6) resulted in medium levels of bioaccumulation in the worms. For input PCB 54, which falls in the medium chlorination range, the highest worm bioaccumulation occurred in the sand cap (E4). This was expected considering chemical activity, as the low fraction of OC in the sand combined with the input sediment created high PCB porewater C_{free} concentrations, which were almost as high as the C_{free} concentration for the input sediment before addition to the mesocosms. For the hexa- to nona-chlorinated bed congeners, the most effective remedy in terms of decreasing worm bioaccumulation was the sand cap used in E4 (Figure 13). This was a surprising result, but may only be a temporary phenomenon, as these congeners have slow sediment-to-AC mass transfer. Adding AC to the caps reduced worm bioaccumulation of the corresponding (in terms of chlorination and hydrophobicity) input congener 173. This may have been possible in the 3-month time frame due to the freshly spiked (aged 2 weeks) nature of the input sediment. In general, the capping treatments caused relatively small decreases in bioaccumulation of native PCBs in worms because they create burrows that extend deeper than the 2-3 cm caps. Therefore, despite the remedies, worms maintained exposure directly to the underlying NBH sediment, while also likely preferentially feeding at the surface on OC-rich fish supplemental food and feces.

Remedies caused a substantial decrease in the bioaccumulation of PCBs in clams (Figure 14), which can be attributed to the clams burrowing and feeding at the sediment-water interface. Mixing AC to the sediment was the most effective remedy for bed congeners. Adding AC to the caps did not greatly enhance remedy performance in the 3 month mesocosms. None of the treatments were effective at treating input congeners, likely due to the ongoing nature of the inputs and the slow kinetics of AC sorption from input sediment.

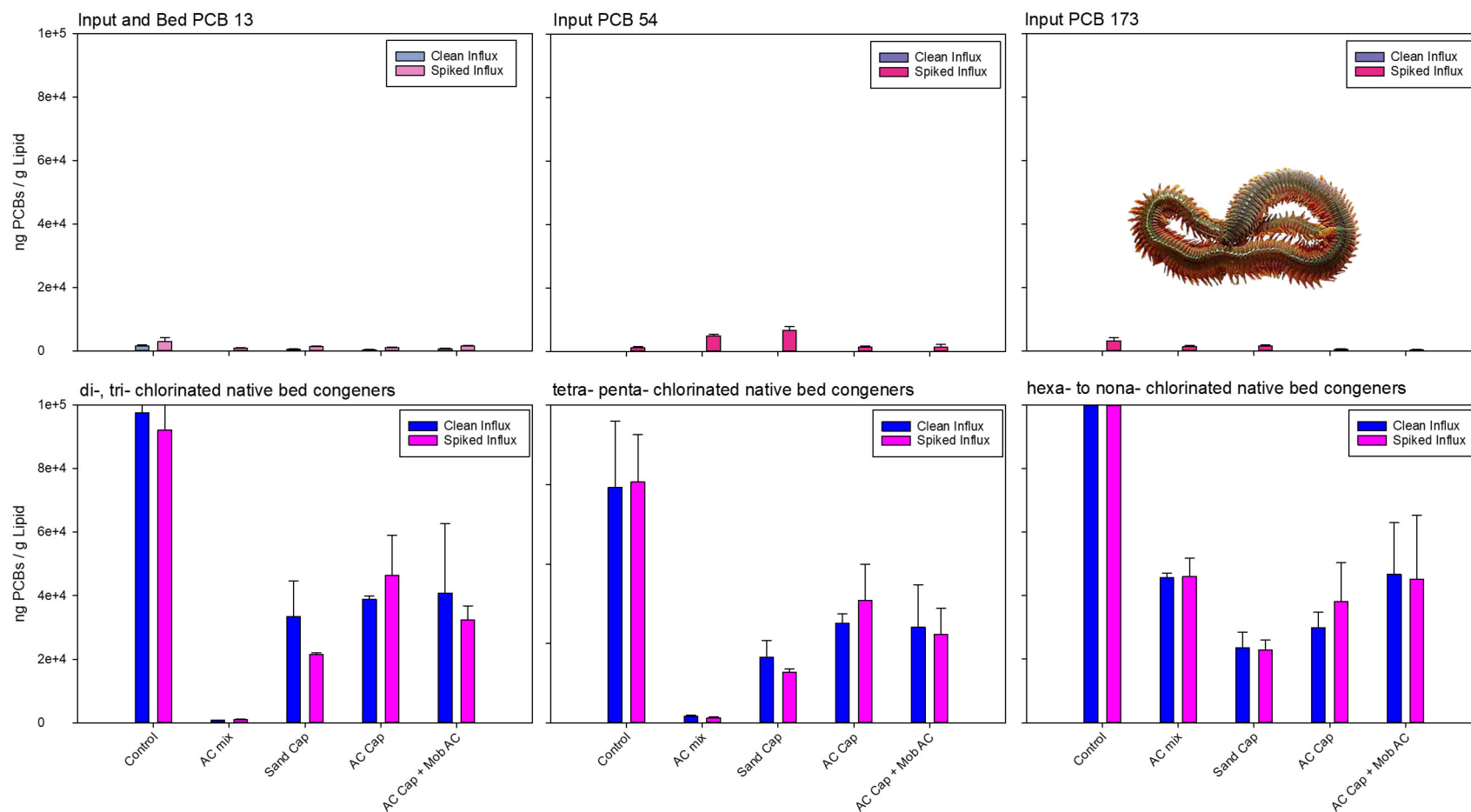


Figure 13. Lipid normalized bioaccumulation in worms for the NBH series of experiments. Top row shows input congeners, bottom row shows native bed congeners. Low chlorinated congeners are on the left and highly chlorinated congeners are on the right.

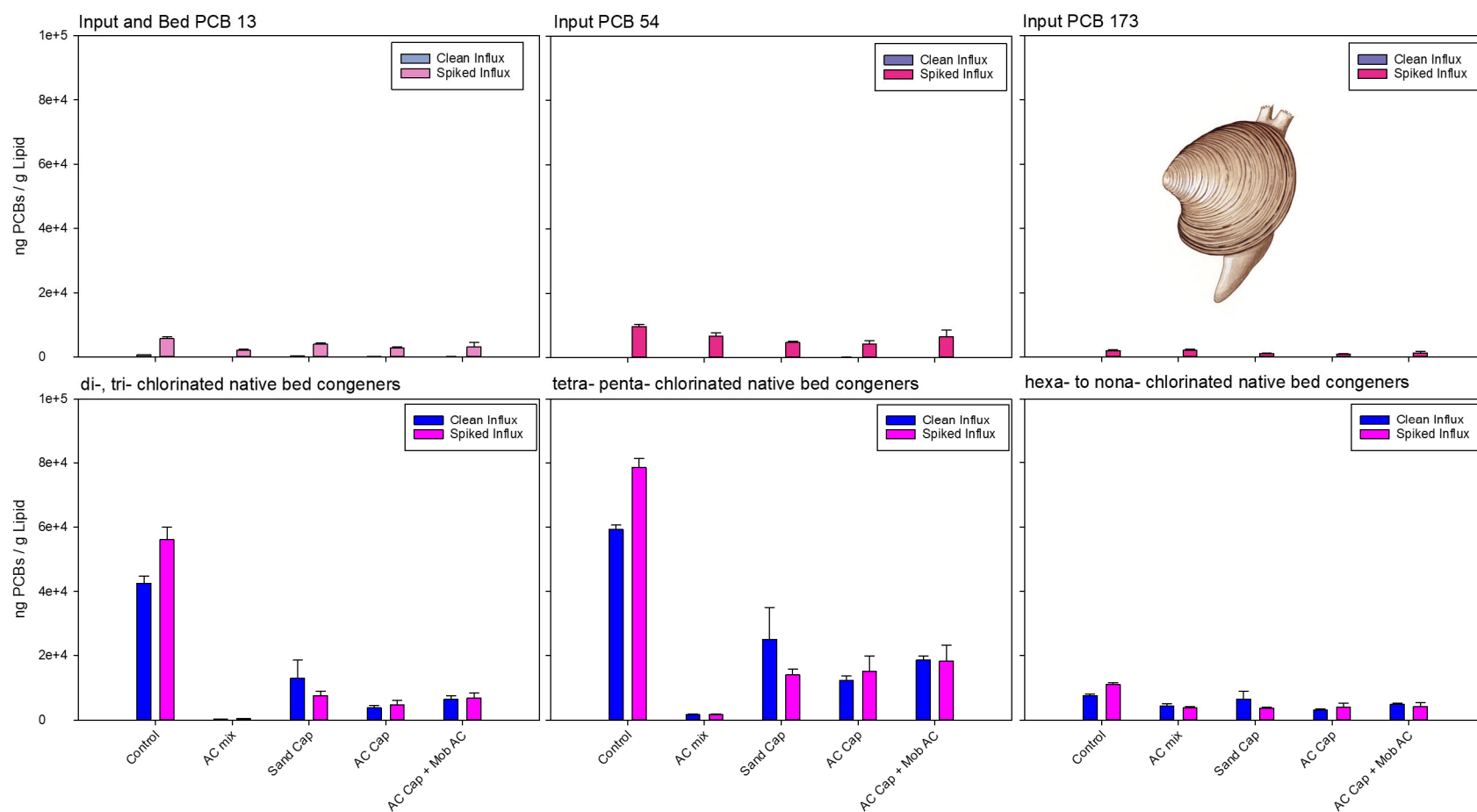


Figure 14. Lipid normalized bioaccumulation in clams for the NBH series of experiments. Top row shows input congeners, bottom row shows native bed congeners. Low chlorinated congeners are on the left and highly chlorinated congeners are on the right.

Fish bioaccumulation for the series of six NBH sediment mesocosm treatments is shown in Figure 15. Fish were only exposed for 60 days, 30 days less than the worms and clams. In 90 days, the worms and clams were likely at steady-state based on Kennedy et al. (2010), while the fish likely below steady-state based on the toxicokinetic study for fathead minnows by van Geest et al. (2011). Differently from the worms and clams, fish were held in a cage in the water column and were therefore influenced by surfaces and processes above the sediment-water interface, where uncaged fish would dwell. For example, the glass side walls in the mesocosms (aquaria) were coated with what appeared to be a biofilm or sediment particles by the end of the 90 days. This process would have been approximately 4-fold more influential on the fish (based on area) than the cap/sediment surface. Finally, the fish cage provided additional surface (similar to the aquarium side walls) that could have influenced the fish. The 5 treatments were all effective in reducing bioaccumulation of native bed PCBs as well as input congeners. Mixing AC to the sediment was the most effective remedy for most bed congeners but the sand cap was surprisingly the most effective remedy for input congeners. One of the reasons for the lower performance of the AC mix is that contact time was likely too short to treat input PCBs, unlike the bed PCBs.

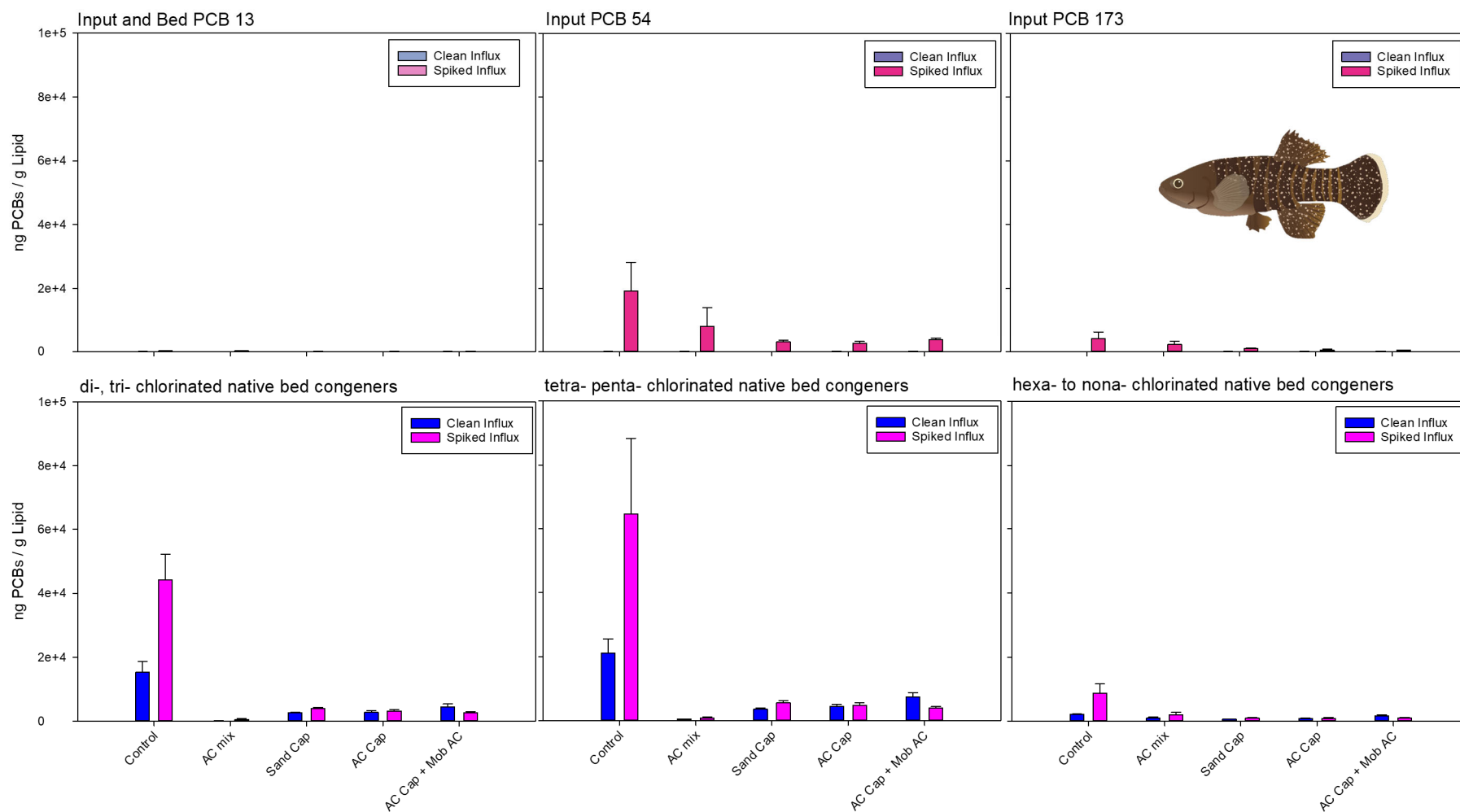


Figure 15. Lipid normalized bioaccumulation in fish for the NBH series of experiments. Top row shows input congeners, bottom row shows native bed congeners. Low chlorinated congeners are on the left and highly chlorinated congeners are on the right.

3.3. Bioaccumulation of Highly Hydrophobic PCBs

AC amendment has been gaining a lot of attention, and rightfully so, in contaminated sediment remediation. Meanwhile sand capping has often provided physical stability and isolation of contaminated sediment particles. Additionally, superhydrophobic organic chemicals ($\log K_{ow} > 6$, Gobas et al. 1989) are an important category of sediment contaminants (e.g., hydrophobic PCBs, dioxins, and furans). Sediment-to-AC mass transfer of this class of HOCs is slow, and numerous studies have shown minimal effectiveness of AC for treating these “slow” congeners. Meanwhile, trophic magnification factors for these “slow” contaminants in the aquatic food web are high relative to “fast” (less hydrophobic) organic contaminants (Khairy et al. 2014).

The importance of cap isolation (i.e., the “layering effect”) should not be overlooked. Here, we present a comparison of bioaccumulation in 90-day marine mesocosm experiments with AC mixed into the bed (“AC mix”), or a thin-layer of sand (“sand cap”) compared to a reference with no treatment (“control”). Ongoing inputs of clean sediment, or clean sediment spiked with marker PCBs, were applied to these mesocosms as a process in addition to the bioturbation. Here we present bioaccumulation data for hexa- to nona-CBs from the field contaminated bed sediment (“native bedded PCBs”) and input marker PCB 173.

Where AC mix had a 1-month “head-start” via premixing, a sand cap with thickness (2-3 cm), which was less than the bioturbation depth, showed greater reductions in bioaccumulation than AC mix after 3 months (2 months exposure for fish). We believe the 1-month premixing of the AC represents a condition years after AC application in the field. While 3-months was not a long period for monitoring the sand caps, caps would also typically be applied at a thickness greater than the bioturbation depth.

The very thin sand capping outperformed AC mix with regard to native bedded congeners and input PCB 173 (Figure 16). The only exception to this was clam bioaccumulation during clean ongoing inputs in terms of native bedded congeners (Figure 16). The “layering effect” was clearly important for controlling superhydrophobic organic contaminant bioaccumulation in fish. The fish also showed reduced bioaccumulation due to the clean ongoing input, which deposited and added to the layering effect (Figure 16). It is unknown why the sand cap also outperformed AC mix with regard to input PCB 173. AC did not have a “head-start” to treat input PCB 173 (like for the native bedded PCBs) relative to the sand cap but input 173 would also have been presumably unaffected by the layering effect.

The bioaccumulation in worms was not shown in Figure 16 because the native bed congener uptake was so high (off the scale in Figure 16). Figure 17 shows the native bedded PCB worm bioaccumulation along with relatively lower levels for the other organisms and input 173. The sand cap outperformed AC mix in terms of native bedded PCB bioaccumulation in worms as well. We hypothesize that worms feed on the surface sediments leading to this outcome.

We do not highlight these results to negate the overall positive effect of activated carbon amendment. Indeed, when all the PCBs in the system are considered, AC mix often performed

best (see Figures 13-15). However, we do claim these results indicate that layers with activated carbon (or capping with activated carbon) might be superior to simply amending sediments with activated carbon.

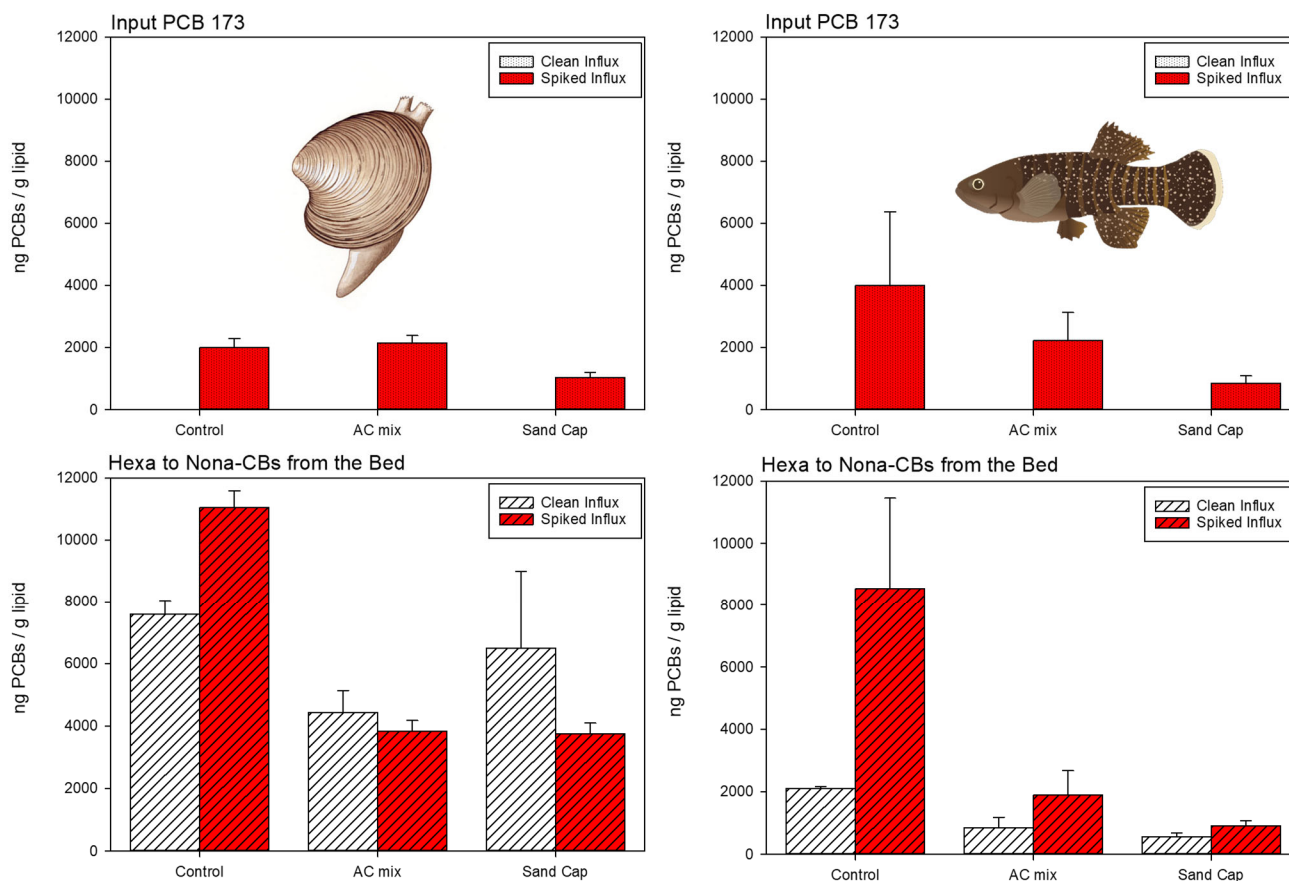


Figure 16. Bioaccumulation in clams and fish for “highly hydrophobic” PCBs (ng PCBs/g lipid) for E2 (control), E3 (AC mix), and E4 (sand cap).

Using a different scale, Figure 17 shows the native bed PCBs and input PCB 173 bioaccumulation in worms, clams, and fish for E2, E3 and E4. Similar to fish and clams, the sand cap outperformed AC mix in terms of native bed PCB bioaccumulation in worms as well. Possibly the worms fed on the surface leading to this result. Even though smaller, the remedy performance of the AC mix treatments to worms was sizable (Figure 17). Indeed, when all the PCBs in the system are considered, AC mix often performed best (see analysis for the full range of hydrophobicity in Figures 13-15).

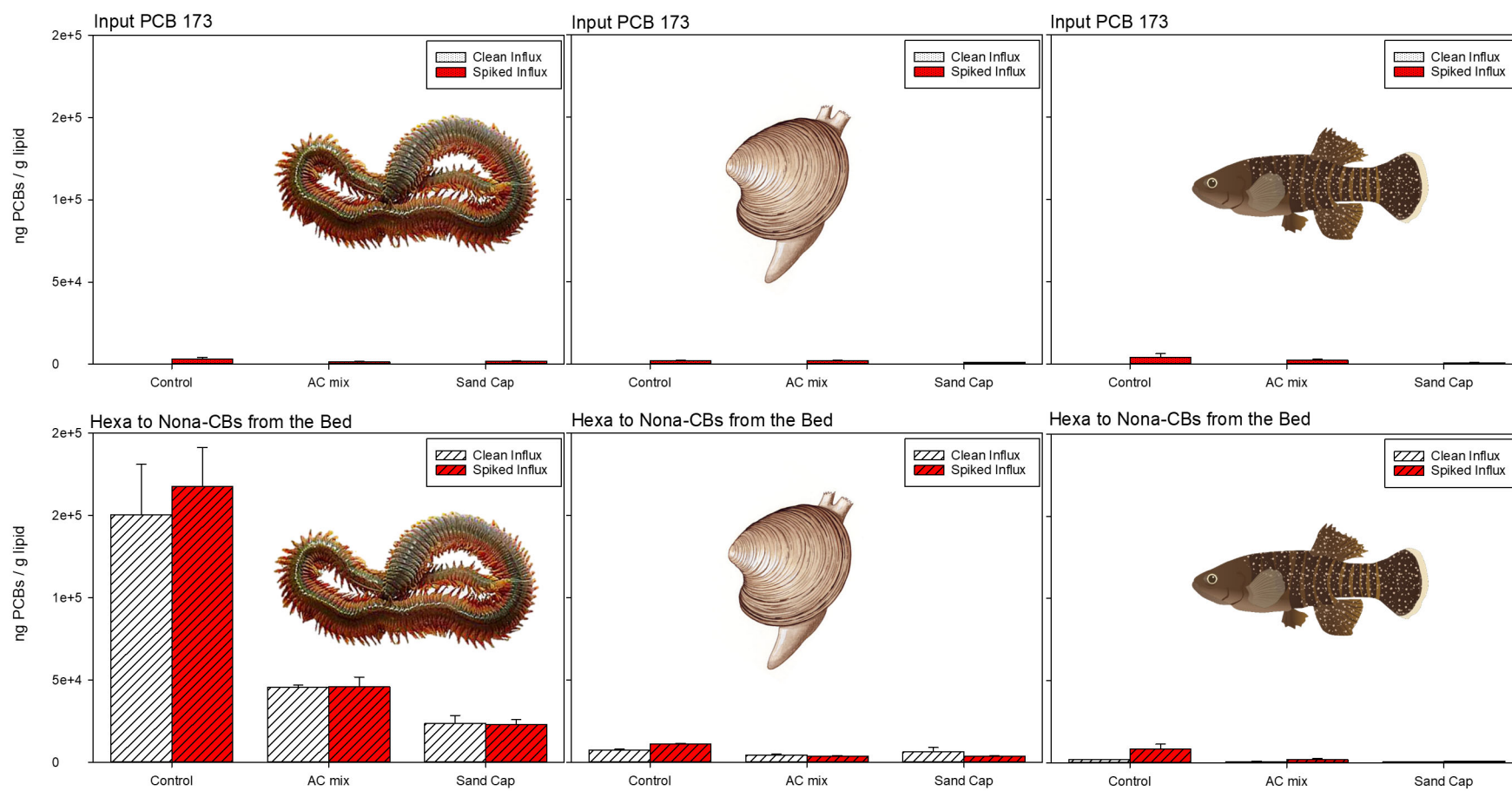


Figure 17. Bioaccumulation worms for “highly hydrophobic” PCBs (ng PCBs/g lipid) for E2 (control), E3 (AC mix), and E4 (sand cap). Bioaccumulation plots from Figure 18 are also shown for comparison.

3.4. “Mobile AC” Amendment to the Surface Water

The addition of AC to the surface water 3x a week as a “chaser” following ongoing input sediment (E6, “mobile AC”) can be considered a novel approach for examining the use of AC in sediment remediation. A comparison of the AC amended sand cap (E5) to the same treatment with the addition of AC to the surface water (E6) is the focus of Figures 18-20 for fish, clams, and worms, respectively. The striking characteristic of all of these plots is the lack of any additional effect relative to AC-sand cap treatment. The highest effect from the addition of mobile AC was approximately 25% reduction in bioaccumulation of total PCBs in worms for spiked influx. One explanation for this is that by the mobile AC that deposited on the bed got mixed into the sediment bed via bioturbation causing a reducing effect after 3 months.

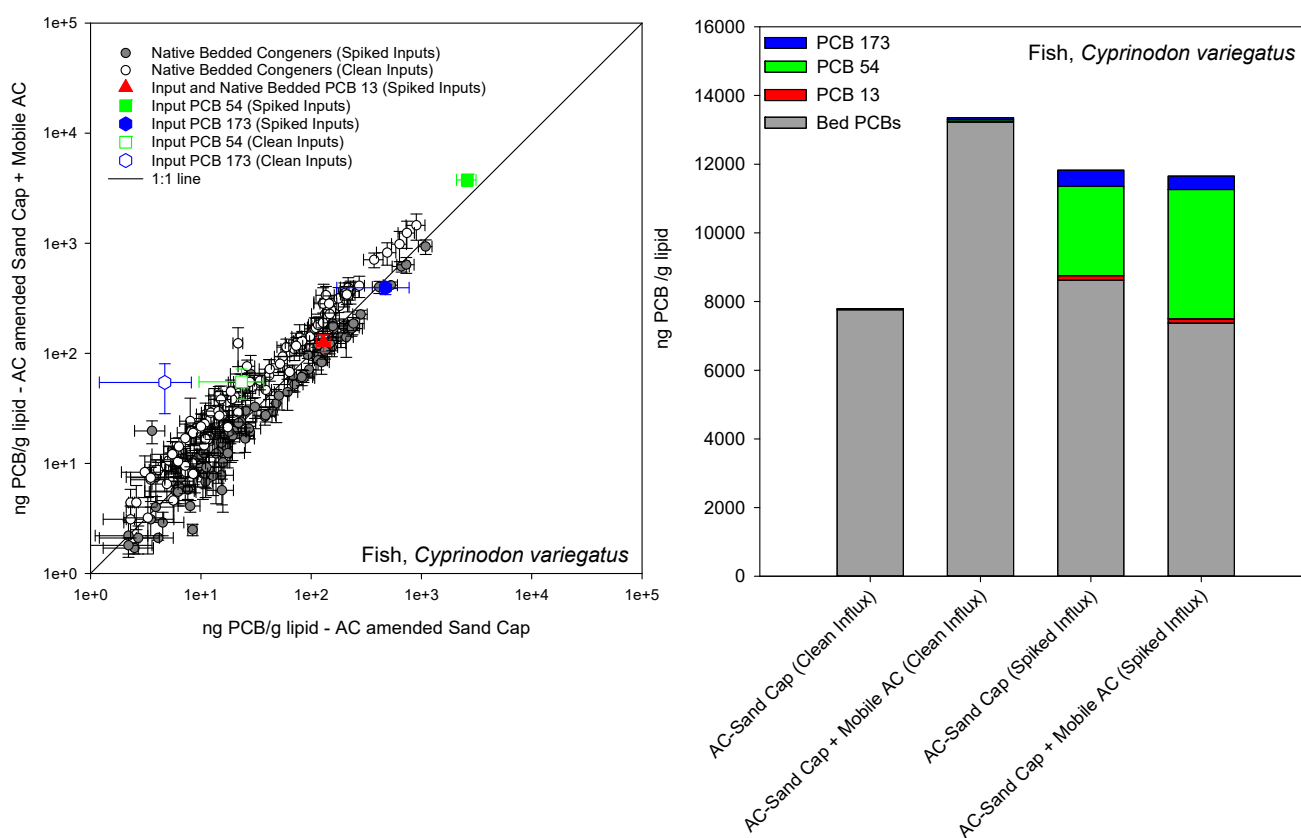


Figure 18. The effect of “mobile” AC on fish bioaccumulation (clean and spiked influx shown).

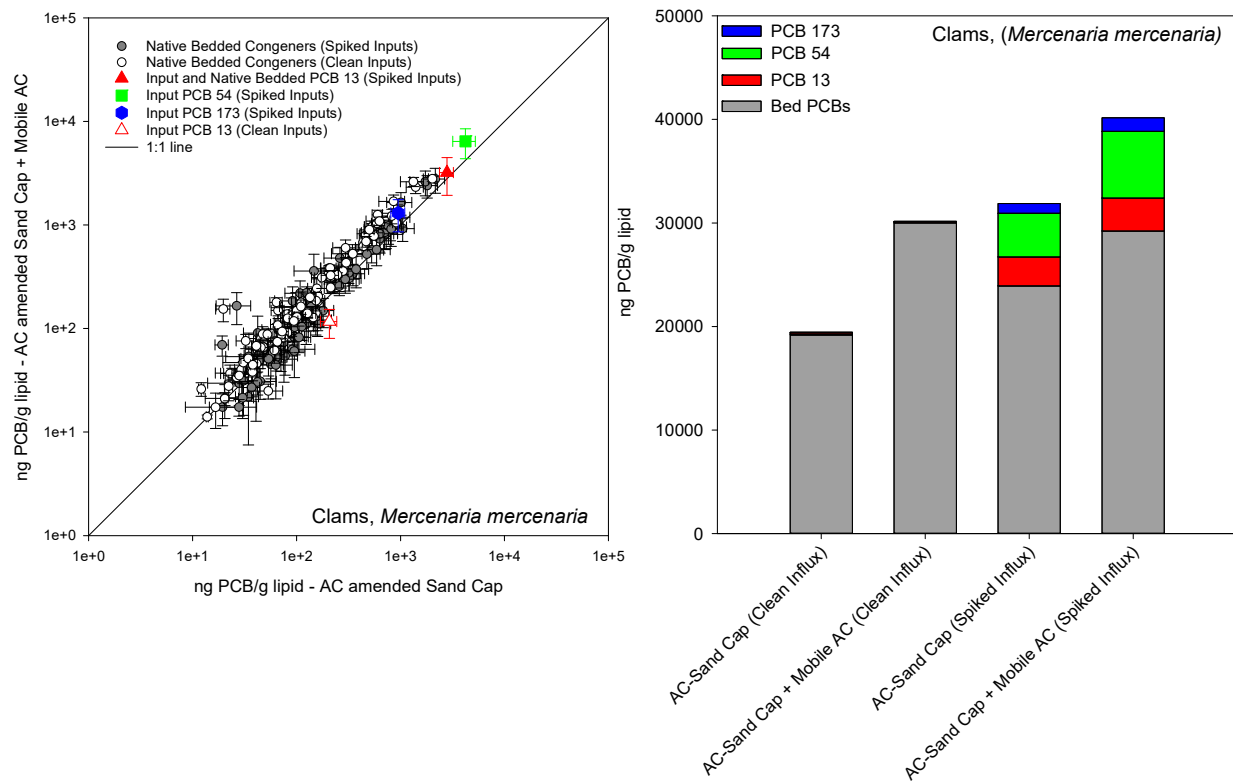


Figure 19. The effect of “mobile” AC on clam bioaccumulation (clean and spiked influx shown).

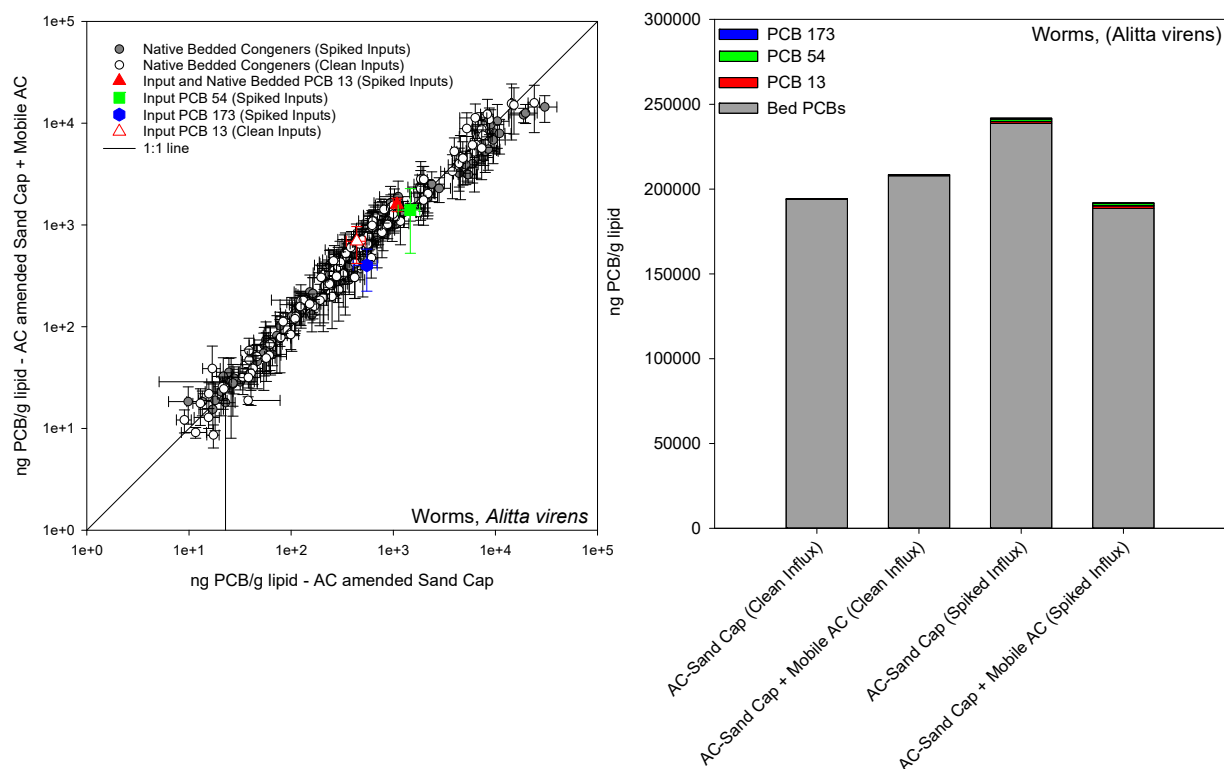


Figure 20. The effect of “mobile” AC on worm bioaccumulation (clean and spiked influx shown).

3.5. Overall trends for treatment effectiveness for reducing the bioaccumulation of input PCBs

The input PCBs were not perfectly replicated across the NBH series as revealed by bulk concentrations in this spiked sediment measured after 2 weeks of aging, but before addition to the mesocosms. Figure 21 is a combination of Figures 13, 14, and 15 for the input congeners only, with bulk phase concentrations of the input batches (prepared for those mesocosm) also presented. General trends show that all capping treatments effectively reduced bioaccumulation of input PCBs in fish. The AC amended sand cap (E5) was the most effective treatment for all species, but sand capping (E4) was also effective for fish and clams. Sand capping (E4) was the least effective remedy for input PCBs for worms and clams, but was effective for fish.

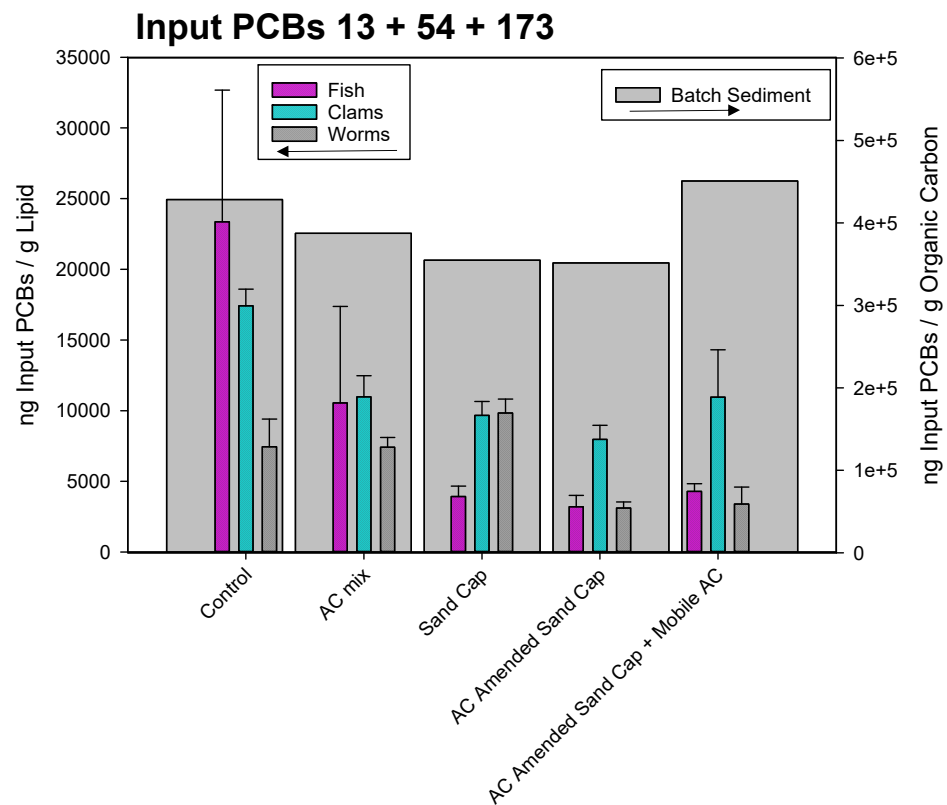


Figure 21. Measurement of the total input PCBs in biota (ng PCB/g lipid; left y-axis) and bulk concentrations OC normalized prior of input sediment (ng PCB/g OC) sampled prior to addition to the mesocosms.

4. New Bedford Harbor sediment mesocosm experiments Cross validation of two polymer sampling approaches

As previously described, two polymer methods were conducted for the mesocosms: *ex situ* equilibrium sampling with silicone coated jars, and *in situ* passive sampling using LDPE loaded with PRCs. Those methods provided equilibrium concentrations in either silicone or LDPE. Comparing the two methods therefore required the conversion of one polymer to the other (using independently determined polymer-polymer partitioning) or conversion of both polymers to C_{free} . Rather than selecting one polymer over the other as a comparison phase, comparisons were made using C_{free} estimated from polymer data. In the literature, there are a limited number of congeners with reported silicone-water partitioning coefficients, thus creating a subset of congeners that could be rigorously compared on the basis of C_{free} was accomplished (Schmidt et al. 2017). Following the publication of Schmidt et al. (2017) we conducted comparison of the coated jar and LDPE passive sampling methods based on C_{free} for all congeners, not just a subset. In order to accomplish this, a regression relating silicone-water partitioning to K_{ow} was created (Figure 22). This allowed for the conversion of all congeners measured in silicone to C_{free} . Then C_{free} based on *in situ* passive sampling with LDPE was plotted versus C_{free} based on *ex situ* equilibrium sampling using silicone coated jars (Figure 23).

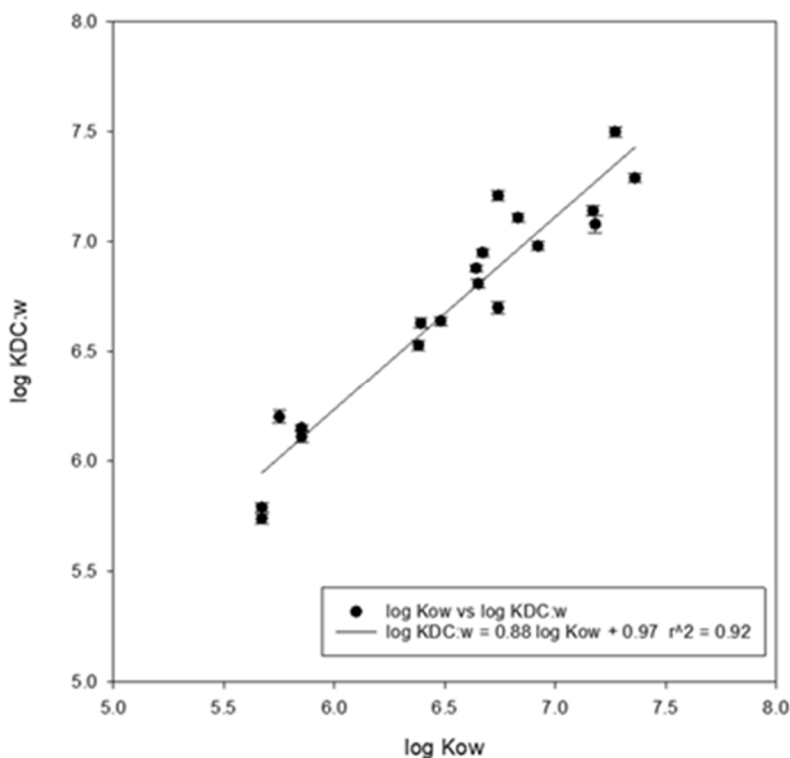


Figure 22. Relation between Dow Corning (DC) silicone: water partitioning ($K_{DC:w}$) (from Gilbert et al. 2016) and octanol: water partitioning (K_{ow}) (from Hawker and Connell, 1988).

In general, most of the individual data points fell along the 1:1 line and were within a factor of 2, which is in general agreement with comparisons of *ex situ* and *in situ* LDPE sampling methods (Apell and Gschwend 2016 and with Jonker et al. 2018) for a variety of passive sampling formats. However, the data points for input PCB 54 in E1 and in E3 fell outside the factor of 2 band (Figure 23). This may be due to the LDPEs providing a spatially weighted averaging of a chemical activity gradient in the top 2-3 cm, whereas the coated jars were measuring the chemical activity of the top 2-3 cm of sediment homogenized. In E1 this gradient occurred because there was no bioturbation. In E3 this gradient occurred because of the activated carbon. In E2 there was bioturbation and no activated carbon, so there was more *in situ* spreading of the input PCBs in the surficial sediment. PCB 13 was also a native bed congener (in addition to being an input), so it did not behave like PCB 54. PCB 173 has slow sediment-to-AC mass transfer, so the AC in E3 did not create the gradient like it did for PCB 54, which has fast sediment-to-AC mass transfer.

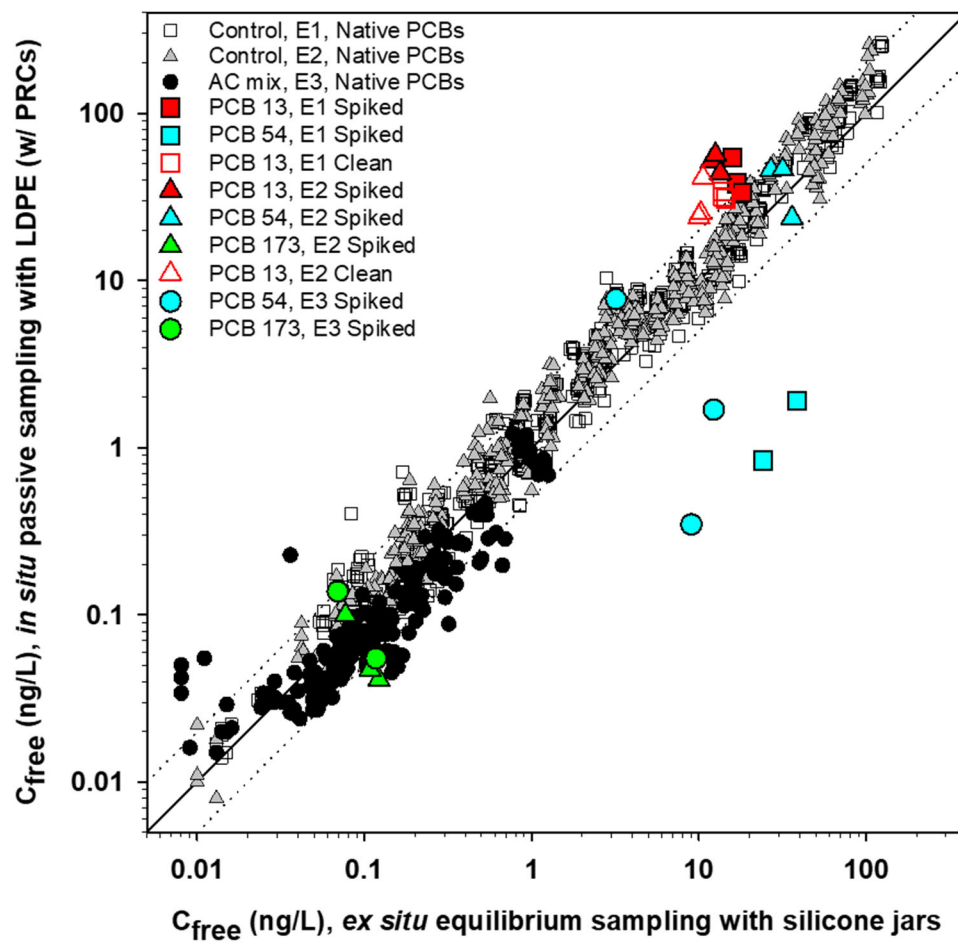


Figure 23. Comparison of the two polymer methods on the basis of C_{free} for all congeners in Experiments 1, 2, and 3. Solid line is the 1:1 and dotted lines show within a factor of 2

5. New Bedford Harbor sediment mesocosm experiments – Thermodynamic exposure assessment (TEA)

A comparison of lipid-normalized tissue concentrations to equilibrium polymer concentrations for a thermodynamic exposure assessment (TEA) was one of the main focuses of the present study and is presented here for E2 and E3. To compare measured bioaccumulation with polymer-predicted bioaccumulation, polymer concentrations were converted to lipid concentrations but only for congeners for which polymer-lipid partition coefficients were available (Gilbert et al. 2016, Smedes et al. 2017), for a tier 2 TEA. When polymer concentrations are converted to lipid concentrations (using appropriate lipid-polymer partitioning coefficients) and related to lipid-normalized tissue concentrations, this is referred to as a tier 2 TEA. Polymer sampler equilibrium concentrations directly related to lipid-normalized tissue concentrations is referred to here as a tier 1 TEA. Polymer concentrations converted to lipid concentrations (using appropriate lipid-polymer partitioning coefficients) and related to lipid-normalized tissue concentrations is referred to as a tier 2 TEA.

Tier 1 TEA of the worms is provided in Figure 24. Overall, a strong relationship between silicone concentrations and worm lipid concentrations was obtained, with much of the data falling within a factor of 2 (within the 2X lines) and most of the data falling within a factor of 10 (within the 10X lines). AC amendment to the bed sediments generally resulted in a similar reduction in both lipid and silicone for native bed congeners. However, for the input congeners the relationship is less clear. AC amendment reduced PCB 13 to non-detect levels (data not shown). PCB 54 showed a concentration reduction in silicone by AC amendment, but a concentration increase in lipid. PCB 173 showed a concentration reduction in lipid by AC amendment, but little change in silicone (Figure 24).

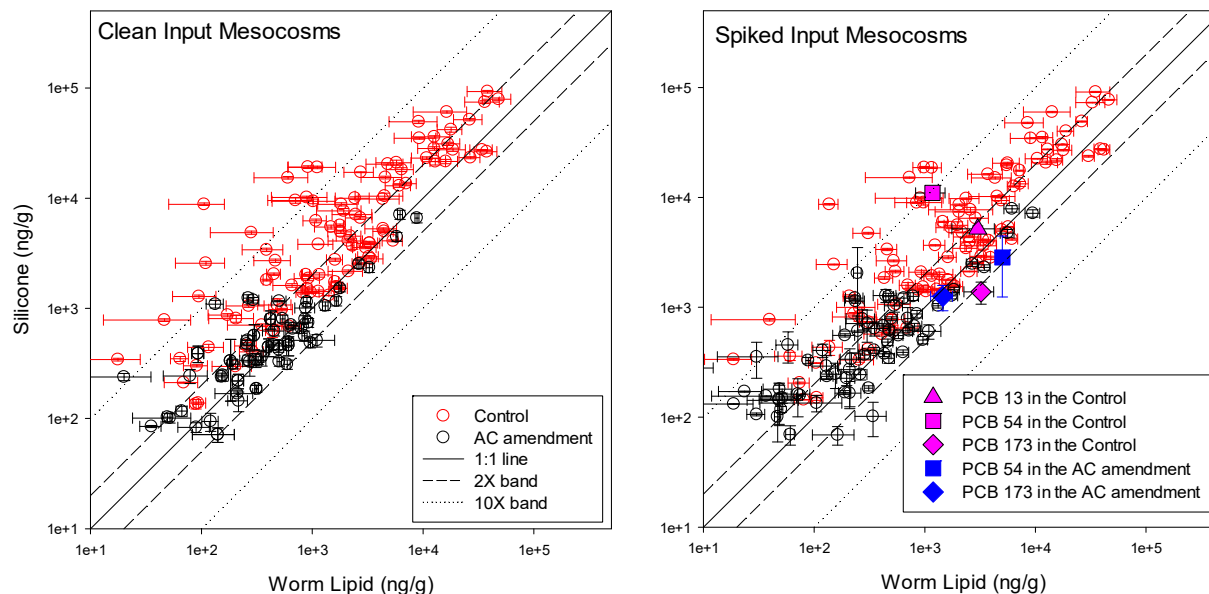


Figure 24. PCB congener concentrations in silicone *Alitta virens* lipid from 90-day mesocosm experiments containing New Bedford Harbor sediment. Either clean (left plot) or spiked (with PCB 13, 54, or 173) (right plot) ongoing input sediment were added in a pulsed fashion for the duration of the experiments. Input congeners (PCB 13, 54, or 173) are larger solid symbols (pink for the control, and blue for the AC amended). The error bars show standard deviation of the mean for 3 replicates.

For clams, an overall good relationship between silicone concentrations and clam lipid concentrations was observed, with much of the data falling at a factor of 10 (i.e., overall, the concentration in silicone was 10-fold higher than in clam lipid) (Figure 25). This factor of 10 difference is partly due to the clams feeding at or above the benthic boundary layer, while the silicone sampled the sediment. AC amendment to the bed sediments generally resulted in reductions in bed congeners that were similar for both clam lipid and silicone. However, for the input congeners concentration in silicone and clam lipid were similar within a factor of 2 or less. This relationship was likely due to the input congener exposure in the surficial sediment closely matching the exposure in the surface water, which is expected to be main bioaccumulation source compartment for clams.

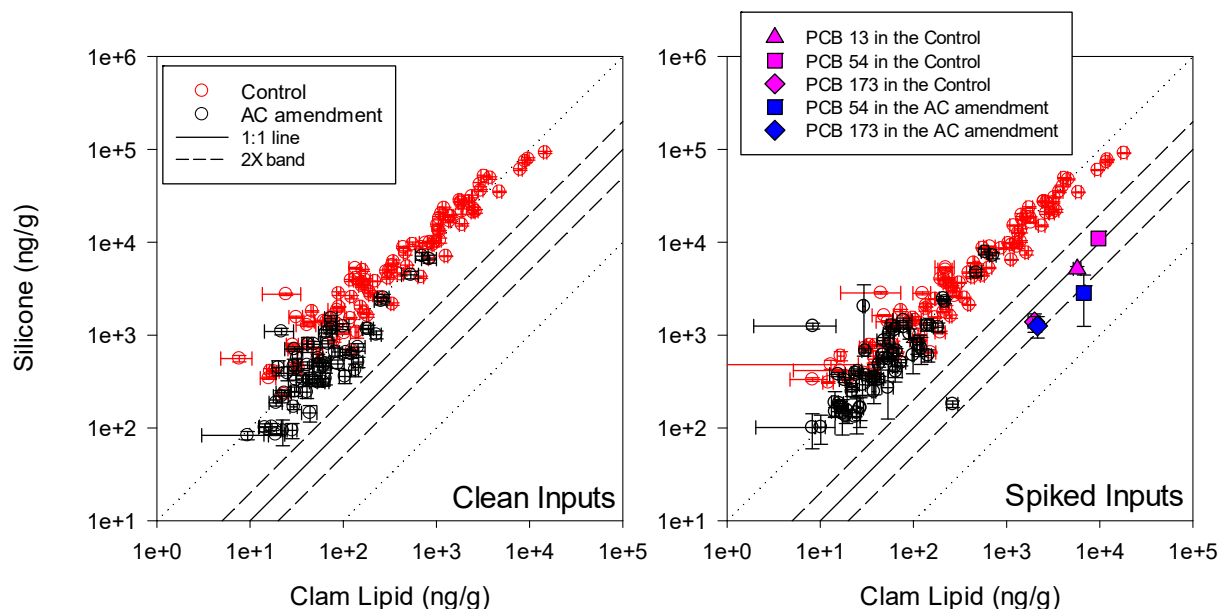


Figure 25. PCB congener silicone concentrations versus PCB congener clam (*Mercenaria mercenaria*) lipid concentration from 90-day mesocosm experiments containing New Bedford Harbor sediment. Either clean (left plot) or spiked (with PCB 13, 54, or 173) (right plot) ongoing input sediment were added in a pulsed fashion for the duration of the experiments. Native bed congeners are smaller hollow symbols (red for the control, and black for the activated carbon (AC mix) amended bed sediment mesocosms). Input congeners are larger solid symbols (pink for the control, and blue for the AC amended).

Tier 1 TEA of the fish is provided in Figure 26. For fish, an overall, good relationship between silicone concentrations and fish lipid concentrations was observed (Figure 26), but the data fell at or above a factor of 10 band. The clean input mesocosms showed a relation that was above the 10X band due to mild treatment of the surface water by the clean inputs, or diffusion of native bed congeners into the clean surficial layers (which was then sampled by the silicone). AC amendment to the bed sediments generally resulted in similar concentration reductions in both lipid and silicone for native bed congeners (though the relation was less strong for AC amended mesocosms). However, for the input congeners the relationship between silicone and polymer still stayed close to the 1:1 line except for input PCB 13 (which was also a bed congener). This approximate 1:1 relationship was probably due to the input congener exposure in the surficial sediment closely matching the exposure in the surface water where the fish were feeding. AC amendment reduced PCB 13 to non-detect levels in the coated jars during the 2-week mixing (data not shown). PCB 54 showed a reduction in silicone and lipid by AC amendment. PCB 173 showed little change in silicone or lipid between the control and AC amendment, probably due to the slower sorption kinetics of PCB 173 relative to PCB 54 (Figure 26).

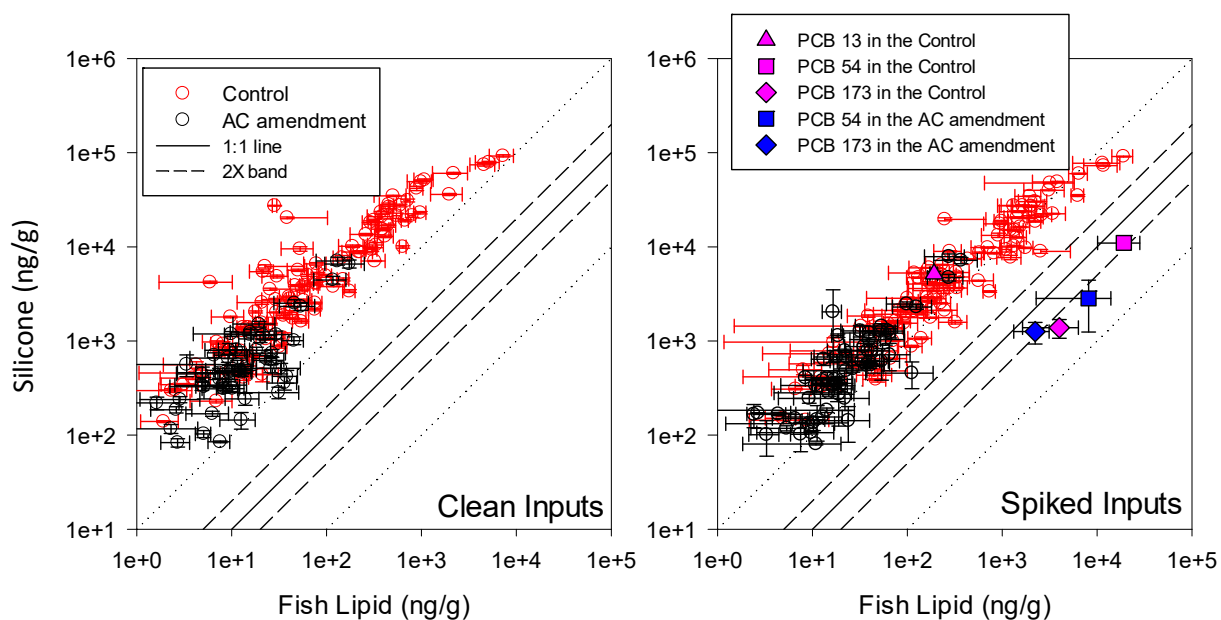


Figure 26. PCB congener silicone concentrations versus PCB congener fish (*Cyprinodon variegatus*) lipid concentration from 90-day mesocosm experiments containing New Bedford Harbor sediment. Either clean (left plot) or spiked (with PCB 13, 54, or 173) (right plot) ongoing input/influx sediment were added in a pulsed fashion for the duration of the experiments. PCB 13 was also a native bed congener. Native bed congeners are smaller hollow symbols (red for the control, and black for the activated carbon (AC mix) amended bed sediment mesocosms). Input congeners are larger solid symbols (pink for the control, and blue for the AC amended).

There are three major processes driving differences between the silicone and measured lipid:

1. Silicone and lipids have different sorption capacities and therefore polymer-lipid partitioning coefficients are needed to cancel-out this effect (the sorption capacity of polymer is less than lipid, but since the organisms are usually under-equilibrated with the sediment, this brings the polymer vs lipid plots closer to the 1:1, which is useful).
2. The fish are under-equilibrated with their environment (have not reached steady-state) and this differs with hydrophobicity of the congener.
3. The coated jars sample a homogenized core of the surficial sediment, while the fish reside above the sediment. Thus, any layers that form in the sediment bed (from depositional influx) will greatly impact the ability of the silicone to match the uptake in fish. This also differs with the hydrophobicity of the congener. Interestingly, the presence of input marker congeners in the surficial layer influences the behavior of the native bed congeners.

The Tier 2 TEA for the data shown in Figures 24-26 is shown in Figure 27. It is important to note that in Figure 27, the polymer derived measurements are now on the X-axis, instead of the Y-axis. Converting the silicone data to lipid data, pushes the data further from the 1:1 line. This indicates that the organisms are far under-equilibrated with the sediment (as measured by *ex situ*

equilibrium sampling with coated jars). For example, for the worms (Figure 24) the silicone data versus the actual lipid data was close to the 1:1 line, but after converting the silicone to lipid (Figure 27), the data is off by a factor of 10 (i.e., worms are at a thermodynamic level that is an order of magnitude less than the sediment). The other organisms (clams and fish) are at even lower levels than the worms. This result was not expected especially for the worms, which were expected to be in equilibrium with the sediment.

There are several likely reasons for the much lower actual concentration in biota relative to that predicted from the thermodynamic level in the sediment:

- 1) Clean fish food was added to these systems, which descended to the sediment surface as food or fish feces. This food source may have been preferentially fed on by the worms, and this food source diluted the tissues (in terms of PCBs).
- 2) Ongoing input was also expected to have diluted the PCB contamination in bed sediments ingested by worms, therefore also contributing to lower-than-expected bioaccumulation for native bed congeners.
- 3) Even worms (not just clams and fish) are influenced by the surface water (the worms irrigate their burrows with surface water), which is at a lower level than the sediment porewater in these systems (as seen in Figure 28, which is similar to Figure 2 in Mäenpää et al. 2015).
- 4) In situ sediment porewater might be at a lower level than ex situ sediment porewater (Apell et al. [2018] explore this in detail in the Lower Duwamish Waterway, Seattle, Washington, USA) measured using the ex situ coated jars (this can be explored more using the in situ LDPE passive samplers [Figure 28 and other figures]).
- 5) Chemical activity is only one side of bioavailability (Reichenberg and Mayer, 2006; Smedes et al. 2013). Accessibility, which is considered the other side, was measured for of the sediments using in E2 and E3 using Tenax extractions (Sinche et al. 2019; Sinche 2018).

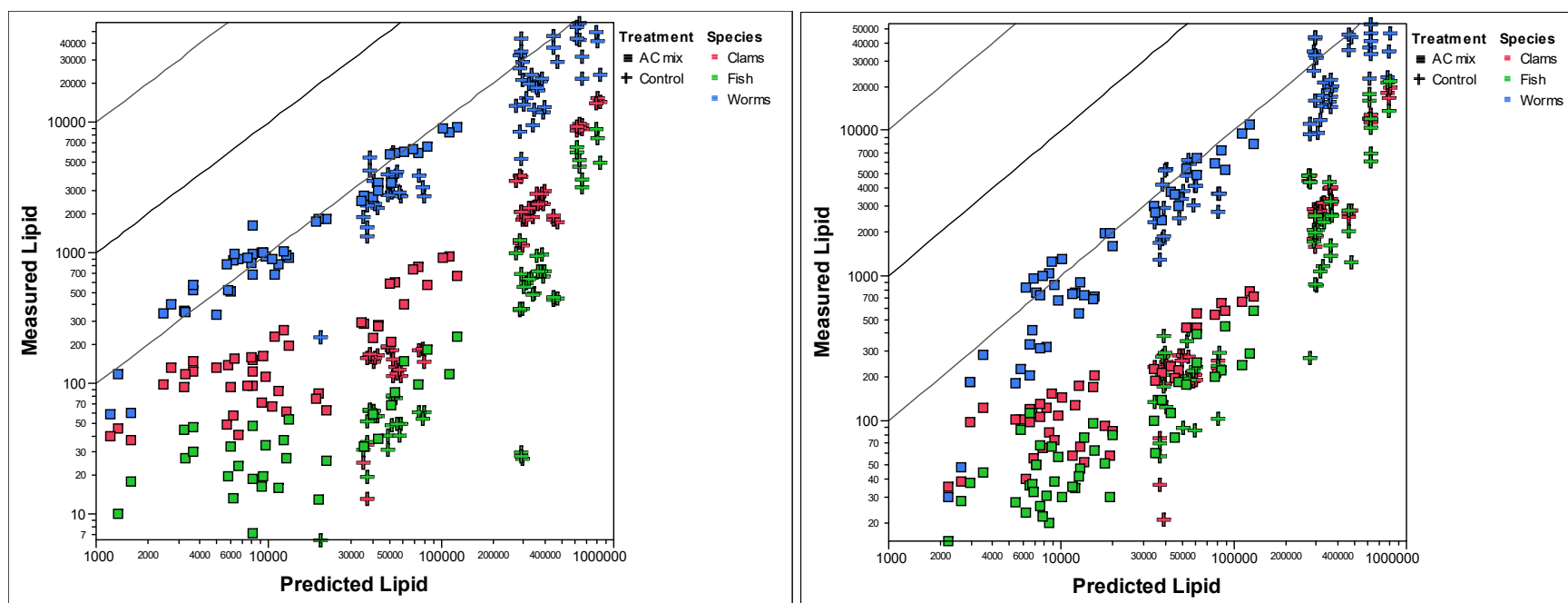


Figure 27. Measured lipid concentrations versus predicted (or the thermodynamic potential from the sediment). Here, silicone concentrations were converted to lipid concentration (using silicone:lipid partitioning from Gilbert et al. 2016). There are no error bars because polymer and lipid values were matched within each mesocosm. Input congeners are not included, because these congeners do not have independently determined silicone:lipid partitioning coefficients. Worms are blue symbols, clams are red symbols, and fish are green symbols. The control (E2) are plus symbols, and the AC mix (E3) are square symbols. Clean influx mesocosms are shown on the left, and spiked influx mesocosms are shown on the right.

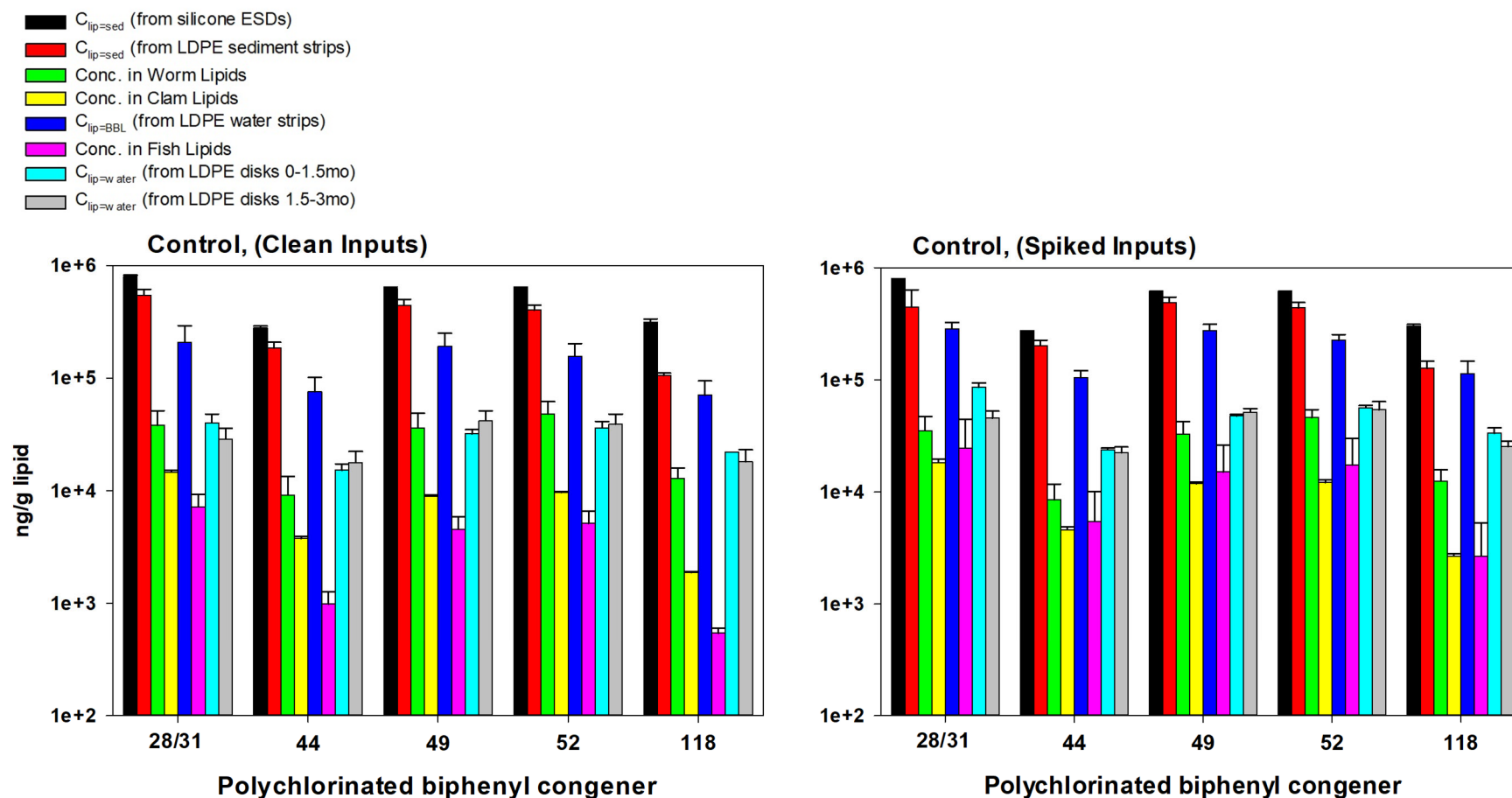


Figure 28. Reference levels in lipid of native bedded PCB congeners in different media of the control (E2). Reference levels in lipid are shown for: silicone ESDs in equilibrium with the sediment, in situ passive samplers in equilibrium with the sediment (LDPE sediment strips), measured worms, measured clams, in situ passive samplers in equilibrium with the benthic boundary layer (BBL) (LDPE water strips), measured fish, and in situ passive samplers in equilibrium with the surface water (LDPE disks) deployed for the first half (0 to 1.5 months) and the second half (1.5 to 3 months) of the experiments. Each bar represents a mean and error bars, the standard deviation ($n=3$ for all media).

In terms of chemical activity vs accessibility (#1 above), this is somewhat beyond the scope of this project. Chemical activity was selected as the focus of this project because it is a theoretical reference level that is not operationally defined (Reichenberg and Mayer, 2006). Therefore, regardless of the polymer used (whether silicones or LDPE), or the time or method to determine equilibrium, the level determined should be the same. Whereas accessibility (such as Tenax extraction, or uptake into a thick strip of LDPE used as an infinite sink) will depend on the type of extraction material and length of extraction. Indeed, Sinche et al. (2019) found that Tenax extraction was highly related to bioaccumulation in benthic amphipod for the NBH and Gould Island sediments used in this project.

It was shown previously that both *in situ* passive sampling with LDPE and *ex situ* equilibrium sampling using silicone agreed (within a factor of two) on the basis of C_{free} (Figure 14), without any apparent bias. However, on a lipid basis, a few select congeners (where polymer-lipid partitioning is available in the literature from Gilbert et al. 2016 and Smedes et al. 2017) show that the *ex situ* method is biased high (Figure 28). This is consistent with the findings of Apell and Gschwend (2016) and Apell et al. (2018), where there is a depletion of the *in situ* porewater PCB concentrations relative to the *ex situ*.

It is quite obvious that the clams and fish are influenced by surface water and clean food/inputs. However, it is helpful to examine the worms, where this may be relatively limited. A tier 1 TEA (similar to Figure 24 above) is provided for the worms compared to both *ex situ* silicone and *in situ* LDPE (Figure 29, native bed congeners only, E2 control only). It appears that *in situ* LDPE is closer to the 1:1 line than *ex situ* silicone, meaning that silicone concentrations are higher than LDPE concentrations. In this way, it is difficult to determine if these differences are due to the different sorption capacities of the polymers or the *in situ* versus *ex situ* method in which they were used. Aside from a few outliers, it appears that the LDPE correlates more strongly with the worms than the silicone. The LDPE was corrected for equilibrium (by PRCs) using the “diffusion method” or Matlab GUI. Sanders et al. (2018) reported that this PRC correction method was inadequate for AC amended sediments. Figure 30 accounts for the possible differences in polymer sorption capacities by putting both silicone and LDPE on a neutral playing field – lipid. Figure 30 also includes the results of the AC amended sediment mesocosms (AC mix, E3). The black and white (or hollow) circles correspond to the blue symbols in Figure 27 (note that X and Y-axes swapped between Figure 30 and 27). In terms of having a metric for assessing contaminated sediments, it appears the *ex situ* silicone coated jars are superior, because the data is well aligned regardless of if the sediment is amended with AC or not (Figure 30). The *in situ* LDPE passive samplers align well with the *ex situ* coated jars when there is no amendment with AC (red squares), but amendment with AC shifts the LDPE data closer to the 1:1 line (blue squares). Is this shift a failure of the PRC correction method (Matlab GUI), or a real phenomenon happening in the mesocosms to the worms? The answer to this question may come back to chemical activity versus accessibility. Ideally, a good bioavailability metric for sediments would predict bioaccumulation similarly regardless of the sediment properties (or amendment added). In this case, the thermodynamic potential of the sediment (predicted lipid

from LDPE) is less relative to actual bioaccumulation when AC is present. But when AC is present, the predicted is closer to the actual (closer to the 1:1) (Figure 30). An explanation might be found in the available pool of PCBs. This available pool (accessibility) also plays a part in determining bioaccumulation. The available pool of PCBs is large in the control (E2), but the pool remains in E3 and contributes to the actual bioaccumulation. The LDPEs are not sampling the available pool that remains, they only see chemical activity, and thus the LDPEs decrease faster than the actual worm lipid in response to the AC after just 3 months. The additional 2 week mixing of the *ex situ* coated jar method, reduces small scale heterogeneities, and advances the mass transfer kinetics of PCBs from sediment to AC, limiting the available pool's contribution to actual bioaccumulation, and allows this measure of chemical activity to remain aligned with actual bioaccumulation with and without AC. Then the question arises, if the available pool was so large in the unamended sediment (E2 control), why did that not lead to a misalignment in the silicone data between E2 and E3? Perhaps when the chemical activity and available pool are both very high, the chemical activity plays the major role as a limiting factor in how much the PCBs can be thermodynamically driven into the tissue. And even under these conditions, the worms only reached about 10% of the maximum from the sediment, due to dilution factors from surface water and clean food (#3, 4 and 5 above). If this reasoning is somehow flawed, perhaps Sanders et al. (2018) was correct, the PRC correction method is compromised in some way by AC (possibly due to AC's nonlinear sorption isotherms). Finally, even though there are differences between the *in situ* passive samplers and *ex situ* equilibrium samplers on a lipid basis, the two methods were essentially equivalent when compared on the basis of C_{free} (Figure 14; see Schmidt et al. 2017 for more details), where the two methods agreed within a factor of 2 (without any apparent bias) when analyzed in the same laboratory.

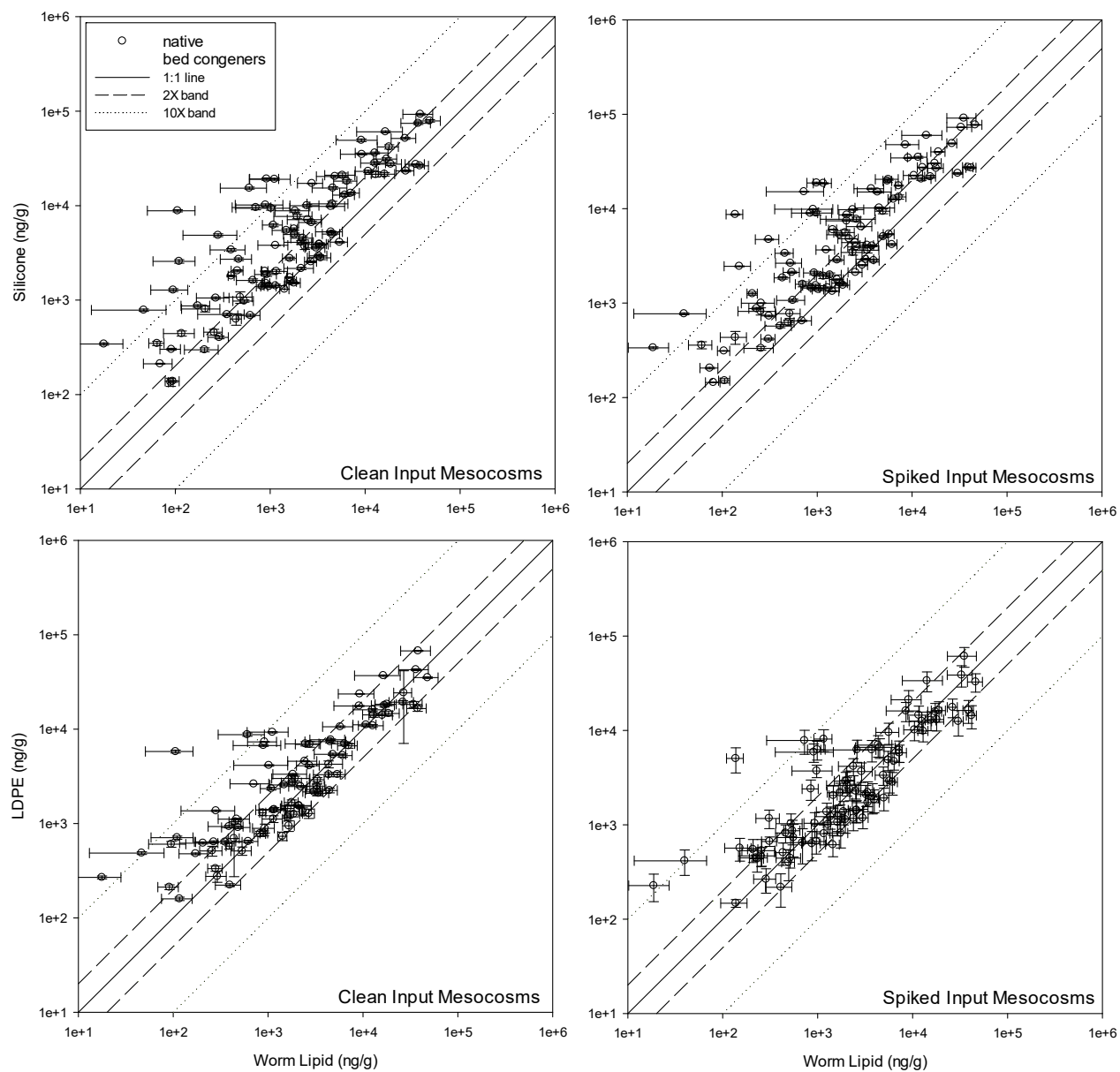


Figure 29. Concentrations in silicone and LDPE (surficial sediment sampled) plotted against worm lipid for clean and spiked input mesocosms of the control experiment. 2X and 10X bands are provided.

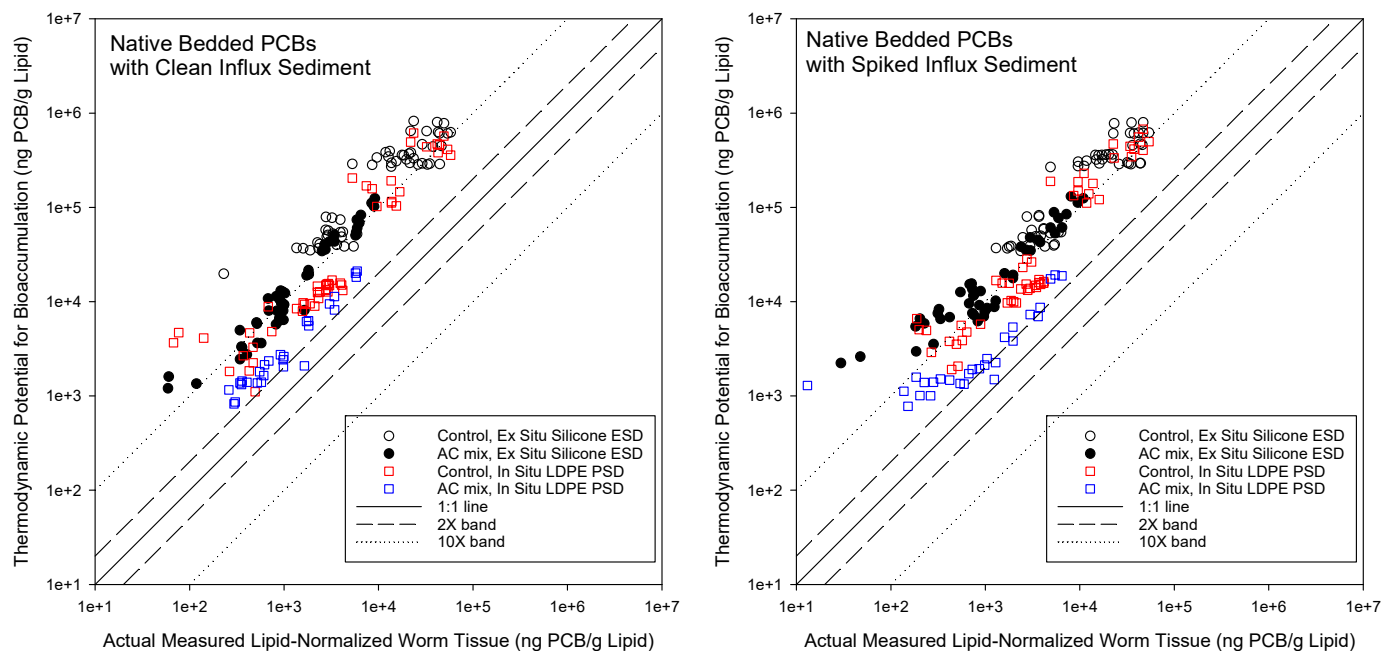


Figure 30. Thermodynamic potential from the sediment (or predicted lipid) versus measured concentrations in lipid (worms only, E2 and E3). Here, polymer concentrations were converted to lipid concentration (using polymer:lipid partitioning from Gilbert et al. 2016 and Smedes et al. 2017). There are no error bars because polymer and lipid values were matched within each mesocosm. Input congeners are not included, because congeners 13, 54 and 173 do not have independently determined polymer:lipid partitioning coefficients. LDPE are red and blue squares, silicone are black and hollow circles. The control (E2) are red or hollow symbols, and the AC mix (E3) are blue or black symbols. Clean influx mesocosms are shown on the left, and spiked influx mesocosms are shown on the right.

Figure 31 expands the analysis in Figure 30 to all species (worms, clams, and fish). Figure 31 is similar to Figure 27 (which only showed silicone coated jars, not LDPE, but with the X and Y-axes switched.) Even though the fish were influenced by factors other than the bed sediment treatment, the passive samplers in the water column should have been affected by these surfaces and processes similarly. As a starting place, LDPE passive samplers in the sediment (sediment strips) and water column (water column discs) (X-axis) were compared to actual fish lipid (Y-axis) in the control (E2) (Figure 32). Indeed, surface water LDPE disks were a better predictor of native bed PCBs in fish tissue than sediment LDPE strips ($r^2 = 0.67$ vs 0.59). The trend for the input congeners with surface water LDPE discs appears to be different from that for bed congeners. PCB 173 and 54 were similar; surface water LDPEs were high and sediment LDPEs were low (because these input PCBs were not getting down into the bed). PCB 13 was different from the other inputs because it was also present in the bed as a native congener.

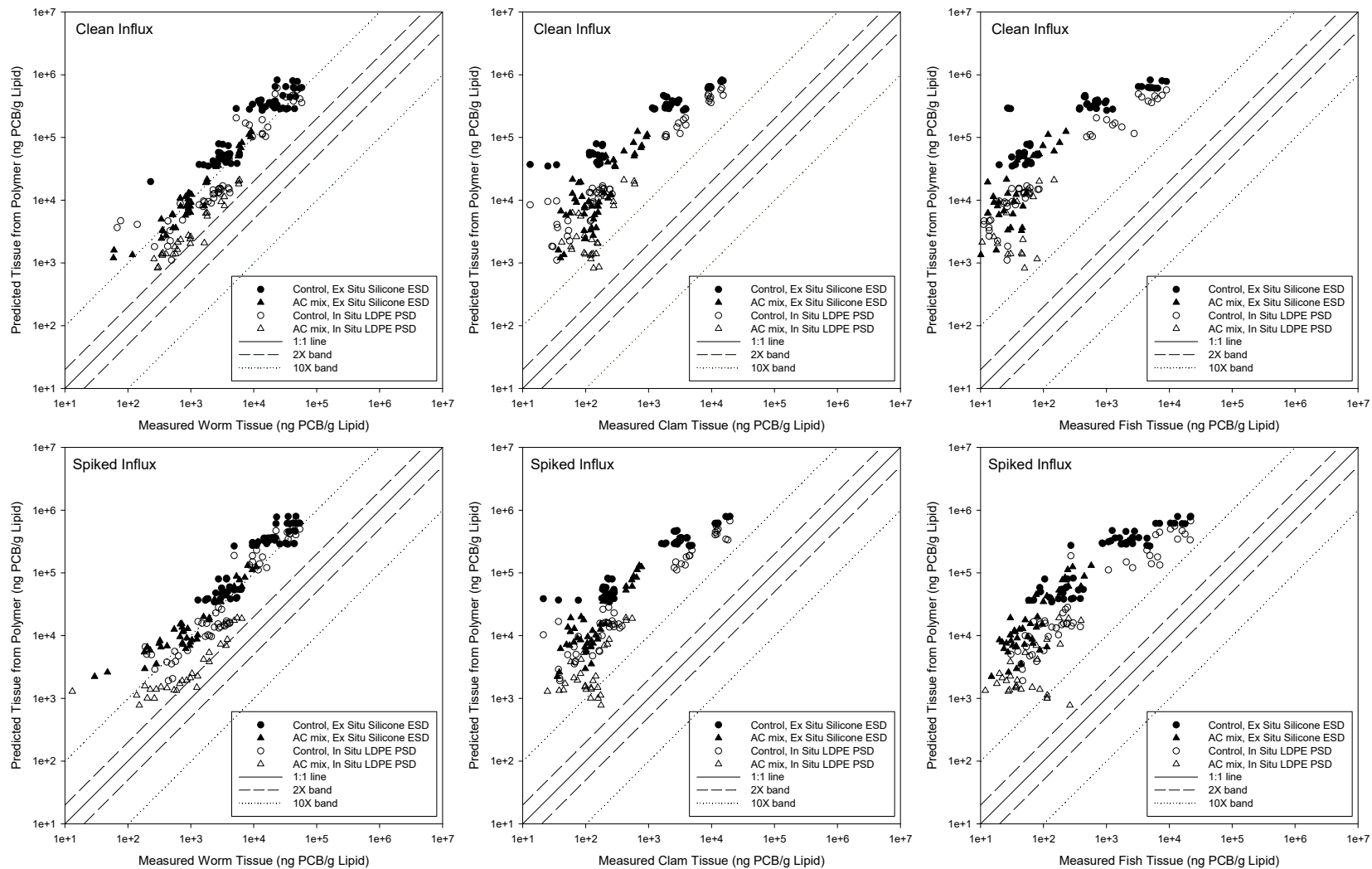


Figure 31. Thermodynamic potential from the sediment (or predicted lipid) versus measured concentrations in lipid (worms, clams, and fish, E2 and E3). Similar to Figure 30 above for worms only.

For the native bed congeners, the relation was plotted for all experiments in the NBH series: fish versus LDPE discs (Figure 33). The relationship was poor. It also seems like it changes depending on the remedy, which was a similar problem with sediment LDPEs and worms in Figure 30.

In a monitoring program, accumulation in polymer and in biota should be used to track remedy efficiency as % reduction in bioavailability, rather than as absolute values. Reductions (as a fraction remaining, i.e., 90% reduction = 0.1) in actual worm lipid concentrations by AC amendment on the X-axis, and the fraction remaining in lipid concentration equilibrated with the sediment (as shown by polymers) on the Y-axis (Figure 34). Since most of the data for the polymers falls along the 1:1 line within a factor of 2, the polymers and tissues are generally tracking together similarly. The tetra-chlorinated congeners fell closest to the 1:1 line, relative to other faster (light) and slower (heavy) congeners. The data for spiked input mesocosms were also closer to the 1:1 line than the clean input mesocosms, but the two different polymer methods were more alike in the clean input mesocosms than the spiked input mesocosms. The silicone coated jar data remained closer to the 1:1 line relative to the in situ passive samplers, showing that the silicone coated jar data more accurately predicted worm bioaccumulation in these mesocosms (E2 and E3) (Figure 34).

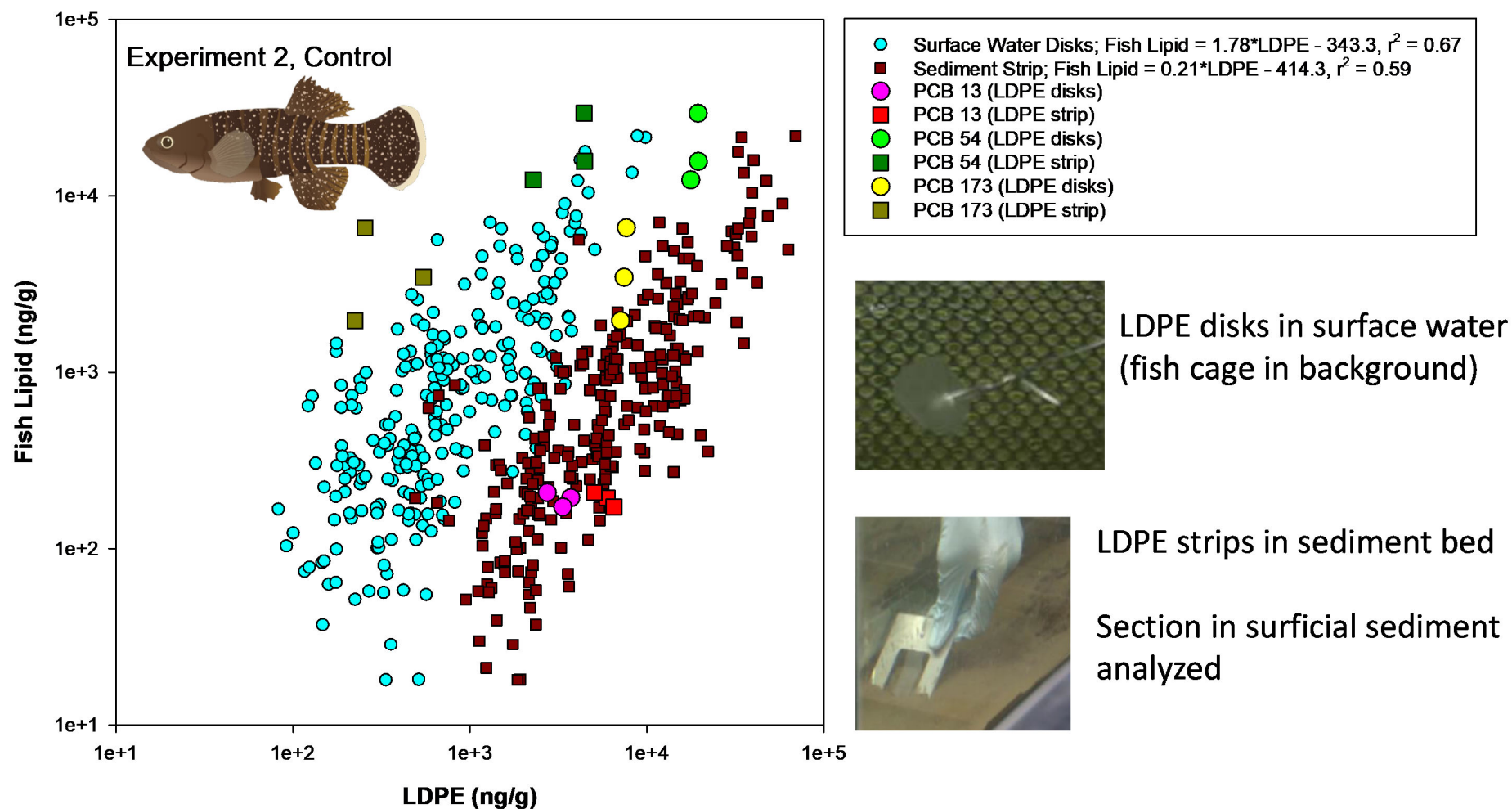


Figure 32. Comparing Fish to LDPE discs in the water column and LDPE strips in the sediment (both corrected for equilibrium using PRCs) for E2.

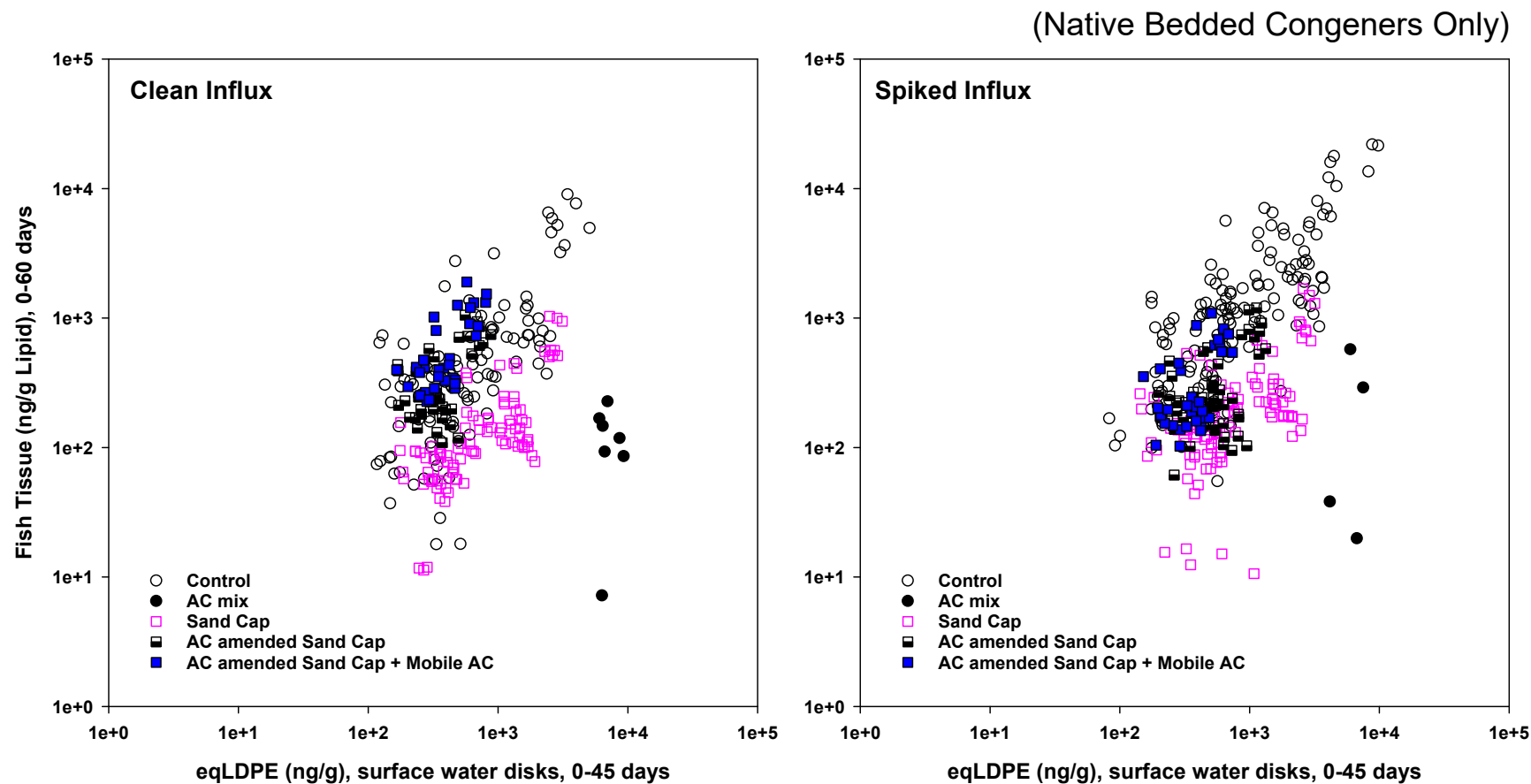


Figure 33. Comparing Fish to LDPE discs in the water column (corrected for equilibrium using PRCs) for E2, E3, E4, E5 and E6.

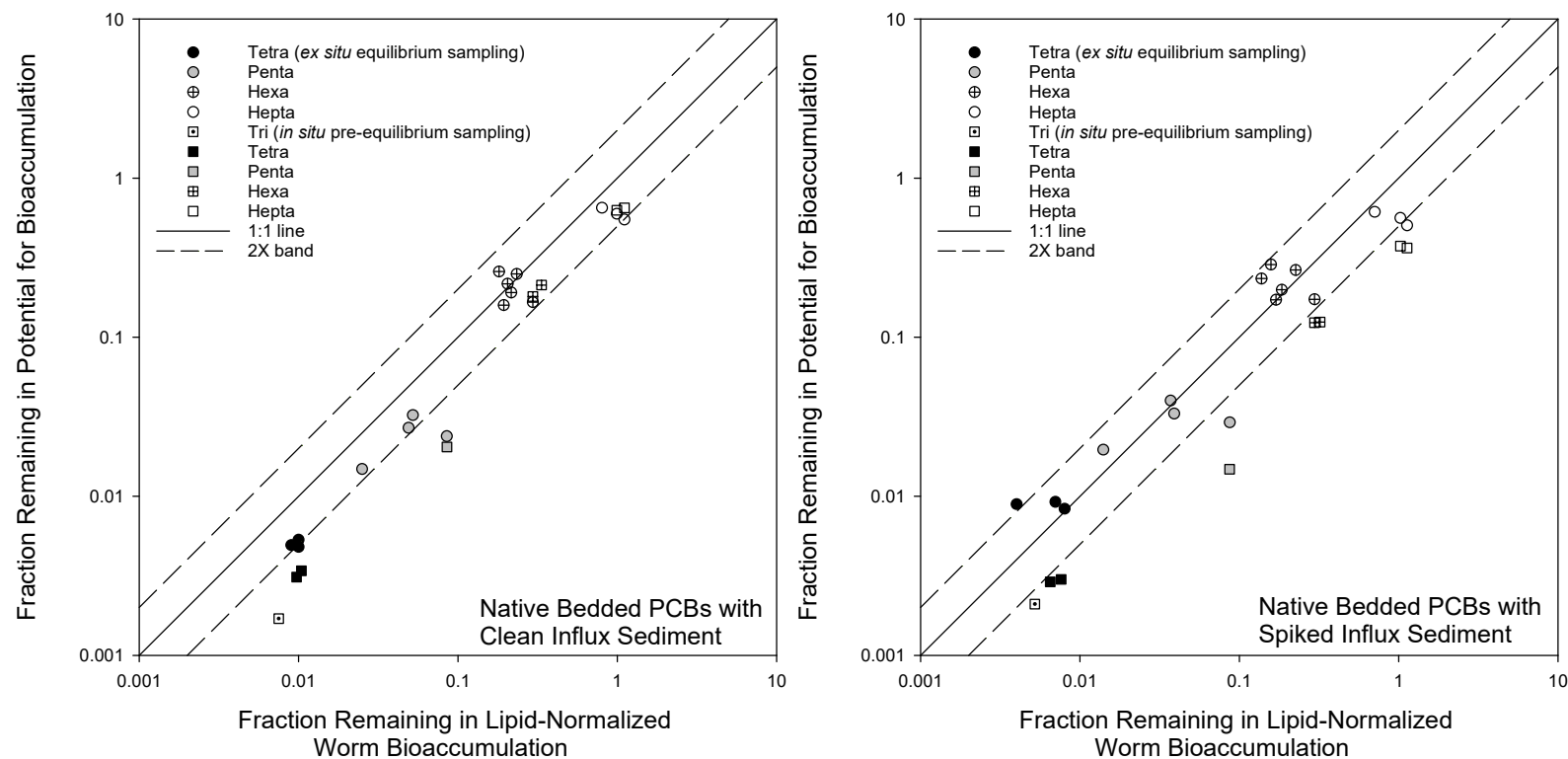


Figure 34. Fraction of PCB congeners remaining in lipid in equilibrium with the sediment determined from silicone coated jars ($C_{\text{Lipid} \rightleftharpoons \text{Sed}}, \text{AC mix} / C_{\text{Lipid} \rightleftharpoons \text{Sed}}, \text{Control}$) versus fraction remaining in worm lipid ($C_{\text{lipid}}, \text{AC mix} / C_{\text{lipid}}, \text{Control}$) for clean input and spiked input mesocosms. A fraction of less than 1 is a reduction in bioaccumulation or exposure, while a fraction of greater than 1 is an increase. If congeners were non-detect in either the control or AC mix, a value was not shown in the plot. Solid symbols are tetra-chlorinated congeners, gray symbols are penta-chlorinated congeners, crossed symbols are hexa-chlorinated congeners, and hollow symbols are hepta-chlorinated congeners. Input congeners were not included in the above plot. For silicone coated jars, data that showed an $r^2 < 0.60$ and/or $\text{RSE} > 20\%$ (by the 3 silicone thicknesses) were excluded. Using only jar data passing strict QA/QC checks, there was a very strong relation between changes in silicone and changes in worm lipid.

6. Gould Island sediment mesocosm experiments

6.1. Remedy effectiveness assessment

A series of three additional experiments were conducted with sediment from Gould Island, Jamestown, RI. The sediment was collected from the “Stillwater” boat basin overall area of the Navy Installation Restoration Program (IRP) Site 17, the Building 32 Area at Gould Island (Tetra Tech, 2011). Relative to the NBH sediment, the PCB bulk phase concentrations of Gould Island are an order of magnitude lower (~ 0.33 mg/kg-dry at initial screening). The sediment TOC was also an order of magnitude lower (0.58%). The additional experiments were a sand cap (E8, similar to E4 with NBH) and an AC mix (E9, similar to E3 with NBH, but at a much lower AC dose). Those treatments were compared to the control (E7, no remedy). The AC mix with Gould Island (GI) had a dose of only 0.026% (5% of TOC) versus the 4.3% (96% of TOC) added to the NBH sediment. An assessment of the Gould Island AC mix versus the control is shown in Figures 35 and 36 for LDPE sediment strips compared to worms, and LDPE compared to clams. The low dose of AC (0.026%) reduced uptake in LDPE strips in surficial sediment corrected for equilibrium, but increased bioaccumulation in biota (worms and clams). Even the sand cap (E8) did not reduce bioaccumulation in the Gould Island experiments as illustrated by clam data in Figure 37. The similar uptake of native bed PCBs in the Gould Island capping experiment (E8) compared to the control (E7) for spiked inputs suggests that the bed sediment was well homogenized and similar across the control (E7), the cap (E8) and the AC mix (E9). The increase in the native bed congeners between E7 and E8 for clean inputs could be due to a mechanism observed with the NBH series of capping experiments, where we speculated that the deposition of clean input sediment “facilitates” uptake of the bed congeners. This could be a mechanism of PCBs dissolving through the sand cap and resorbing to input sediment in a bioavailable state at the sediment-water interface. The increased bioaccumulation of native bed congeners in the AC mix (E9) relative to the control (E7) for the clean input might be explained by a reduction in C_{free} that led to an increase in organism feeding rates. An alternative explanation is that the bed sediment was well homogenized and therefore similar between the control (E7) and the cap (E8), but was a portion containing higher contamination was used for the AC mix (E9). Material collected at the termination of the GI experiments showed that bulk phase concentrations were a factor of 2.3 and 4 higher, respectively, between the control (E7) and AC mix (E9) for spiked and clean input replicates, respectively. Although this was based on single measurements (1 replicate), it supports the possibility that a poorly homogenized portion containing higher contamination was used for E9.

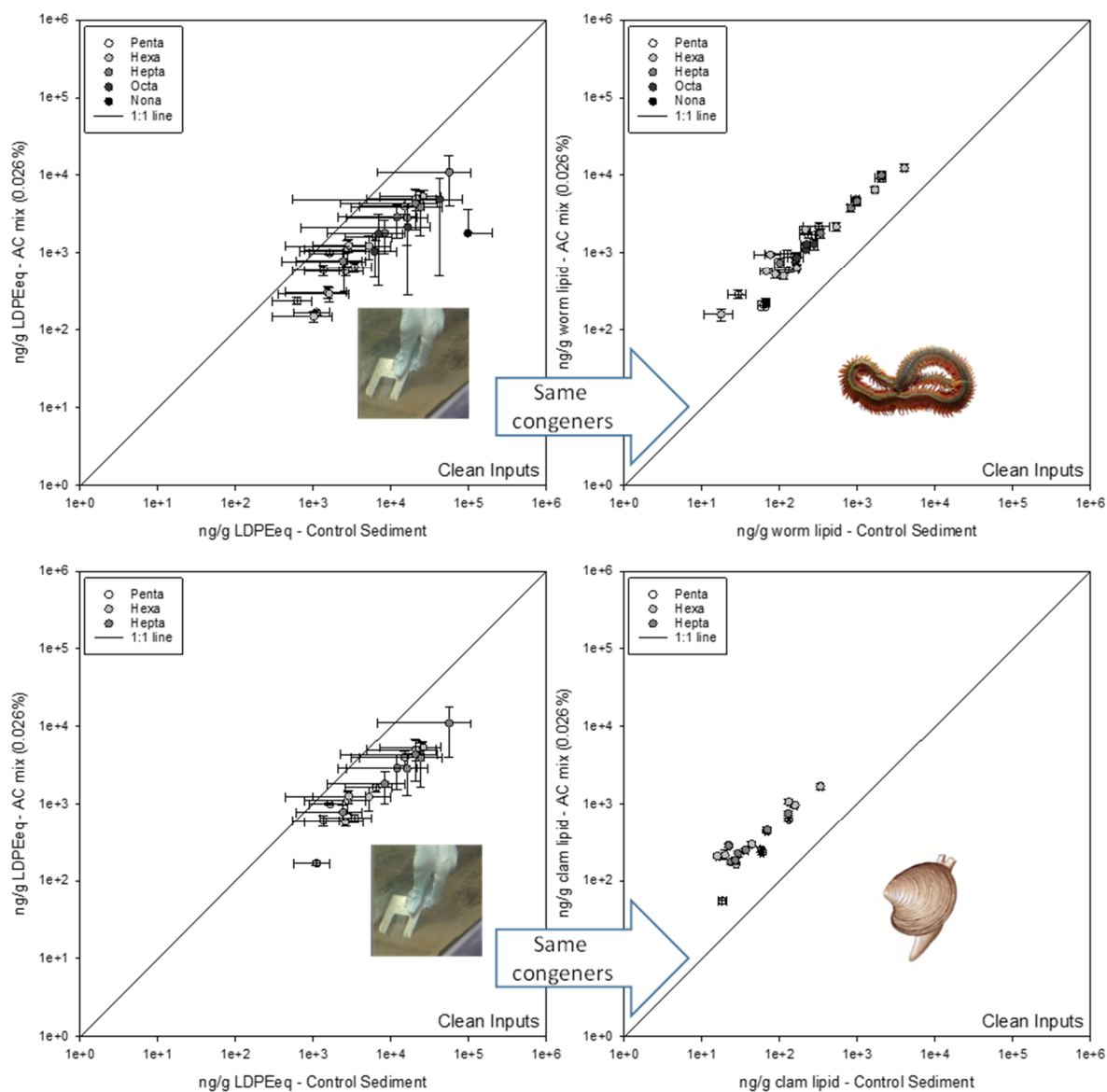


Figure 35. Matched congeners in LDPE and worms, or LDPE and clams. Each plot shows AC mix versus the control (clean input mesocosms).

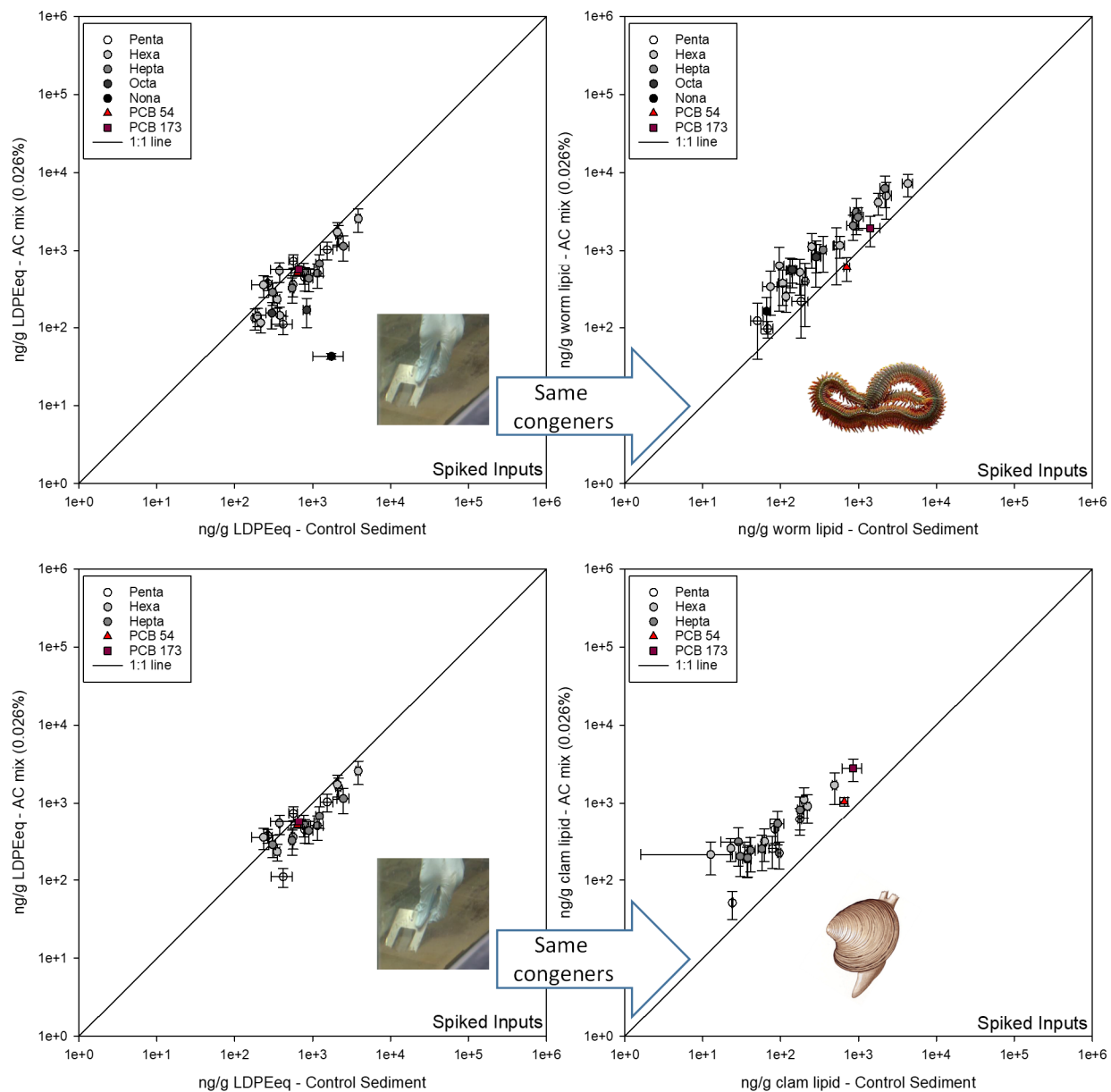


Figure 36. Matched congeners in LDPE and worms, or LDPE and clams. Each plot shows AC mix versus the control (spiked input mesocosms).

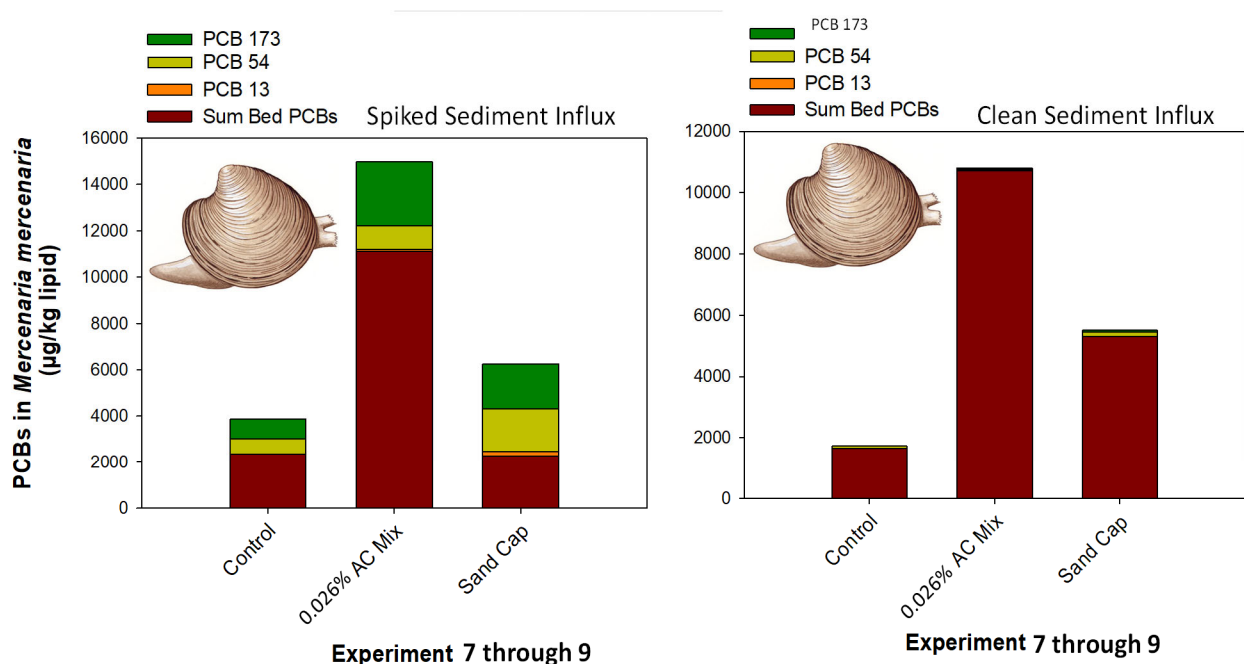


Figure 37. Bioaccumulation in clams for the Gould Island experiments.

Sinche et al. (2019) and Sinche (2018) examined PCB accessibility in NBH and GI sediments used in this study. Using Tenax and bioaccumulation in the amphipod, *Leptocheirus plumulosus*, Sinche (2018) reported that PCB uptake in both Tenax and amphipod were lower for the AC-amended sediment. It was suspected that additional contact with the AC was responsible for the effectiveness of the low dose AC treatment. Further testing of the AC amended Gould Island sediment (using the silicone coated jars) was conducted to see if additional mixing and contact time could further reduce C_{free} (Figure 38). Additional mixing for up to 6 months and at two different mixing intensities did not show a noticeable change in PCB chemical activity of the GI sediment amended at 0.026% (by wt). Therefore, differences between mesocosms experiments and experiments reported in Sinche (2018) remain unexplained.

6.2. Tier 1 TEA – A comparison of NBH and GI

Using TEA, the NBH sediment (E2) is compared to the GI sediment (E7) in Figure 39. The LDPE data are the calculated equilibrium concentrations in the sediment strips. The strong relation determined for the NBH sediment mesocosms was not always held for the GI sediment mesocosms. GI mesocosms seem to hold the strong relation in the spiked input mesocosms for worms and clams. For fish, a strong relation exists for spiked inputs, but it is weaker as that observed for NBH. The relation really breaks down with clean input mesocosms for the GI mesocosms. The differences between NBH and GI for clean inputs (top row in Figure 39) might be explained by location if the clams feed higher in the water column for GI than NBH. If the spiked input discouraged this behavior, then that would explain the closer match between NBH and GI for spiked inputs (bottom row). The caged fish are higher up in the water column and were not expected to have changed change their feeding, other than by increasing or decreasing feeding rate. The fish would also be expected to be more associated with the water column than

the other organisms, and this should be factored into any interpretation of the LDPE sediment strips. In Figure 39 (bottom right plot) the GI data might be shifted down due to the levels of bioturbation and resuspension compared to the NBH mesocosms. Because the GI sediment was much denser than the NBH sediment, the clams, and especially worms, might have been more successful in bioturbating the NBH sediment relative to the GI sediment.

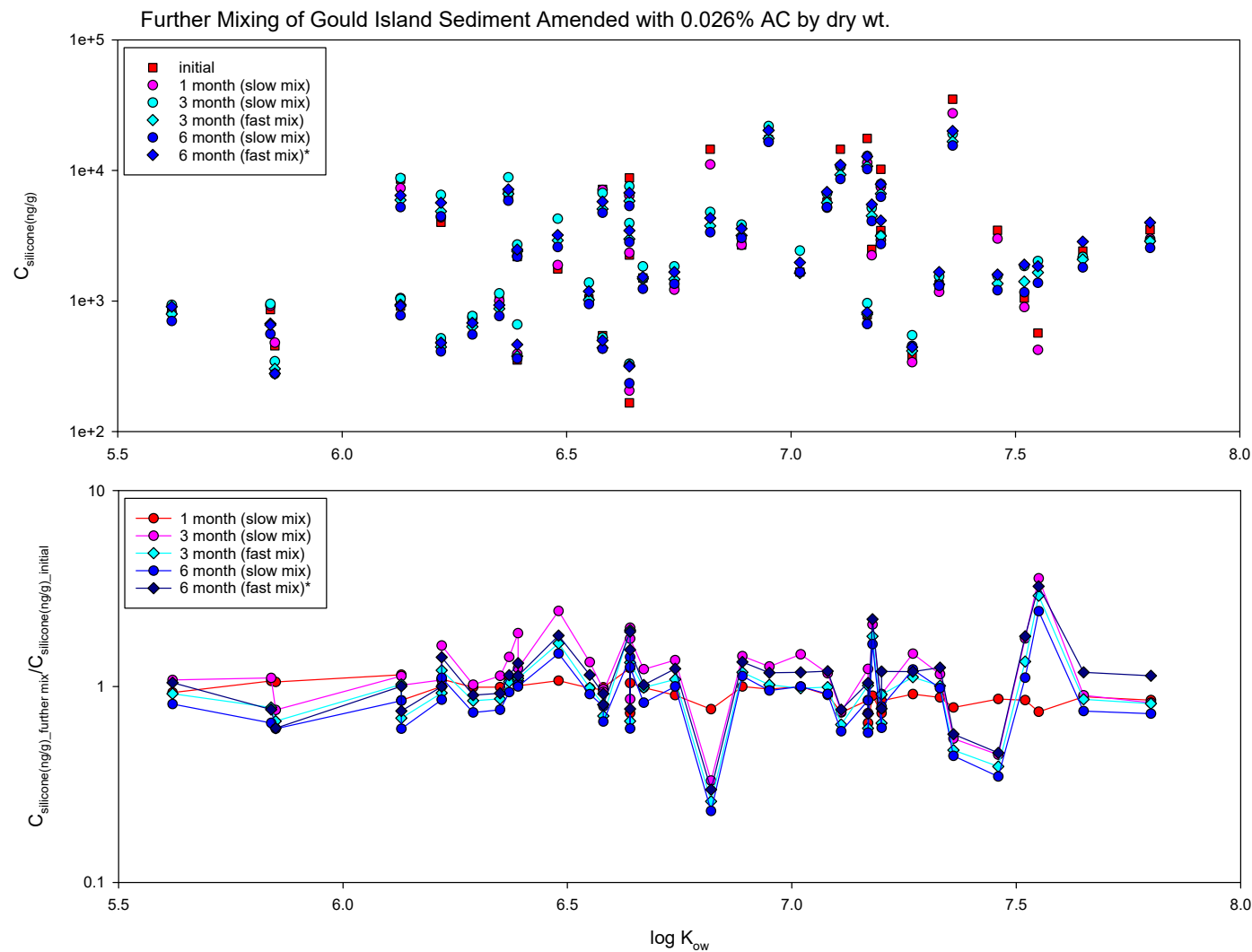


Figure 38. Equilibrium concentrations in silicone vs $\log K_{ow}$ (top plot) for GI sediment amended with 0.026% AC by dry wt. (0.05% of the TOC). Fraction of equilibrium silicone uptake in further mix treatment over the control (initial) (bottom plot) for the same batch experiments. Six month (fast mix) was not confirmed to be in equilibrium using 3 silicone thicknesses.

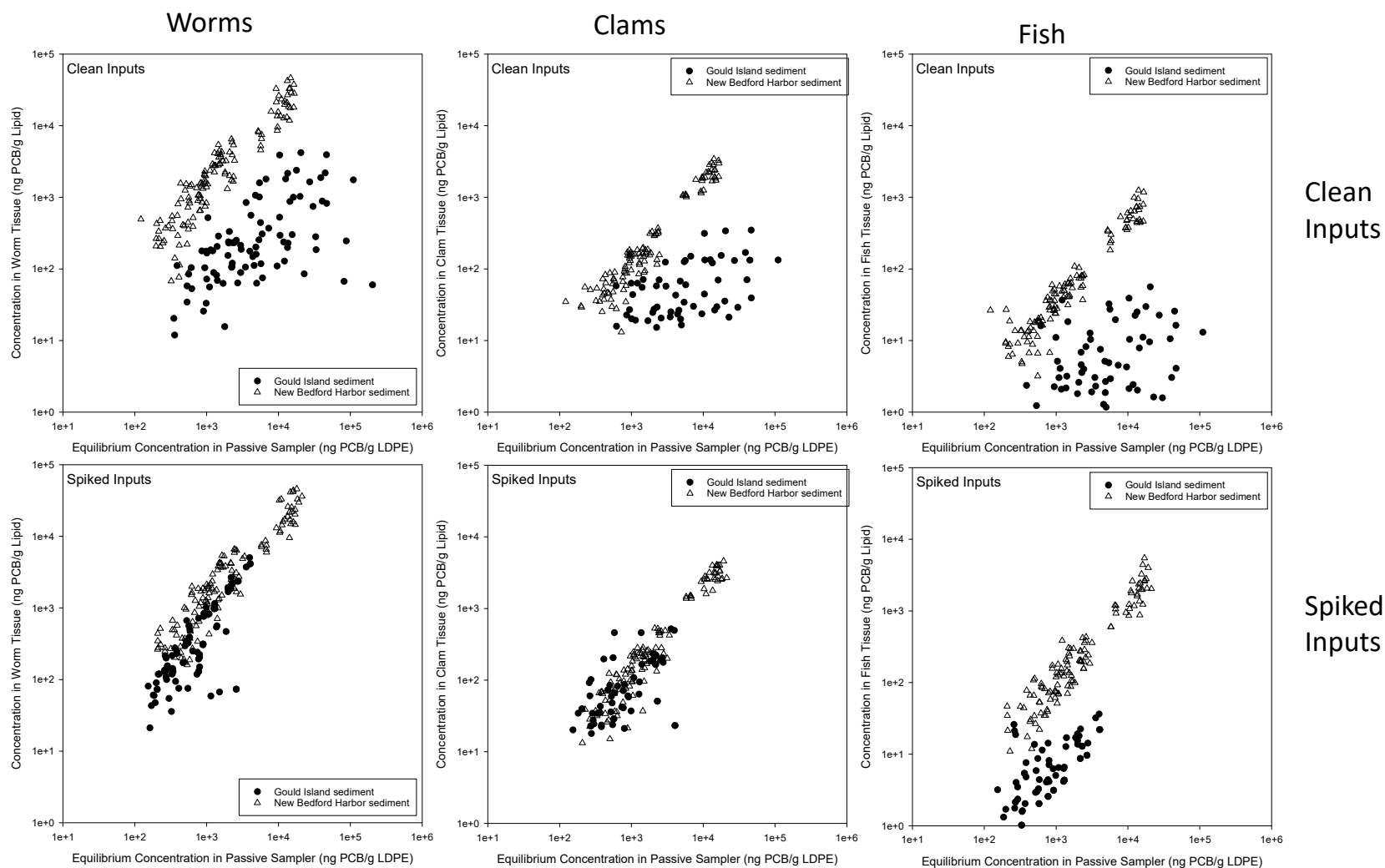


Figure 39. Bioaccumulation of bed congeners in organisms vs. sediment LDPE strips (two sediments: GI and NBH).

7. Batch experiments evaluating the benefit of low-level activated carbon application

Additional batch experiments using silicone coated jars sampling method were conducted to explore the efficacy of low doses of activated carbon. A related study in our laboratory using sediment from Ashtabula Harbor (OH, USA) generated evidence for a low dose of AC providing a significant reduction in PCB bioavailability. That prompted us to conduct additional batch experiments using PCB-contaminated sediments obtained from GI and also from Hunters Point (HP), a coastal site near San Francisco (California, USA).

Total PCB bulk phase concentration in Ashtabula Harbor sediment (~ 0.08 mg/kg-dry) was lower than in the GI sediment, but the range of TOC was higher (1.3 to 2.8%). The AC-sediment batches were continually mixed on rotary agitator at 24 RPM end-over-end rotation for 60 days. They were sampled with the coated jars for two weeks, and then analyzed. Figure 40 shows the uptake in silicone for doses of AC equal to 1% and 10% of the TOC. AC doses equal to the TOC (100%) resulted in non-detects for all congeners. These results indicate that an AC dose equal to 10% of the native TOC caused reductions in chemical activity of PCBs in the sediment. From a practical standpoint, a dose of AC should be at least half the native TOC.

The efficacy of AC amendment to remedy HP has been studied extensively (see Ghosh et al. 2011 and references therein). The PCB bulk phase concentrations of the HP sediment used in these experiments was 0.6 mg/kg-dry and a TOC of 1.8%. The aim was to test low doses of AC to HP sediment using the silicone coated jars. Unlike Ashtabula sediment, the HP experiments had many more congeners detected in all the treatments, allowing for a much more robust analysis. In addition, many congeners could be confirmed to be in equilibrium with the silicone (by three thicknesses of silicone per rep) for all treatments. Doses of 5% and 50% of the TOC (three reps of each dose) were compared to a no-AC control. Mixing the AC-sediment batches was conducted at 22 RPM end-over-end rotation for 58 days. Figure 41 shows the 5% of TOC dose (top plots) and the 50% of TOC dose (bottom plots). The left side plots show data in the form of bar plots, while right side plots show cross-plots (Figure 41). A dose of AC at 5% of the TOC to HP sediment caused a 19% reduction in 36 matched congeners. An AC dose of 50% of the TOC to HP sediment caused a 63% reduction in chemical activity for 26 matched congeners. This also confirms our conclusions from the Ashtabula Harbor sediment batch experiments, that an AC dose equal to 50% the TOC would be required for significant reductions. However, often >90% reductions are desired. In this case, a dose of AC equal to the TOC is likely required.

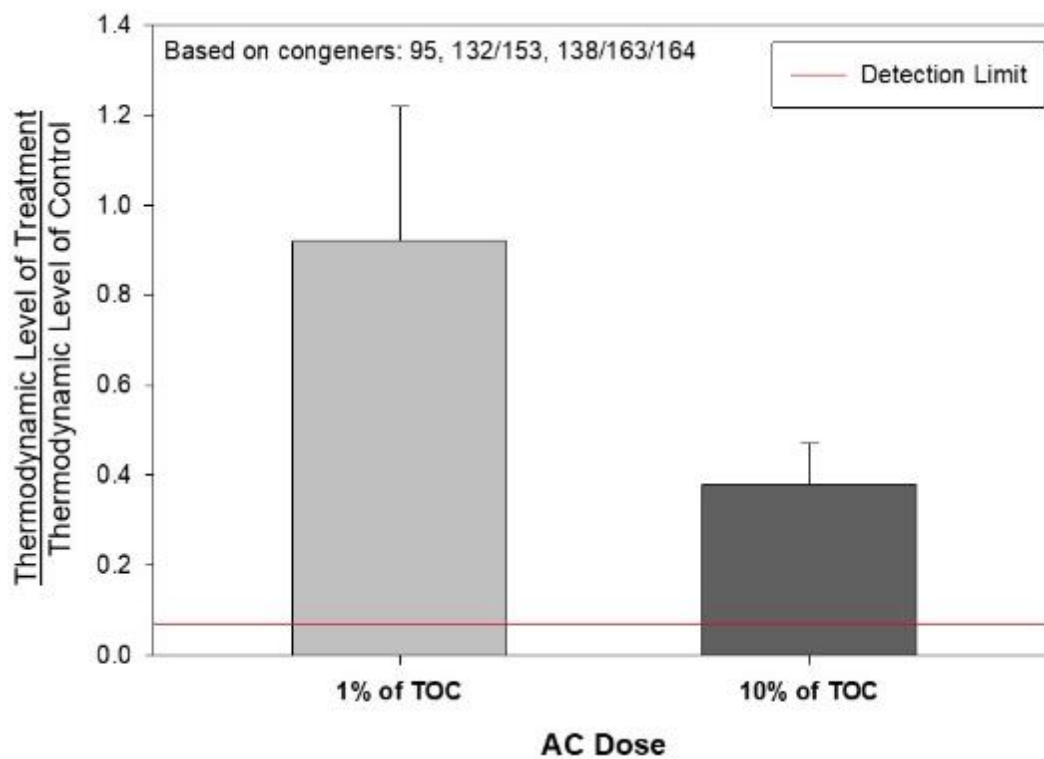


Figure 40. Fraction of silicone uptake in treatment over the control for Ashtabula sediment (2.8% TOC) amended with low doses of AC. An AC dose equal to 100% of the TOC resulted in levels in silicone that were below detection.

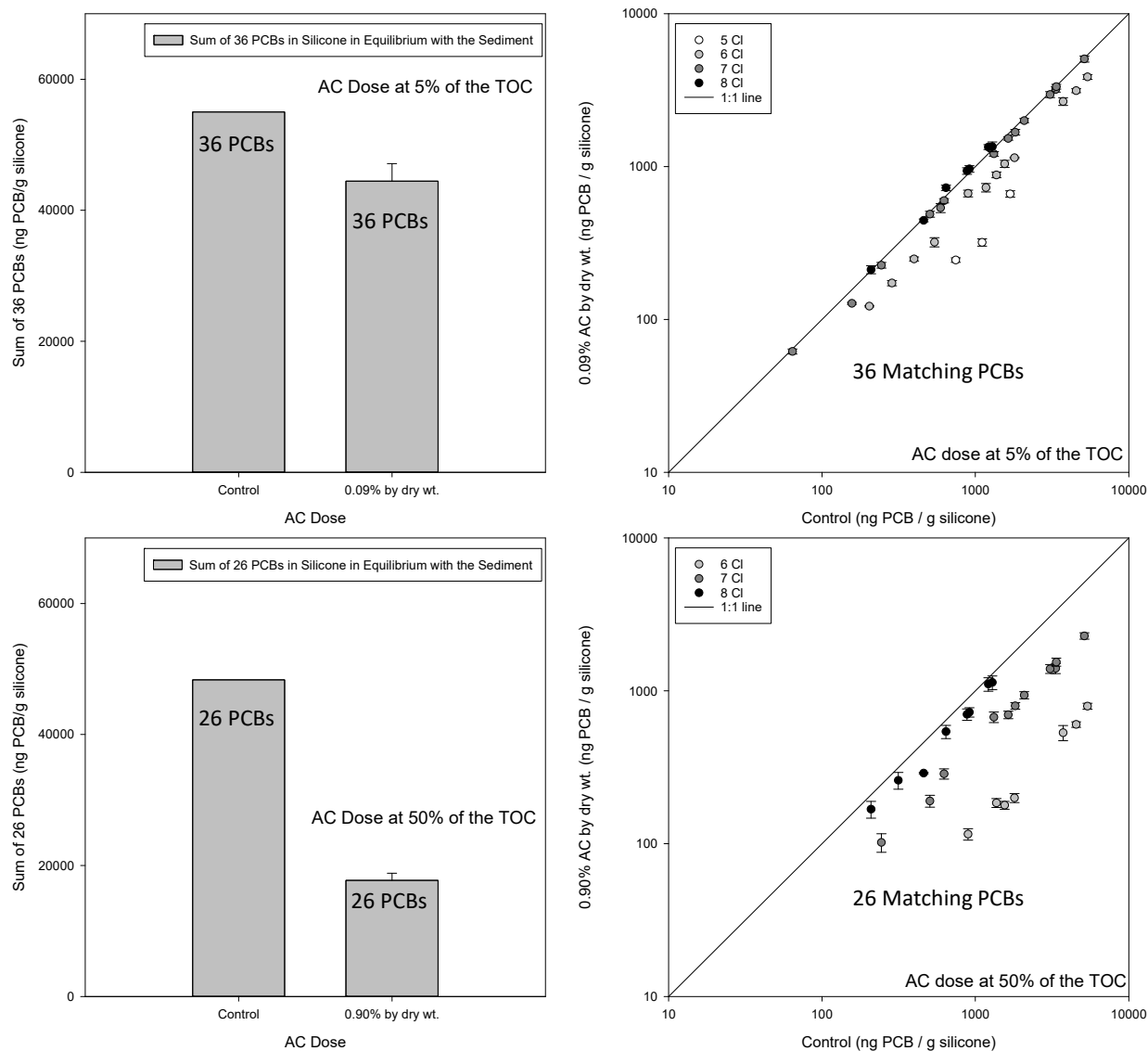


Figure 41. Equilibrium silicone concentrations from Hunters Point sediment amended with low doses of activated carbon. Top plots show AC dose at 5% of the TOC and bottom plots show dose at 50% of TOC. Left side show simple bar plots, while the right side shows cross-plots of the same congeners (amended vs unamended control).

8. Food Web Model predictions for PCB uptake in functionally diverse aquatic organisms used in mesocosm experiments

Background

Laboratory mesocosm experiments described in Chapter 3 were conducted to observe PCB uptake in three functionally different aquatic organisms from NHB sediment under a range of sediment treatment scenarios. The modeling work presented here is aimed at providing interpretation of the observed measurements in the context of how the organisms interact differently based on the differences in their feeding and ventilation behaviors in laboratory mesocosms and under the different treatment scenarios. The work focusses on the control with biota (E2), sediment treated with AC (E3), and sediment treated with a thin layer of sand cap (E4).

Food web modeling approach and assumptions

A food web model based on the Arnot and Gobas (2004) bioaccumulation model and described in Ghosh et al. (2021) was developed to simulate exposure to a range of aquatic organisms. The model describes the kinetics of uptake and loss processes for each organism based on their specific biology and interaction with the rest of the food web and the environment under the constrained laboratory mesocosms. The model was then used to predict steady state concentrations in each organism used in the mesocosm experiments. Several changes were made in the model to allow inputs of directly measured parameters such as the freely dissolved concentrations in sediment porewater and surface water. The original model (Ghosh et al. 2021) uses a partitioning calculation to estimate the freely dissolved concentration in sediment porewater and surface water. For the mesocosms experiments, freely dissolved concentrations were directly measured using passive sampling and thus, the directly measured values were used in the predictions. Major components of a food web model are the assumptions made for the composition of the diet and the type of water ventilated (surface water or porewater). Diet composition of native organisms in New Bedford Harbor were obtained from personal communications with Dr. Lawrence Burkhard from the USEPA and modified as necessary to address specific exposure conditions within the laboratory mesocosms and different treatments used for the laboratory experiments. Organism wet weight and lipid content were based on measured values. All simulations were performed at 20°C and measured oxygen saturation. Organisms were fed clean food. This is a major departure from what one would expect to see in the natural environment and had to be accounted for in the predictions for the laboratory experiments.

Bioaccumulation prediction in *Alitta virens* in E2

For the worm, assuming 100% ingestion of sediment as food and 100% ventilation of sediment porewater leads to a significant overprediction of uptake of PCBs as shown in Figure 42 below. For both the native sediment congeners (black circles) and the input congener PCB 13 (also present in sediment; red circle), the predictions are about an average factor of 3 higher. While

polychaetes live primarily within the sediment bed, they largely ventilate surface water to access oxygen necessary for survival. Work by USEPA in modeling PCB uptake in New Bedford Harbor (Burkhard 2013) assumes 100% ventilation of surface water by the polychaetes. As shown in Figure 43, assuming 100% ventilation of surface water by the polychaetes while ingesting 100% sediment in their diet, improves the prediction to within a factor of 2, but still overpredicts the uptake, especially for the more hydrophobic congeners. In the mesocosms experiments, clean food was introduced in the exposure chambers periodically and it is reasonable to assume that the clean food that settled on the sediment surface was ingested by the worms. A further simulation was performed assuming that the worms ingested 50% clean food and 50% sediment as part of their diet. The results of this simulation are shown in Figure 44. The close match between predicted and observed uptake as shown in Figure 44 indicates that it is necessary to account for the ingestion of clean food to adequately describe the behavior of the organisms in the mesocosms.

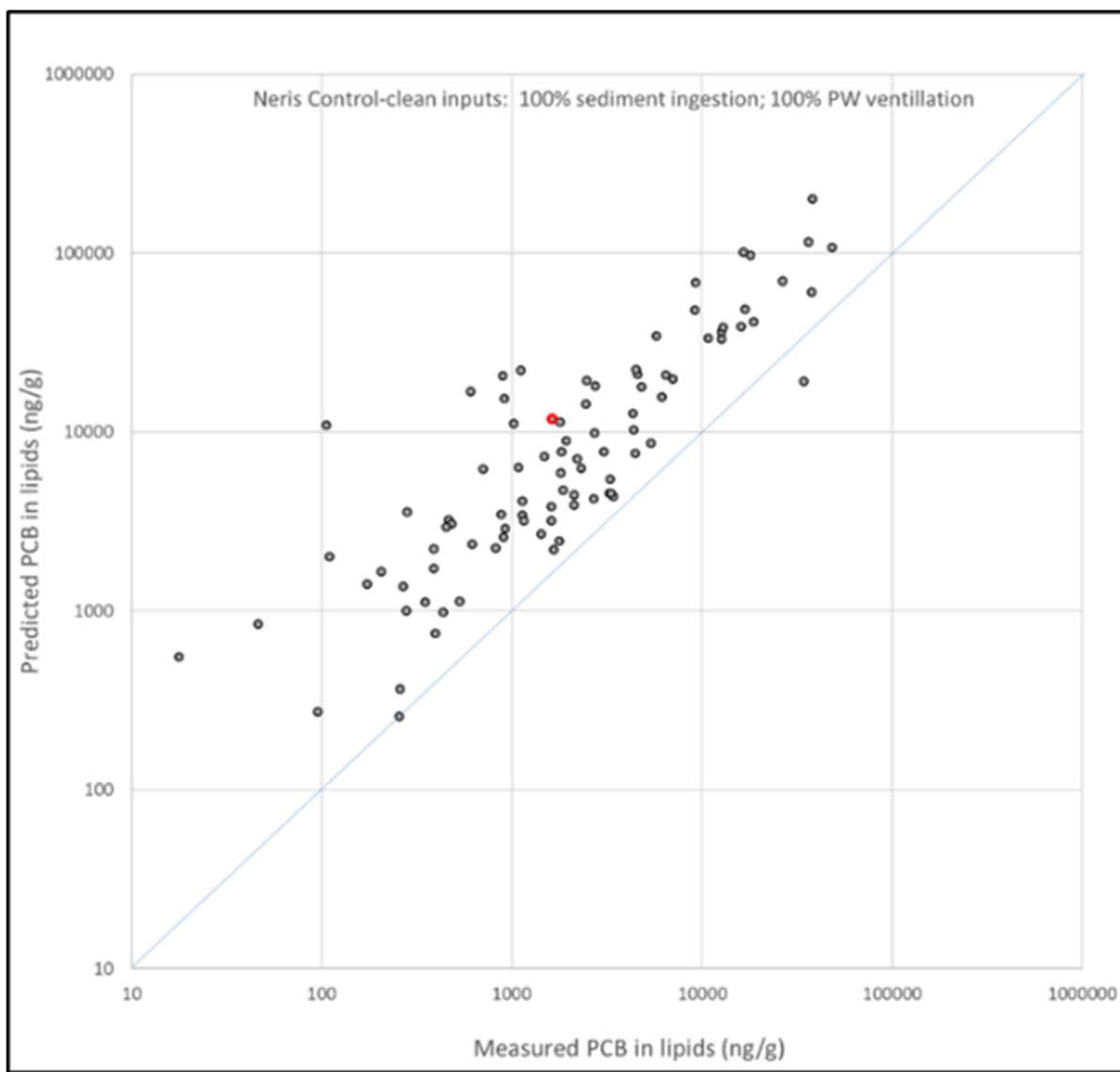


Figure 42. Comparison of predicted and measured tissue concentration of PCB congeners in the benthic worm *Alitta virens* exposed to untreated NBH sediment in E2. In this modeled scenario, the worm diet is composed of sediment only and the worm solely ventilates porewater.

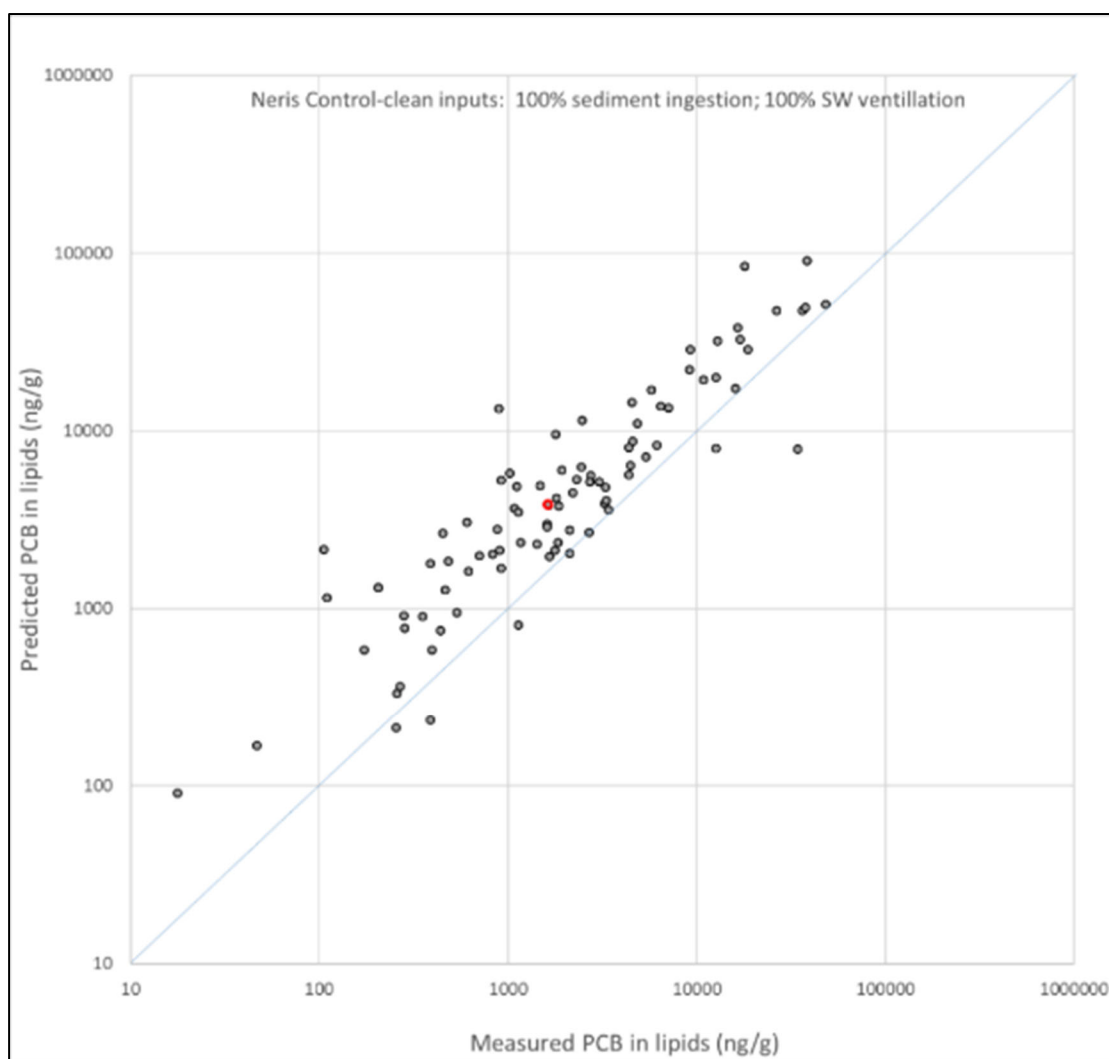


Figure 43. Comparison of predicted and measured tissue concentration of PCB congeners in the benthic worm *Alitta virens* exposed to untreated NBH sediment in E2. In this modeled scenario, the worm diet is composed of sediment only and the worm solely ventilates surface water.

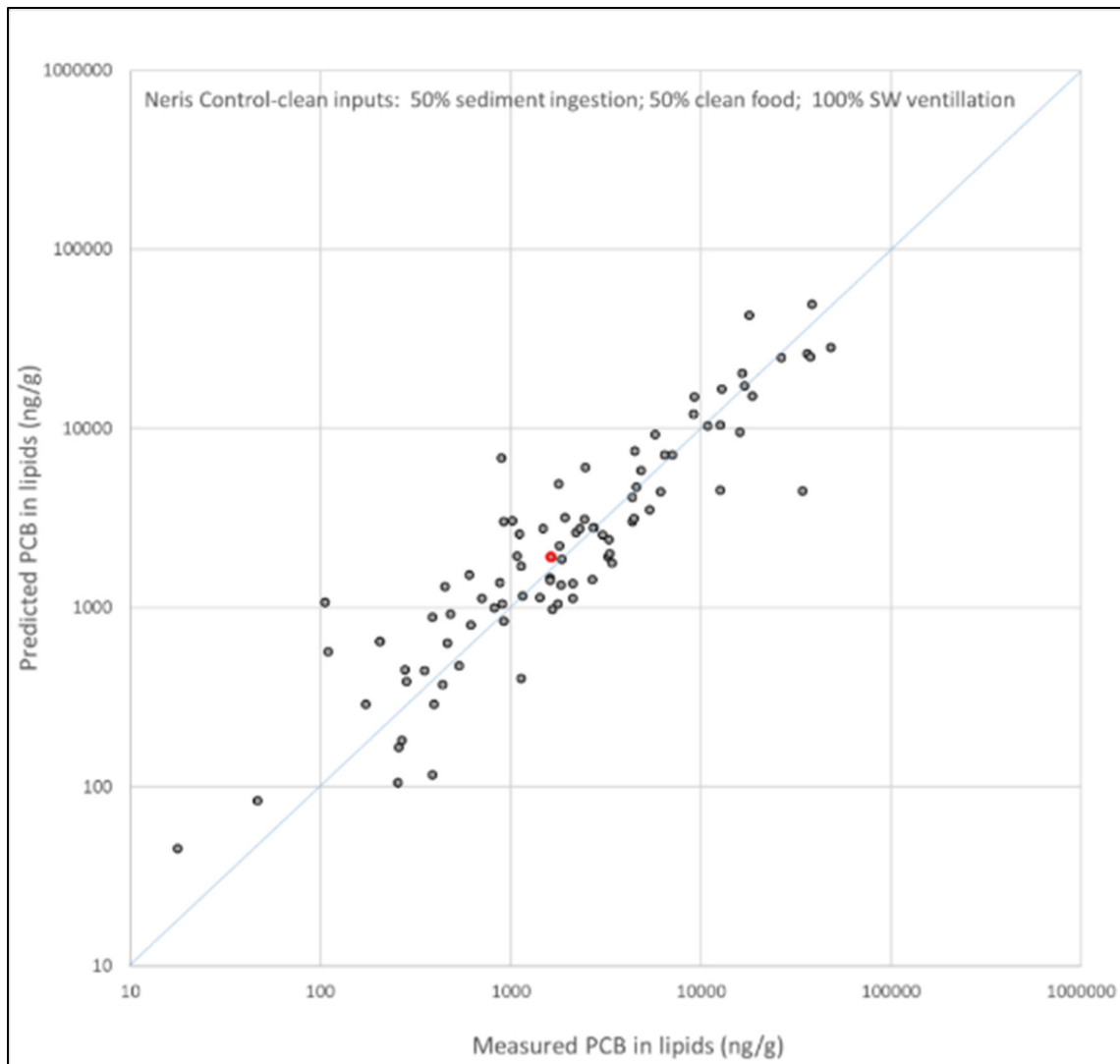


Figure 44. Comparison of predicted and measured tissue concentration of PCB congeners in the benthic worm *Alitta virens* exposed to untreated NBH sediment in E2. In this modeled scenario, the worm diet is composed of 50% clean food and 50% sediment and the worm solely ventilates surface water.

Bioaccumulation prediction in *Mercenaria mercenaria* in E2

Mercenaria mercenaria clams are filter feeders and are expected to feed on phytoplankton and resuspended sediment/detritus. These hard clams obtain some nutrition from dissolved organic matter, but their primary food source is suspended particles (Grizzle et al. 2001). They can retain particles >3 to $4\ \mu\text{m}$ in diameter with 100% efficiency, and $2\ \mu\text{m}$ particles with about 50% efficiency. Hard clams can effectively use picoplankton-sized particles ($0.2\text{--}3\ \mu\text{m}$). They can selectively ingest algae and reject sediment particles (coarse mineral particles) as pseudofeces from mixed suspensions, but this ability varies greatly among species varieties and populations. The diet of *M. mercenaria* is composed of 50% sediment and 50% phytoplankton above the hurricane barrier in New Bedford Harbor, and 100% phytoplankton past the hurricane barrier

(Burkhard 2013). Thus, both scenarios were modeled to test the effect of different feeding behavior assumptions in the modeled uptake of PCBs in the mesocosms. For the present simulation, first a 50% sediment and 50% phytoplankton were assumed. However, in the laboratory exposures, most of the suspended food ingested by clams in our experiments was the clean algae that was introduced into the mesocosms. Thus, phytoplankton that would have equilibrated with the surface water was replaced with clean algae. As shown in Figure 45, this approach generally overpredicts the exposure to the *M. mercenaria* in the laboratory mesocosms. Total PCBs are overpredicted by a factor of about 7. In contrast, if we assume that the clams does not feed on any sediment like the native organisms past the hurricane barrier (Burkhard 2013), then the prediction is very close to the observed measurements in the exposure chambers fed with clean food (see Figure 46). Thus, it appears that the *M. mercenaria* had minimal ingestion of the bed sediments in the experimental mesocosms.

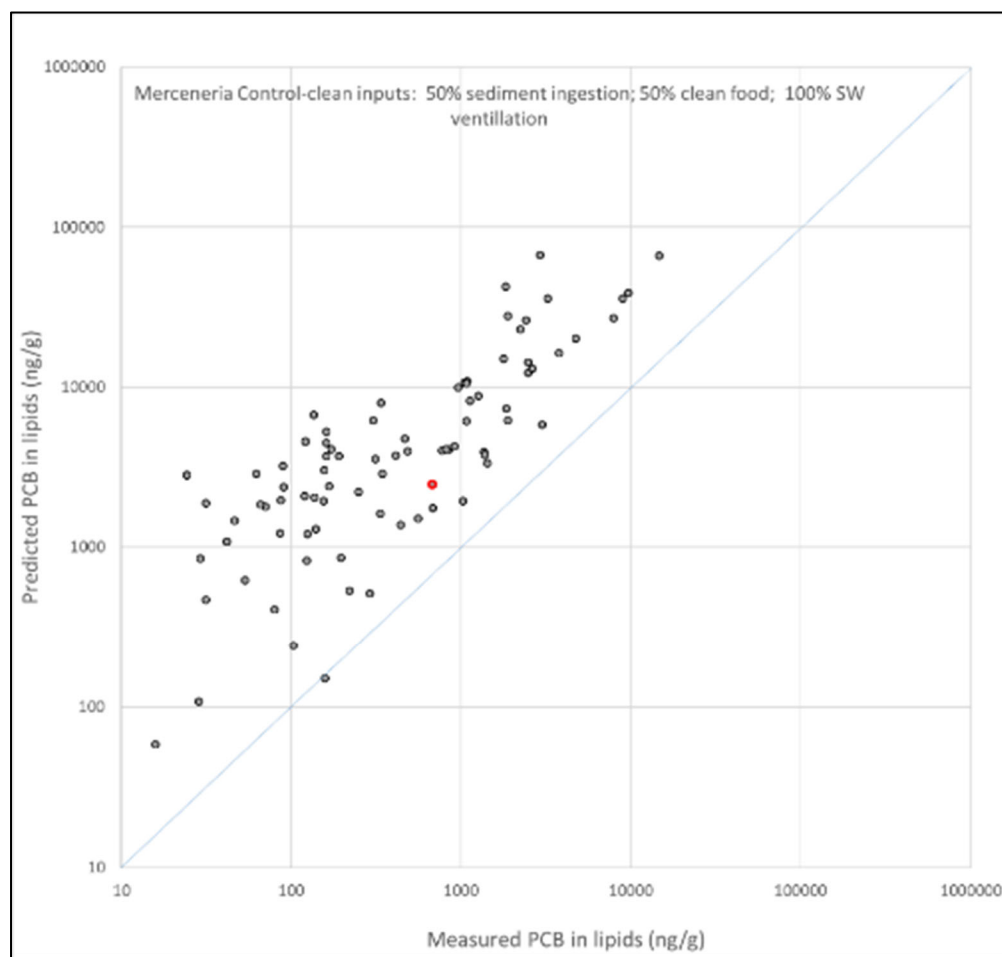


Figure 45. Comparison of predicted and measured tissue concentration of PCB congeners in the clam *Mercenaria mercenaria* exposed to untreated NBH sediment in E2. In this modeled scenario, the clam diet was assumed to comprise of 50% clean food and 50% sediments. Ventilation was surface water only.

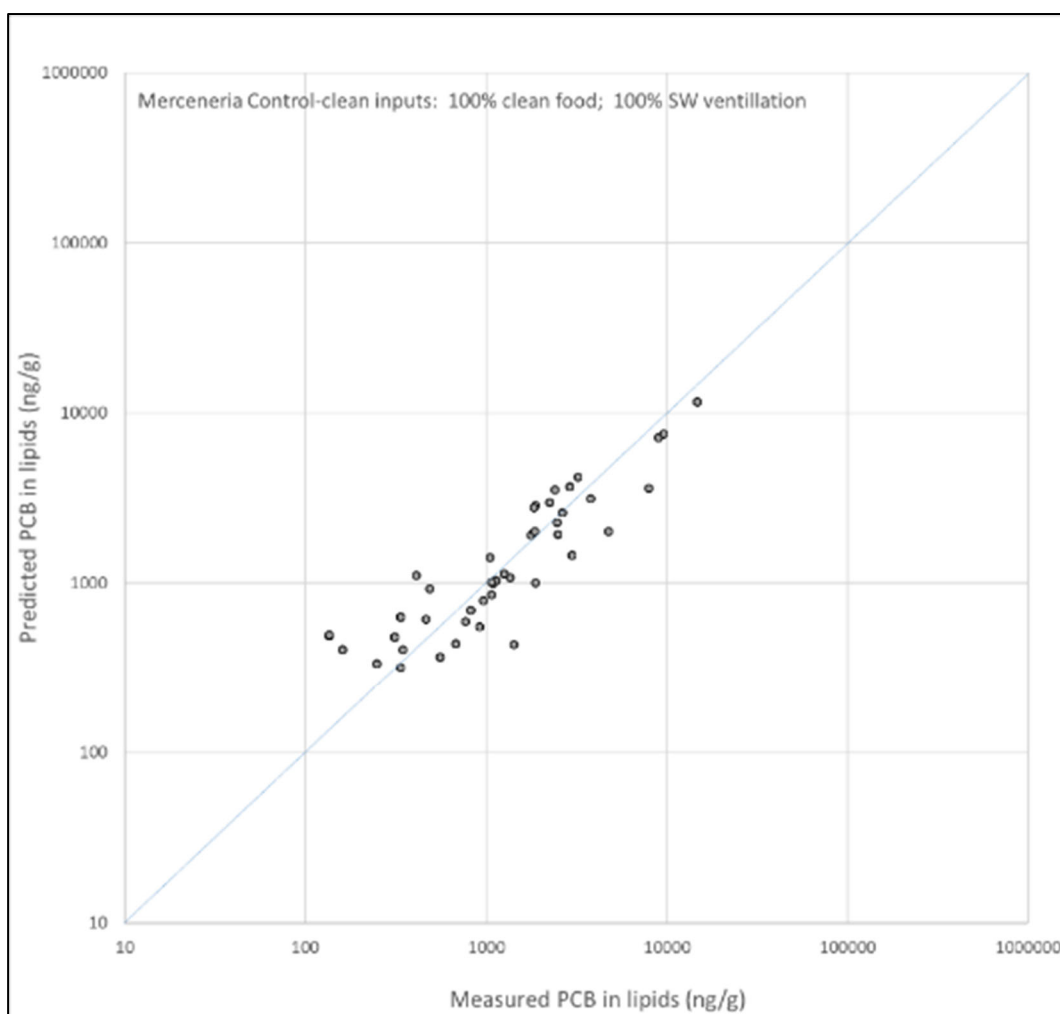


Figure 46. Comparison of predicted and measured tissue concentration of PCB congeners in the clam *Mercenaria mercenaria* exposed to untreated NBH sediment in E2. In this modeled scenario, the clam diet was assumed to comprise of 100% clean food. Ventilation was surface water only.

Bioaccumulation prediction in *Cyprinodon variegatus* in E2

The laboratory exposure chambers isolated the fish in cages to prevent major resuspension of sediment by the fish. Thus, the fish had minimal contact with bedded sediments. Also, the fish exclusively fed on the supplied clean food. In the native environment, the fish at a similar trophic level would be expected to feed on a combination of phytoplankton, zooplankton, and some benthic invertebrates that would have accumulated PCBs from their respective environments. Thus, the same fish in the native environment would be expected to accumulate more PCBs than what was measured in the mesocosms. To simulate conditions within the mesocosms, the fish were assumed to ventilate surface water only, and the food was set to clean food only. Thus, the only PCB exposure to the fish in the laboratory mesocosms was coming from surface water ventilation. As shown in Figure 47, the lipid normalized PCB concentrations predicted in the fish closely match the measured values.

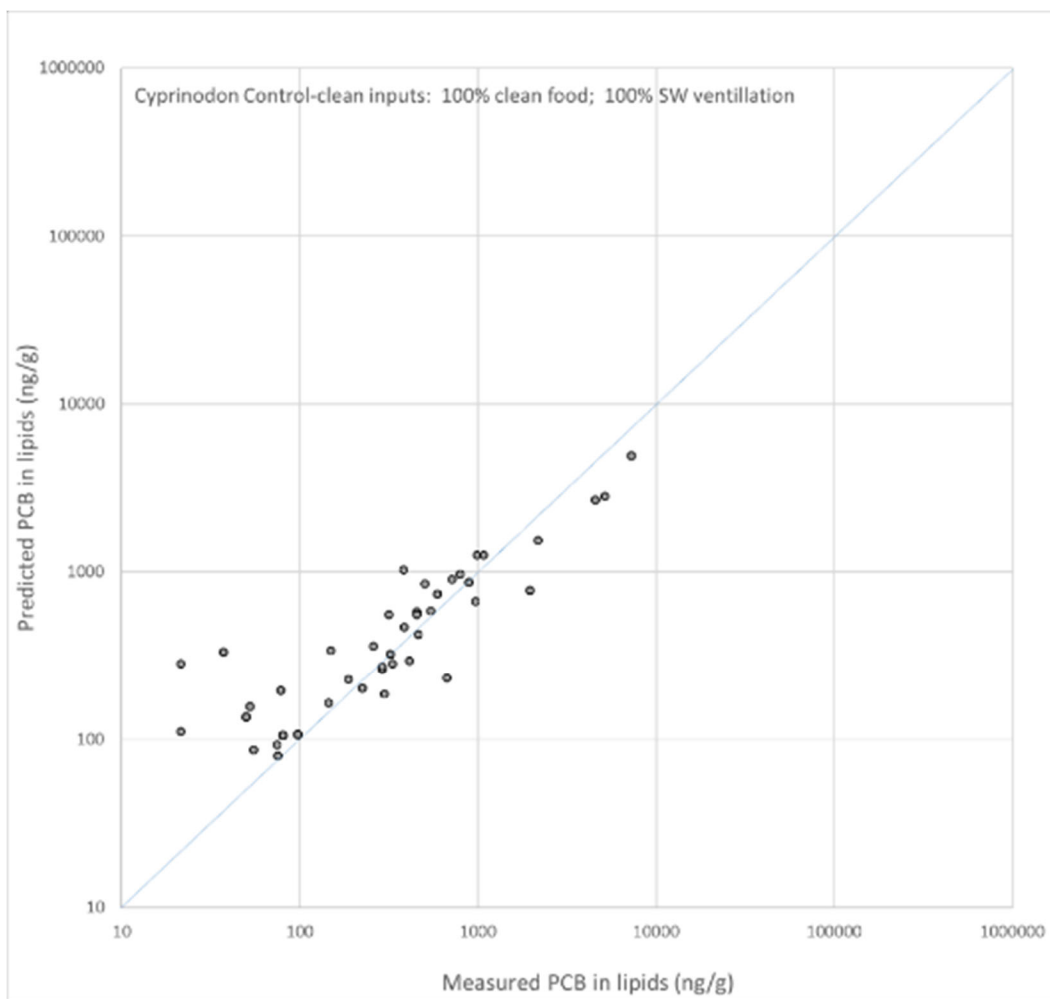


Figure 47. Comparison of predicted and measured tissue concentration of PCB congeners in the fish *Cyprinodon variegatus* exposed to untreated NBH sediment in E2. In this modeled scenario, the fish were fed with clean food and kept isolated in the surface water in cages.

Bioaccumulation prediction for all organisms in E3 and E4

The food web model parameterized as described above for the control sediment exposures was used to generate the fractional contribution of surface water and apparent organism partitioning for the deconvoluted thermodynamic model as described in Appendix A. The deconvoluted model then was used to predict the uptake of PCBs in the three experimental organisms for the control sediment and the treatments with a sand cap and AC mix. The deconvoluted model used the measured concentrations of freely dissolved porewater and surface water concentrations in the mesocosms to predict organism concentrations. As shown in Figure 48, the predicted uptake generally match with the measured PCB concentrations of PCBs in the three organisms in the untreated and two treated sediments. For the AC-mix treatment most of the water concentrations were below detection limits making it difficult to correctly inform the model on the applicable thermodynamic drivers. Nonetheless, the deconvoluted thermodynamic model is able to provide

a good representation of the changing exposure conditions and resulting biouptake of PCBs in the three organisms under the different treatment scenarios.

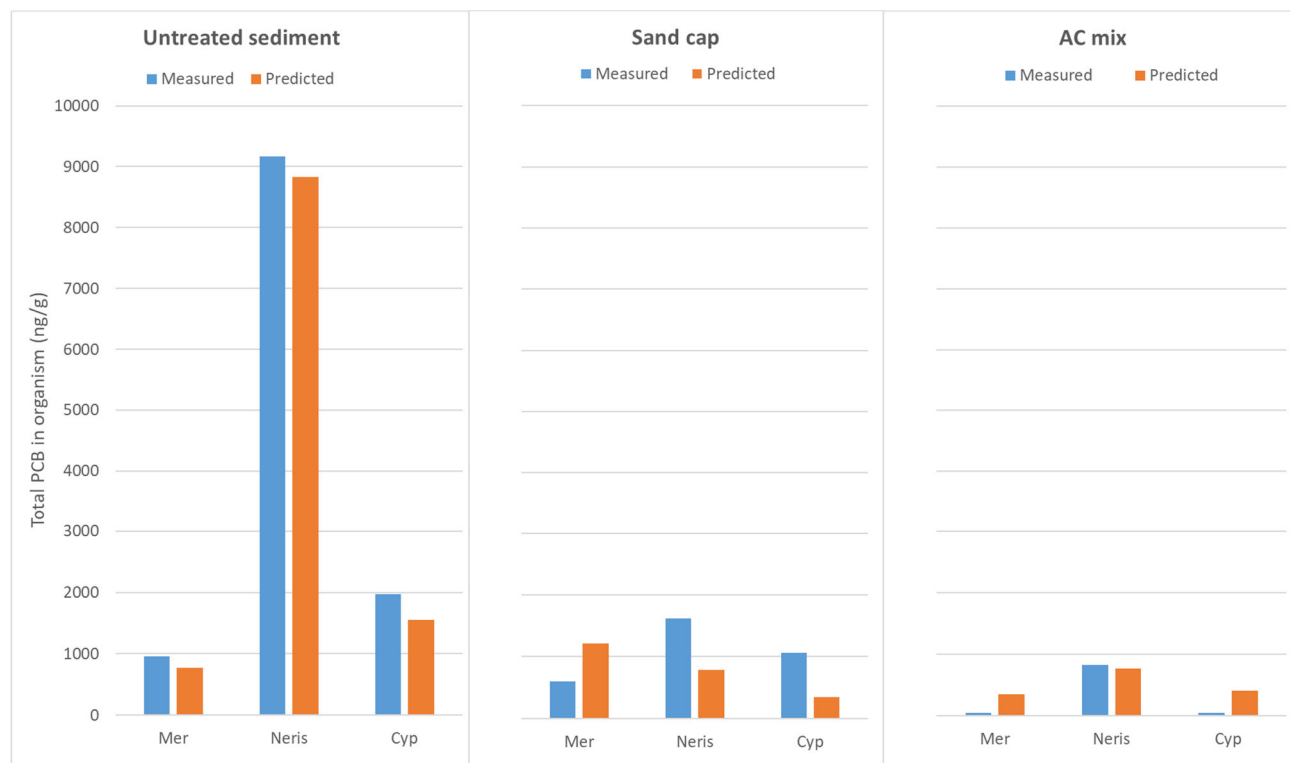


Figure 48. Comparison of predicted and modeled uptake of total PCBs in functionally diverse aquatic organisms (*Mercenaria mercenaria* [Mer], *Alitta virens* [Ner], *Cyprinodon variegatus* [Cyp]) using the deconvoluted thermodynamic model or different treatment scenarios.

Key Observations

While the freely dissolved PCB concentration in sediment porewater provides one extreme boundary of thermodynamic potential for bioaccumulation in aquatic organisms, the actual steady state concentrations measured are greatly impacted by the specific exposure conditions. To accurately predict uptake in the organisms, the specific exposure pathways and exposure concentrations need to be correctly accounted for. As seen for the three functionally different aquatic species studies here, PCB concentrations in the surface water and diet greatly impact bioaccumulation. Using accurate measures of the two primary thermodynamic drivers – the freely dissolved concentrations in the sediment porewater and surface water, it is possible to predict uptake in the aquatic organisms and anticipate changes after sediment treatment.

9. RECOVERY 5.0: A contaminated sediment-water interaction model

This chapter describes the U.S. Army Corps of Engineers screening-level contaminant fate and transport model (RECOVERY version 5.0) for assessing long-term impacts of contaminated bottom sediments on surface waters and ecological resources. The model was developed to provide exposure data for risk assessment of contaminated sediment sites and to screen remedial alternatives, in particular, no action, monitored natural recovery or enhanced monitored natural recovery, residuals management, and capping. Major improvements have been made to allow a user to better simulate advection through the bottom sediment such as ground water flow and flow resulting from consolidation of the contaminated material, foundation, and/or cap. Both of these processes can disrupt a remedial action and these impacts can be better predicted over both the short and long-term. This new model incorporates formulations to enhance capabilities and better represent in situ remedial alternatives. As with the previously released version, a Windows-based graphical user interface will allow the user to simulate multiple contaminants in the same run.

9.1. Introduction

Toxic substances are known to associate strongly with fine-grained particulate matter; therefore, contaminants tend to accumulate in the bottom sediments of natural waters. Pollutants in bottom sediments can be released by resuspension of particles, mixing by benthic organisms, and diffusion and advection from the sediment pore water. Conversely, pollutants in the water column can be transferred to the sediment layer by settling and to the atmosphere by volatilization. Understanding the extent that contaminated sediments effect overlying water quality and contaminant bioaccumulation is necessary for environmental impact assessment and design of remediation to minimize their impact. This paper describes the modeling framework of RECOVERY (version 5.0) used to assess the impact of contaminated bottom sediments on the surface water quality.

RECOVERY (version 5.0) is the U.S. Army Corps of Engineers screening-level water quality model for assessing the long-term effects of contaminated bottom sediments on surface waters. . It is an extension of previous version of the RECOVERY model (Ruiz et al. 2007, Ruiz and Gerald, 2001, Ruiz et al. 2001), developed by Boyer et al. (1994). The system is idealized as a well-mixed surface water layer underlain by a vertically stratified sediment column. As shown in Figure 49, the sediment is uniform horizontally but segmented vertically into a well-mixed surface layer and layers with varying thicknesses, porosities, and contaminant concentrations underlain by an uncontaminated region. The discretized sediment layer configuration is useful for assessing capping scenarios and sites where contamination occurred over a long time resulting in the system appearing to have contaminant layers. The specification of a mixed surface layer is included because an unconsolidated layer is often observed at the surface of sediments due to a number processes, including bioturbation and mechanical mixing.

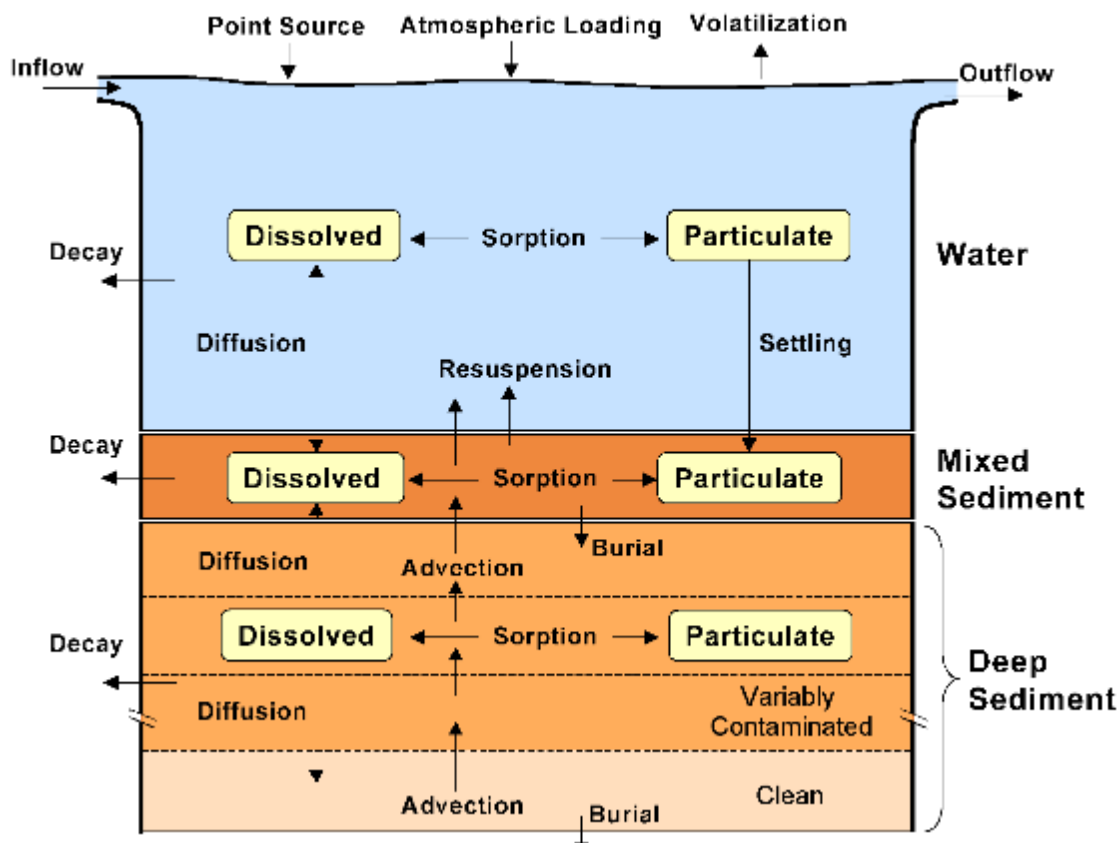


Figure 49. Schematic of the sediment-water system as modeled in RECOVERY.

The model couples contaminant interaction between the water column and the bottom sediment, as well as between contaminated and clean bottom sediments. The analysis is intended primarily for organic contaminants with the assumption that the overlying water column is well mixed vertically. The contaminant is assumed to follow linear, reversible, equilibrium sorption and first-order decay kinetics. The system is physically represented as a well-mixed water column (i.e., zero dimensional) underlain by a vertically stratified sediment column (i.e., one-dimensional). The sediment is well-mixed horizontally but segmented vertically into a well-mixed surface layer and deep sediment. The deep sediment is segmented into variably contaminated and clean sediment regions. Processes incorporated in the model are sorption, decay, volatilization, burial, resuspension, settling, bioturbation, and pore-water diffusion.

A major update to the RECOVERY model as a part of version 5.0 is the ability to better simulate the process of advection through the bottom sediments such as occurs with groundwater flow and flow resulting from the consolidation of sediment.

9.2. Model formulation

Contaminants Mass Balance

For a well-mixed water column, the mass balance for a single contaminant in the water column can be written as

$$V_w \frac{d c_w}{dt} = Q c_i - Q c_w - k_w V_w c_w - k_v V_w c_w - v_s A_w F_{pw} c_w + v_r A_m c_m + v_d A_m (F_{dp} c_m - F_{dw} c_w) + W \quad (1)$$

where V_w = volume of water body, m^3 ;

c_w and c_m = concentrations of toxicant in water and mixed sediments, respectively, mg/m^3 ;

c_i = inflow concentration, mg/m^3 , which reflects both direct and tributary loadings; t = time, years;

Q = flushing flow rate, m^3/yr ;

k_w = decay rate constant of the contaminant in the water, yr^{-1} ;

k_v = volatilization rate of contaminant, yr^{-1} ;

v_s = settling velocity of particulate matter, m/yr ;

A_w and A_m = surface areas of water and mixed sediment, respectively, m^2 ;

F_{pw} = fraction of contaminant in particulate form in the water;

v_r = resuspension velocity of sediments, m/yr ;

v_d = diffusion mass-transfer coefficient at the sediment-water interface, m/yr ;

F_{dp} = ratio of contaminant concentration in the sediment pore water to contaminant concentration in total sediment;

F_{dw} = fraction of contaminant in the dissolved form in the water; and W = external loads, kg/yr .

The model assumes that the movement of one contaminant is independent of the presence of other contaminants. The term on the left-hand side of Equation 1 represents the rate of change of contaminant mass in the water column. The first term after the equal sign represents the rate at which the contaminant is introduced into the water body. The second term represents the outflow rate of the contaminant by flushing flow. The third term is rate of contaminant decay, and the fourth term is the rate of contaminant mass volatilization. The next two terms are rate of contaminant transfer between the sediments in the water column and the mixed layer as a result of deposition and resuspension, respectively. The next term represents the net rates of contaminant transfer by diffusion between the water column and the mixed sediment. The last term in the equation is the rate of point source input (W).

To complete the representation of the interaction between contaminants in the water column and the mixed sediment layer, the contaminant mass balance in the mixed sediment is written as

$$V_m \frac{dc_m}{dt} = - k_m V_m c_m + v_s A_w F_{pw} c_w - v_r A_m c_m - v_b A_m c_m + v_d A_m (F_{dw} c_w - F_{dp} c_m) + v_d A_m (F_{dp} c_w(0) - F_{dp} c_m) \quad (2)$$

where V_m = volume of mixed layer, m^3 ; k_m = decay rate constant of the contaminant in the mixed layer, yr^{-1} ; v_b = burial velocity, m/yr ; and $c_s(0)$ = contaminant concentration at the top of the deep contaminated layer, mg/m^3 .

In Equation 2, the term on the left-hand side of the equation represents the rate of contaminant mass accumulation in the mixed layer. The first term after the equal sign is the decay rate of the contaminant in the mixed layer. The next three terms represent the transfer of contaminants between the mixed layer and the water column and the deep sediments by settling, resuspension and burial of sediment particles. The last two terms represent the interaction between the mixed layer and the water column and the deep sediment by diffusive transfer.

Coupling between the contaminants in the mixed sediment layer and the deep sediment takes place by diffusive transfer as well as by the burial of contaminated particles from the mixed sediments layer into the deep layer. Both the deep contaminated and clean sediments can be modeled with one-dimensional advection-diffusion-decay equations of the form

$$\frac{\partial c_z}{\partial t} = \phi F_{dp} D_s \frac{\partial^2 c_z}{\partial z^2} - v_b \frac{\partial c_z}{\partial z} - k_z c_z \quad (3)$$

where c_s = contaminant concentration in the deep sediments mg/m^3 , ϕ = sediment porosity;

D_s = diffusion rate in the sediment pore water, m^2/yr ; z = depth into the sediment, m , where $z = 0$ at the top of the deep sediments; and k_s = decay rate constant of the contaminant in the deep sediments, yr^{-1} . The term on the left-hand side of the equation is the rate of contaminant concentration change in the sediment. The first term after the equal sign is the rate of contaminant transfer by diffusion in the sediment pore water. The second term represents the rate of contaminant transfer due to sediment particle burial, and the last term represents the decay rate of contaminants in the pore water of the deep sediment.

9.3. Modifications to allow upwelling of groundwater

RECOVERY (5) ability to better simulate the process of advection through the bottom sediments requires the modification of the original formulation to include the Darcy Upwelling velocity. The modified well-mixed water column mass balance for a single contaminant in the water column can be written as:

$$V_w \frac{dc_w}{dt} = Qc_i - Qc_w - k_w V_w c_w - k_v V_w c_w - v_s A_w F_{pw} c_w + v_r A_m c_m + v_d A_m (F_{dp} c_m - F_{dw} c_w) + v_u A_m F_{dp} c_m + W \quad (4)$$

where v_u =Darcy upwelling velocity (m/yr), not the pore water upwelling velocity and all other variables were previously defined.

The contaminant mass balance in the mixed sediment layer needs the following modification to the right side of the sediment mixed layer mass balance equation (2)

$$+ v_u A_m F_{dp} c_s(0) \quad (5)$$

The deep contaminated and clean sediments can be modeled with one-dimensional advection-diffusion-decay equations and to include the Darcy upwelling, the following term must be added to the right side of the deep sediment layers mass balance Equation (3)

$$+ v_u F_{dp} \frac{\partial c_s}{\partial z} \quad (6)$$

Solids mass balance

In addition to the contaminant mass, the sediment mass must be conserved. The velocity terms v_s , v_r and v_b in Equations 1 and 2 are computed according to a steady-state mass balance for mixed sediment layer solids as described by Chapra and Reckhow (1983). The mass balance is

$$0 = v_z A_w s_w - (v_r + v_b) A_m (1 - \phi) \rho_p \quad (7)$$

where ρ_p is the density of the sediment solids, gm/m³. The framework assumes that suspended solids concentration, s_w , is given. Therefore, if two of the three velocities are specified, the equation can be employed to calculate the third.

In addition to these transfer velocities, the other facet of the physical system is the sediment porosity. Different porosities may occur in the mixed layer and the deep sediments. Within the layers of the deep sediment region, porosity can vary from layer to layer, but is assumed constant over time. This means that compaction is not included. The same argument is assumed for particle density and partitioning.

Partitioning.

The F terms in Equations 1-3 are dimensionless ratios that reflect how a contaminant partitions between solid matter and water, assuming a linear sorption mechanism. Denoting the contaminant as A, the fraction of contaminants in particulate form in the water column is

$$F_p = \frac{\left[\frac{\text{Mass of A (Particulate Form)}}{\text{Total Volume}} \right]}{\left[\frac{\text{Mass of A (Dissolved Form)} + \text{Mass of A (Particulate Form)}}{\text{Total Volume}} \right]} = \frac{K_{dw} s_w}{1 + K_{dw} s_w} \quad (8)$$

and the fraction of the contaminant mass in dissolved form is $1-F_{pw}$:

$$F_{dw} = \frac{\left[\frac{\text{Mass of A (Dissolved Form)}}{\text{Total Volume}} \right]}{\left[\frac{\text{Mass of A (Dissolved Form)} + \text{Mass of A (Particulate Form)}}{\text{Total Volume}} \right]} = \frac{1}{1 + K_{dw} s_w} \quad (9)$$

and the fraction of contaminant mass in the dissolved phase of the mixed sediment pore water is

$$F_{dp} = \frac{\left[\frac{\text{Mass of A (Dissolved Form)}}{\text{Volume of pore water}} \right]}{\left[\frac{\text{Mass of A (Dissolved Form)} + \text{Mass of A (Particulate Form)}}{\text{Total Volume}} \right]} = \frac{1}{\phi + K_{dw}(1 - \phi)\rho_s} \quad (10)$$

where K_{dw} and K_{ds} = contaminant partitioning coefficient in the water and sediments, respectively, m^3/g ; and s_w = suspended solids concentration in the water, g/m^3 . The contaminant partitioning coefficients can be specified directly by the user or computed using a default relationship for hydrophobic organic contaminants. Note that the model allows different values of this parameter to be employed in the mixed layer and the vertically segmented sediments (F_{dpm} and F_{dps})

The partitioning coefficient for organic contaminants is computed via (Karickhoff, Brown, and Scott 1979)

$$K_d = 0.617 f_{oc} K_{ow} \quad (11)$$

Where K_d = equilibrium partitioning coefficient, L/kg

f_{oc} = the weight fraction of organic carbon in the solid matter, g-orgC/g

K_{ow} = octanol-water partitioning coefficient, (mg/m³-octanol)/(mg/m³-water).

Note that the model assumes a default of 0.05 for f_{oc} . Different values for f_{oc} are allowed for the water column, mixed layer, and the deep sediments. Analogous to other physico-chemical characteristics of the sediments, the f_{oc} can vary with depth (layers) in the deep sediments.

Contaminant losses

The decay rate constants, k_w , k_m and k_s , represent all mechanisms for decay except volatilization, which is accounted for separately. These mechanisms include photolysis, hydrolysis, and bacterial degradation.

9.4 RECOVERY Testing

RECOVERY (5.0), was applied to a series of scenarios to verify that RECOVERY ability to adequately model a variety of remediation alternatives. In addition, to test its advective component a series of groundwater flows were simulated. Simulations for each scenario

Included three contaminants of concern (COC) with different of Octanol-Water Partitioning Coefficients (Kow). The COCs include Anthracene, Pyrene, and PCBs. Table 4 shows the properties of each COC.

Table 4. Contaminant parameters

Contaminant	Molecular Weight	log Kow	Molecular Diffusivity (cm ² /sec)	Concentration (mg/kg)
Anthracene	178	4.45	5.00E-06	1
Pyrene	202	5.32	5.00E-06	2
PCB	328	6.04	5.00E-06	3

The scenarios and remediation alternatives modeled include no action (existing conditions), sand cap, amended sand cap, and advective flow through both sand caps. To verify the groundwater component of RECOVERY, realistic groundwater flows were selected and simulated. The following sections detail each of the scenarios and remediation alternatives.

No action/existing conditions

Figure 50, show an unremediated/existing conditions of a contaminated site scenario modeled with RECOVERY. This is also an example of no-action/enhance natural recovery in which the natural ongoing processes are used to accelerate the site recovery. The existing conditions consist of a sediment bed with 1 meter of contaminated sediments. The top 5 cm of the contaminated sediments is the mixed layer, which accounts for the assumed bioturbation layer. A 3 m water column overlies the sediment bed. The contaminated sediment has a specific gravity of 2.65, a f_{oc} of 1% and a porosity of 0.67. The existing condition will be the basis for the remediation scenarios modeled.

Sand cap

The first remediation alternative simulated is a sand cap. The most basic form of capping is the addition of a clean sand cap over the contaminated sediment (Figure 51). The cap is a 30cm

clean sand cap including a 5cm bioturbation layer. The cap has a specific gravity of 2.65, f_{oc} of 1%, and a porosity of 0.5.

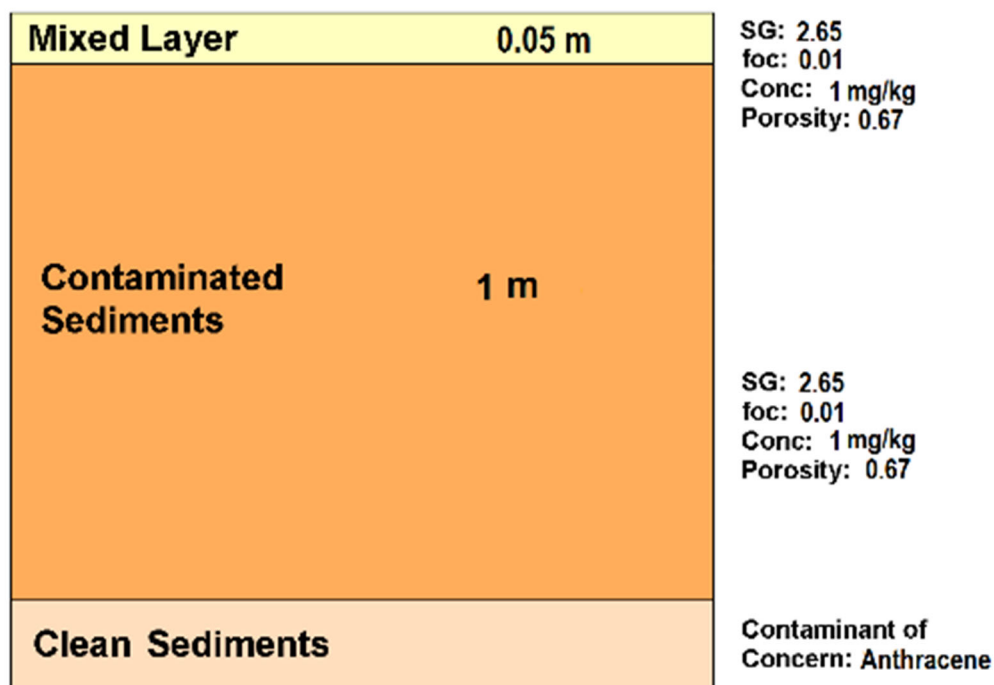


Figure 50. No action/existing conditions scenario

Activated carbon amended sand cap

The third scenario included a sand cap eroded to 18 cm, and rehabilitated with a 5cm mixed layer, an amendment layer consisting of 2cm activated carbon and 4 cm sand overlaid with a 6 cm sand layer for stabilization as shown in Figure 52. Parameters for the sand layers are those of Scenario 2, a specific gravity of 2.65, f_{oc} of 2.0%, and a porosity of 0.5.

Activated carbon amended sand cap #2

The fourth remediation alternative simulated is an amended sand cap of 10 cm. The K_d for the mixed sediments layer was set to be two orders of magnitude greater than the sediment K_d (previously defined) to account for the sorptive capacity of the activated carbon. This cap is typical when contaminated uncontrolled sources are near the site (Figure 53). This exercise shows the flexibility of RECOVERY 5.0 in setting user defined properties like the K_d for the different compartments.

Mixed Layer	0.05 m	SG: 2.65 foc: 0.01 Conc: 0 mg/kg Porosity: 0.5
Clean Sand Cap	0.25 m	
Contaminated Sediments	1 m	SG: 2.65 foc: 0.01 Conc: 1 mg/kg Porosity: 0.67
Clean Sediments		

Contaminant of Concern: Anthracene

Figure 51. Sand cap scenario

Mixed Layer	0.05 m	SG: 2.65 foc: 0.01 Conc: 0 mg/kg Porosity: 0.5
Clean Sand Cap	0.06 m	
AC (2 cm)/Clean Sand Mix (4 cm)	0.06 m	SG: 2.65 foc: 0.01 Conc: 0 mg/kg Porosity: 0.5
Clean Sand Cap	0.13 m	
Contaminated Sediments	1 m	SG: 2.65 foc: 0.01 Conc: 1 mg/kg Porosity: 0.67
Clean Sediments		

Contaminant of Concern: Anthracene

Figure 52. AC/sand cap scenario.

Mixed Layer	AC/Sand Mix	0.10 m	SG: 2.65 foc: 0.01 Conc: 0 mg/kg Porosity: 0.5
Clean Sand Cap		0.10 m	SG: 2.65 foc: 0.01 Conc: 0 mg/kg Porosity: 0.5
Contaminated Sediments		1 m	SG: 2.65 foc: 0.01 Conc: 1 mg/kg Porosity: 0.67
Clean Sediments			Contaminant of Concern: Anthracene

Figure 53. Mixed layer AC/sand cap scenario

Advective flux

The fifth scenario adds groundwater upwelling to the no action/current conditions scenario to demonstrate the advective capabilities of the model (Figure 54). Constant groundwater velocities between 10 and 200 cm/yr were simulated.

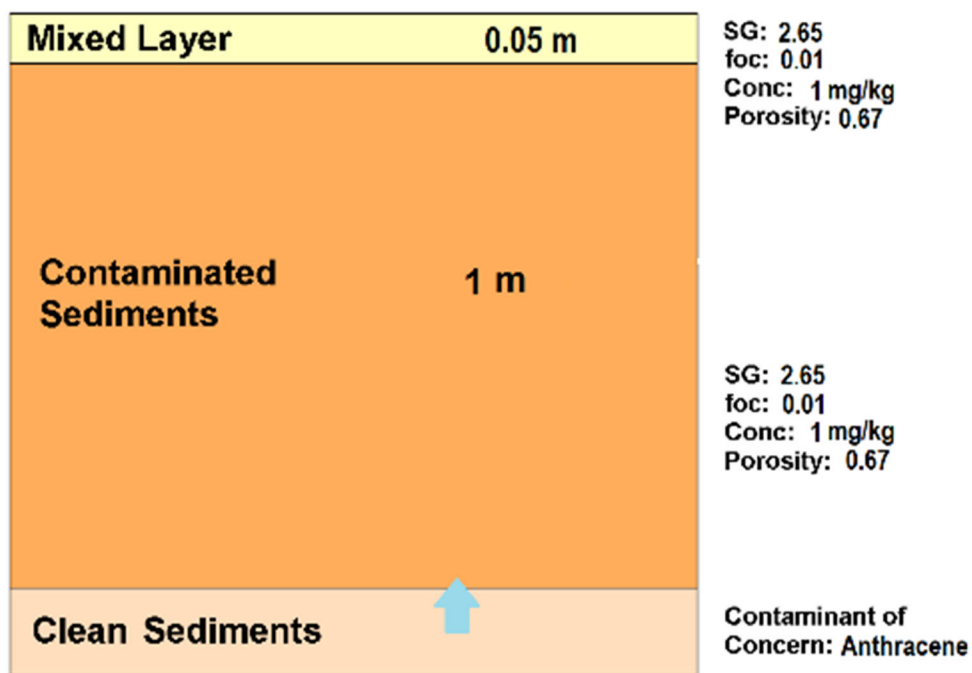


Figure 54. No action/existing conditions advective scenario.

9.5. Results

The results from the simulation of the six different scenarios will show the COC concentration over time for the water column (WC), sediment mixed layer (SML), and the pore water (PW) of the sediment mixed layer.

Figure 55 shows the simulations for the no action alternative or the current conditions for the water column and the mixed layer, both sediment and pore water concentration. The sediment concentration reflects the initial concentration for the three COC (1, 2, and 3 mg/l for Anthracene, Pyrene, and PCBs respectively). Note that PCBs decrease almost 1 mg/kg over 100 years, while Pyrene decreases over 1 mg/kg. Anthracene shows the greatest decrease over time, over an order of magnitude in 100 years. The decrease correlates with the K_d and K_{ow} of the COC, the greater the K_d the longer the persistence.

In the water column, the K_d is inversely correlated to the amount of dissolved COC; the greater the K_d , the lower the dissolved concentration in the pore water, and thus the water. The pore water concentration for Anthracene decreases the most over time as it diffuses into the water column, thus leaving the SML. Pyrene and PCBs diffusion out of the SML is much lower, since it's controlled by the amount in the dissolved phase (pore water), that is a function of the K_d .

Figure 56 shows the effect of placing a sand cap (clean based on concentration, but high in f_{oc}) over the existing conditions scenario. The cap provides isolation (to the water column and benthic

resources) from the COCs and their impact. Anthracene concentration is the greatest in WC, SML, and PW; however, the concentration is orders of magnitude lower than in the no action results of Figure 55.

The PW concentration in the SML is nine (9) orders of magnitude reduced for the period of simulation. The sand cap simulations show that for the COC and Kd simulated, a 30 cm sand cap provides isolation and risk reduction for over a hundred years.

Figure 57 shows how adding AC to the previously described sand cap enhances the protection by increasing the isolation and further reducing the risk. Anthracene reduction of nearly 10 orders of magnitude in the SML was achieved with the addition of 2 cm of AC. This shows that when rehabilitating a sand cap an amended sand cap requires less depth and probably increases the performance of the layer by a factor of at least ten.

The performance of adding AC to the top of the sediment (sediment mixed layer) is shown in Figure 58. The 10 cm addition of AC or AC/sand is typical of a thin layer cap (TLC); it provides risk reduction and might provide isolation. The cap was described in Figure 53; although the total of 20 cm (10 cm AC/sand and 10 cm sand) might be in the higher end of a TLC. Anthracene reduction of at least three orders of magnitude was achieved by the addition of AC/sand. It was the thinnest cap evaluated and was the one that lowest performer; however, it achieves all remediation goals of risk reduction and isolation.

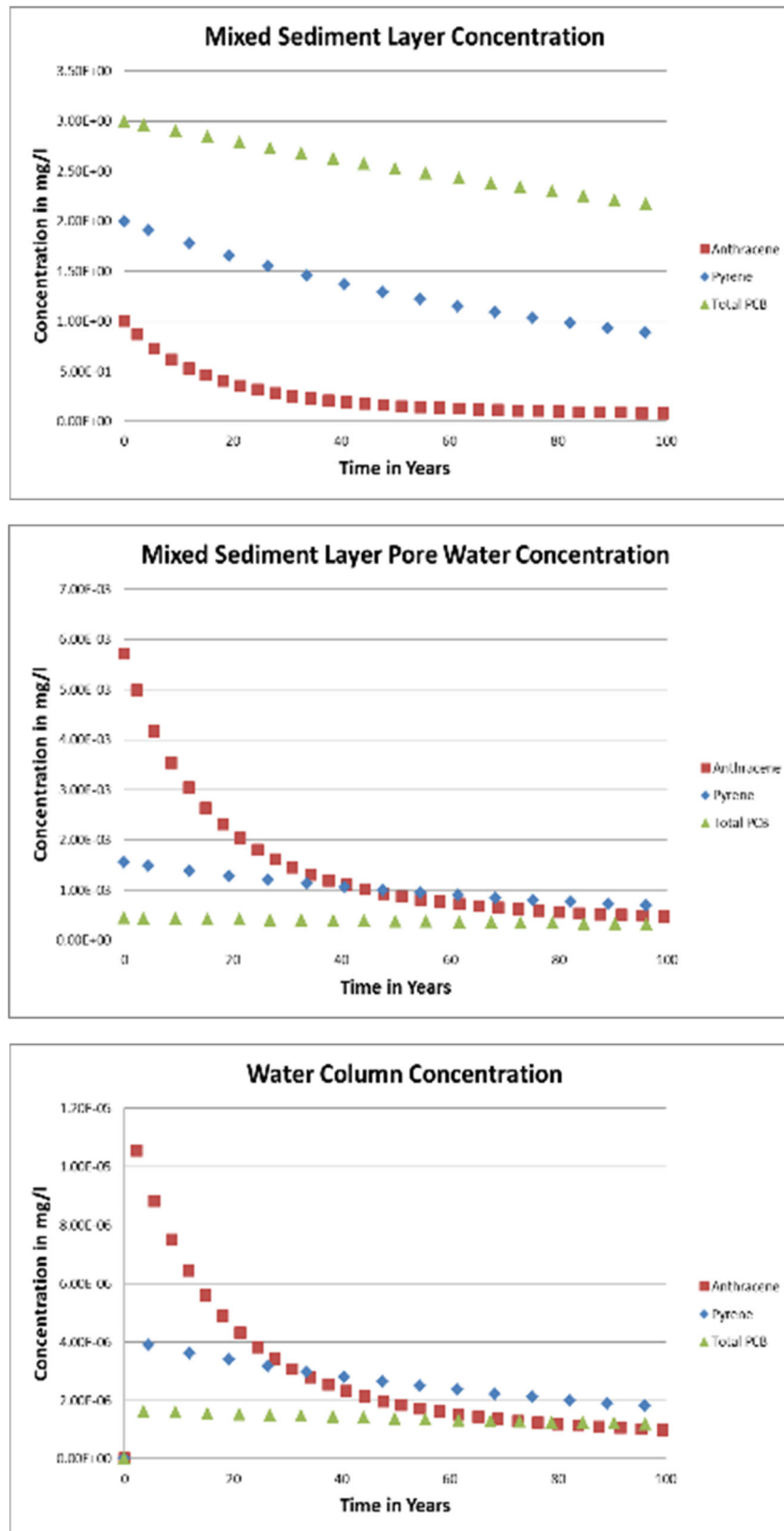


Figure 55. No action/existing conditions (sediment, PW, and WC).

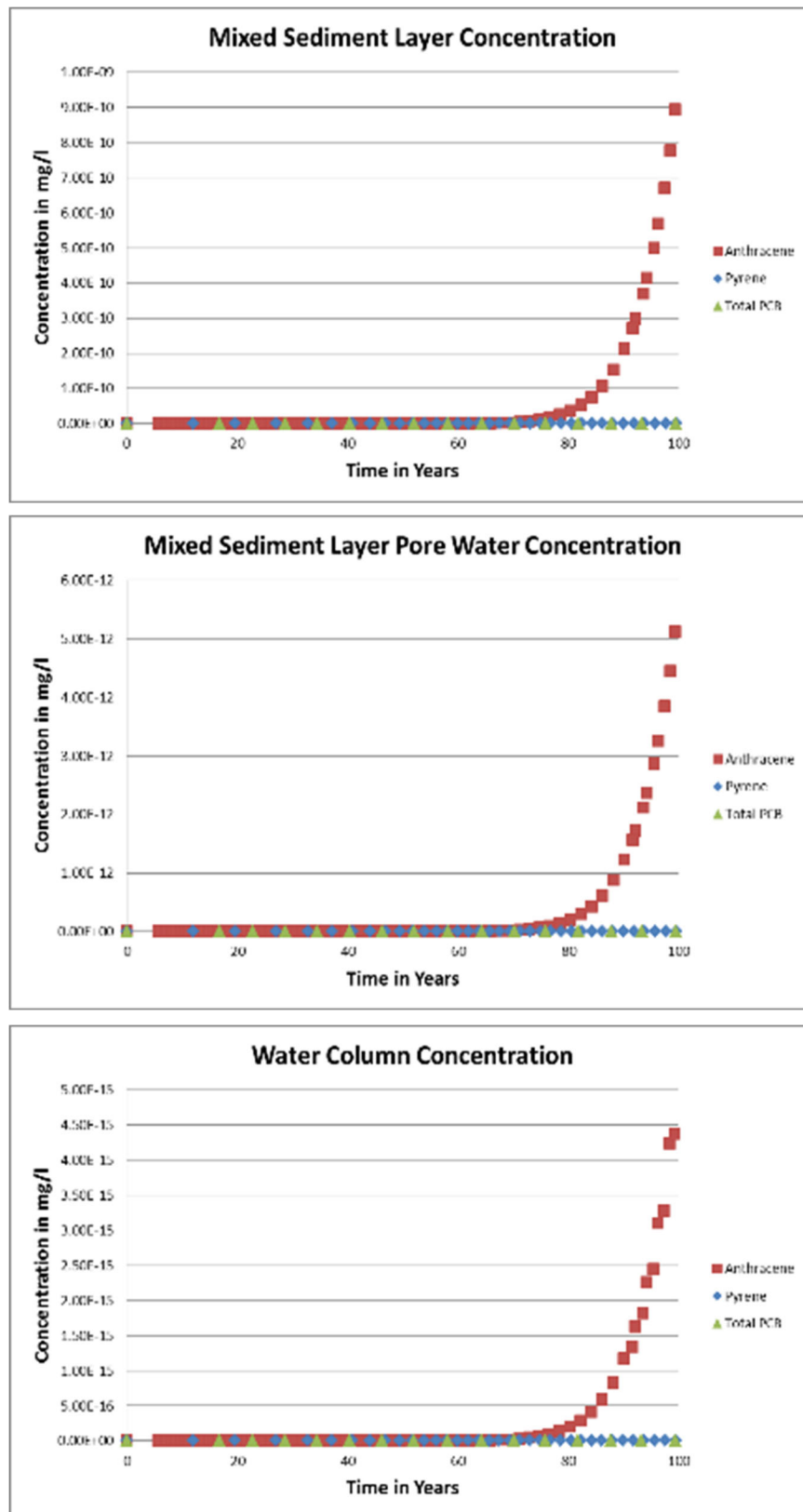


Figure 56. Sand cap scenario (sediment, PW, and WC).

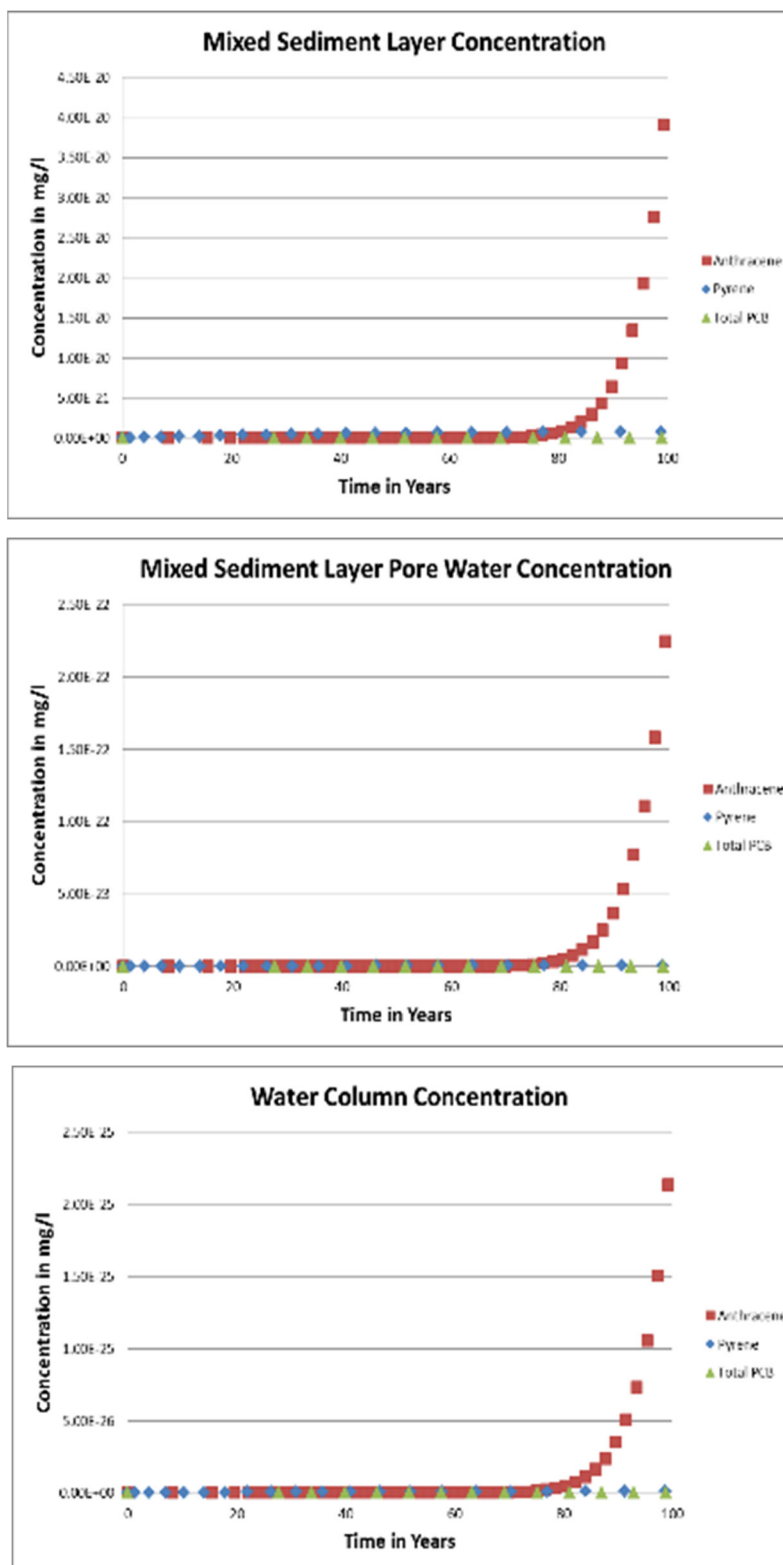


Figure 57. AC/sand cap scenario (sediment, PW, and WC).

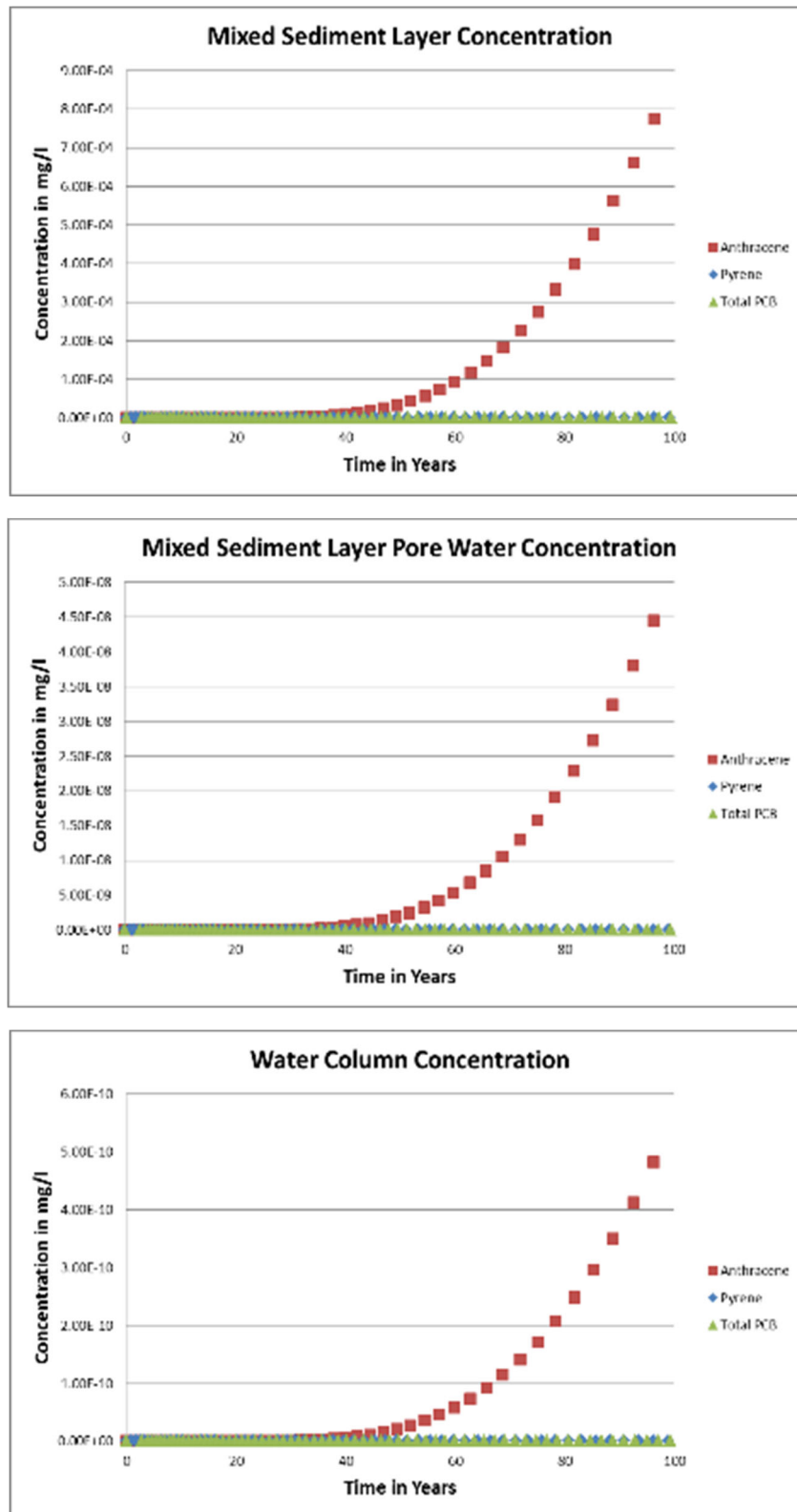


Figure 58. Mixed layer ac/sand cap scenario (sediment, PW, and WC).

Overall, the cap as described in Figure 53 provides risk reduction and does provide isolation for a period of at least 100 years (see Figure 59). Figures 59 and 60 show the Pyrene profile for both an AC mixed layer sand cap and a sand cap. Both profiles show isolation of nearly 10 cm for the AC mixed cap and over 20 cm for the sand cap after 100 years.

The last scenario simulated was that of the groundwater upwelling. This feature is new in RECOVERY 5.0. Figure 61 shows the PCBs profile for the no action scenario subjected to two different upwelling or Darcy velocities of 10 cm/yr and 70 cm/yr. There is a slight difference on the profile as it goes from 3 mg/kg toward the other end of 0 mg/kg. It's easier to see the effects in the SML compartment, specifically PW over time. Figure 62 shows the COC Anthracene over time (100 years) subject to a range of upwelling velocities. Note that as the groundwater velocity increases the concentration profile of Anthracene increases too. Eventually the concentration will be constant based on the maximum dissolved anthracene that can be generated (desorbed) from the layer above, and thus able to move with the advective flux.

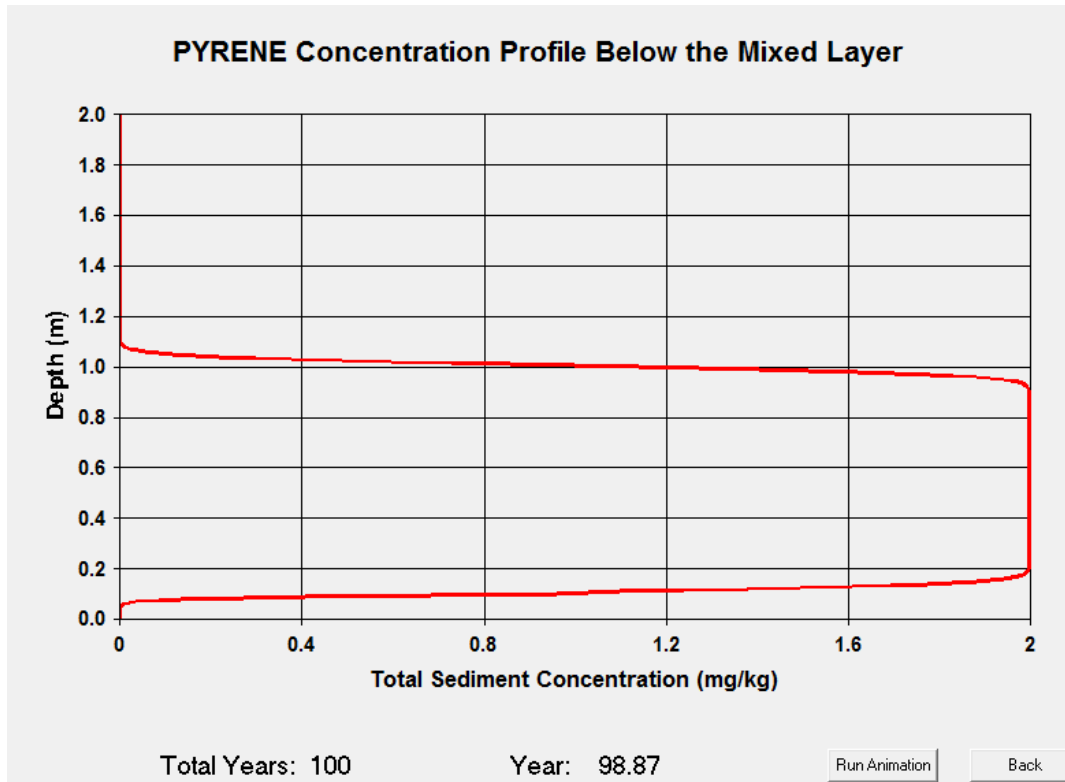


Figure 59. Pyrene mixed layer ac/sand cap profile

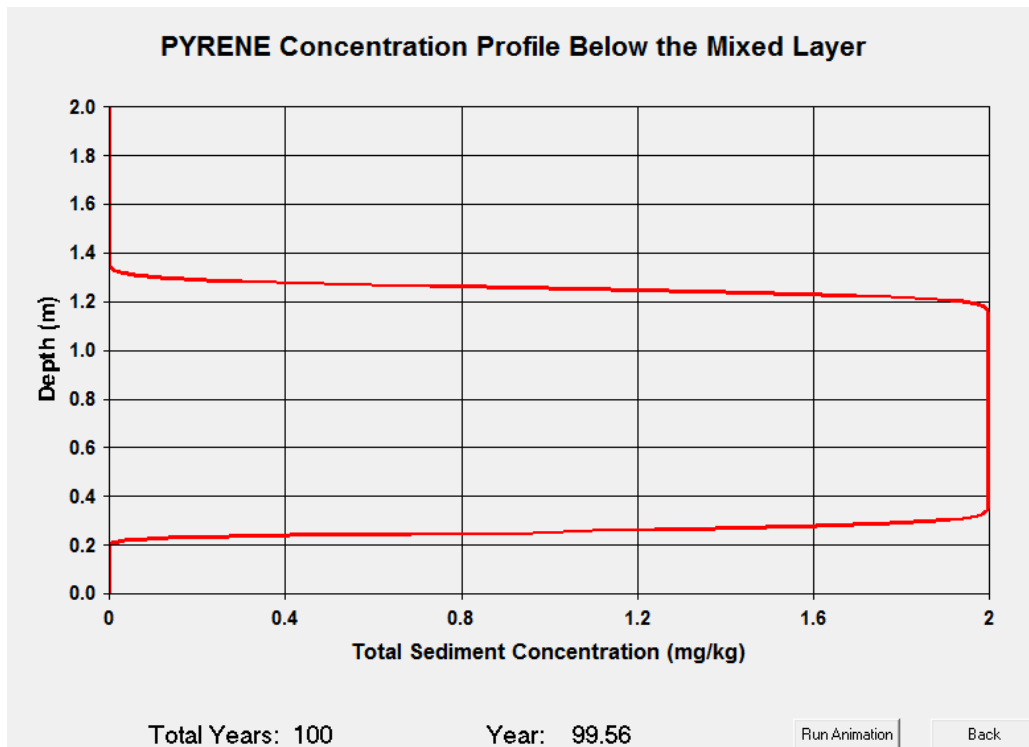


Figure 60. Pyrene sand cap profile

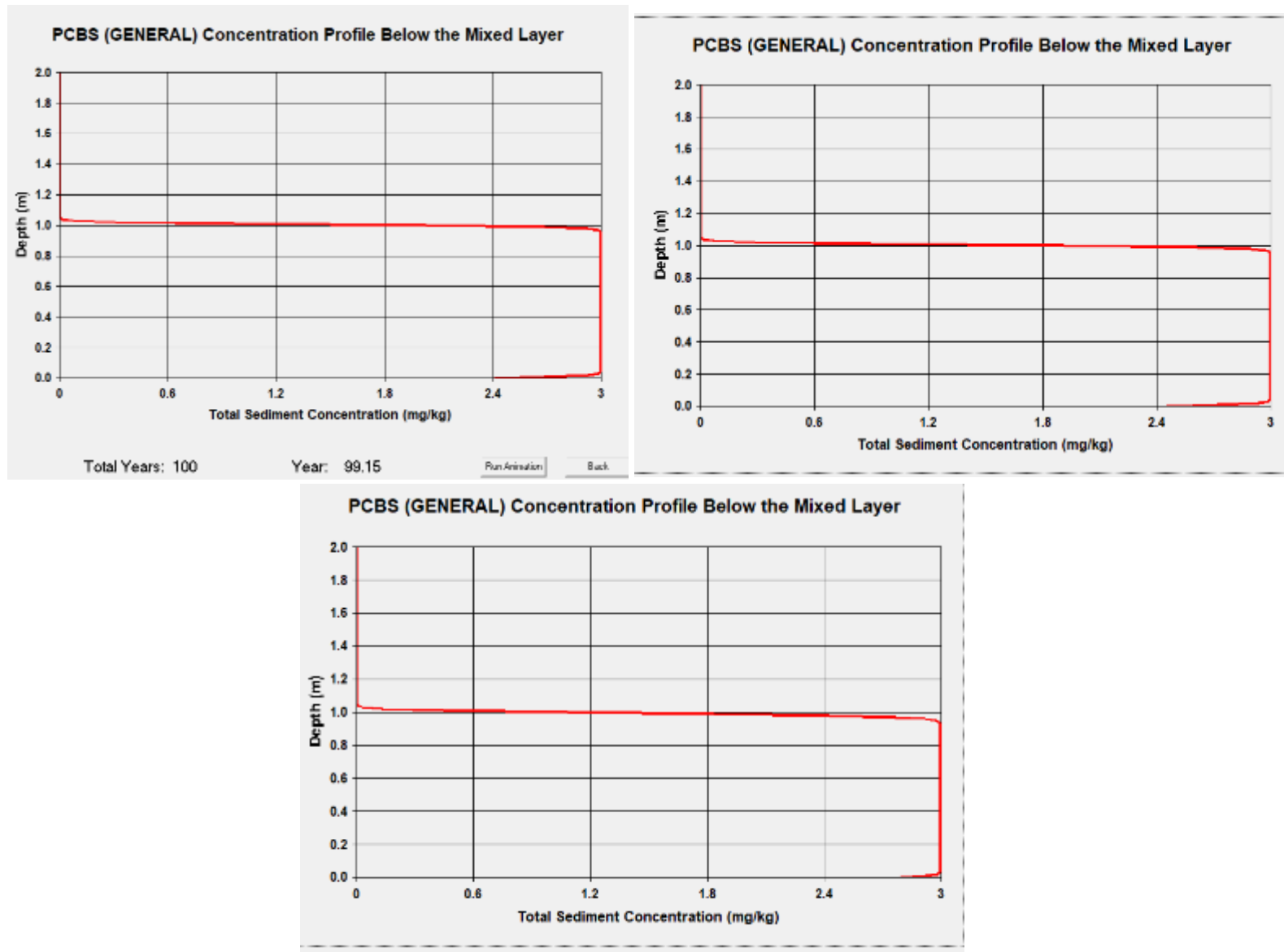


Figure 61. Sediment profile for groundwater upwelling of 0 (a), 10(b), and 70(c) cm/yr

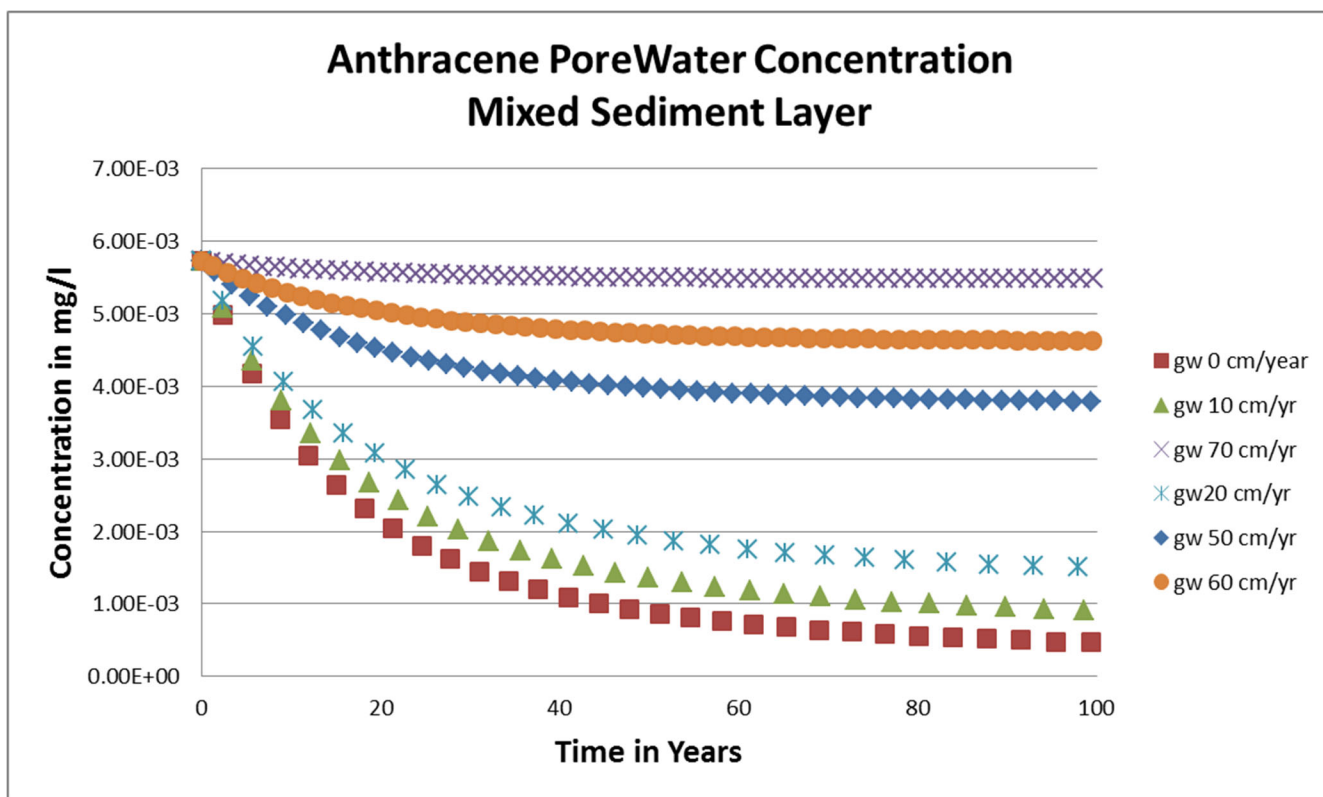


Figure 62. Porewater mixed layer concentration for groundwater upwelling.

9.6. Summary

RECOVERY 5.0, a screening-level contaminant fate and transport model for assessing long-term impacts of contaminated bottom sediments was developed to provide exposure data for risk assessment of contaminated sediment sites and to screen remedial alternatives, in particular, no action, monitored natural recovery or enhanced monitored natural recovery, residuals management, and capping. The model evaluated for different remedial action alternatives, show accurate simulations of the processes, and provides insight into the mechanisms interacting in all the different alternatives. A new User Guide will be developed and distributed with the model in our ERDC model website.

10. RECOVERY-NL A contaminated sediment-water interaction model

This paper describes the U.S. Army Corps of Engineers screening-level contaminant fate and transport model (RECOVERY-NL) for assessing long-term impacts of contaminated bottom sediments on surface waters and ecological resources. RECOVERY-NL stands for RECOVERY with a nonlinear partition coefficient, i.e., modeling using linear partition coefficient, but also nonlinear (e.g., Freundlich and Langmuir, or any other formulation). The model was developed to provide exposure data for risk assessment of contaminated sediment sites and to screen remedial alternatives, in particular, the addition of amendment in in situ treatment and capping. The model couples contaminant interaction between the water column and the bottom sediment, as well as between contaminated and clean bottom sediments. The analysis is intended primarily for organic contaminants with the assumption that the overlying water column is well mixed vertically. The contaminant is assumed to follow linear, reversible, equilibrium sorption and first-order decay kinetics (optional) or nonlinear partition equilibrium. The system is physically represented as a well-mixed water column (i.e., zero dimensional) underlain by a vertically stratified sediment column (i.e., one-dimensional). The sediment is well-mixed horizontally but segmented vertically into a well-mixed surface (active) layer and deep sediment. The specification of an active surface layer is included because an unconsolidated layer is often observed at the surface of sediments due to several processes including bioturbation and mechanical mixing. The deep sediment is segmented into variably contaminated and clean sediment regions.

This major revision of RECOVERY allows a user to better simulate the addition of amendments, in particular activated carbon, which like natural black carbon exhibits nonlinear equilibrium/partition. The ability to capture the long-term performance of black carbon is important for remedial actions, since these impacts can be better predicted over both the short and long-term. This new model incorporates formulations to enhance capabilities and better represent in situ remedial alternatives. As with the previously released version, a Windows-based graphical user interface has been included that permits the user to simulate multiple contaminants in the same run.

10.1 Introduction

Toxic substances are known to associate strongly with fine-grained particulate matter. Therefore, contaminants tend to accumulate in the bottom sediments of natural waters. Pollutants in bottom sediments can be released by resuspension of particles, mixing by benthic organisms, and diffusion and advection from the sediment pore water. Conversely, pollutants in the water column can be transferred to the sediment layer by settling and to the atmosphere by volatilization. Understanding the extent that contaminated sediments effect overlying water quality and contaminant bioaccumulation is necessary for environmental impact assessment and design of remediation to minimize their impact. This paper describes the modeling framework of

RECOVERY-NL used to assess the impact of contaminated bottom sediments on the surface water quality.

RECOVERY-NL is an extension of previous version of the RECOVERY model (Ruiz and Gerald 2021, Ruiz et al. 2007, Ruiz and Gerald, 2001, Ruiz et al. 2001), developed by Boyer et al. (1994). RECOVERY is the U.S. Army Corps of Engineers screening-level water quality model for assessing the long-term effects of contaminated bottom sediments on surface waters. The RECOVERY-NL redevelopment brings in the capability of simulating black carbon, both natural occurring and manmade (activated carbon). Like in its predecessor, the system is idealized as a well-mixed surface water layer underlain by a vertically stratified sediment column. As shown in Figure 63, the sediment is uniform horizontally but segmented vertically into a well-mixed surface layer and layers with varying thicknesses, porosities, and contaminant concentrations underlain by an uncontaminated region. The discretized sediment layer configuration is useful for assessing capping scenarios and sites where contamination occurred over a long time resulting in the system appearing to have contaminant layers. The specification of a mixed surface layer is included because an unconsolidated layer is often observed at the surface of sediments due to a number processes, including bioturbation and mechanical mixing.

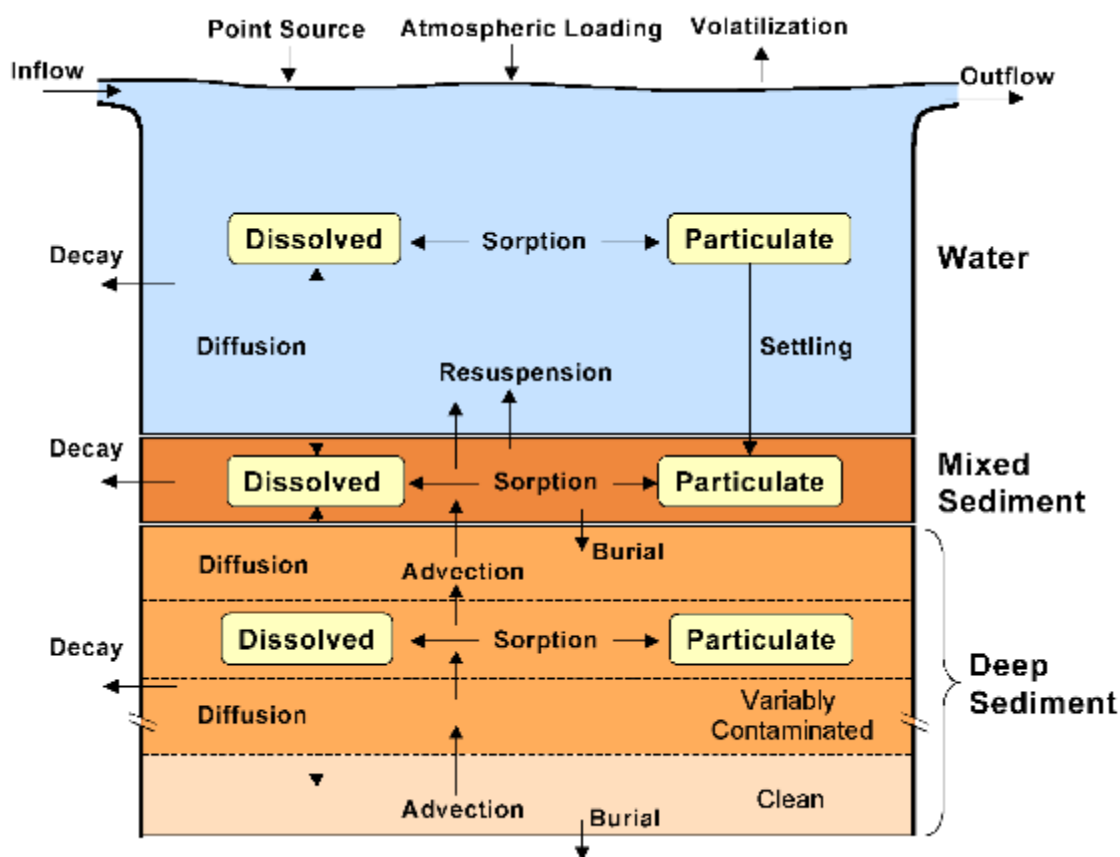


Figure 63. Schematic of the sediment-water system as modeled in RECOVERY-NL.

The model couples contaminant interaction between the water column and the bottom sediment, as well as between contaminated and clean bottom sediments. The analysis is intended primarily for organic contaminants with the assumption that the overlying water column is well mixed vertically. The contaminant is assumed to follow linear, reversible, equilibrium sorption, nonlinear equilibrium sorption, and first-order decay kinetics. The system is physically represented as a well-mixed water column (i.e., zero dimensional) underlain by a vertically stratified sediment column (i.e., one-dimensional). The sediment is well mixed horizontally but segmented vertically into a well-mixed surface layer and deep sediment. The deep sediment is segmented into variably contaminated and clean sediment regions. Processes incorporated in the model are sorption, decay, volatilization, burial, resuspension, settling, bioturbation, advection, and pore-water diffusion.

RECOVERY-NL, a major update to the RECOVERY (5) exhibits the ability to better simulate black carbon, through nonlinear sorption in the form of either Langmuir or Freundlich isotherms/parameters. This is critical in the long-term simulation of remedial alternatives where the contaminant is sequestered by black carbon.

10.2. Partitioning.

The linear partitioning coefficient for organic contaminants can be computed via (Karichhoff, Brown, and Scott 1979) like in RECOVERY (5)

$$K_d = 0.617 f_{oc} K_{ow} \quad (1)$$

Where K_d = equilibrium partitioning coefficient, L/kg

f_{oc} = the weight fraction of organic carbon in the solid matter, g-orgC/g

K_{ow} = octanol-water partitioning coefficient, (mg/m³-octanol)/(mg/m³-water).

Note that the model assumes a default of 0.05 for f_{oc} . Different values for f_{oc} are allowed for the water column, mixed layer, and the deep sediments. Analogous to other physico-chemical characteristics of the sediments, the f_{oc} can vary with depth (layers) in the deep sediments.

The model can use four different partition formulations/models for each of the compartments (water, mixed layer, and sediment). The four partition models are linear, Langmuir, Freundlich, and user defined (measured). The deep sediment can have a different partition model for each layer defined; thus, the user can designate layers with activated carbon using a nonlinear model and layers with natural sediment using a linear model providing a much accurate representation of the remedial action.

10.3. RECOVERY Testing

RECOVERY-NL was applied to a scenario to verify its ability to adequately model a variety of remediation alternatives/processes. The output was compared to that of RECOVERY (5). The comparison is the first hurdle in evaluating the applicability of the model and its versatility. Both models will simulate the same scenario and the results compared for accuracy.

The Contaminant of Concern (COC) selected for the model check is Anthracene. Table 5 shows the properties of Anthracene.

Table 5. Contaminant Parameters

Contaminant	Molecular Weight	log Kow	Molecular Diffusivity (cm ² /sec)	Concentration (mg/kg)
Anthracene	178	4.45	5.00E-06	3

10.4. No Action/Existing Conditions

The scenario simulated is a mixture of no action (existing conditions) with a clean layer of natural sediment. Figure 64 shows an unremediated/existing conditions of a contaminated site

scenario modeled with both RECOVERY and RECOVERY-NL. This is also an example of no-action/enhance natural recovery in which the natural ongoing processes are used to accelerate the site recovery. The existing conditions consist of a sediment bed with 20 centimeter of clean sediment and 80 centimeters of contaminated sediments for a total of 1 meter. The top 5 cm of the contaminated sediments is the mixed layer, which accounts for the assumed bioturbation layer. A 3 m water column overlies the sediment bed. The contaminated sediment has a specific gravity of 2.65, a f_{oc} of 1% and a porosity of 0.67. The existing condition will be the basis for the comparison of the two models. Table 6 summarizes most of the parameters used in both RECOVERY models.

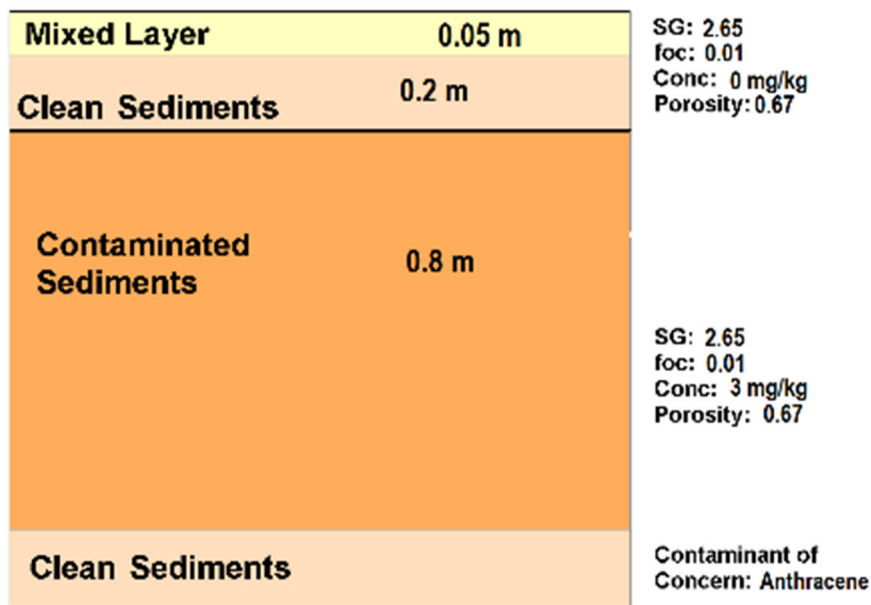


Figure 64. No Action/Existing Conditions Scenario

Table 6. Values Used in the RECOVERY Evaluation

Parameter	Value
Mixed layer thickness (cm)	5
Cap thickness (cm)	0
Porosity of cap	.67
Specific gravity of cap	2.65
Sediment thickness (m)	1
Porosity of sediment	.67
Specific gravity of sediment	2.65
Settling velocity (m/yr)	17.5
Burial velocity (m/yr)	0.0001
Molecular diffusivity (cm ² /sec)	5x10-6
Biodiffusion coefficient (cm ² /sec)	2x10-5
Biodiffusion depth (cm)	0

10.5. Results

The results from the simulation of the scenario will show the COC concentration over time for the water column (WC), sediment mixed layer (SML), and the sediment profile after 200 years.

Figures 65 and 66 show the simulations for the no action alternative or the current conditions for the water column and the mixed layer sediment concentration for the RECOVERY-NL model. The sediment concentration reflects the concentration for Anthracene from an initial clean layer to beginning of contamination to a slightly contaminated layer after 200 years. Anthracene moves from the contaminated sediment layer through the clean layer into the mixed layer over the 200 year period. Figure 67 shows the profile for the no action scenario for the RECOVERY-NL model.

Figures 68 and 69 show the simulations for the no action alternative or the current conditions for the water column and the mixed layer sediment concentration for the RECOVERY model. The sediment concentration reflects the concentration for Anthracene from an initial clean layer to a slightly contaminated layer after 200 years. The simulations for the WC and SML are almost identical. Figure 70 presents the profile for the RECOVERY simulation; both profiles Figures 67 and 68 show almost identical profiles. Note that the profile for RECOVERY-NL has the sediment column from top to bottom, while RECOVERY has it upside down.

This is the first step in the verification and testing of the newly developed RECOVERY-NL model.

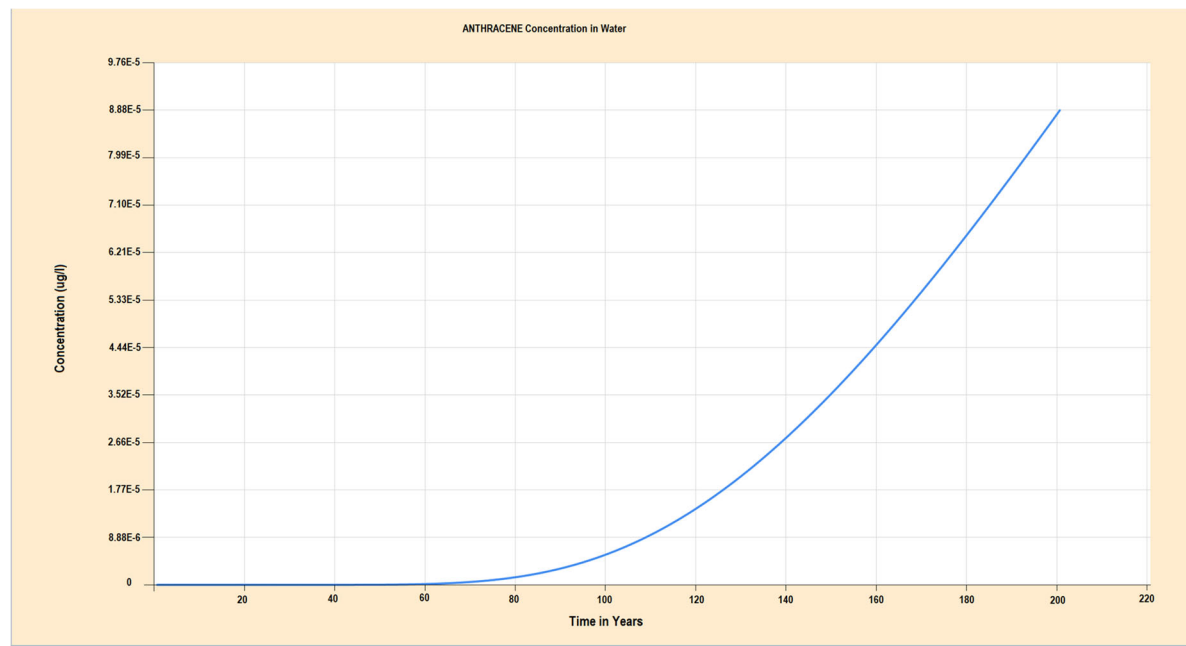


Figure 65. No Action Scenario Water Column Compartment (RECOVERY-NL).

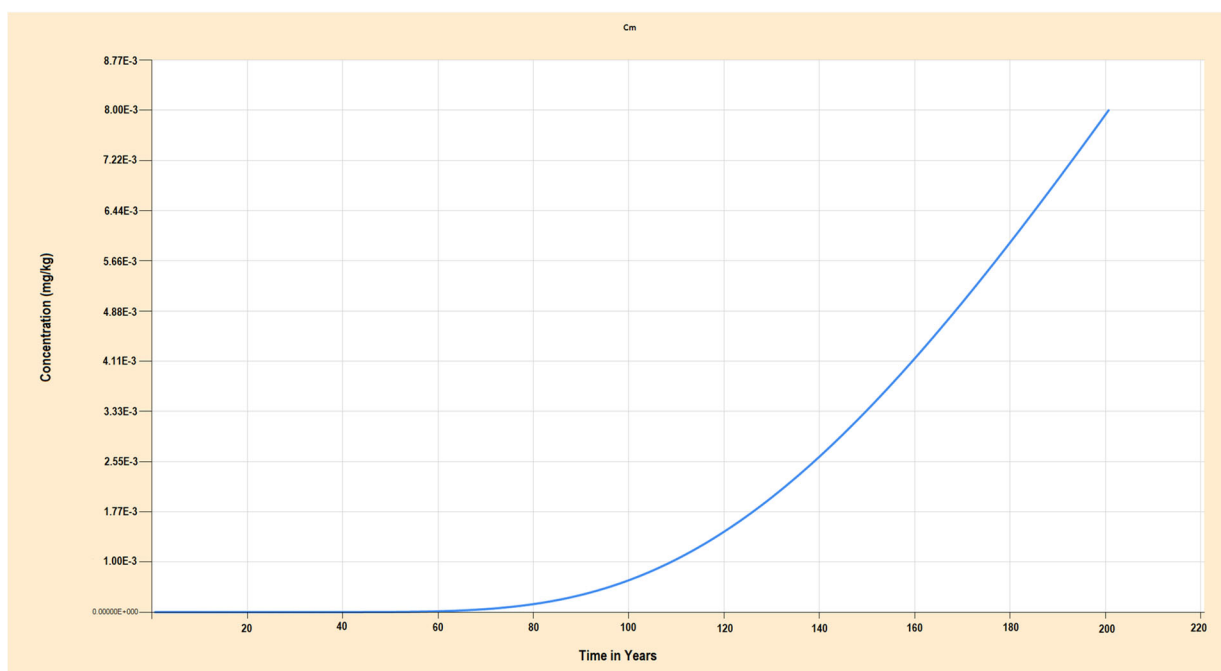


Figure 66. No Action Scenario Mixed Sediment Layer Concentration (RECOVERY-NL).

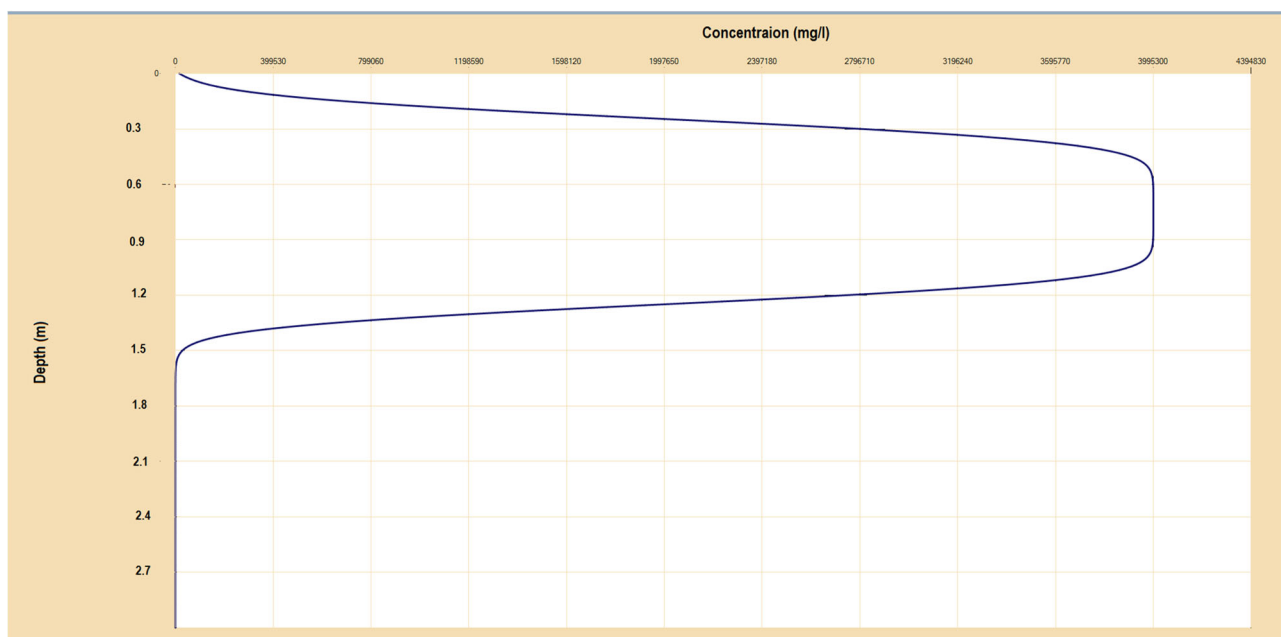


Figure 67. Anthracene Sediment Profile after 200 years (RECOVERY-NL).

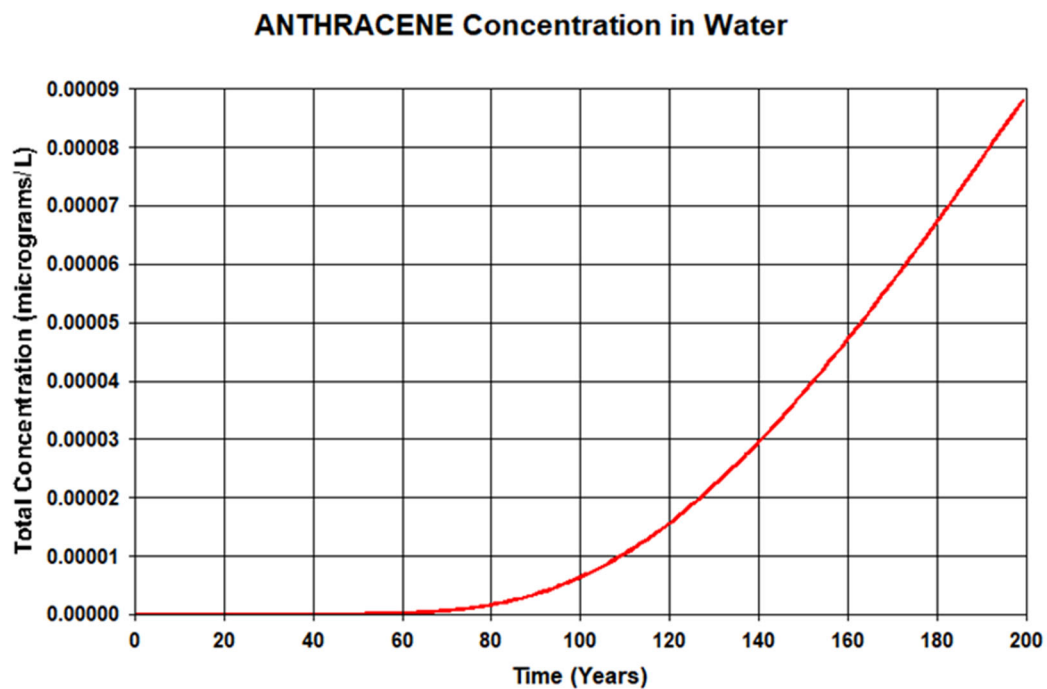


Figure 68. No Action Scenario Water Column Compartment (RECOVERY).

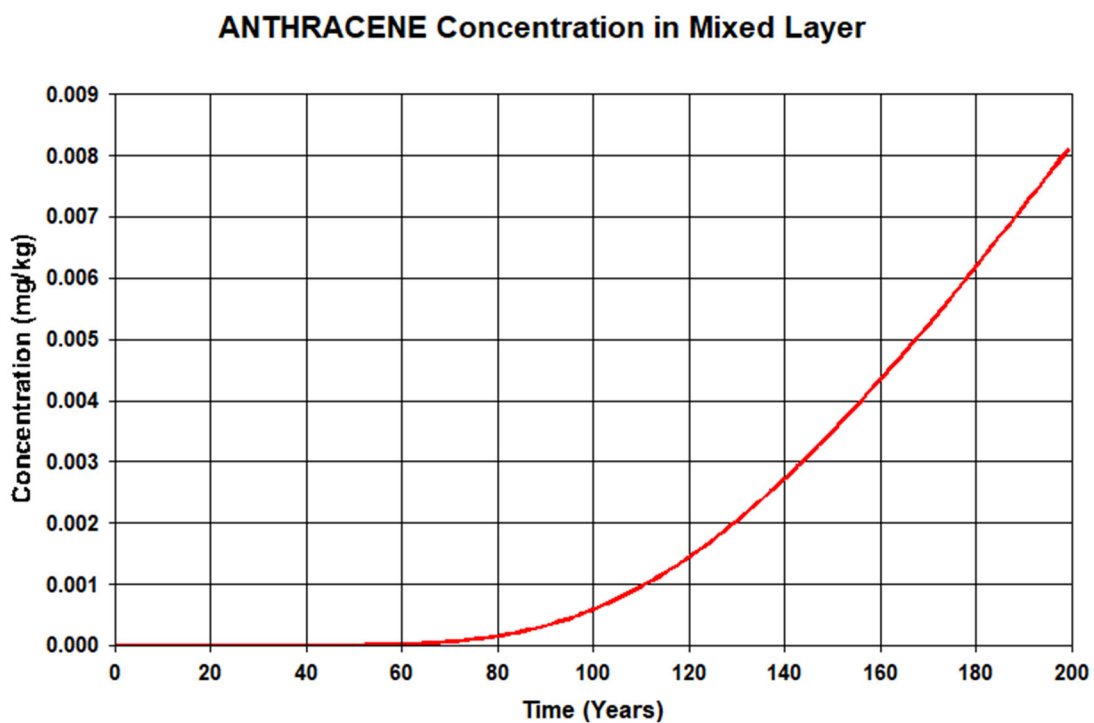


Figure 69. No Action Scenario Mixed Sediment Layer Concentration (RECOVERY).

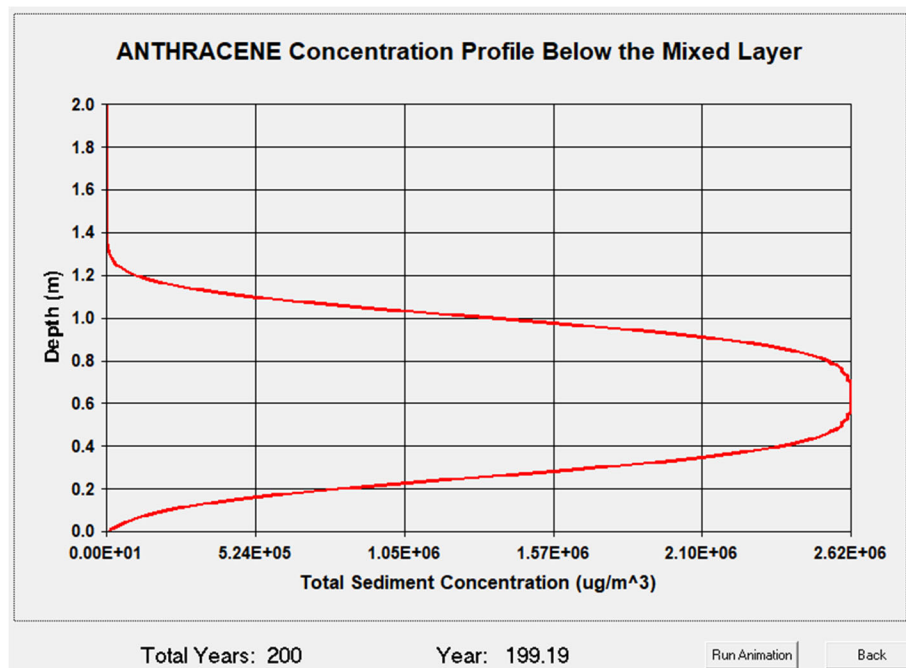


Figure 70. Anthracene Sediment Profile after 200 years (RECOVERY).

10.6. Summary

RECOVERY-NL, a screening-level contaminant fate and transport model for assessing long-term impacts of contaminated bottom sediments was developed to provide exposure data for risk assessment of contaminated sediment sites and to screen remedial alternatives, in particular residuals management, and capping with the addition of black carbon. The model was compared to the current RECOVERY version 5 for the simulation of a scenario with a clean layer over contaminated sediments. The results were almost identical, showing accurate simulations of the processes and providing insight into the mechanisms interacting in all the processes. A new User Guide is included and a comprehensive one is being developed and will be distributed with the model in our ERDC/EL model website.

11. Conclusions

A series of nine mesocosm experiments were conducted to explore the use of AC to treat PCB-contaminated sediments. A unique feature of the experiments were ongoing inputs of clean sediment or PCB-spiked sediment. The key measurements were biouptake of PCB congeners in biota and polymeric samplers. Additional batch experiments addressed the efficacy of low dose AC treatments. The experiments demonstrated several important principles relevant to contaminated sediment site remediation and restoration:

1. No remedy using AC or thin-layer capping was effective (i.e., significant reduction >50%) to ongoing inputs of contamination. Ongoing inputs must be controlled or at least minimized.
2. Different polymer methods (*in situ* passive sampling with PRCs versus *ex situ* equilibrium sampling with multiple polymer thicknesses) provided similar results, within a factor-of-two.
3. Despite general agreement between biota uptake and polymer equilibrium concentrations the two matrices show three common differences: (1) a greater number of congeners were detected in tissue than polymers, which is likely an analytical artifact; (2) AC sometimes caused greater reductions in polymers than tissue, which might be due to spatial and temporal differences; and (3) the thermodynamic level of the polymers was usually greater than the tissue (primarily with controls, but also with E3), meaning that the sediment porewater and surface water were sources not sinks.
4. AC amendment remedies require some patience and should not be considered a rapid remedy. Sorption kinetics are slow from the sediment to the AC, especially for the most hydrophobic, highly chlorinated congeners (hepta- and higher). Within the three-month timeframe of the experiment, di-, tri-, tetra-, penta-, and hexa-chlorinated PCB congeners were treated effectively with AC, while the hept-, octa-, nona-chlorinated congeners were treated more effectively by the “layering effect” of the thin-layer caps.
5. Large reductions in bioavailability by AC (aside from continued inputs) requires a dose equal the natural TOC of the sediment. The concept being that in order to ensure effective treatment, the fundamental nature of the sediment TOC in the bioactive zone must be altered from labile (i.e., amorphous) carbon to black carbon. Some sediments may be effectively treated at lower doses, but almost all sediments, dominated by PCB partitioning to TOC, should show reductions at a dose equal to the TOC.

The results of this work showed AC and thin-layer capping can provide value separately and in combination beyond what may be achievable by MNR alone. Thin-layer capping with AC should be considered as an early, first-step intervention at sites requiring remediation beyond MNR. Repeated application of thin sediment layers without AC also showed benefits. Polymers can provide useful information for monitoring remedy performance, but the polymers may not be able to fully replace the need to measure uptake by biota from a range of functional feeding strategies.

While freely dissolved PCB concentration in sediment porewater provides one extreme boundary of thermodynamic potential for bioaccumulation in aquatic organisms, the actual steady state bioaccumulation are greatly impacted by the specific exposure conditions (e.g., differing contributions of sediment and water column exposures) and organism-specific biological

attributes. Therefore, polymer sampling may not be able to completely replace the need to measure uptake by biota.

This study demonstrated that the complex biological interaction and thermodynamic influences in a food web model can be deconvoluted to express the concentration of each PCB congener in an organism as a function of surface water and porewater concentrations. Uptake in mesocosm organisms was accurately predicted using this simplified model that captures the complexity of the aquatic food web. The use of polymer sampling to characterize exposure to sediment and water column compartments, coupled with a deconvoluted food web model may be used as a streamlined and less costly monitoring approach.

The expansive experimental and modeling efforts performed for this present study generated a large amount of information. A portion of the information has been presented in the published literature (Appendix A). Efforts are underway to develop manuscripts addressing primarily two topics 1) comparisons of lipid-normalized tissue concentrations to equilibrium polymer concentrations towards a thermodynamic exposure assessment; and 2) an evaluation the benefit of low-level activated carbon application using different sediments.

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Appendix A – List of ER-2431 Peer-reviewed Publications and Dissertations

Main project publications

Ghosh U, Bokare M, Gobas FAPC. 2021. Deconvoluting thermodynamics from biology in the aquatic food web model. *Environmental Toxicology and Chemistry* 40: 2145-2155.
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Gidley PT, Lotufo GR, Kennedy AJ, Ruiz CE., Melby NL, Wooley AH, Laber CH, Burgess RM, Bridges TS. 2022. Effect of activated carbon in thin sand caps challenged with ongoing PCB inputs from sediment deposition: PCB uptake in clams (*Mercenaria mercenaria*) and passive samplers. *Archives of Environmental Toxicology and Contamination* 82: 95-104
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Publications of studies partially funded by ER-2431

Sinche FL, Lotufo GR, Landrum P, Lydy MJ. 2019. Can Tenax extraction be used as a surrogate exposure metric for laboratory-based bioaccumulation tests using marine sediments? *Environmental Toxicology and Chemistry* 38: 1188-1197. <https://doi.org/10.1002/etc.4398>.

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Appendix B – List of ER-2431-related Presentations

Wang AP, Gidley PT, Kennedy, AJ, Wooley AH, Lotufo GR, Ruiz CE, Melby NL, Schmidt SN, Mayer P, Ghosh U, Burgess RM, Bridges TS, Fernandez LA. **2018**. *In Situ* Activated Carbon (AC) Amendment to Limit Biouptake from PCB Contaminated Sediment – a Mesocosm Study with three Organisms (Poster). North America 39th Annual Meeting of the Society of Environmental Toxicology and Chemistry, Sacramento, California.

Wang AP, Gidley PT, Kennedy AJ, Wooley AH, Lotufo GR, Ruiz CE, Melby NL, Schmidt SN, Mayer P, Ghosh U, Burgess RM, Bridges TS, Fernandez LA. **2018**. Clean Sand Capping to Reduce Bioaccumulation of PCBs – a Sediment Mesocosm Study with Three Organisms of Different Functional Traits (Poster). American Chemical Society National Meeting. Boston, Massachusetts.

Bridges TS, Lotufo GR, Gidley PT, Kennedy AJ, Melby NL, Wooley AH, Mayer P, Schmidt SN, Fernandez LA, Wang AP, Ghosh U, Burgess RM. **2017**. Equilibrium Status of Aquatic Organisms with Different Functional Traits Exposed to PCB Contaminated Sediment Treated with Activated Carbon (Platform). North America 38th Annual Meeting of the Society of Environmental Toxicology and Chemistry, Minneapolis, Minnesota.

Wang AP, Gidley PT, Kennedy AJ, Schmidt SN, Mayer P, Wooley AH, Lotufo GR, Ruiz CE, Ghosh U, Burgess RM, Bridges TS, Fernandez LA. **2017**. Calculating Diffusive Flux of Polychlorinated Biphenyls between Sediments and Water Column from New Bedford Harbor using Polyethylene Passive Samplers (Poster). North America 38th Annual Meeting of the Society of Environmental Toxicology and Chemistry, Minneapolis, Minnesota.

Gidley PT, Lotufo GR, Kennedy AJ, Ruiz CE, Ghosh U, Mayer P. **2018**. New Approaches of Performance Monitoring for Activated Carbon Amendment and Thin-Layer Capping of PCB Contaminated Sediments. In: Advancements in *In Situ* Management using Caps and Activated Carbon. Presentation to the Sediment Management Working Group (SMWG) Fall Members Meeting, October 2nd, 2018. Nashville, Tennessee.

Gidley PT, Bridges TS, Lotufo GR, Ruiz CE, Kennedy AJ, Melby NL, Wooley AH, Mayer P, Schmidt SN, Fernandez LA, Wang AP, Ghosh U, Burgess, RM. **2017**. From “Project Phoenix” to Thermodynamic Exposure Assessment. Presentation to Exxon Mobil. May 31st 2017. Vicksburg, Mississippi.

Bridges TS, Gidley PT, Lotufo GR, Ruiz CE, Kennedy AJ, Melby NL, Wooley AH, Mayer P, Schmidt SN, Fernandez LA, Wang AP, Ghosh U, Burgess RM. **2017**. Quantitative Thermodynamic Exposure Assessment (QTEA) for Supporting Resilient Contaminated Sediment Site Restoration (Platform). Battelle 7th International Conference on Remediation and Management of Contaminated Sediments. New Orleans, Louisiana.

Schmidt SN, Bridges TS, Gidley PT, Lotufo GR, Ruiz CE, Kennedy AJ, Wooley AH, Mayer P, Fernandez LA, Wang AP, Ghosh U, Burgess RM. **2016**. Remediation of PCB Contaminated Sediments using Activated Carbon: Thermodynamic Exposure Assessment (Platform). North America 37th Annual Meeting of the Society of Environmental Toxicology and Chemistry. Orlando, Florida.

Mayer P, Schmidt SN, Sjöholm KK, Christensen J, Gidley PT, Wooley AH, Vorkamp K, Witt G, Jahnke A. **2016**. Multiple Coating Thicknesses for Sampling of Organic Pollutants – Linear Regressions Confirm Equilibrium even in Challenging Environmental Media (Platform). North America 37th Annual Meeting of the Society of Environmental Toxicology and Chemistry. Orlando, Florida.

Gidley PT. **2016**. Polymer-Based Sampling Technologies. Presentation to the Sediment Management Working Group (SMWG) Spring Sponsors Meeting, May 20th, 2016. Vicksburg, Mississippi.

Schmidt SN, Bridges TS, Gidley PT, Lotufo GR, Ruiz CE, Kennedy AJ, Rogers NS, Ghosh U, Burgess RM, Fernandez LA, Wang AP, Mayer P. **2016**. Remediation of PCB Contaminated Sediments using Activated Carbon: Thermodynamic Exposure Assessment (Poster). Europe 26th Annual Meeting of the Society of Environmental Toxicology and Chemistry. Nantes, France.

Mayer P, Schmidt SN, Mäenpää K, Witt G, Schäfer S, Gidley PT, Jahnke A. **2015**. Equilibrium Sampling of Hydrophobic Organic Contaminants in Sediment (Platform). North America 36th Annual Meeting of the Society of Environmental Toxicology and Chemistry. Salt Lake City, Utah

Appendix C: New Bedford Harbor RECOVERY Simulations Coupled with Food Web Model: Implementing Sediment Remediation

Introduction

Contaminant bioaccumulation from benthos to fish, wildlife and humans is the exposure pathway responsible for the risks driving most contaminated sediments cleanup decisions. Improved approaches for quantifying bioavailability and exposures within the sediment bed is key to reducing uncertainties in descriptions of risks to benthos and fish that feed on benthos. More accurate exposure characterizations are also necessary to support the challenges of designing, implementing, and monitoring the performance of cost-effective in situ remedies for contaminated sediments.

Approaches, which explicitly consider the functional ecology of the diverse array of species comprising benthos, will produce more accurate exposure assessments and predictions for remedial decision-making. Benthic species vary in their position within the sediment column, relation to sediment particles and porewater (e.g., tube building vs. free burrowing), and feeding behavior (filter feeding vs. deposit feeding), all of which contribute to differences in contaminant exposure to the water column vs. sediment and porewater, and the notion of bioavailability.

SERDP project ER-2431 measured uptake differences among different organisms to enable incorporating differences among benthic functional groups into risk assessments and evaluations of alternative remedy designs; those differences were incorporated into a Deconvoluted Food Web Model. The model can be coupled to a contaminant transport model like RECOVERY to predict effectiveness of alternative remedy designs. Both the Deconvoluted Food Web Model and the RECOVERY Model require less data and thus provides a Screening level assessment in a fraction of time as compared to a comprehensive coupled hydrodynamic, contaminant transport and Food Web Model. To evaluate the performance of the remedial action the RECOVERY model is used to estimate the future contaminant concentration in the bioactive zone over time for the current conditions and after a remedy such as a cap.

Objective

The objective of this effort was to demonstrate the RECOVERY model as a Sediment Remediation Assessment Tool and the coupling to the Food Web Model. The model was used to evaluate the New Bedford Harbor's EPA selected remediation plan. EPA selected remediation plan for the widespread PCB contamination in NBH (EPA, 1998) involves dredging and containment of approximately 688,000 m³ (900,000 cubic yards) of PCB-contaminated sediment spread over about 1,000 acres. In summary, the plan has three major remediation sites: the Upper Harbor, the Lower Harbor, and the Outer Harbor (Figure C1). The main goals of the planned remediation are to reduce health risks due to consumption of PCB-contaminated seafood, and reduce health risks due to contact with PCB-contaminated shoreline sediments. The Remedial Action Objectives evaluated are based on prescribed sediment concentration in the NBH:

1. In the Upper Harbor, the concentration of total PCBs in the bottom sediment was set equal to 10 ppm;
2. In the Lower Harbor, the PCB bed concentrations was set to 15 ppm in the areas where dredging has been performed; and
3. In the Outer harbor, the concentration of total PCBs in the bottom sediment was set equal to 1 ppm.

Site

EPA's long-term sediment and biota sampling program that began in 1993 analyzes 18 PCB congeners utilized by the National Oceanic and Atmospheric Administration's (NOAA) Status and Trends Program (Bergen et al. 1998; Nelson et al. 1996; Nelson and Bergen, 2012). These specific congeners, listed in Table C1, are the most pervasive and make up about half of the total mass of PCBs in marine biota. In Figure C2, collection areas are shown for the on-going seafood monitoring program for the New Bedford Harbor Superfund site performed by the State of Massachusetts, Department of Environmental Protection and Division of Marine Fisheries.

In order to compare the RECOVERY simulations against previous New Bedford Harbor (NBH) Contaminant Modeling Studies the approach from Hayter et al (2017) was used in evaluating the weighted Total PCB partition coefficient for the Fish Closure Areas (FCA) (Figure C2). The Total PCBs use a weighted average of NOAA's PCB 18 congeners for NBH based on occurrence in the area. Tables C1 and C3 show the octanol-water partition coefficient (K_{ow}) for all 18 congeners and their occurrence in the two FCAs. The Total PCB saltwater Log K_{ow} for FCA 1 and 2 were 6.67 and 6.88 respectively.

A small tributary at the north end of the Inner Harbor is the Acushnet River. Its annual average flow is $0.54 \text{ m}^3/\text{s}$ ($19.1 \text{ ft}^3/\text{s}$). Surface waters in the harbor usually contain 1-4 mg/l of suspended matter (Massachusetts Division of Water Pollution Control, 1975), similar to the amount in suspension in Buzzards Bay (New England Aquarium, 1973), and in other Atlantic coastal estuaries (Meade and others, 1975).

Upper Harbor, concentration of Total PCBs in the bottom sediment in the subtidal and mudflat areas was set equal to 10 ppm. Average depth of the Upper Harbor is 4 ft (1.22 m) and the area was estimated to be 185.8 acres (751946.3 m^2) (Figures C3 and C4). In the Lower Harbor, the PCB bed concentrations were set to 15 ppm. Average depth of the Lower Harbor is 12 ft (3.66 m) and the area was estimated to be 759.4 acres (3069095 m^2) (Figures C5 and C6). The Outer Harbor, Total PCB bed concentration was set to 1 ppm. Average depth of the Outer Harbor is 20 ft (6.10 m) and the area was estimated to be 3404.7 acres (13778251 m^2) (Figure C7).

Upper Harbor sediments were generally more fine-grained, with mean values of 61.3% fines (silt + clay), 32.7% sand, and 6.67% gravel (Table C3). The Lower Harbor was more evenly distributed with mean values of 50.7% fines, 42% sand and 7.2% gravel. The Outer Harbor was characterized more as a sandy environment with the mean values of 50.0% fines, 43.1% sand, and 6.96% gravel. TOC levels were higher on average in the Upper Harbor (mean = 4.76%), and decreased in a north-to south direction (means of 2.69% and 1.41% in the Lower and Outer Harbors, respectively) (Table C3).

The goal of the RECOVERY model evaluation is to compare the surficial sediment contaminant concentration, porewater concentration, and surface water concentration for the prescribed conditions with two remediation scenarios for a 100-year design. The remediation scenarios selected for the demonstration are TLC, a sand cap (10 cm) and an amended sand cap (10 cm). The remediation will be implemented in the Upper and Lower Harbors. The contaminant migration into and through the caps and accumulation within the cap are simulated for Total PCBs using a weighted average partition coefficient of NOAA's PCB 18 congeners for the NBH. Contaminant concentrations in the sediment mixed layer, porewater and water column concentrations resulting from flux from the sediment bed are simulated to determine the effect of the remediation goal for the two harbor sites.

Table C1. K_{ds} for Fish Closure Area 1 (Upper and Lower Harbor).

New Bedford										
Fish Closure Area 1										
Congener	Log Kow	Log Kow-sw	Kow-sw	%	Fraction	Water Column (sw)			Sediment	
						Log Kow	Log Kdoc	Log Kpoc	Log Kdoc	Log Ksoc
PCB8/5	5.26	5.46	288403.2	2.14%	0.02136	0.1166	0.0932	0.1166	0.0932	0.1069
PCB18	5.45	5.68	478630.1	6.90%	0.06899	0.3919	0.3162	0.3919	0.3162	0.3604
PCB28	5.89	6.11	1288249.6	16.02%	0.16023	0.9790	0.8032	0.9790	0.8032	0.9060
PCB44	5.96	6.21	1621810.1	5.17%	0.05168	0.3209	0.2642	0.3209	0.2642	0.2974
PCB52	6.06	6.3	1995262.3	17.93%	0.17926	1.1293	0.9327	1.1293	0.9327	1.0476
PCB66	6.41	6.66	4570881.9	5.57%	0.05566	0.3707	0.3096	0.3707	0.3096	0.3453
PCB101/90	6.57	6.84	6918309.7	10.10%	0.10097	0.6906	0.5799	0.6906	0.5799	0.6446
PCB105	6.88	7.14	13803842.6	2.34%	0.02335	0.1667	0.1411	0.1667	0.1411	0.1561
PCB118	6.97	7.23	16982436.5	10.30%	0.10302	0.7448	0.6318	0.7448	0.6318	0.6979
PCB128	6.95	7.23	16982436.5	1.37%	0.01374	0.0993	0.0843	0.0993	0.0843	0.0931
PCB138/160/163	7.03	7.31	20417379.4	7.88%	0.07879	0.5760	0.4895	0.5760	0.4895	0.5400
PCB153	7.17	7.45	28183829.3	10.51%	0.10511	0.7831	0.6678	0.7831	0.6678	0.7351
PCB170/190	7.48	7.78	60255958.6	0.97%	0.00965	0.0751	0.0645	0.0751	0.0645	0.0707
PCB180	7.6	7.9	79432823.5	1.28%	0.01276	0.1008	0.0868	0.1008	0.0868	0.0950
PCB187/182	7.38	7.68	47863009.2	1.14%	0.01141	0.0876	0.0751	0.0876	0.0751	0.0824
PCB195	7.77	8.09	123026877.1	0.16%	0.00157	0.0127	0.0110	0.0127	0.0110	0.0120
PCB206	8.3	8.64	436515832.2	0.15%	0.00147	0.0127	0.0111	0.0127	0.0111	0.0120
PCB209	8.39	8.75	562341325.2	0.10%	0.00098	0.0086	0.0075	0.0086	0.0075	0.0081
Total PCBs					1	6.67	5.57	6.67	5.57	6.21

Table C2. Kds for Fish Closure Areas 2 and 3 (Outer Harbor).

New Bedford										
Fish Closure Areas 2 and 3										
Congener	Log Kow	Log Kow-sw	Kow-sw	%	Fraction	Water Column (sw)			Sediment	
						Log Kow	Log Kdoc	Log Kpoc	Log Kdoc	Log Ksoc
PCB8/5	5.26	5.46	288403.2	3.19%	0.0319	0.1742	0.1392	0.1742	0.1392	0.1597
PCB18	5.45	5.68	478630.1	3.40%	0.0340	0.1929	0.1557	0.1929	0.1557	0.1775
PCB28	5.89	6.11	1288249.6	10.42%	0.1042	0.6366	0.5223	0.6366	0.5223	0.5891
PCB44	5.96	6.21	1621810.1	3.90%	0.0390	0.2420	0.1993	0.2420	0.1993	0.2242
PCB52	6.06	6.3	1995262.3	8.16%	0.0816	0.5143	0.4248	0.5143	0.4248	0.4771
PCB66	6.41	6.66	4570881.9	7.84%	0.0784	0.5223	0.4363	0.5223	0.4363	0.4866
PCB101/90	6.57	6.84	6918309.7	11.35%	0.1135	0.7761	0.6516	0.7761	0.6516	0.7243
PCB105	6.88	7.14	13803842.6	3.73%	0.0373	0.2660	0.2252	0.2660	0.2252	0.2490
PCB118	6.97	7.23	16982436.5	13.63%	0.1363	0.9852	0.8357	0.9852	0.8357	0.9230
PCB128	6.95	7.23	16982436.5	2.71%	0.0271	0.1958	0.1661	0.1958	0.1661	0.1834
PCB138/160/163	7.03	7.31	20417379.4	12.18%	0.1218	0.8900	0.7564	0.8900	0.7564	0.8345
PCB153	7.17	7.45	28183829.3	12.64%	0.1264	0.9418	0.8032	0.9418	0.8032	0.8842
PCB170/190	7.48	7.78	60255958.6	2.17%	0.0217	0.1687	0.1449	0.1687	0.1449	0.1588
PCB180	7.6	7.9	79432823.5	1.87%	0.0187	0.1473	0.1269	0.1473	0.1269	0.1388
PCB187/182	7.38	7.68	47863009.2	1.33%	0.0133	0.1025	0.0878	0.1025	0.0878	0.0964
PCB195	7.77	8.09	123026877.1	0.60%	0.0060	0.0486	0.0420	0.0486	0.0420	0.0459
PCB206	8.3	8.64	436515832.2	0.43%	0.0043	0.0374	0.0327	0.0374	0.0327	0.0354
PCB209	8.39	8.75	562341325.2	0.47%	0.0047	0.0409	0.0357	0.0409	0.0357	0.0387
Total PCBs				1	1	6.88	5.79	6.88	5.79	6.43

Table C3. Total Organic Carbon, Grain Size, and PCB Summary Results for New Bedford Harbor LTM VI Survey

Area	Parameter	Units	No. Obs.	% Detected	MIN	Mean	Std. Dev.	Median	MAX	Location of MAX (Station ID)
Upper Harbor	Gravel	%	27	100	0.00	6.67	9.04	3.00	30.0	154-14LTM
	Sand ¹	%	27	100	1.00	32.7	26.4	26.0	84.0	151-14LTM
	Fines ²	%	27	100	4.00	61.3	31.8	68.0	99.0	111-14LTM; 138-14LTM
Lower Harbor	Gravel	%	29	100	0.00	7.2	11.1	3.00	44.0	218-14LTM; 333-14LTM
	Sand ¹	%	29	100	3.00	42.0	23.4	46.0	86.0	208-14LTM
	Fines ²	%	29	100	7.00	50.7	28.2	42.0	97.0	235-14LTM
Outer Harbor	Gravel	%	23	100	0.00	6.96	11.8	2.00	44.0	333-14LTM
	Sand ¹	%	23	100	4.00	43.1	28.5	35.0	92.0	306-14LTM; 311-14LTM
	Fines ²	%	23	100	3.00	50.0	30.9	63.0	92.0	323-14LTM
Upper Harbor	TOC	%	27	100	0.26	4.76	2.49	5.14	8.38	108-14LTM
Lower Harbor		%	29	100	0.38	2.69	1.49	2.35	5.71	230-14LTM
Outer Harbor		%	23	100	0.07	1.41	0.98	1.38	3.49	334-14LTM
Upper Harbor	Total PCB ³	ppm	27	NA	0.502	83.1	184	24.6	934	115-14LTM
Lower Harbor		ppm	29	NA	0.226	2.82	2.34	1.98	8.70	230-14LTM
Outer Harbor		ppm	23	NA	0.003	0.166	0.222	0.055	0.766	304-14LTM

¹ Sand is a sum of all sand fractions (very coarse, coarse, medium, fine, very fine).

² Fines is a sum of the silts and clays.

³ Total PCB is the sum of 18 NS&T congeners using surrogate corrected data and ½ the RL for non-detects.

³ Total PCB is the sum of 18 NS&T congeners using surrogate corrected data and ½ the RL for non-detects.

Contaminant Transport Modeling

Background

RECOVERY (version 5.0) is the U.S. Army Corps of Engineers screening-level water quality model for assessing the long-term effects of contaminated bottom sediments on surface waters. It is an extension of previous version of the RECOVERY model (Ruiz et al. 2007, Ruiz and Gerald, 2001), developed by Boyer et al. (1994). The system is idealized as a well-mixed surface water layer underlain by a vertically-stratified sediment column. As shown in Figure C8, the sediment is uniform horizontally but segmented vertically into a well-mixed surface layer and layers with varying thicknesses, porosities, and contaminant concentrations underlain by an uncontaminated region. The discretized sediment layer configuration is useful for assessing capping scenarios and sites where contamination occurred over a long time resulting in the system appearing to have contaminant layers. The specification of a mixed surface layer is included because an unconsolidated layer is often observed at the surface of sediments due to a number processes, including bioturbation and mechanical mixing.

The model couples contaminant interaction between the water column and the bottom sediment, as well as between contaminated and clean bottom sediments. The analysis is intended primarily for organic contaminants with the assumption that the overlying water column is well mixed vertically. The contaminant is assumed to follow linear, reversible, equilibrium sorption and first-order decay kinetics. The system is physically represented as a well-mixed water column (i.e., zero dimensional) underlain by a vertically-stratified sediment column (i.e. one-dimensional). The sediment is well mixed horizontally but segmented vertically into a well-mixed surface layer and deep sediment. The deep sediment is segmented into variably contaminated and clean sediment regions. Processes incorporated in the model are sorption, decay, volatilization, burial, resuspension, settling, bioturbation, pore-water diffusion and advection through the bottom sediments from groundwater upwelling and water expulsion resulting from the consolidation of sediment.

Input Parameters

The goal of the contaminant modeling was to demonstrate the capability of using RECOVERY as a Sediment Remediation Assessment Tool to evaluate the three different Harbor Sites and two thin layer remedial alternatives, a sand cap and an amendment sand cap. The evaluation uses sediment properties, simple transport, and partitioning data in addition to COC contaminant concentration data. Table C4 summarizes most of the parameters used in RECOVERY. Figures C9, C10 and C11 show the conceptual configuration for the current conditions at the three harbor sites and the two remedial alternatives. The modeling of at the three harbor sites shows the results for the proposed goals and the incorporation of two remediation alternatives. The partition coefficient for the Total PCBs is a weighted average of the NOAHs PCB 18 as described in the previous section.

The partition coefficient for the sand layer was estimated based on the clean sand f_{oc} (0.009) and the Log Kow for the FCA 1 of 6.67. The partition coefficient of the activated carbon amended sand cap was set to two orders of magnitude larger than the sediment partition coefficient. RECOVERY version 5 allows the user to enter the partition coefficient for amended layers (mixed layer in this simulation) and for heavy metals. All other parameters are in the conceptual configuration (Figures C9, C10, and C11).

Table C4. Values Used in the RECOVERY Evaluation

Parameter	Value
Mixed layer thickness (cm)	10
Cap thickness (cm)	10
Porosity of cap	0.5
Specific gravity of cap	2.65
Sediment thickness (m)	3
Porosity of sediment	0.65
Specific gravity of sediment	2.65
Settling velocity (m/yr)	126
Burial velocity (m/yr)	0.001
Molecular diffusivity (cm ² /sec)	5x10-6
Biodiffusion coefficient (cm ² /sec)	2x10-5
Biodiffusion depth (cm)	0

Results and Discussion

Total PCBs and the 18 congeners are the primary COCs, requiring the greatest reduction in exposure. RECOVERY simulations for the COC of NBH were Total PCBs. The simulations were performed for a period of 100 years.

Figure C12 shows surface water, porewater, and the mixed layer Total PCBs concentrations of the Upper Harbor for a 100-year simulation. Reduction in the bulk mixed layer concentration varied from around 1 ppm for the first decade to less than 0.5 per decade after 50 years. Surface water concentration was reduced by a third over the simulation period. Note that the hydrodynamics of RECOVERY are yearly average thus might be conservative. Porewater concentration follows the decrease of the bulk mixed layer Total PCBs.

Figure C13 shows surface water, porewater, and the mixed layer Total PCBs concentrations of the Lower Harbor for a 100-year simulation. Reduction in the bulk mixed layer concentration varied from 1 ppm for the first decade to less around 0.8 per decade after 50 years. Surface water concentration was reduced by a fourth over the simulation period. Porewater concentration

follows the decrease of the bulk mixed layer Total PCBs; they are much higher than the Upper Harbor porewater concentration.

Figure C14 shows surface water, porewater, and the mixed layer Total PCBs concentrations of the Outer Harbor for a 100-year simulation. Note that the partition coefficient for the Outer Harbor is calculated based on the Log K_{ow} of 6.688 for the FCA 2. Surface water concentrations are two or at least two orders of magnitude lower than the Upper Harbor. Porewater concentration in the Outer Harbor are at least one order of magnitude lower than the Lower Harbor. Total PCBs sediment bed reduction over the 100th simulation ranged from 0.2 ppm for the first 10 years to 0.18 for the last 10 years.

Figure C15 shows the effect of a 10 cm clean layer of sand over the Upper Harbor. Surface water concentration was reduced by at least two orders of magnitude over the 100-year simulation. Bed sediment concentration was reduced from (10 ppm @ T=0) to (~0.03 ppm @ T=100 years). Porewater Total PCBs concentration max at 1 ppt versus 70 ppt for the uncapped sediments.

Figure C16 shows the effect of a 10 cm clean amended layer of sand over the Upper Harbor. Surface water concentration was reduced by at least two orders of magnitude over the 100-year simulation. Bed sediment concentration was reduced from (10 ppm @ T=0) to (~0.03 ppm @ T=100 years). Porewater Total PCBs concentration max at 1 ppt versus 70 ppt for the uncapped sediments.

Figure C17 shows the effect of a 10 cm clean layer of sand over the Lower Harbor. Surface water concentration was reduced by at least two orders of magnitude over the 100-year simulation. Bed sediment concentration was reduced from (15 ppm @ T=0) to (~0.046 ppm @ T=100 years). Porewater Total PCBs concentration max at 1.8 ppt versus 193 ppt for the uncapped sediments.

Figure C18 shows the effect of a 10 cm clean amended layer of sand over the Lower Harbor. Surface water concentration was reduced by at least two orders of magnitude over the 100-year simulation, like that for the clean sand. Bed sediment concentration was reduced from (15 ppm @ T=0) to (~0.046 ppm @ T=100 years), like that of the clean sand. Porewater Total PCBs concentration max at 0.018 ppt versus 193 ppt for the uncapped sediments, two orders of magnitude lower than that of the clean sand.

In summary, the thin layers of sand and amended sand (TLC) provide a significant reduction in the porewater concentration and thus in the surface water concentration of the Upper and Lower New Bedford Harbor by reducing the flux contaminant flux from the bed to the water column. Both sand and amended sand TLC provided a reduction of the bed concentration (sediment dilution). Over the simulation period the mixed layer concentration did not reach a tenth of the concentration of the uncapped sediment bed for both the upper and Lower NBH.

Integration with Food Web Modeling

A food web model based on the Arnot and Gobas (2004) bioaccumulation model was set up to simulate exposure to a range of aquatic organisms. The model describes the kinetics of uptake

and loss processes for each organism based on their specific biology and interaction with the rest of the food web and the environment. The original model uses a partitioning calculation to estimate the freely dissolved concentration in sediment porewater and surface water. Major components of a food web model are the assumptions made for the composition of the diet and the type of water ventilated (surface water or porewater). Diet composition of native organisms in New Bedford Harbor was obtained from Dr. Lawrence Burkhard from the USEPA, the model was then used to predict steady state concentrations in each organism. Several changes were made in the model to allow inputs of RECOVERY simulated parameters such as the freely dissolved concentrations in sediment porewater and surface water. As described in Section 8 of this report and in Ghosh et al. (2021), after site specific parameterization, the complex biological interaction and thermodynamic influences in a food web model can be deconvoluted to express the concentration of each PCB congener in an organism as a function of surface water and porewater concentrations. We demonstrated that a deconvoluted food web model parameterized for site specific conditions can predict the bioaccumulation of PCBs in aquatic organisms similar to that of existing complex food web models. The final deconvoluted form of the model is a product of a bioaccumulation factor for Fish A ($BAF_{Fish,A}$) and fractional influence of surface water or porewater (f_{SW} or f_{PW}) as shown in Equation 1.

$$C_{Fish,A} = C_{SW} \times [f_{SW} \times BAF_{Fish,A}] + C_{PW} \times [f_{PW} \times BAF_{Fish,A}] \quad - \text{Equation (1)}$$

Where, C_{SW} and C_{PW} are the freely dissolved concentrations in surface water and sediment porewater respectively. The water concentrations for each congener for the modeled scenarios were generated using the RECOVERY model. The bioaccumulation factors and fractional contribution of surface water and porewater were estimated for each modeled congener and organism modeled as described in Ghosh et al. 2021 and shown in Tables C5 and C6.

Table C5. Log BAF values estimated for the different species using the deconvoluted food web model (Ghosh et al. 2021)

	log BAF											
	L/Kg											
PCB congener	Phytoplankton	Zooplankton	Hard clams	Polychaete	Blue mussel	Blue crabs	Crayfish	Mummichog	Winter flounder	Lobster	Black sea bass	Scup
18	3.68	3.56	3.52	3.83	3.64	3.65	3.78	4.40	4.03	3.74	4.48	4.46
28/31	4.09	4.01	4.02	4.33	4.21	4.26	4.35	4.85	4.68	4.46	5.18	5.08
44	4.16	4.10	4.10	4.39	4.28	4.35	4.45	4.93	4.77	4.57	5.30	5.17
52	4.25	4.19	4.19	4.47	4.38	4.46	4.57	5.01	4.87	4.70	5.43	5.28
66	4.56	4.57	4.61	4.87	4.81	4.94	5.07	5.34	5.34	5.23	5.93	5.69
90/101	4.69	4.73	4.74	4.96	4.92	5.06	5.22	5.45	5.44	5.37	6.06	5.79
105	4.89	5.00	5.11	5.38	5.32	5.48	5.62	5.64	5.85	5.79	6.40	6.08
118	4.95	5.08	5.13	5.36	5.32	5.46	5.62	5.65	5.82	5.78	6.37	6.06
128	4.95	5.08	5.20	5.47	5.41	5.56	5.70	5.68	5.93	5.88	6.46	6.14
132/153	4.95	5.09	5.14	5.38	5.34	5.48	5.63	5.66	5.83	5.79	6.38	6.07

Table C6. Fraction contribution of surface water estimated for the different species using the deconvoluted food web model (Ghosh et al. 2021).

	Fraction SW contribution											
PCB congener	Phytoplankton	Zooplankton	Hard clams	Polychaete	Blue mussel	Blue crabs	Crayfish	Mummichog	Winter flounder	Lobster	Black sea bass	Scup
18	1.00	1.00	0.90	0.81	0.75	0.89	0.90	0.99	0.87	0.89	0.96	0.92
28/31	1.00	1.00	0.78	0.59	0.58	0.70	0.79	0.96	0.64	0.70	0.83	0.80
44	1.00	1.00	0.78	0.59	0.60	0.69	0.79	0.96	0.64	0.69	0.82	0.80
52	1.00	1.00	0.78	0.58	0.61	0.67	0.77	0.95	0.62	0.68	0.80	0.79
66	1.00	1.00	0.66	0.38	0.51	0.47	0.62	0.91	0.41	0.50	0.63	0.68
90/101	1.00	1.00	0.67	0.38	0.54	0.47	0.62	0.91	0.40	0.50	0.62	0.69
105	1.00	1.00	0.47	0.19	0.35	0.26	0.40	0.82	0.21	0.30	0.40	0.49
118	1.00	1.00	0.51	0.22	0.39	0.30	0.45	0.85	0.24	0.34	0.44	0.53
128	1.00	1.00	0.43	0.17	0.32	0.23	0.37	0.80	0.18	0.27	0.36	0.45
132/153	1.00	1.00	0.50	0.21	0.38	0.29	0.44	0.84	0.23	0.33	0.43	0.52

The merit of this approach is that once the thermodynamic and biological contributions to food-web bioaccumulation are computed for an ecosystem, the deconvoluted model provides a relatively simple approach for calculating concentrations of chemicals in organisms for a range of possible surface water and sedimentary concentrations. This approach is especially useful for calculating bioaccumulation of pollutants from freely dissolved concentrations measured using passive sampling devices or predicted by fate and transport models. Simulations were performed for the Lower New Bedford Harbor for a period of 100 years.

The model was verified with the SERDP experiments where direct measurement of freely dissolved concentrations using passive sampling values was used in the predictions (see section 8 in report).

Results and Discussion

The RECOVERY model was used in simulating the Lower NBH scenarios of no action/no treatment, a 10 cm sand cap layer, and a 10 cm activated carbon/sand layer as described in Figures C9, C10, and C11. The model results were further decomposed to four time periods over the 100-year simulation as shown in Figure C19. The Food Web Model was then coupled from

the RECOVERY results for the three scenarios of Figure C19. All model calculations were performed at the congener level for each of the 10 congeners listed in Table C5.

Figure C20 shows the Food Web Model simulations for the Lower Harbor for the no treatment scenario (actual conditions/EPA selected remediation plan); fish Total PCBs concentration was higher than the 1991 U.S Food and Drug Administration's tolerance level of 2 ppm PCBs for human seafood consumption. The simulations agree with the fish advisory for the NBH as shown in Figure C2.

Figure C21 shows the effect of the TLC sand layer; lower porewater concentration, thus lower surface water concentration resulting in lower Food Web concentration across all species and in particular the higher trophic species. Fish concentrations are in the range of 0-0.5 ppm and are below the FDA recommended tolerance of 2 ppm.

Incorporation of AC in the sand layer resulted in further reductions in porewater for the Lower Harbor and subsequent reduction in surface water concentration (Figure C19). These reductions resulted in further reductions in the PCB bioaccumulation across the food web by a factor of 5 for the case of amended sand compared to the sand only scenario.

Summary

The coupling and demonstration of the Sediment Remediation Assessment Tool: RECOVERY and the Deconvoluted Food Web Model illustrate the advantage of these simple tools in planning and developing sediment remediation strategies and alternatives. Both tools are rigorous, easy to apply, while maintaining the comprehensive mechanisms of the more sophisticated and advanced tools in the remediating arena.

References

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FIGURES



Figure C1. New Bedford Harbor, MA

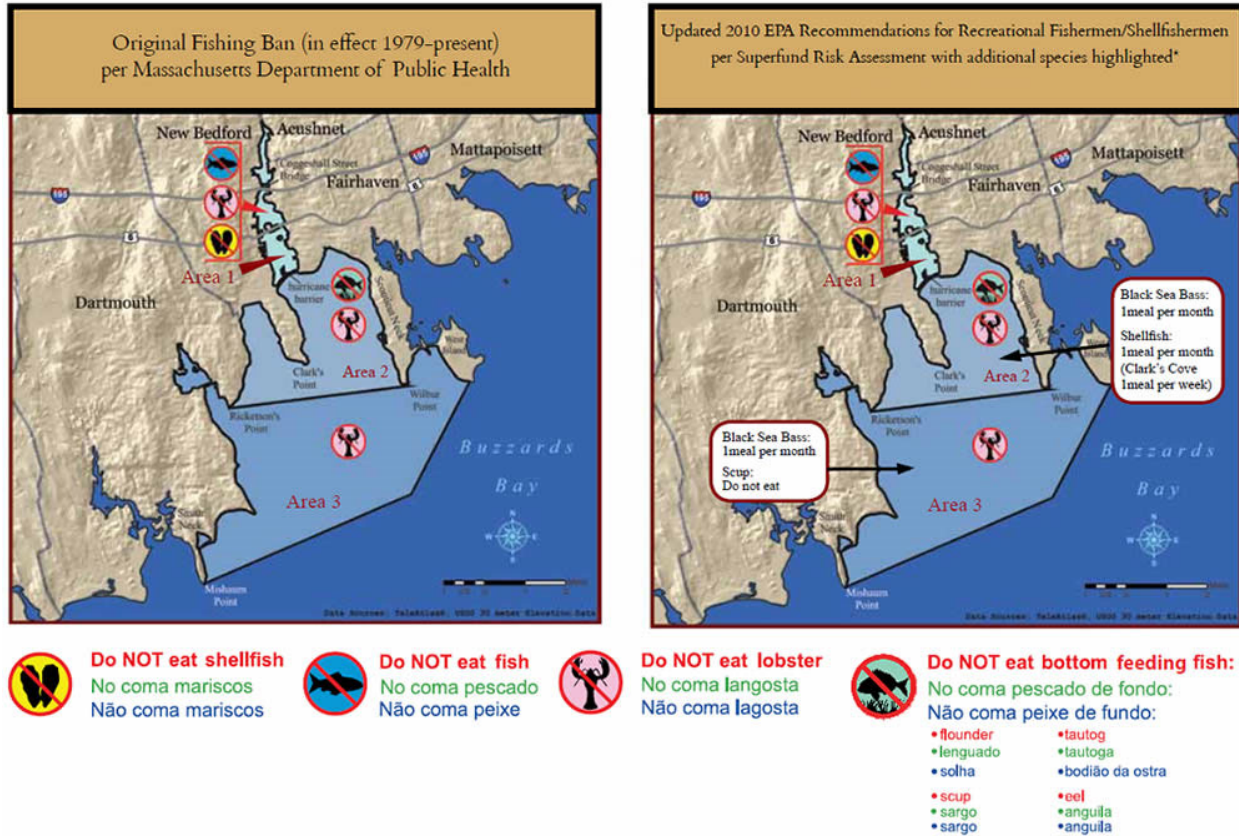


Figure C2. Fishing Ban in Effect, New Bedford Harbor.

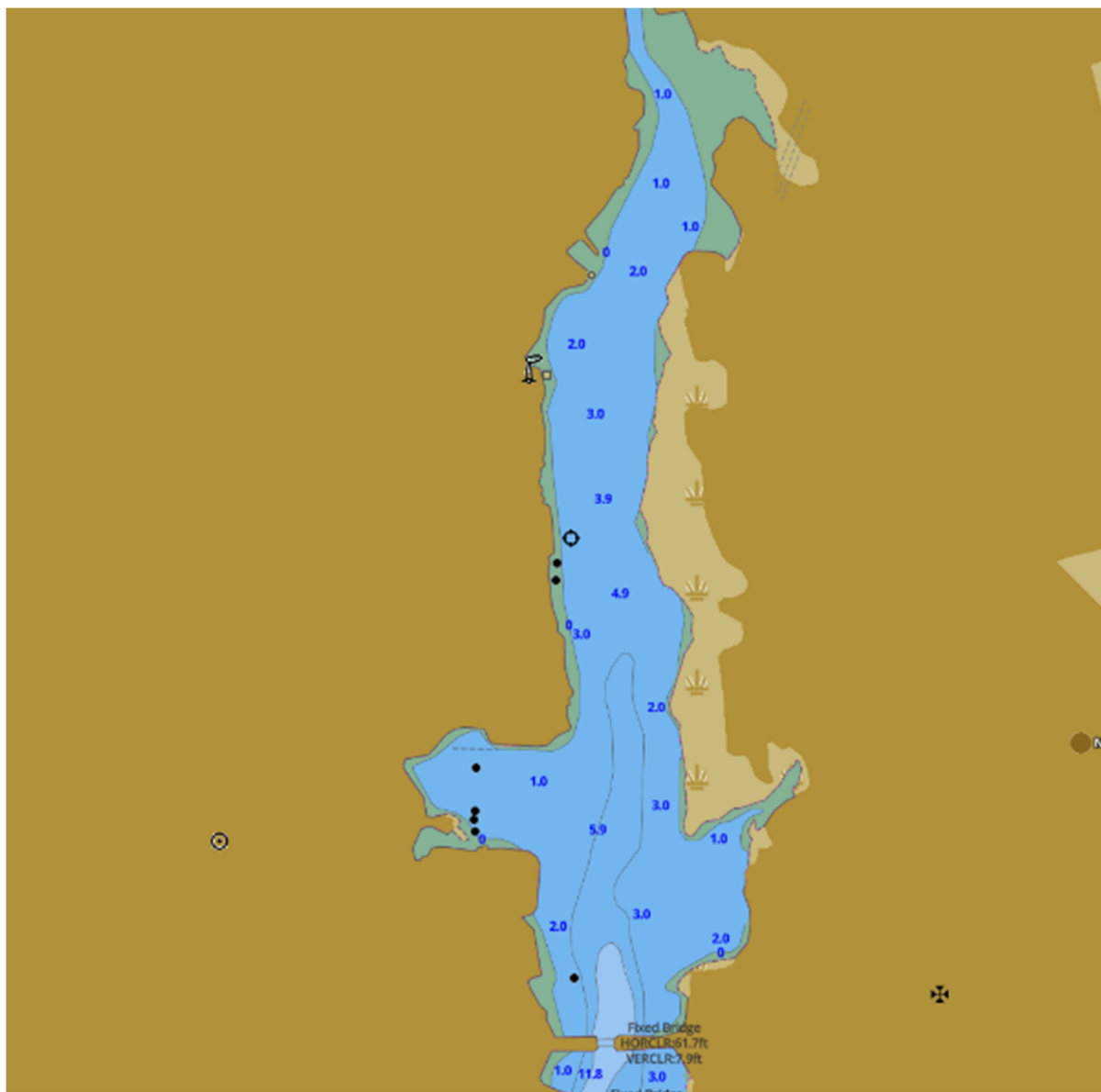


Figure C3. Upper New Bedford Harbor, MA Average Depth



Figure C4. Upper New Bedford Harbor, MA (Area)

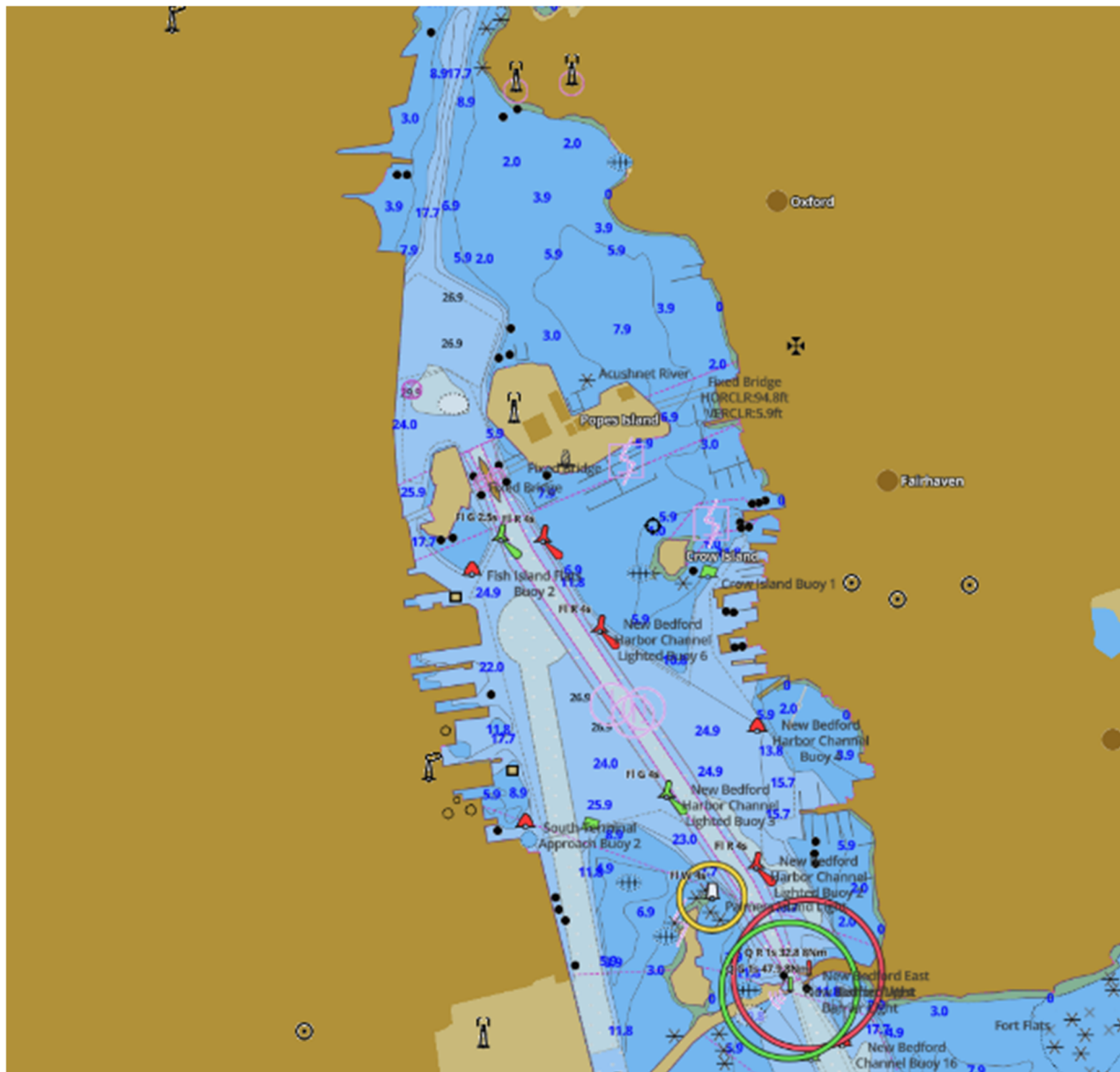


Figure C5. Upper New Bedford Harbor, MA (Average Depth).



Figure C6. Upper New Bedford Harbor, MA (Area).

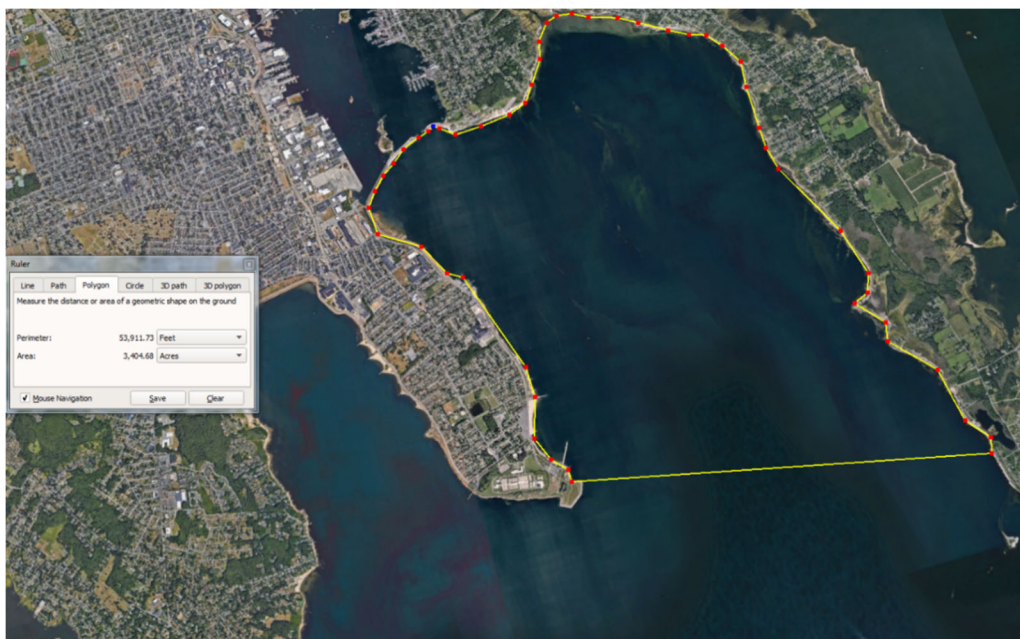


Figure C7. Outer New Bedford Harbor, MA (Area).

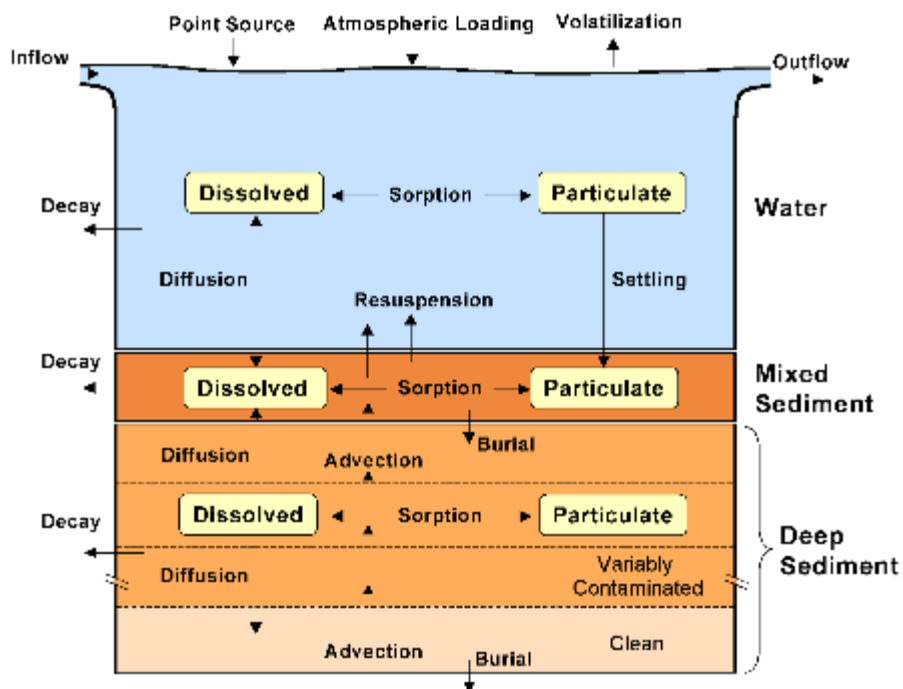


Figure C8. Schematic of the sediment-water system as modeled in RECOVERY.

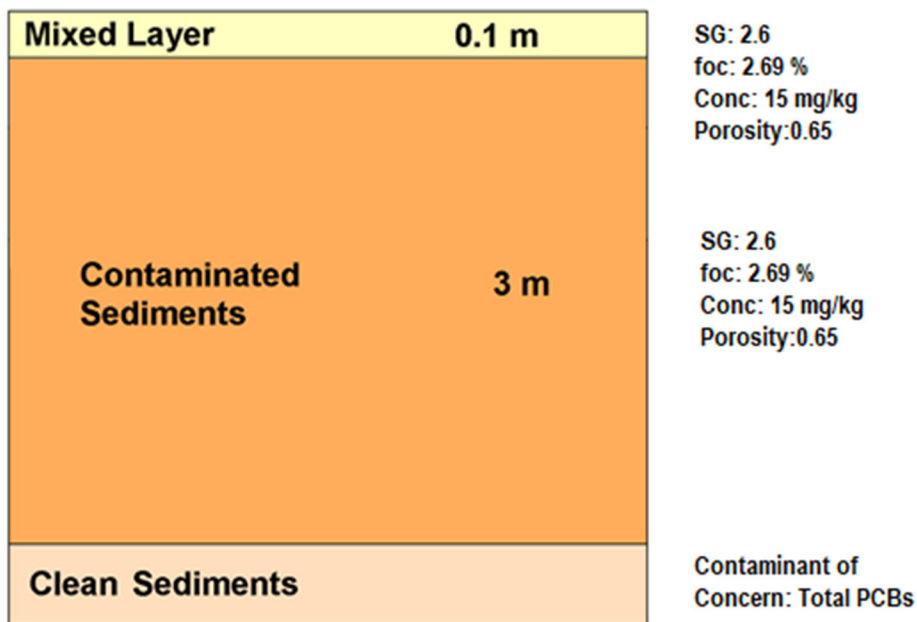


Figure C9. Lower New Bedford Harbor bed configuration for modeling Total PCBs using RECOVERY.

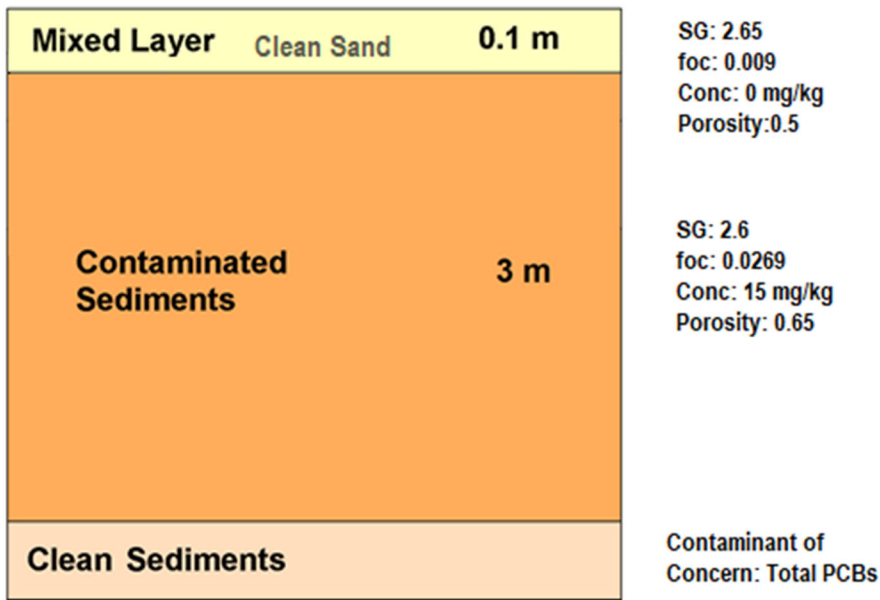


Figure C10. Lower New Bedford Harbor sand cap for modeling Total PCBs using RECOVERY.

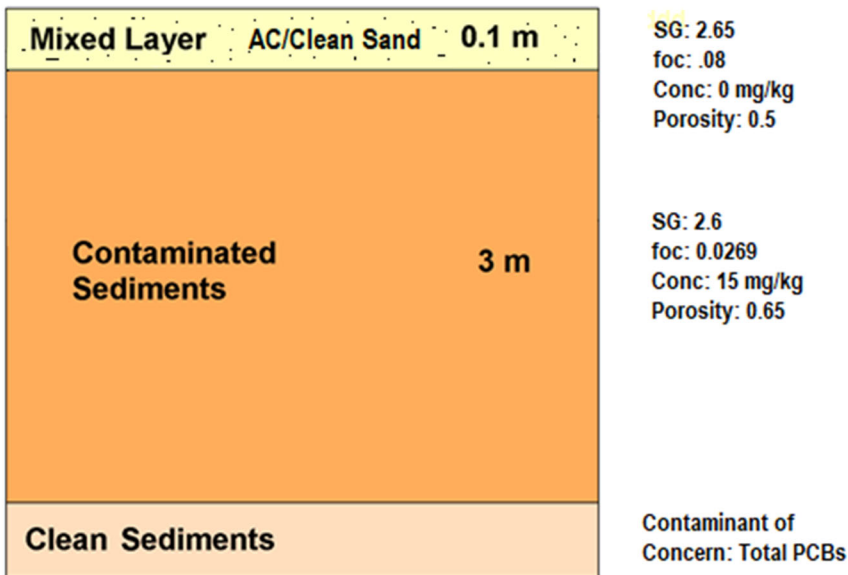
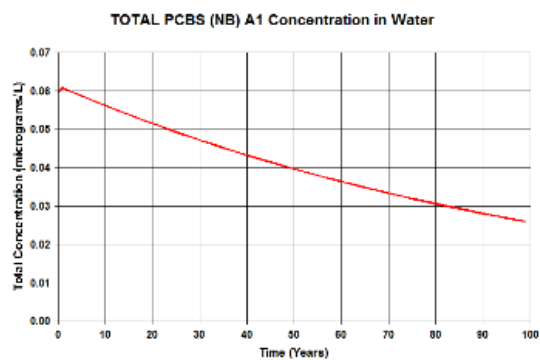
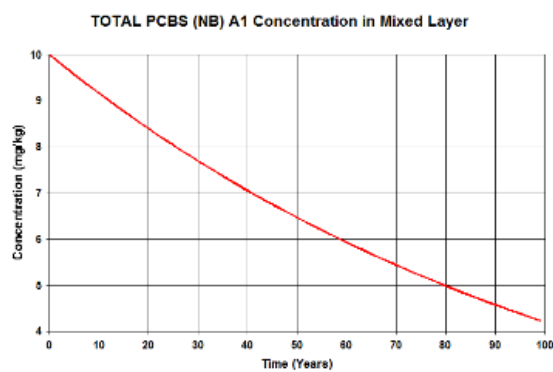


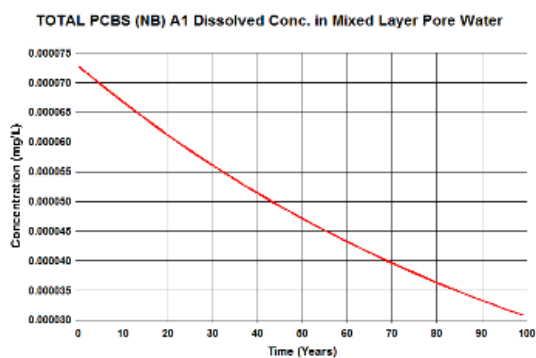
Figure C11. Lower New Bedford Harbor ac/sand cap for modeling Total PCBs using RECOVERY



(a)

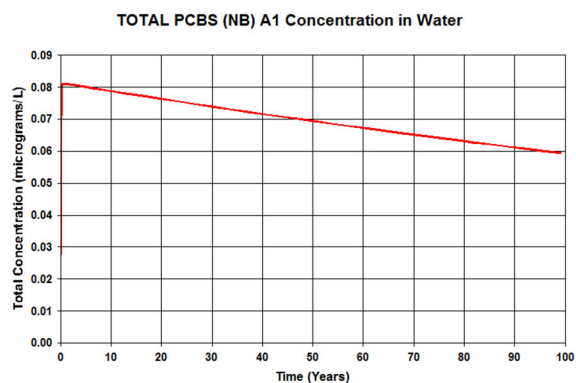


(b)

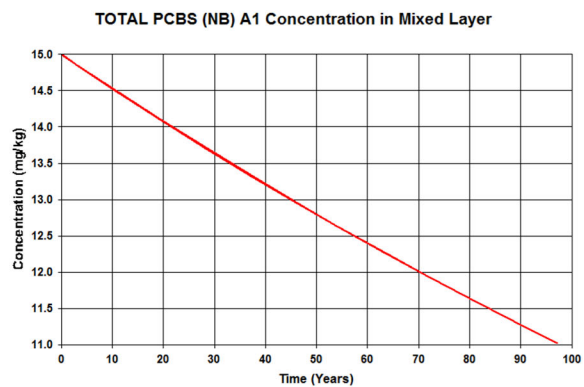


(c)

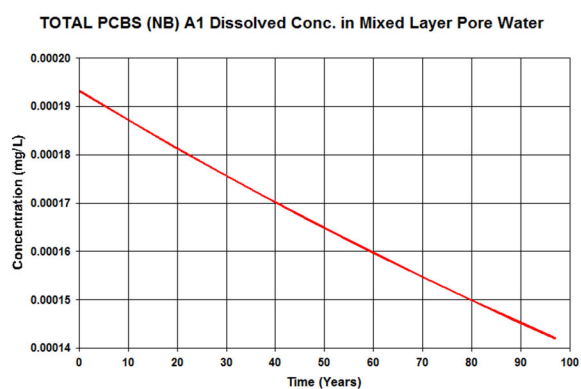
Figure C12. Upper Harbor Total PCBs concentration in the water column (a), sediment mixed layer (b), and porewater in the mixed



(a)

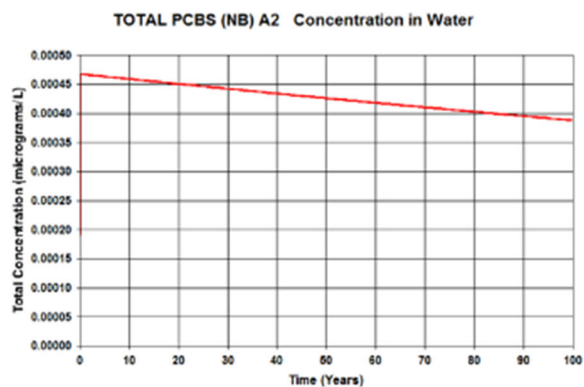


(b)

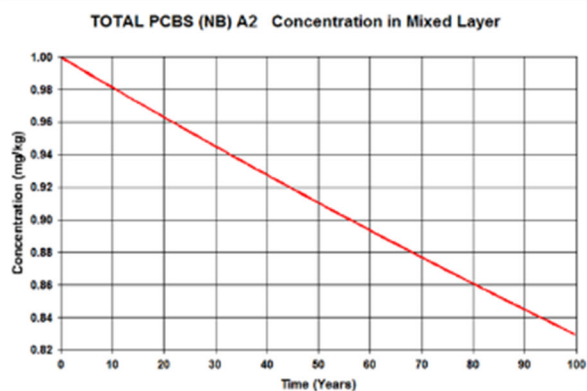


(c)

Figure C13. Lower Harbor Total PCBs concentration in the water column (a), sediment mixed layer (b), and porewater in the mixed layer(c).



(a)



(b)

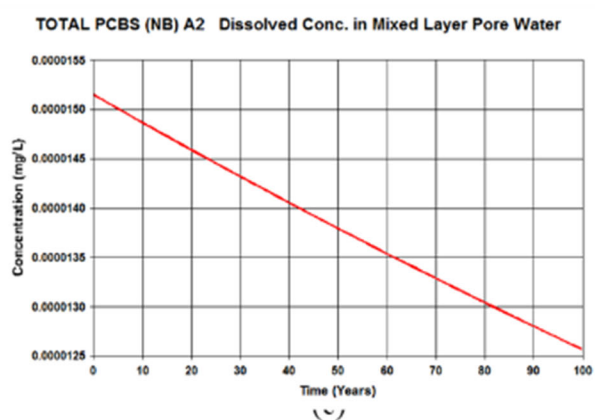
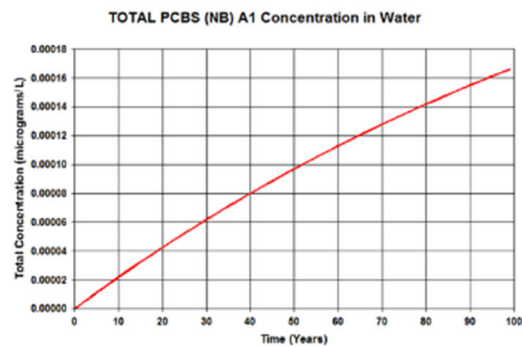
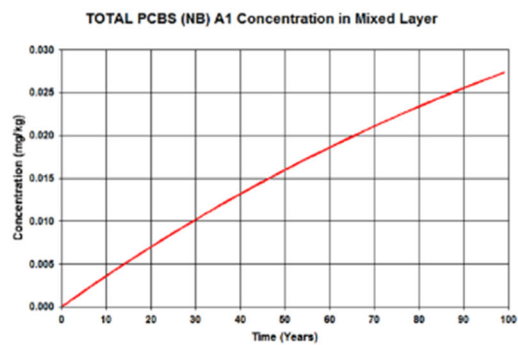


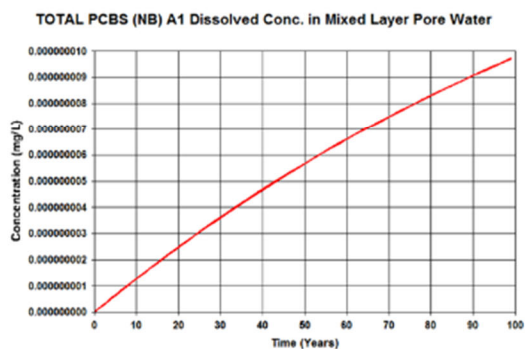
Figure C14 Outer Harbor Total PCBs concentration in the water column (a), sediment mixed layer (b), and porewater in the mixed layer(c).



(a)

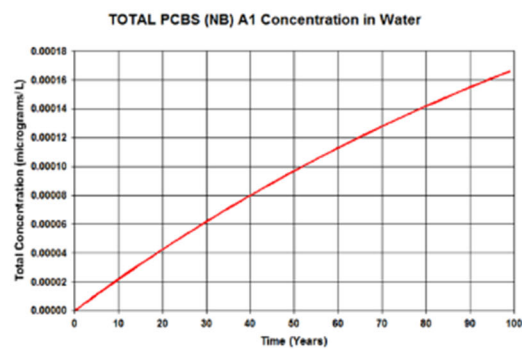


(b)

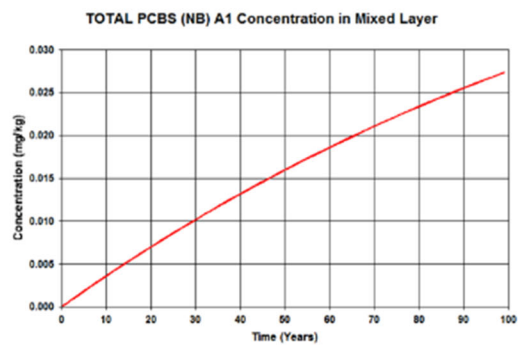


(c)

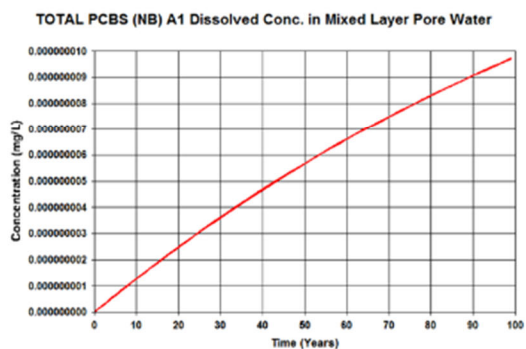
Figure C15. Upper Harbor Total PCBs concentration in the water column (a), sediment mixed layer (b), and porewater in the mixed layer(c) with a 10 cm clean sand layer



(a)

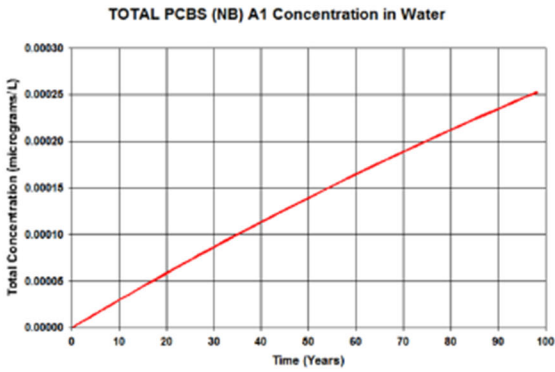


(b)

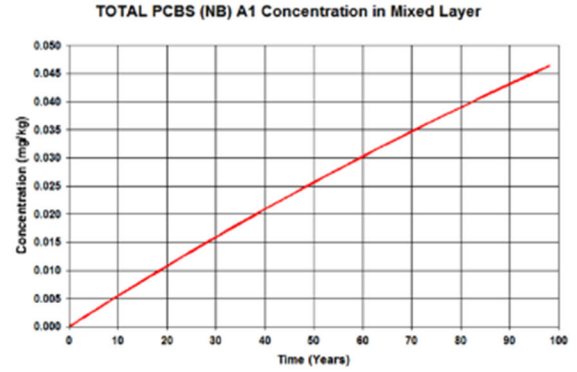


(c)

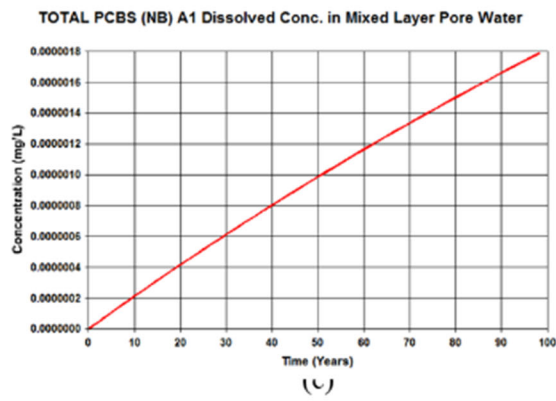
Figure C16. Upper Harbor Total PCBs concentration in the water column (a), sediment mixed layer (b), and porewater in the mixed layer(c) with a 10 cm activated carbon/clean sand layer.



(a)

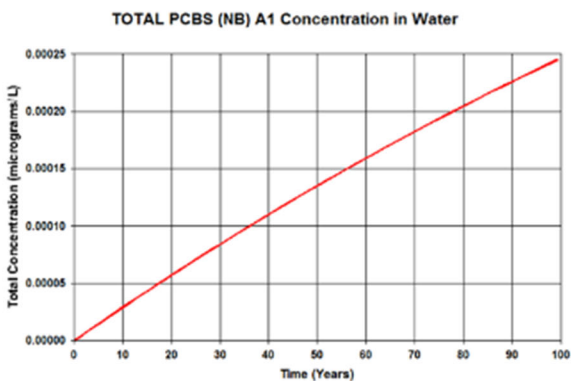


(b)

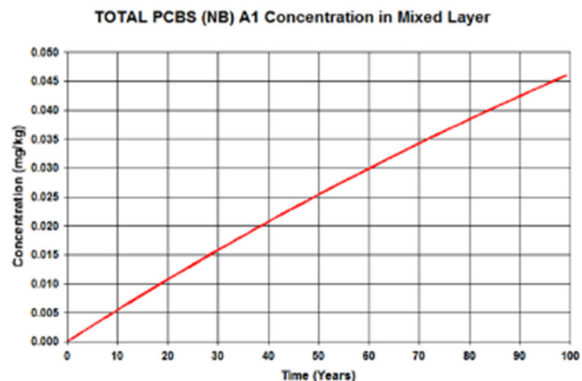


(c)

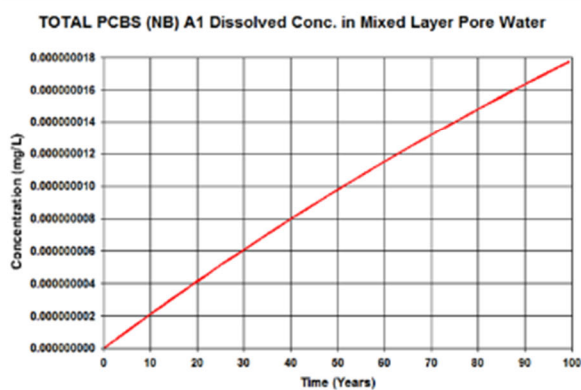
Figure C17. Lower Harbor Total PCBs concentration in the water column (a), sediment mixed layer (b), and porewater in the mixed layer(c) with a 10 cm clean sand layer.



(a)

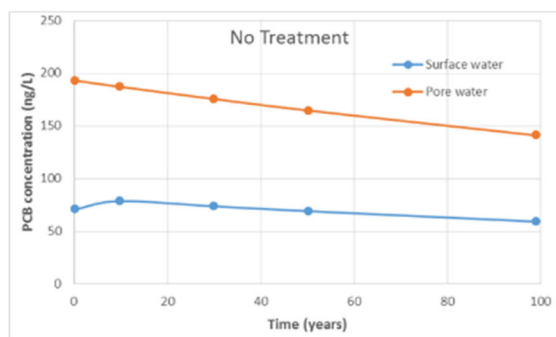


(b)

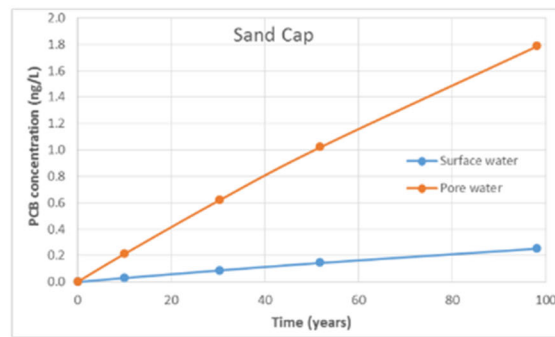


(c)

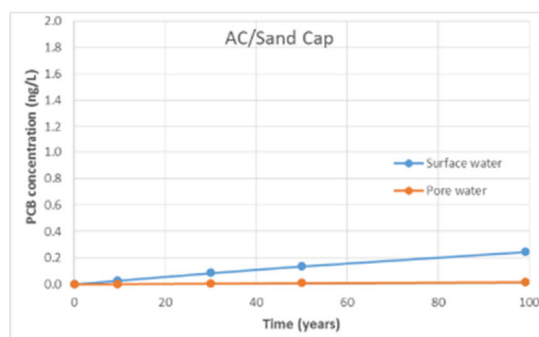
Figure C18. Lower Harbor Total PCBs concentration in the water column (a), sediment mixed layer (b), and porewater in the mixed layer(c) with a 10 cm activated carbon/clean sand layer.



(a)



(b)



(c)

Figure C19. Lower Harbor Total PCBs (a) uncapped sediments, (b) clean sand cap, and (c) activated carbon/clean sand cap

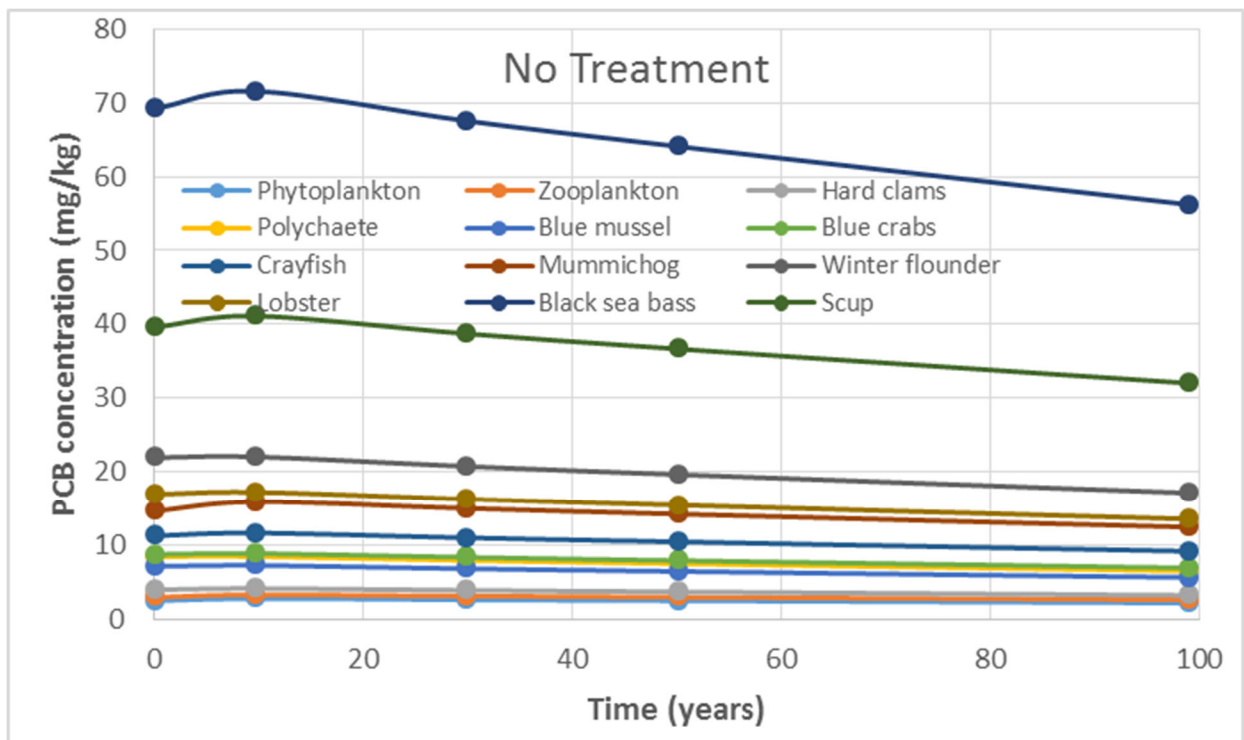


Figure C20. Predicted Food Web Total PCBs concentration in NBH Lower Harbor

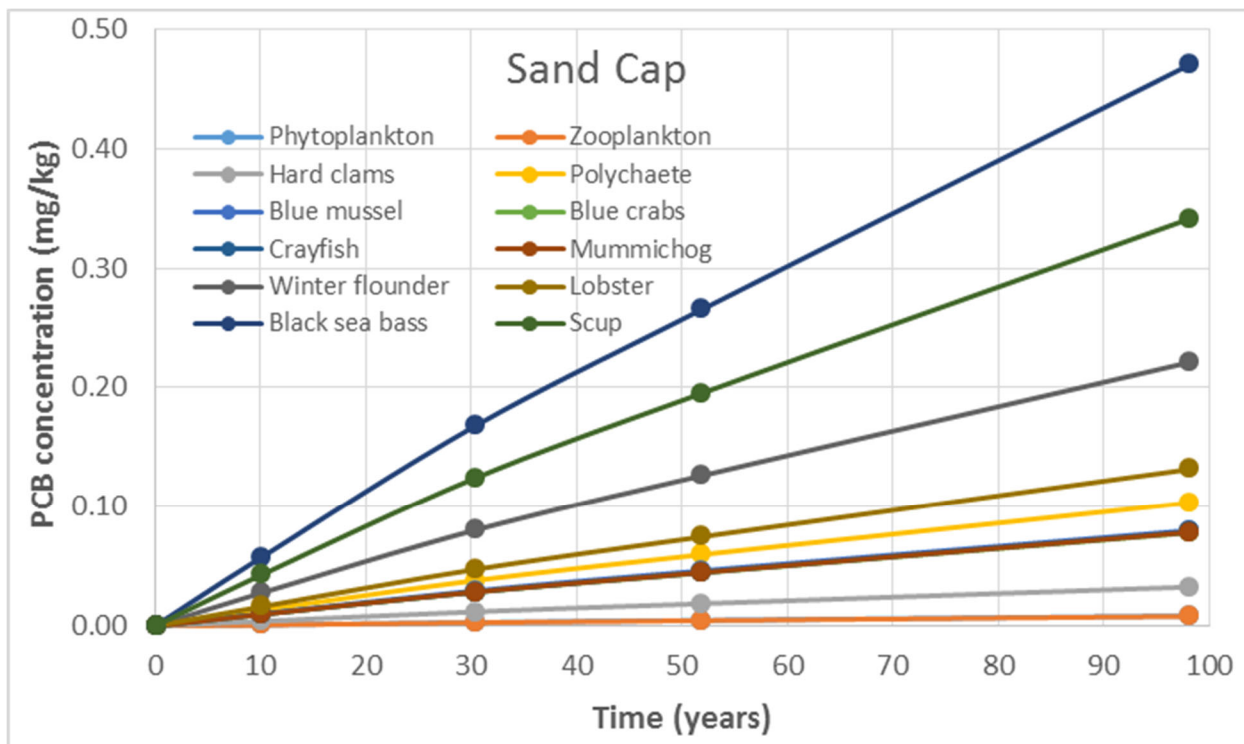


Figure C21. Predicted Food Web Total PCBs concentration in NBH Lower Harbor with a 10 cm clean sand layer.

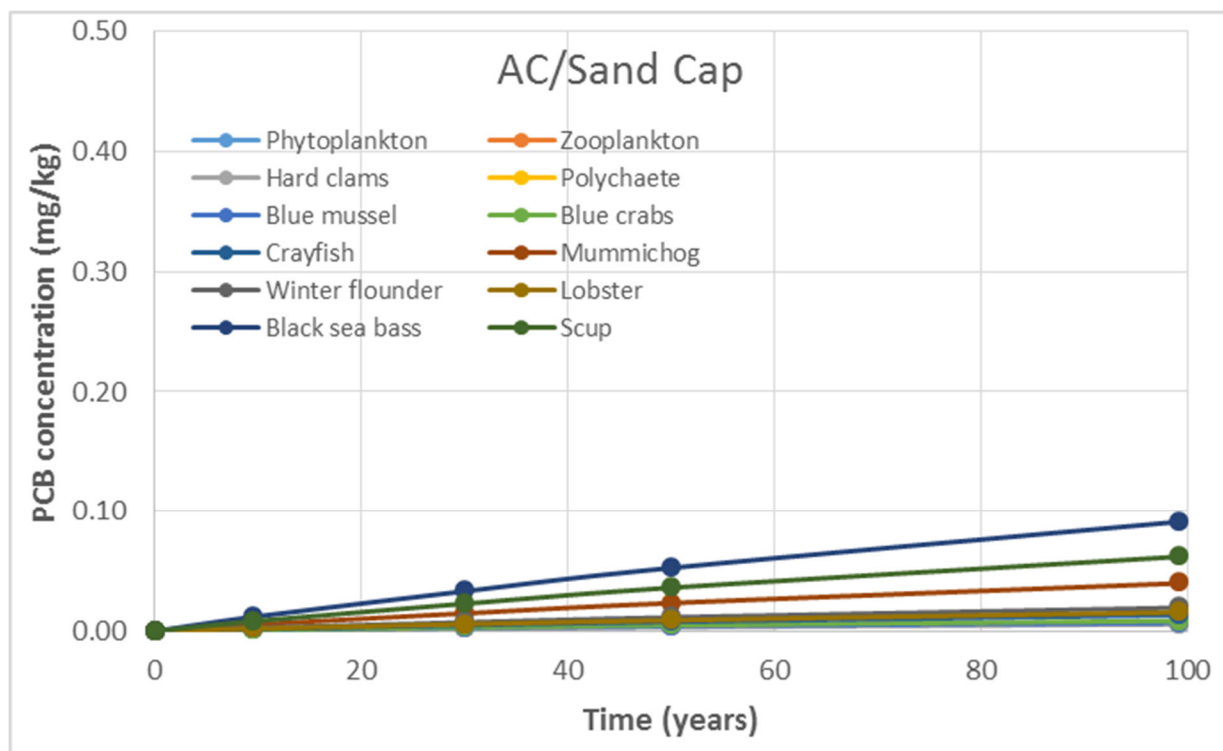


Figure C22. Predicted Food Web Total PCBs concentration in NBH Lower Harbor with a 10 cm activated carbon/clean sand layer